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Enzymatic Hydrolysis of Poly (Caprolactone) and its Blend with Styrene–Butadiene–Styrene (40% PCL/60% SBS)

Abir Ben Abdallah^{1,2}  · Achraf Kallel³ · Fehmi Gamaoun^{4,5} · Abbas Tcharkhtchi¹

Abstract

In this study, we aim to evaluate the effect of enzymatic hydrolysis on aliphatic polyester and on its shape memory blend. Therefore, the hydrolysis of poly (ϵ -caprolactone) (PCL) and of its shape memory polymer (SMP) blend [40% PCL/60% styrene–butadiene–styrene (SBS)] in a solution containing an Amano lipase from *Pseudomonas fluorescens* and a phosphate buffered saline (PBS), is achieved. An appropriate characterization helps to better understand the behaviour of these polymers. So, the properties of these materials prior and after hydrolytic degradation are investigated. When they are submitted to enzymatic hydrolysis, the physico-chemical and mechanical properties of PCL and its blend (PCL/SBS) change. PCL undergoes a significant decrease in weight during enzymatic hydrolysis. Yet, blending PCL with SBS considerably reduces its degradation rate in terms of weight drop, compared with pure PCL. The enzymatic hydrolysis causes chains splitting, which rises their mobility and facilitates their reorientation. Consequently, for PCL and its blend, the degree of crystallinity X_c rises during hydrolytic degradation, which confirms that the amorphous regions of PCL are more susceptible to hydrolysis. Besides, this continuous rise in crystallinity causes the augmentation of PCL and its blend melting, crystallization and glass transition temperatures. Moreover, the PCL brittleness increases, and the blend ductility decreases with the enzymatic hydrolysis time. For both, PCL and its blend, the young modulus displays two opposite effects; it goes up due the growth of crystallinity, but at the end of hydrolysis, its value goes down because of weight loss.

Keywords Poly (ϵ -caprolactone) · SMP blend (40% PCL/60% SBS) · Enzymatic hydrolytic degradation · Weight loss · Properties alteration

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Introduction

Studies on polymers and biodegradable polymers, such as aliphatic polyesters in general and shape memory polymer (SMP) blends in particular, have been focused on improving the design, functionality and thermal and mechanical properties of these polymers to meet specific needs and to develop new applications.

Aliphatic polyesters, such as polylactide (PLA) and Poly (ϵ -caprolactone) (PCL), have lately attracted significant attention of researchers thanks to their appealing characteristics. These biodegradable polymers have good and varied elastic, mechanical and chemical properties and a foreseeable degradation behavior [1]. Thus, they are extensively used in diverse fields such as tissue engineering [2], environmental applications and biomedical applications, especially in drug delivery systems and in absorbable sutures [2].

Among promising polyesters, we mention PCL as a semi-crystalline thermoplastic. It is non-toxic and biodegradable

aliphatic polyester with the permeability, compatibility and capacity to mix with many other polymers [3]. In fact, this material is compatible with numerous polymers, such as poly (vinyl chloride), polyethylene chlorinated, polycarbonate and poly (styrene-co-acrylonitrile) [3, 4]. Indeed, PCL can be blended with many other copolymers like styrene-butadiene-styrene (SBS) to form a new material with novel properties [5]. Previous studies [5, 6] have shown that PCL and SBS form an immiscible blend that constitutes a new intelligent polymer with Shape Memory Effect (SME). A shape memory polymer is a material that has the ability to deform to a temporary shape and to recover its initial shape under a stimulus like temperature [5]. These SMP blends have gained big interest as they are useful in a lot of domains such as the design of biomedical devices, intelligent clothing, and aero-spatial equipment [7–9].

Concerning the aliphatic polyester degradation, it is mentioned that hydrolysis is the main mechanism of the degradation of these polymers because they have ester linkages that are easily cleavable [10]. The hydrolysis of these polyesters begins with a water absorption stage followed by the hydrolytic fractionation of the ester bonds. This leads to molecular fragmentation and chain splitting. The two principal mechanisms of hydrolytic degradation are surface erosion (heterogeneous) and volume erosion (homogeneous) [10]. Benedict et al. [11] reported that amorphous regions would degrade more rapidly before crystalline regions. In other cases, only the amorphous phase degrades. Divers agents seem to be crucial in the determination of the biodegradation rate of polyesters [12]. It is important to mention the chemical structure, the porosity, the degree of crystallinity, and the molecular weight [12–14]. Moreover, hydrolysis conditions as pH, temperature, components concentration and enzymes have an impact on the hydrolytic degradation of polyesters [14, 15]. As for the PCL degradation, this material can be degraded in multiple natural environments such as compost, soil and rivers [16, 17] and in the presence of microbes [18] and enzymes [2, 15, 19]. Indeed, it has been found that several lipases can catalyze the hydrolysis of PCL [16]. Among these enzymes, we cite pseudomonas and *Rhizopus arrhizus* ones [15, 16]. It has been reported that the pseudomonas lipase shows preferential hydrolytic degradation of PCL [20]. In fact, the authors in [20] reported that the enzymatic hydrolysis of PCL took place by the rupture of ester bonds. A lipase enzyme would attack these ester bonds and cause chain splitting [21]. Particularly, the amorphous regions were the mainly attacked by enzymes [21]. In addition, many factors would influence the enzyme catalyzed hydrolysis of PCL, such as its morphology, its surface conditions, its porosity, and its physical and chemical properties, including crystallinity, transition and melting temperatures, as well as molecular weight [2, 12, 22, 23]. Moreover, it was shown in [24] that the presence of cavities and lipase concentration

promotes the enzymatic hydrolysis of PCL. The hydrolytic degradation of PCL and its blends has given rise not only to the mass loss [25, 26] but also to the decrease in molecular weight [10, 11, 27, 28]. Furthermore, the enzymatic hydrolysis of PCL causes the degradation and alteration of its mechanical properties like the Young modulus, the tensile yield and the strain at break [2, 16, 29]. This degradation engenders also the alteration of the transition and melting temperatures and of the crystallinity degree [1, 2, 24, 29].

The aim of this study is to investigate the effect of hydrolytic degradation on PCL and on its blend (40% PCL/60% SBS). Thus, mechanical properties (young modulus, elongation to fracture...) and physico-chemical properties (crystallinity rate, melting and glass transition temperatures...) of these materials are evaluated, prior and after enzymatic hydrolysis.

Materials and Methods

Materials

PCL CAPA 6800 is used and is provided by Perstrop Limited UK. It is a semi-crystalline biodegradable aliphatic polymer with a density of 1140 kg/m^3 and a number-average degree of polymerization of 1.5. Its chemical formula is: $[-O-(CH_2)_5-CO-]$. PCL has a transition temperature of $-40 \text{ }^\circ\text{C}$ and a relatively low melting temperature between 58 and $62 \text{ }^\circ\text{C}$ [30].

SBS, supplied by Sinopec Group, is an amorphous copolymer whose main chain is made of two rigid polystyrene segments on both sides and a flexible segment of polybutadiene in the middle [31]. SBS is an elastomer with a transition temperature of $-80 \text{ }^\circ\text{C}$ and a degree of polydispersity of 1.09.

These two materials are blended to form a mixture of (40%) PCL and (60%) SBS. This immiscible blend shows almost a total shape memory effect [6].

In order to get the final form, the pure materials and the blend (PCL/SBS) are firstly extruded into pellets through a twin screw extruder machine (Brabender, Duidburg, Germany). The extruded pellets are then injected in an injection molding machine to get samples with a size of $25 \times 4 \times 2 \text{ mm}^3$.

Enzymatic Hydrolysis

Enzymatic hydrolysis is carried out. PCL, blend (40% PCL/60% SBS) and SBS specimens are immersed in a container filled with enzymatic solution for 4 weeks at $37 \text{ }^\circ\text{C}$. This solution is prepared by dissolving, in distilled water, an Amano lipase from pseudomonas fluorescence ($2.5 \text{ } \mu\text{g/ml}$) and a Phosphate Buffered Saline (PBS). The solution is changed twice

a week in order to conserve the enzyme activity. The pseudomonas lipase and the PBS are supplied by Sigma Aldrich. At specific periods, samples are removed from solution and dried under a vacuum. Then these hydrolyzed specimens are submitted to mechanical and physico-chemical tests.

Properties and Degradation's Evaluation

In order to characterize materials before and after hydrolytic degradations, mechanical and physico-chemical tests are performed.

After the degradation process, the mass loss is determined. In fact, the mass loss is evaluated using the following equation:

$$\text{weight loss}(\%) = \frac{w_0 - w_f}{w_0} \times 100, \quad (1)$$

where w_0 is the weight before hydrolysis and w_f is the weight after hydrolysis.

A balance Mettler Toledo with a sensitivity of 0.01 mg is used to weigh the specimens.

The melting and crystallization temperatures (respectively T_m and T_c), the enthalpies of melting (ΔH_m) and crystallization (ΔH_c) are measured by means of a Differential Scanning Calorimetric (DSC) machine Q1000 V9.0 Build 275 TA Instruments. All DSC tests are carried out at a constant rate of 5 °C/min. The device is calibrated with indium, and T_m , T_c , ΔH_m and ΔH_c are measured from the first heating cooling and second heating curves. The degree of crystallization (X_c) is determined according to the following equation:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_{m0}} \times 100. \quad (2)$$

ΔH_m represents the enthalpy of melting from DSC tests, and ΔH_{m0} represents the reference enthalpy of PCL which has the value of 142 j/g [32].

Table 1 Mechanical properties of reference materials

Material	Young modulus (Mpa)	% elongation to fracture	Fracture stress (Mpa)
PCL	406 ± 12.2	14 ± 0.5	23 ± 0.6
SBS	27 ± 1	149 ± 4.5	4 ± 0.5
Blend	116 ± 3.5	292 ± 8.8	7 ± 0.5

The glass transition temperature (T_g) is determined using dynamical mechanical analysis DMA Q800 TA Instruments type machine. These experiments are carried out with a frequency of 1 Hz; a temperature range between – 100 °C and 100 °C, and a heating rate of 5 °C/min.

Uniaxial tensile tests are performed on a standard Instron mechanical testing 5966-type machine with a load of 10KN at a deformation rate of 6 mm/min. A camera is installed to measure the deformation of the specimen. The stress as a function of the deformation is then recorded

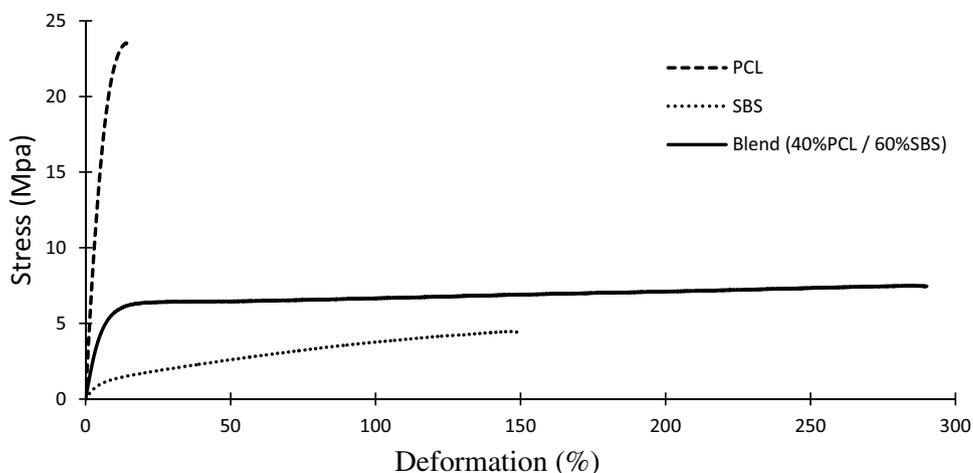
Results and Discussion

Materials Properties Prior to Hydrolytic Degradation

In order to investigate mechanical properties of PCL, blend (40% PCL/60% SBS), and SBS before hydrolysis, tensile tests at ambient temperature are realized. Figure 1 presents the tensile curves of reference materials until fracture. During our study, we consider the reference materials as the materials before hydrolysis. The mechanical properties are recapitulated in Table 1.

According to Fig. 1 and Table 1, the three materials show largely different mechanical properties. PCL displays a young modulus of 406 ± 12.2 Mpa, which is much higher than those of SBS and even the blend (27 ± 1 Mpa, and

Fig. 1 Tensile curves of: PCL, SBS, blend (60% SBS/40% PCL)



116 ± 3.5 Mpa, respectively). The fracture stress of PCL is equal to 23 ± 0.6 Mpa, which is much higher than those of SBS and the blend (4 ± 0.5 Mpa, and 116 ± 3.5 Mpa). PCL is obviously the most rigid material, compared SBS and even the blend. The tensile curve of the blend presents two different zones of linear deformation, consisting of an elastic zone (6–8% of deformation) and a plastic zone ($> 10\%$ of deformation). The blend has an elongation to fracture of $292 \pm 8.8\%$. We remark that the (PCL/SBS) mixture shows a ductile character since it exhibits the capacity to undergo an important plastic deformation before rupture. It is more ductile than SBS. The enhancement in the blend ductility compared with pure SBS and pure PCL can be explained with the good compatibility between these two polymers. In previous work, Massardier et al. [33] reported that for the blend [polyamide 6 (PA6)/Acrylonitrile Butadiene Styrene (ABS)] a good compatibility between the polymers constituting a blend would ameliorate its mechanical properties. In addition, they showed that when a certain quantity of the maleic anhydride was added as a compatibility agent to the (PA6/ABS) blend, the mechanical properties of this blend were improved. They explained that when the compatibility of the blend rose, the young modulus was enhanced and the elongation to fracture was increased. Therefore, in our case, the increase in the total elongation of the blend could be explained by the good compatibility between PCL and SBS.

The DMA tests are carried out to determine the transition temperatures of PCL, the blend, and SBS. Figure 2 represents the curves of Tan Delta versus temperature. Tan Delta represents the loss or damping factor and it is a measure of the energy dissipation in the polymer. The peak in the Tan Delta curve gives directly the value of the glass transition temperature.

According to these results, PCL shows a single peak at -40.1 °C, which corresponds to its transition temperature ($T\alpha$). Similarly, SBS displays a single pic at -76 °C, which corresponds to its transition temperature. However, the Tan

Delta curve of the blend (40% PCL/60% SBS) presents two separate peaks corresponding to two various glass transition temperatures: The first one appears at -80.7 °C and the second at -39.7 °C. In fact, the existence of these two distinct glass transition temperatures indicate that the two materials forming the mixture are immiscible. These results are in accordance with the work of Zhang et al. [5] who indicated that PCL and SBS formed an immiscible blend that had two different glass transition temperatures ($T\alpha$). The lowest $T\alpha$ corresponds to the flexible phase, which is SBS. While the second $T\alpha$ corresponds to the hard phase, which is PCL in our case. Besides, according to Tan Delta curves, the loss factor related to SBS is significantly more important than the loss factor related to the blend. This results could be explained by the fact that PCL decreases the damping property of SBS in the blend.

The DSC experiments are performed to investigate the melting temperature, the crystallization temperature and the crystallinity rate of PCL and its blend (40% PCL/60% SBS). SBS is an amorphous elastomer that has neither a crystallization temperature nor a melting temperature. The crystallinity rate of the blend corresponds to the crystallinity of PCL. Figure 3 illustrates the heat flow of PCL and the blend versus temperature.

According to the PCL heat flow curve (Fig. 3), a first peak appears, from the first cooling, at 35.7 °C. It corresponds to the PCL crystallization temperature T_c . During heating, the second one appears at 59.7 °C. It represents the melting point T_m of PCL. The crystallinity ratio X_c of PCL is calculated from Eq. (2) and it is equal to 50.5%. This value confirms the semi-crystalline character of PCL. Likewise, the blend heat flow curve (Fig. 3) displays two peaks; the first one, which represents the crystallization temperature T_c , appears at 34.1 °C, and the second one, for the melting temperature T_m , is at 58.9 °C. The crystallinity rate X_c of the blend is 51.4%. It is important to indicate that the percentage of SBS in the blend is eliminated when we calculate the

Fig. 2 Tan delta curves versus temperatures of: PCL, SBS, and blend (60% SBS/40% PCL)

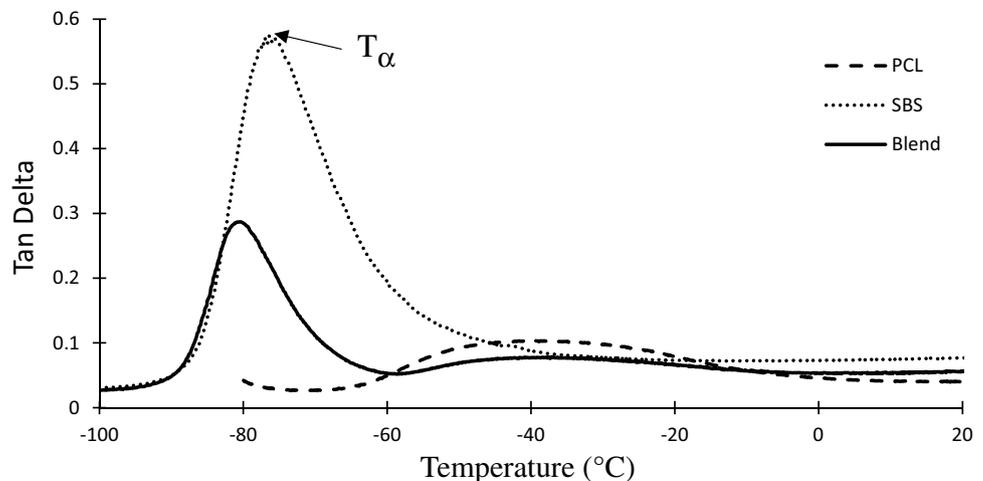
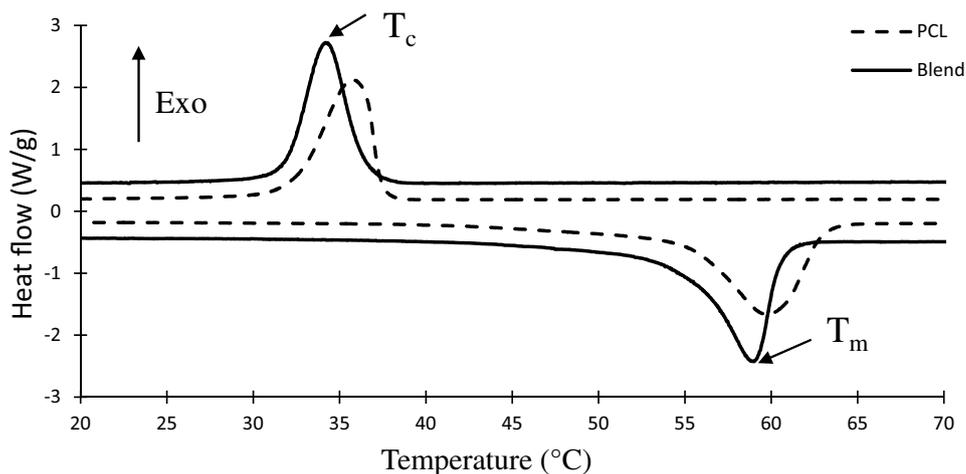


Fig. 3 DSC curves of: PCL and blend



crystallinity of the blend. Hence, this X_c (51.4%) is only related to the PCL phase. This high degree of crystallinity induces blend components separation. This outcome is in accordance with DMA results that shows the immiscibility between the blend components since the blend presents two T_{α} . Table 2 summarizes the thermal properties of the reference: PCL, SBS, and blend.

PCL, SBS and their blend are submitted to DMA and DSC tests in order to investigate their physico-chemical properties. We notice that the blend has two distinct glass transition temperatures T_{α} . The first one corresponds to T_{α} of SBS, and the second one corresponds to T_{α} of PCL. This outcome can confirm the immiscibility of this blend. Moreover, the crystallinity rate X_c of the blend is related to the PCL phase. The melting and crystallization temperatures (respectively T_m and T_c) of the blend match those of PCL, which can confirm the compatibility of the blend. Moreover, this result is in coherence with the tensile test results, where we show that the ductility and rigidity of SBS is enhanced when we mix it with PCL, since we obtain a blend with higher elongation to fracture. Afterwards, enzymatic hydrolysis is achieved in order to evaluate its effect on PCL and the mechanical (Young modulus, elongation to fracture, and fracture stress) and physico-chemical (T_m , T_c , T_{α} , and X_c) properties of the blend.

Mass Loss

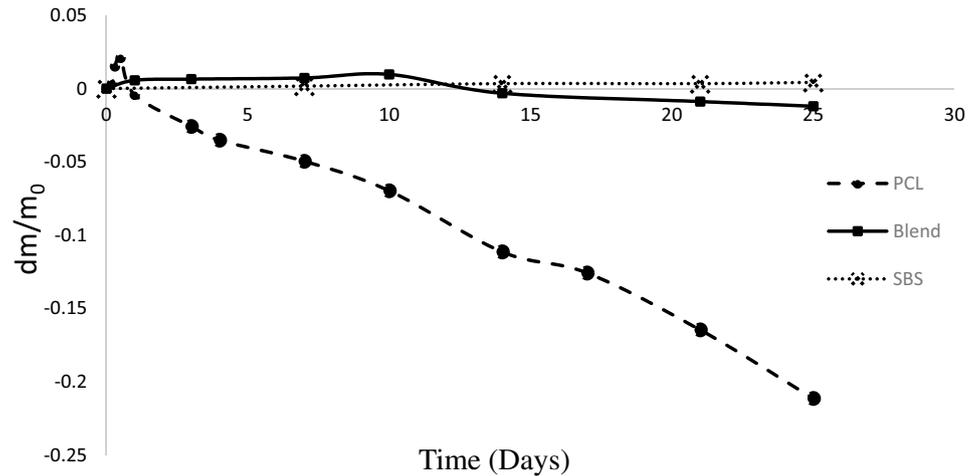
Figure 4 illustrates the weight losses of PCL, SBS, and the blend (40% PCL/60% SBS) after 25 days of hydrolysis.

After a rapid phase of water absorption, PCL starts to lose mass after only 24 h. PCL undergoes a significant and fast decrease in weight during enzymatic hydrolysis. In addition, the polymer loses 5% of its initial mass after 1 week and it loses up to 21% of its mass at the end of hydrolysis. In fact, the use of the lipase enzyme promotes the mechanism of PCL hydrolysis. It causes the hydrolytic fractionation of the ester bonds, which leads to molecular fragmentation and chain splitting. Moreover, the release of degradation products causes the important mass loss [26]. Tkanori et al. [34] pointed out that PCL hydrolytic degradation manifested from the surface of the material inward. Yet, for the SMP blend, the hydrolysis begins with a water absorption phase, up to the tenth days, followed by a phase of mass loss. After 25 days of enzymatic hydrolysis, the mixture loses 1.2% of its initial weight. Consequently, we remark that blending PCL with SBS considerably reduces its degradation rate in terms of weight drop, compared with pure PCL. This could be due to the morphological change in the PCL surface. This result is in accordance with the work of Li et al. [24] who reported the enzymatic degradation of PCL and PCL mixture with polylactide-based polymer (BPLLA). They mentioned that a significant drop in the degradation rate in terms of weight loss for PCL/(BPLLA) compared with pure PCL occurred because of the change in the PCL surface. Concerning SBS, as we can see in Fig. 4, there is no obvious change in its weight during hydrolysis time. As a matter of fact, SBS is an amorphous elastomer whose principal degradation mechanism is thermos-oxidation. Consequently, we can estimate that SBS is not susceptible to hydrolytic

Table 2 Thermal properties of PCL, SBS, and blend prior to hydrolyze

Material	$T_{\alpha 1}$ (°C)	$T_{\alpha 2}$ (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)
PCL		-40.1	59.7	35.7	71.7	50.5
SBS	-76					
Blend	-80.7	-39.7	58.9	34.1	73	51.4

Fig. 4 Evolution of material weight during hydrolytic degradation



degradation. To confirm this assumption, SBS samples are submitted to tensile tests at varied hydrolyze time. The results are presented in Fig. 5. We can clearly notice that mechanical properties of SBS do not alter under the effect of enzymatic hydrolysis. Nevertheless, in the following parts, only the hydrolytic degradation influence on PCL and the physical and mechanical properties of its blend are studied.

Crystallization and Thermal Properties Variation

In this part, we are interested in the hydrolytic degradation influence on the thermal properties and the crystallinity of PCL and its blend. These properties are monitored and compared using DSC and DMA tests.

The DSC results of PCL during enzymatic hydrolysis are depicted in Fig. 6 and Table 3. According to this table, the degree of crystallinity (X_c) of the polymer undergoes a significant increase during enzymatic degradation. It passes from 50.5% for reference PCL to 67.2% after 25 days of hydrolysis. The rise in X_c is explained by the fact that the amorphous phase of PCL is more susceptible to hydrolytic

degradation and degrades before the crystalline one, since amorphous regions have less Van Der Waals' links than crystalline ones. This result is in harmony with the work of Malberg et al. [1] and the work of Fukushima et al. [35], where they indicated that the amorphous regions of PCL degraded more rapidly than the crystalline ones. They explained this assumption by the easier water diffusion into the amorphous phase. On the other hand, the hydrolysis causes the shortening of the PCL chains, leading to the increase in the mobility of these chains, which facilitates their reorientation and recrystallization. Furthermore, we remark that the melting temperature (T_m) of PCL arises during hydrolytic degradation. T_m passes from 59.7 °C for the virgin sample to 60.1 °C after 2 weeks and it attains 60.5 °C after 25 days of hydrolytic degradation. The growth of the melting temperature T_m could be due to the continued crystallization which is characterized by the enlargement of the crystalline thickness during hydrolysis [35]. Furthermore, the formation of thicker lamellas may lead to the increase in T_m , since the lower melting temperatures are associated with thinner crystals [36].

Fig. 5 SBS tensile curves during hydrolysis time

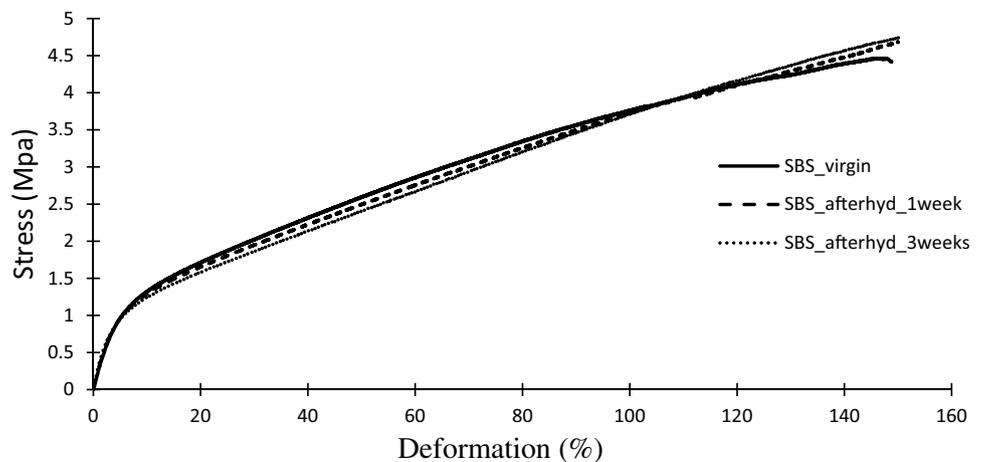


Fig. 6 DSC curves of PCL during hydrolysis

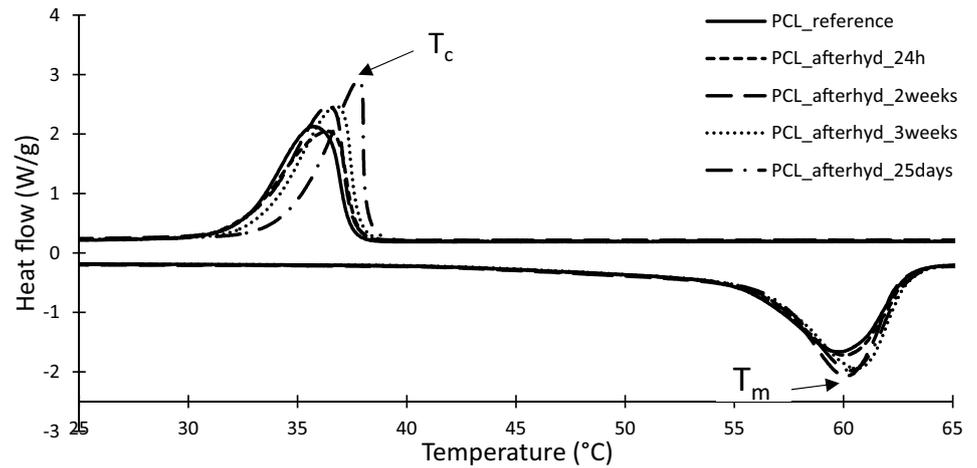
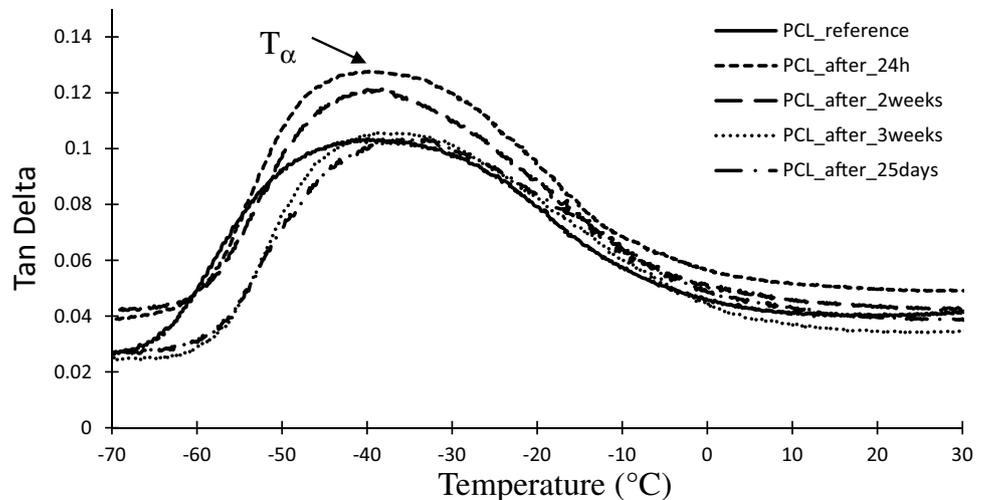


Table 3 PCL thermal properties evolution during hydrolysis

PCL	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_α (°C)
Reference	35.7	59.7	71.7	50.5	-40.1
24 h	36.4	59.9	83.4	58.7	-39.7
2 weeks	36.4	60.1	89.4	62.9	-39.2
3 weeks	36.7	60.3	94.3	66.4	-38.7
25 days	37.8	60.5	95.5	67.2	-35.4

The DMA results of PCL during hydrolysis are represented in Fig. 7 and Table 3. We remark that the glass transition temperature T_α of the polymer grows during the enzymatic hydrolysis. It passes from -40.1 °C before hydrolysis to -35.2 °C at the end. This could be associated to the buildup of intermolecular interactions, which characterize the cohesive forces between polymer chains, as the rise in the crystallinity leads to the reinforcing cohesion of the material. For aliphatic polymers, the T_α goes up when the cohesion forces are enhanced.

Fig. 7 DMA curves of PCL during hydrolysis



Concerning the blend (40% PCL/60% SBS), the DSC results are summarized in Fig. 8 and Table 4. The same trend of the X_c evolution is observed. In fact, X_c increases from 51.4 to 69.7%. This confirms again that the amorphous regions of PCL are more susceptible to hydrolysis than crystalline ones. Indeed, the melting temperature T_m of the blend rises with hydrolysis time. The T_m passes from 58.9 °C for the virgin sample to 59.4 °C after 3 weeks and it reaches 59.6 °C after 25 days of hydrolytic degradation. The increase in T_m during the enzymatic hydrolysis is explained by the crystallization of the material and the growth of the crystalline thickness [1].

The DMA results of the blend during hydrolysis are recapitulated in Table 4. We notice that $T_{\alpha 1}$, corresponding to the glass transition temperature of the PCL, goes up during hydrolysis. It passes from -39.7 °C before hydrolysis to -33.1 °C at the end. This increase in T_α is due to the reinforcing of the cohesion forces of the material because of the rise in crystallinity. $T_{\alpha 2}$, corresponding to the glass

Fig. 8 DSC curves of blend during hydrolysis

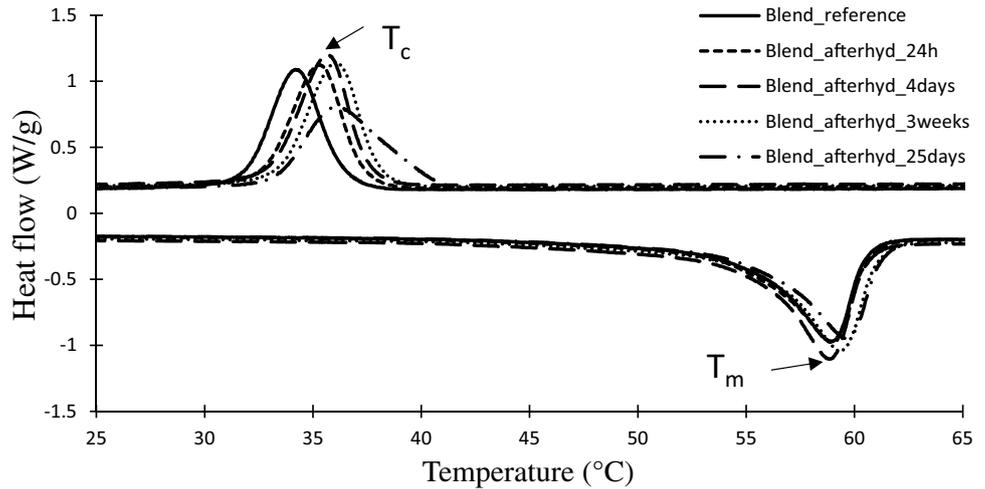


Table 4 Thermal properties evolution during hydrolysis of mixture (40% PCL/60% SBS)

Blend (40% PCL/60% SBS)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	$T\alpha_1$ (°C)	$T\alpha_2$ (°C)
Reference	34.1	58.9	73	51.4	-80.7	-39.7
24 h	35.3	58.8	78.2	55.1	-81.8	-38.9
4 days	35.7	58.9	86.5	60.9	-81.8	-36.7
3 weeks	36	59.4	96.2	67.7	-80.5	-35.3
25 days	36.1	59.6	99	69.7	-79.9	-33.1

transition temperature of SBS, is more or less constant since SBS is not affected by hydrolysis.

For PCL and the blend, hydrolysis causes the fractionation of ester bonds and the shortening of the polymers chains, which allow them to reorient and to recrystallize. Therefore, the crystallinity rate increases with enzymatic hydrolysis time, which confirms that hydrolysis affects the amorphous phase more than the crystalline one. This continuous increase in crystallization enhances the cohesive forces between the chains, which induces the rise in the glass transition temperature. Moreover, the augmentation of crystallization explains the growth of the materials melting temperature. As a result, after 25 days of hydrolysis, we obtain samples of the blend (PCL/SBS) with different crystallization rates and various thermal properties (T_α , T_c , and T_m). These samples will be used, in a later study, to examine the relation between the thermal properties of the blend and its shape memory effect.

Mechanical Properties Alteration

To investigate the mechanical properties, different tensile tests are realized at various periods of hydrolysis with a strain rate of 6 mm/min. Young-modulus, elongation-to-fracture, and fracture-stress values are obtained.

Stress-strain curves of PCL at varied hydrolysis time are presented in Fig. 9. Young-modulus, elongation-to-fracture and fracture-stress values at varied enzymatic hydrolysis time are summarized in Table 5.

After 24 h of hydrolysis, the total elongation of PCL is almost the same, but its young modulus E decreases from 406 ± 12.2 Mpa for the reference specimen to 380 ± 11.4 . This decrease in E is expected as the material gains in plasticity at the beginning of hydrolysis. After that, the young modulus shows a significant increase; it goes up from 487 ± 14.6 Mpa after 4 days of hydrolysis to 599 ± 18 Mpa after 3 weeks. This rise implies the growth of PCL rigidity, which means that PCL chains tend to create additional bonds, since materials rigidity is related to crystallinity. This is coherent with the DSC results where we show that the degree of crystallinity rises with hydrolysis time. Castilla et al. [29] studied the hydrolysis of PCL networks and indicated that the young modulus went up during degradation as the crystallinity rate rose because of the faster degradation of the amorphous regions. However, at the end of hydrolytic degradation, the young modulus value shows a slight diminution, and it becomes 503 ± 15 Mpa. This fall can be due to the formation of pores and the significant loss of weight at the end of hydrolysis. Concerning the elongation to fracture, and the fracture stress, their values indicate a slip with hydrolytic degradation time.

Fig. 9 PCL tensile curves during hydrolysis time

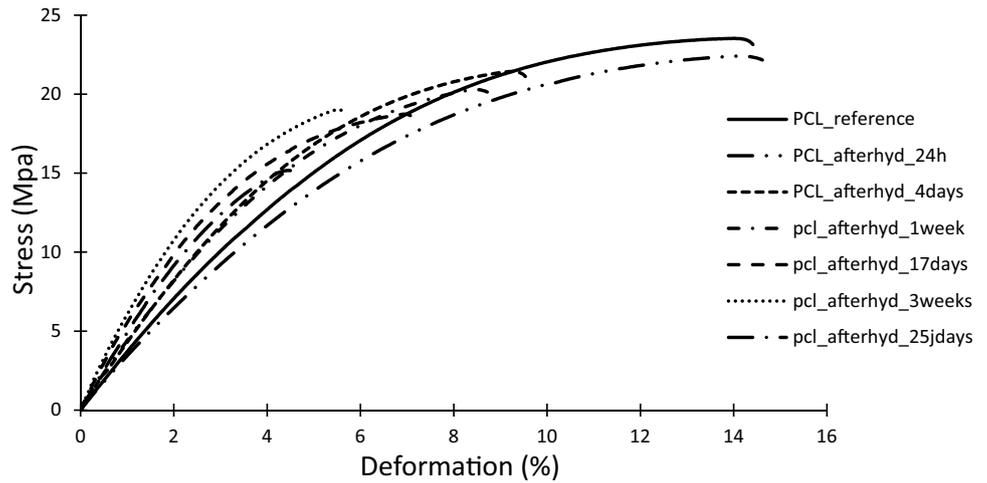


Table 5 PCL mechanical properties variation during hydrolytic degradation

PCL	Young modulus (Mpa)	% Elongation to fracture	Fracture stress (Mpa)
Reference	406 ± 12.2	14 ± 0.5	23 ± 0.6
24 h	380 ± 11.4	14 ± 0.6	22 ± 0.7
4 days	487 ± 14.6	9 ± 0.5	21 ± 0.6
1 week	495 ± 14.9	8 ± 0.4	20 ± 0.6
17 days	542 ± 16.3	6 ± 0.4	18 ± 0.7
3 weeks	599 ± 18	5 ± 0.3	19 ± 0.6
25 days	503 ± 15	4 ± 0.3	15 ± 0.5

The elongation to fracture passes from $14 \pm 0.5\%$ for the reference specimen to $8 \pm 0.4\%$ after 1 week of hydrolysis, and it reaches $4 \pm 0.3\%$ at the end of hydrolysis, which implies that the brittleness of PCL grows. The decline of elongation to fracture is explained by the formation of pores and the weight loss, which engenders the embrittlement of PCL.

To recap, the variation in the Young's modulus can be explained by two different phenomena. On the one hand, the results demonstrate that hydrolysis occurs and affects the amorphous phase more than the crystalline one, which causes the fractionation of the PCL chains leading to a better crystallization. Consequently, the crystallinity of the polymer increases, thus the increase in the Young modulus. On the other hand, after 25 days of enzymatic hydrolysis, a significant weight loss occurs in the material, which leads to the decrease in the Young modulus. For the elongation to fracture and the fracture stress, their decrease is due to the continuous weight loss of the polymer and to its embrittlement during enzymatic hydrolysis.

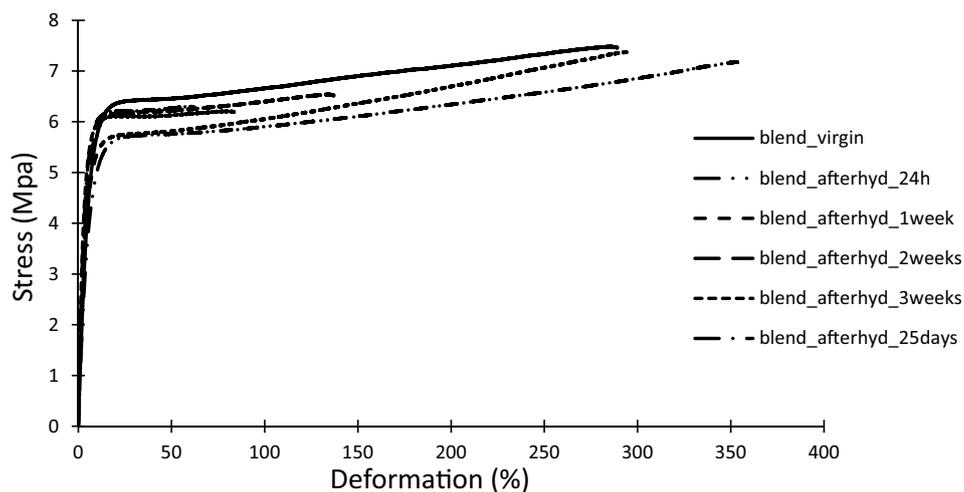
Tensile curves of the blend (40% PCL/60% SBS) at varied hydrolysis time are given in Fig. 10. Young-modulus,

elongation-to-fracture, and fracture-stress values at different enzymatic hydrolysis time are recapitulated in Table 6.

Initially, the ductility of the blend rises as its elongation to fracture increases from $292 \pm 8.8\%$, for the reference specimen, to $356 \pm 10.7\%$, after 24 h of hydrolysis. This result is expected as materials gain in plasticity at the beginning of hydrolysis. The blend Young modulus undergoes a diminution after 24 h. It becomes 108 ± 3.2 Mpa compared with 116 ± 3.5 Mpa for the reference material. This reduction is explained by the mechanism of the hydrolysis of the blend that begins with a water absorption phase, which implies the augmentation of its plasticity. Then the water absorption phase is followed by a phase of weight loss. Consequently, both the elongation to fracture and the fracture stress drop, which indicates that the ductility of the blend clearly shows a decrease with hydrolytic degradation time. The elongation to fracture reaches $61 \pm 2\%$, after 25 days of hydrolysis. The formation of pores and the mass loss could cause the diminution of the elongation to fracture [36]. Moreover, this decrease could be due to the embrittlement of the mixture during enzymatic hydrolysis. Subsequently, the Young modulus value is found to be higher. It becomes 141 ± 4.2 Mpa, after 2 weeks, and then 219 ± 6.6 Mpa, after 3 weeks of enzymatic hydrolysis; i.e., the rigidity of the blend rises. This could be associated to the continuous augmentation of the crystallinity rate during hydrolysis. The DSC results confirm this outcome. Yet, after 25 days of hydrolysis, the Young modulus undergoes a decrease: It reaches 187 ± 5.6 Mpa. This can be due to the mass loss at the end of hydrolytic degradation.

The mechanism of the hydrolysis of the (PCL/SBS) blend starts with a water absorption stage allowing the material to gain in plasticity. Consequently, its elongation to fracture rises and its Young modulus decreases. Afterwards, the weight drops with hydrolysis time, causing the embrittlement of the blends which engenders the decrease in the

Fig. 10 Blend (40% PCL/60% SBS) tensile curves during hydrolysis time



values its elongation to fracture and its fracture stress. However, the continuous crystallization of the mixture during hydrolysis time causes the increase in the Young modulus value. After 25 days of hydrolysis, we acquire samples of the blend (PCL/SBS) with different mechanical properties (Young modulus, elongation to fracture, and fracture stress). These samples with distinct properties will be used, in following works, to study the relation between the mechanical properties of the blend and its shape memory effect.

Conclusions

In this paper, hydrolytic degradation, using a pseudomonas fluorescence lipase, of PCL and of its SMP blend (40% PCL/60% SBS) has been achieved. Prior to degradation, PCL has shown a rigid character with a higher Young modulus and a higher fracture stress, compared with SBS and even the blend. However, the blend has been the most ductile because it has had an elongation to fracture equal to $292 \pm 8.8\%$, which has been higher than that of SBS ($149 \pm 4.5\%$). This result could be associated to the compatibility between the two polymers that constitute the mixture

(SBS/PCL). Likewise, the DMA and DSC results have confirmed the compatibility of the (SBS/PCL) blend, since its T_m , T_c , and X_c have matched those of PCL. Also, the blend has displayed two distinct T_α : one that corresponds to T_α of SBS and the other that corresponds to T_α of PCL. This result has indicated the immiscibility of the mixture. PCL and its Blend (PCL/SBS) have not kept the same properties when submitted to enzymatic hydrolysis. In fact, PCL has undergone a significant decrease in weight: It has lost up to 21% of its mass at the end of hydrolysis. Nevertheless, blending PCL with SBS has considerably reduced its degradation rate in the meaning of the weight drop, due to morphological changes. Moreover, the enzymatic hydrolysis has caused chains splitting, which has increased their mobility and facilitated their reorientation. Thus, for both, PCL and its blend, the degree of crystallinity X_c has gone up during hydrolysis. X_c of PCL has reached 67.2%, and X_c of the blend has attained 69.7%, which confirms that the amorphous regions of PCL are more susceptible to hydrolysis and degrade faster than the crystalline ones. Besides, the continuous crystallization causes the increase in the PCL and its blend glass transition, melting, and crystallization temperatures. Furthermore, for PCL and its blend, the Young-modulus value has shown two opposite evolutions. It has firstly risen, which is explained by the growth of crystallinity during hydrolysis time. However, the modulus value has dropped, after 25 days of hydrolysis, due to the weight loss and the materials embrittlement. Besides, the elongation to fracture and the fracture stress, for both polymers, have decreased with the hydrolytic degradation time. This diminution is explained by the mass loss and the polymers embrittlement.

Table 6 Blend mechanical properties alteration during hydrolytic degradation

Blend (40% PCL/60% SBS)	Young modulus (Mpa)	% Elongation to fracture	Fracture stress (Mpa)
Reference	116 ± 3.5	292 ± 8.8	7 ± 0.5
24 h	108 ± 3.2	356 ± 10.7	7 ± 0.2
1 week	144 ± 4.3	294 ± 8.8	7 ± 0.4
2 weeks	141 ± 4.2	123 ± 3.7	6 ± 0.5
3 weeks	219 ± 6.6	75 ± 2.2	6 ± 0.2
25 days	187 ± 5.6	61 ± 2	6 ± 0.3

At the end of enzymatic hydrolysis, we have obtained samples of the blend (40% PCL/60% SBS) with different physico-chemical and mechanical properties. Thus, the results in this work have been well used to investigate the

influence of hydrolytic degradation on the shape memory effect of the SMP blend (40% PCL/60% SBS) and to investigate the relation between the mechanical, thermal and microstructural properties of this blend and its shape memory properties.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Malberg S, Hoglund A, Albertsson AC (2011) Macromolecular design of aliphatic polyesters with maintained properties mechanical properties and a rapid, customized degradation profile. *Biomacromolecules* 12(6):2382–2388
- Gan Z, Liang Q, Zhang J, Jing X (1997) Enzymatic degradation of poly (ϵ -caprolactone) film in phosphate buffer solution containing lipases. *Polym Deg Stab* 56(2):209–213
- Tjong SC, Xu Y, Meng YZ (1999) Compatibility and degradation of blends of poly (caprolactone)–Poly (ethylene glycol) blocks copolymer and polypropylene. *Polymer* 40(13):3703–3710
- Tjong SC, Bei JZ (1998) Degradation behavior of poly (caprolactone)–poly (ethylene glycol) block copolymer/low-density polyethylene blends. *Polym Eng Sci* 38(3):392–402
- Zhang H, Wang H, Zhong W (2009) A novel type of shape memory polymer blend and the shape memory mechanism. *Polymer* 50(6):1596–1601
- Ben Abdallah A, Kallel A, Gamaoun F (2017) Shape memory property and driving force of the shape memory blend (40% PCL/60% SBS). In: 7th international conference design modeling mechanical system, Tunisia
- Behl M, Lendlein A (2007) Shape memory polymers. *Mater Today* 10(4):20–28
- Tcharktchi A, Abdallah-Elhirsiti S, Ebrahimi K, Fitoussi J, Shirinbayan M, Farzaneh S (2014) Some new concepts of shape memory effect of polymers. *Polymers* 6(4):1144–1163
- Farzaneh S, Fitoussi J, Lucas A, Bocquet M, Tcharktchi A (2012) Shape memory effect and shape memory properties of polyurethane. *J Appl Polym Sci* 28:3240–3249
- Hakkarainen M, Albertsson AC, Karlsson S (1996) Weight losses and molecular weight changes correlated with the evolution of hydroxyl-acids in simulated in vivo degradation of homo- and copolymers of PLA and PGA. *Polym Deg Stab* 52(3):283–291
- Benedict CV, Cook WJ, Jarrett P, Cameron JA, Huang SJ, Bell JP (1983) Biodegradable polymers. *J Appl Polym Sci* 28:327
- Mochizuki M, Hirano M, Kanmuri Y, Kudo K, Tokiwa Y (1995) Hydrolysis of poly (caprolactone) fibers by lipase: effect of draw ratio on enzymatic degradation. *J Appl Polym Sci* 55(2):289–296
- Marten E, Muller E, Deckwer WD (2003) Studies on the enzymatic hydrolysis of polyesters I. Low molecular mass model esters and aliphatic polyesters. *Polym Deg Stab* 80(3):485–501
- Liu L, Li S, Garreau H, Vert M (2000) Selective enzymatic degradations of poly (L-lactide) and poly (ϵ -caprolactone) blend films. *Biomacromolecules* 1(3):350–359
- Tokiwa Y, Ando T, Suzuki T (1976) Degradation of poly (caprolactone) by a fungus. *J Ferment Technol* 3:603–608
- Tsuji H, Ikarashi K (2004) In vitro hydrolysis of poly (L-lactide) crystalline residues as extended-chain crystallites: III. Effects of pH and enzyme. *Polym Deg Stab* 85(1):647–656
- Doi Y, Kasuya KI, Abe H, Koyama N, Koichi T, Shin I, Yoshida Y (1996) Evaluation of biodegradability's of biosynthetic and chemosynthetic polyesters in river water. *Polym Deg Stab* 51(3):281–287
- Jarrett P, Benedict CV, Bell JP, Cameron JA, Huang SJ (1984) In: Shalaby W (ed) *Polymers as biomaterials*. Springer, New York, p 181
- Tokiwa Y, Suzuki T (1977) Hydrolysis of polyesters by lipases. *Nature* 270:76–78
- Hakkarainen M, Albertsson AC (2008) Degradation products of Aaiphatic and aliphatic–aromatic polyesters. *Adv Polym Sci* 211(1):85–116
- Rizzarelli P, Impallomeni G, Montaudo G (2004) Evidence for selective hydrolysis of aliphatic copolyesters induced by lipase catalysis. *Biomacromolecules* 5(2):433–444
- Tsuji H, Ishizaka T (2001) Porous biodegradable polyesters. II. Physical properties, morphology, and enzymatic and alkaline hydrolysis of porous poly(ϵ -caprolactone) films. *J Appl Polym Sci* 80(12):2281–2291
- Tokiwa Y, Calabia BP, Ugwu CU, Aiba S (2009) Biodegradability of plastics. *Int J Mol Sci* 10(9):3722–3742
- Li S, Liu L, Garreau H, Vert M (2003) Lipase-catalyzed biodegradation of poly (ϵ -caprolactone) blended with various poly (lactide): based polymers. *Biomacromolecules* 4(2):372–377
- Patel HN, Thai KN, Chowdhury S, Singh R, Vohra YK, Thomas V (2015) In vitro degradation and cell attachment studies of a new electro-spun polymeric tubular graft. *Prog Biomater* 4(2–4):67–76
- Göpferich A (1996) Mechanisms of polymer degradation and erosion. *Biomaterials* 17(2):103–114
- Tsuji H, Ishizaka T (2001) Blends of aliphatic polyesters. VI. Lipase-catalyzed hydrolysis and visualized phase structure of biodegradable blends from poly (ϵ -caprolactone) and poly (L-lactide). *Inter J Biol Macromol* 29:83–89
- Tilstra L, Johnsonbaugh D (1993) The biodegradation of blends of poly (caprolactone) and polyethylene exposed to defined consortium of fungi. *J. Environ Polym Deg* 1(4):257–267
- Castilla-Cortázar I, Más-Estellés J, Meseguer-Dueñas JM, Escobar Ivirico JL, Marí B, Vidaurre A (2012) Hydrolytic and enzymatic degradation of a poly (ϵ -caprolactone) network. *Polym Deg Stab* 97(8):1241–1248
- Manandhar S (2011) Bioresorbable polymer blend scaffold for tissue engineering. University of North Texas, Denton, TX
- Biron M (2000) *Elastomères thermoplastiques (TPE)*. Technique de l'ingénieur, Saint-Denis
- Elzein T, Nasser-Eddine M, Delaite C, Bistac S, Dumas P (2004) FTIR study of polycaprolactone chain organization at interfaces. *J Colloid Int Sci* 273(2):381–387
- Massardier V (2001) Etat de l'art concernant la compatibilité des matières plastiques. INSA de Lyon, Villeurbanne
- Hayashi T, Kanai H, Hayashi T (2001) Enzymatic degradation of poly (ϵ -caprolactone) fibers in vitro. *Polym J* 33(1):38–41
- Fukushima K, Feijoo JL, Yang MC (2012) Abiotic degradation of poly (L-lactide), poly (caprolactone) and their blends. *Polym Deg Stab* 97:2347–2355
- Meseguer-Duenas JM, Mas-Estellés J, Castilla-Cortazar I, Escobar Ivirico JL, Vidaurre A (2011) Alkaline degradation study of linear and network poly (ϵ -caprolactone). *J Mater Sci Mater Med* 22(1):11–18