EXPERIMENTAL DEGRADATION CHARACTERIZATION OF PLA-PCL, PGA-PCL, PDO AND PGA FIBRES

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SUMMARY

Aliphatic polyesters, such as polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL) and polydioxone (PDO), have been commonly used in biodegradable products. In this experimental study, fibres of PLA-PCL, PGA-PCL, PDO and PGA were characterized in terms of their degradation rate under three different environments (water, NaCl and PBS).

INTRODUCTION

Aliphatic polyesters, such as polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL) and polydioxone (PDO), have been commonly used, alone or combined in blends or composites, in a variety of application on different markets. In the case of commodity products, biodegradable plastics claim clear environmental advantages in several brief use applications, mainly in the final stage of life (waste disposal), which can clearly be evident through life cycle assessment. In the biomedical field, an important application is on regenerative medicine, where they temporarily replace the biomechanical functions while the natural tissue regenerates. They have been also used in many controlled drugs release devices.

Performance of a device is conditioned by the materials selection and dimensioning of the product. For a biodegradable product, performance will decrease along its degradation. From the final user point of view, performance should be enough for the predicted use, during all its life cycle. Biodegradable plastics can present short term performances similar to conventional plastics. There are many biodegradable polymers commercially available to produce a great variety of plastic products, each of them with suitable properties according to the application. So, it is possible to find a large range of mechanical properties and degradation rates useful for a great variety of products for brief use.

The poly-α-hydroxyesters, polylactic acid (PLA), polyglycolic acid (PGA) and copolymers are the most popular aliphatic polyesters that have been synthesized for more than 30 years. The left-handed (L- lactide) and right-handed (D-lactide) are the two enantiometric forms of PLA, with PDLA having a much higher degradation rate

than PLLA. PLLA is a rather brittle polymer with a low degradation rate, and compounding with PCL is frequently employed to improve mechanical properties. PCL is also hydrophilic with a low degradation rate, much more ductile than PLA. PGA, since it is a hydrophilic material presents a high degradation rate. The combination of PGA with PLA is usually employed to tune degradation rate. In table 1, some physical properties of these aliphatic polyesters are resumed.

Table 1- Physical properties of PLLA, PDLA, PGA, PCL, PDO (based on [1] and [2])

Materials	Tg (ºC) [1]	Tm (ºC) [1]	Elastic Modulus (GPa) [1]	Tensile Strength (MPa) [1]	Tensile Elongation (%) [1]	Degradation Time (months) [2]
PLA	45-60	150-162	0.35-3.5	21-60	2.5-6	12-16
PLLA	55-65	170-200	2.7-4.14	15.5-150	3-10	> 24
PDLA	50-60	-------------	1.0-3.45	27.6-50	2-10	6-12
PLA/PGA (50:50)	40-50	-------------	1.0-4.34	41.4-55.2	2-10	3
PGA	35-45	220-233	6.0-7.0	60-99.7	1.5-20	6-12
PCL	-60 - -65	58-65	0.21-0.44	20.7-42	300-1000	> 24

Hydrolytic degradation

The degree of degradation is usually estimated from measurements of mass loss, mechanical strength or molecular weight. The percentage of weight loss, *WL%,* is computed from:

$$WL\% = 100(W_0 - W_r)/W_0 \qquad (1)$$

where W_0 and W_r are, respectively, the initial and the residual weight of the specimen.
The degradation of biopolymers consists essentially on two sequential processes: diffusion of an aqueous solution within the polymer, followed by hydrolytic degradation mediated either by water and/or enzymes. The overall rate is determined by the slowest reaction, named the rate-limiting step [3]. In the particular case of biodegradable polymers, water diffusion is very fast compared to water mediated hydrolysis. Therefore, water can be assumed to be uniformly distributed within the polymer and hydrolysis promotes homogeneous bulk erosion [4].
For aliphatic polyesters, hydrolysis rates are affected by temperature, molecular structure, ester group density and type of degradation media. The crystalline degree may be also a crucial factor, since the crystalline domains are less permeable to water penetration, slowing down hydrolysis.

The polymeric ester groups can be easily hydrolyzed, leading to chain scission (see figure 1). A general consequence is the lowering of the plastic flow ability of the polymer, thus causing an increase in brittleness.
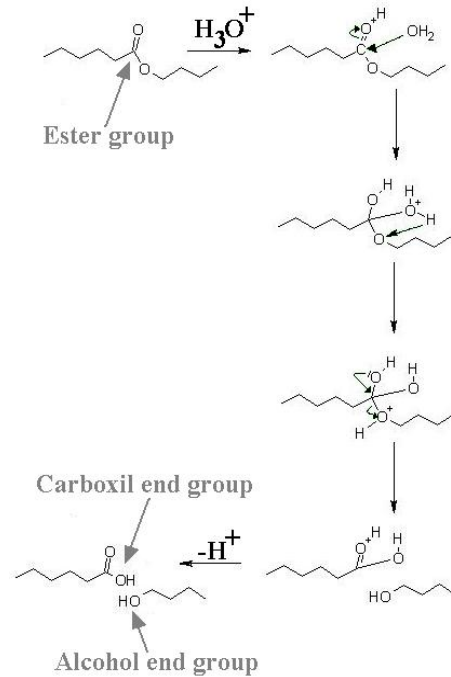

Figure 1 – Scheme of the most important hydrolysis mechanism

Polyester hydrolysis has been traditionally modeled using a first order kinetic mechanism, following the Michaelis–Menten scheme [5]. The following first-order equation describes the hydrolytic process [6], in terms of the rate of formation of carboxyl end groups:

$$\frac{dC}{dt} = kEWC = u_m C \qquad (2)$$

where E, C and W are the concentrations of ester groups, carboxyl groups and water in the polymer matrix, respectively, k is the kinetic constant and u_m is the apparent kinetic constant, assuming that E and W are constant in the early stages of the reaction. It is also assumed that water is uniformly distributed within the sample volume (no diffusion control). Since the concentration of carboxyl end groups is given by $C = 1/M_{n_t}$, where M_n is the number-average molecular weight of the polymer, equation 2 becomes, after integration:

$$M_{n_t} = M_{n_0} e^{-u_m t} \qquad (3)$$

It has been shown [7] that the fracture strength of a generic thermoplastic polymer can, in many cases, be related to M_n through the relationship:

$$\sigma = \sigma_\infty - \frac{B}{M_{n_t}} = \sigma_\infty - \frac{B}{M_{n_0} e^{-u_m t}} \qquad (4)$$

where σ is the fracture strength, σ_∞ is the fracture strength at infinite molecular weight, and B is a constant. Equation (4) provides a description of the time dependence of the material's mechanical strength, which is relevant in the design phase of a biodegradable device. As this is an empirical equation, constant B must be experimentally determined for each material.

EXPERIMENTAL WORK

Four different biodegradable plastics (PLA-PCL, PGA-PCL, PDO and PGA), representing a wide range of degradation times and mechanical properties, were provided by *Chirmax*. Suture fibers with two different diameters (150 μm and 400 μm) were used for measuring degradation properties. Three test pieces, each of 100 mm long, were cut from sterile suture fibres in biological safety chamber to avoid contamination. Fibres specimens were then placed in 50 ml test tubes and submitted to six different degradation steps under water, saline solution and PBS (phosphate buffer solution), at constant temperature (37°C) in a thermostatic bath. The duration of stages was previously determined, according to the supplier durability claims, until a maximum of 7 months.

Dry weight (24 h in incubator at 37°C) was measured initially and at the end of each step, to determine material erosion. For PLA-PCL specimens the number-average molecular weight was determined at the end of each step, by GPC Polymer PL50 (Gel Permeation Chromatography), using a *Polymer ResiPore* column (300 x 7.5 mm), and chloroform as solvent and eluent. Mechanical properties were also repeatedly evaluated at the end of each stage. A universal mechanical test machine (*TIRAtest 2705*) was used, with a load cell off 100 N, and pneumatic grips commonly used in fibre testing. The distance between grips was set for 50 mm. Three specimens were used for each fibre sample. The displacement rate was 500mm/min. The evolution curve of these physical properties was determined during degradation using this methodology.

RESULTS

Weight loss

Experimental results of weight loss are presented in figure 2 for the four materials immersed in the three degradation media. PGA-PCL fibres are the fastest in terms of weight loss. Although PCL has a low degradation rate, the combination with PGA results in a less crystalline plastic, and this may explain the faster degradation compared to PGA alone. It has become very fragile just after 2 weeks. It is followed by PGA, PDO and the less degradable PLA-PCL. Alkaline solution of PBS is the fast degrading media, except for PDO where water, with pH closed to neutral, degrades much faster

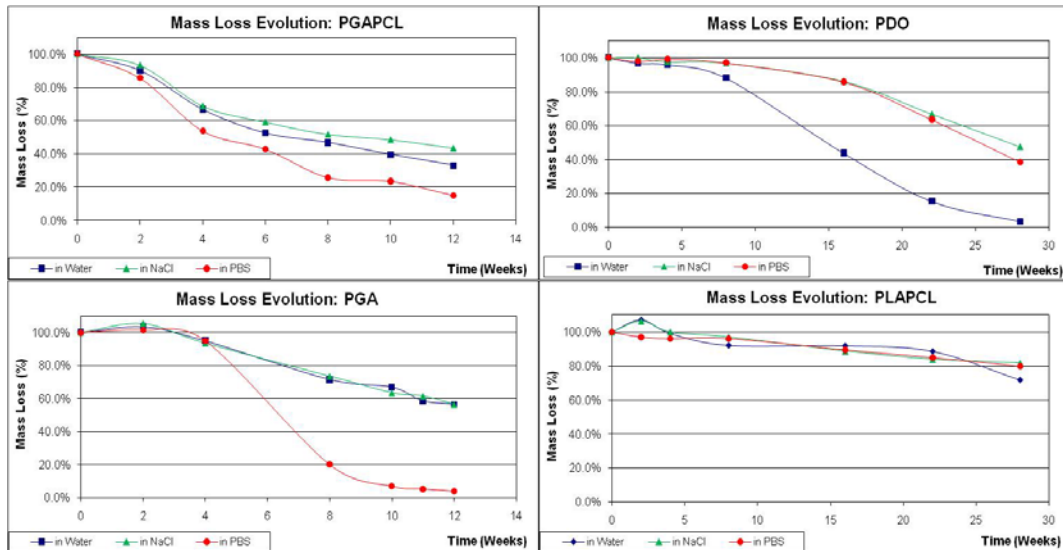than the other two media. For PLA-PCL no significant differences were observed between the three media.

Figure 2 – Relative weight loss of PGA-PCL, PDO, PGA and PLA-PCL suture fibres

Molecular weight evolutions

Molecular weight of PLA-PCL was steadily reduced. Results along degradation can be fitted into a first-order equation, with a very good approximation (see figure 3). No big differences in the molecular weight evolutions were found between different dimensions of specimens and between different degradation media.
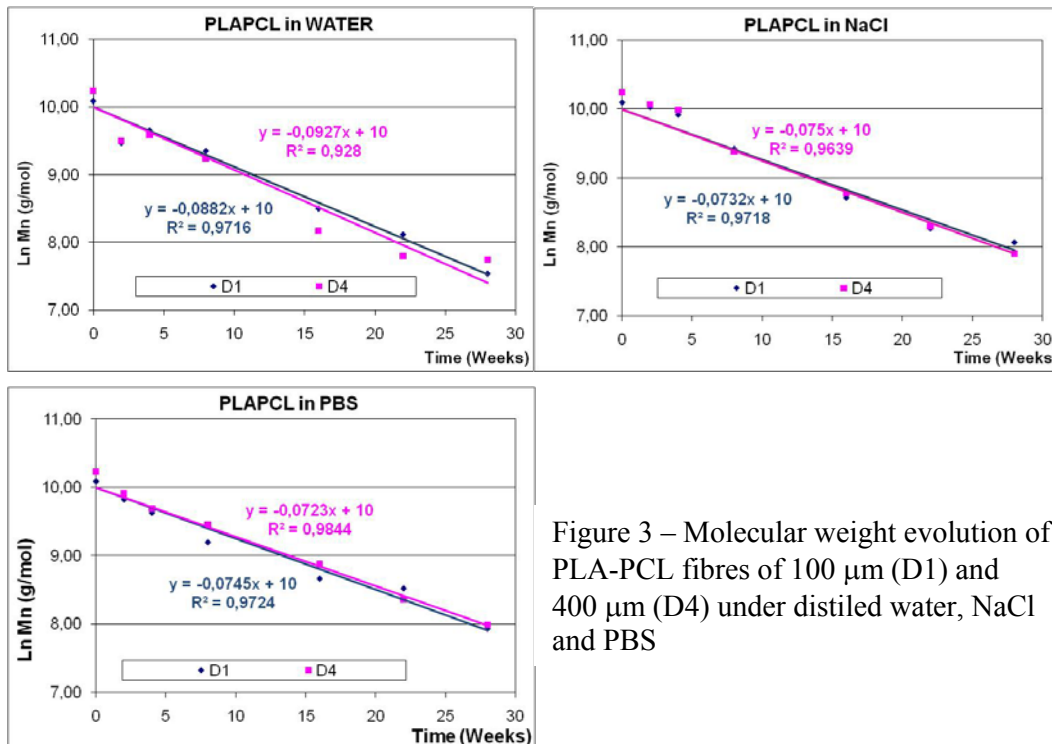

Figure 3 – Molecular weight evolution of PLA-PCL fibres of 100 μm (D1) and 400 μm (D4) under distiled water, NaCl and PBS

Mechanical Behaviour Evolutions

After two weeks of degradation, maximum load of PGA decrecased from 15 N to arround 2,5 N for the small diameter fibres and from 80 N to about 15 N for the larger diameter fibres. Their rupture has become brittle, not showing any plastic deformation. When considering relative results, there was no significant differences between dimensions, meaning that difusion has neglective influence on degradation.

Comparing the relative strength evolution of PDO suture fibres, significant differences between dimension were observed (see figure 4a) . These were more significant for slower degrading media (NaCl and PBS). A faster degradation is observerved for the biger diameter fibres, probably due to a more cristalline structure of small fibers. Water was much faster to degrade PDO strenght, while no significant differences in degradation rate was found between the other two media.
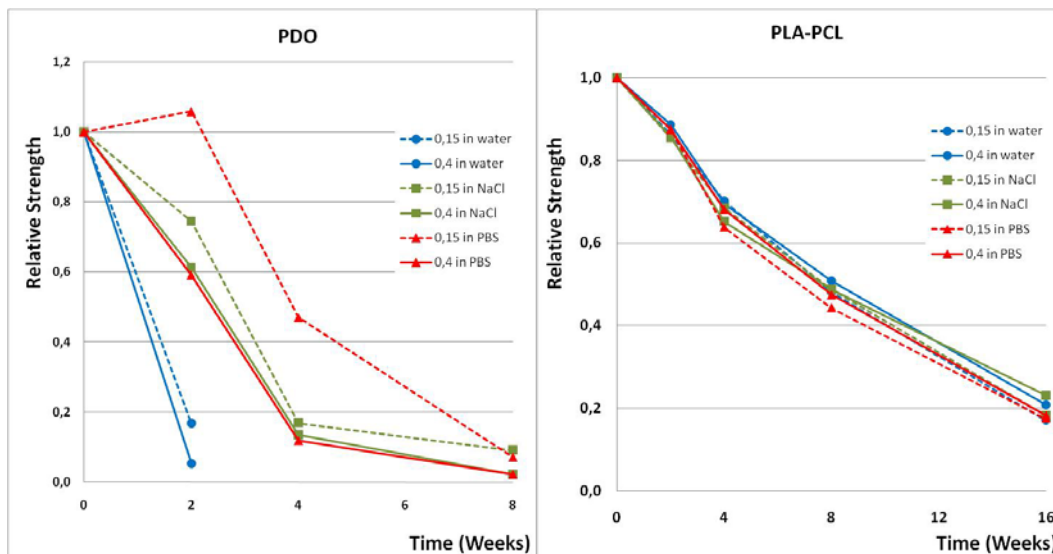

Figure 4 – Relative tensile strength evolution along degradation of: a) PDO and b) PLA-PCL fibres, of 150 µm and 400 µm diameter, under distiled water, NaCl and PBS

PLA-PCL has become brittle only after 16 weeks, but strength was progressevly reduced (see figure 5b). No significant differences between dimension were observed. One can assume that, also for PLA-PCL, difusion has neglective influence on degradation and hydrolisys starts homogenousely.

No tensile test results were available for PGA-PCL, since it was already very fragile without degradation, and it was impossible to test it after two weeks of degradation.
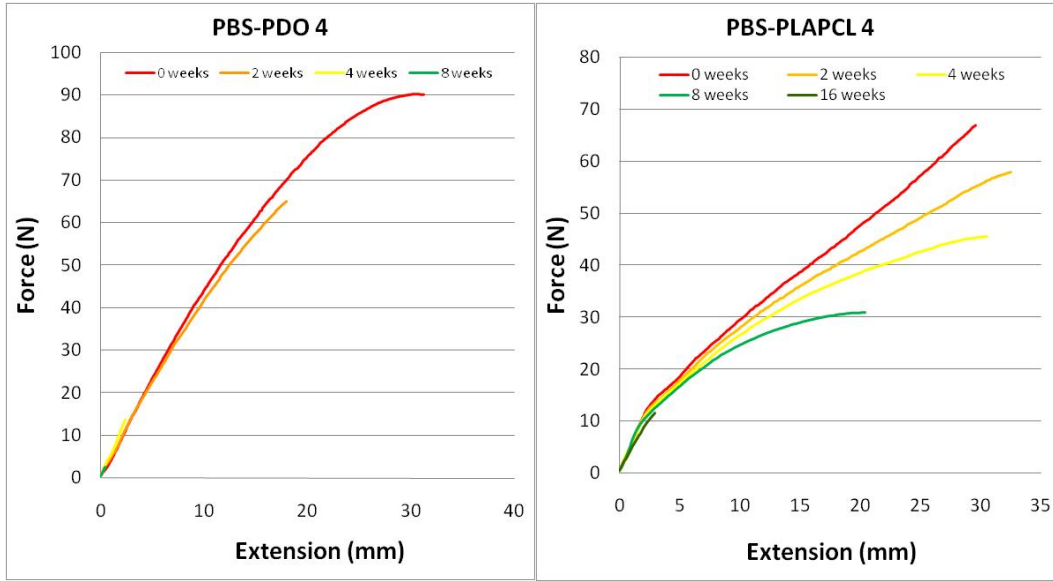
Figure 5 – Tensile curves along degradation of PLA-PCL and PDO fibres, 0.4mm diameter, under PBS.

From figure 5, no significant variation of Young modulus along degradation was found for the materials studied in this experimental work.

Furthermore, we had found that the strength evolution follows the same trend as the molecular weight. Instead of equation 4, it can be represented through a similar relationship obtained for the molecular weight,

$$\sigma = \sigma_0 e^{-u_s t} \qquad (5)$$

where u_s is the strength decrease rate of the material. Obviously the strength degradation rate, u_s, is directly related with the kinetic constant of the material, u_m, as can be seen in figure 6. In table 2 strength decrease rate of the three materials tested are presented. Based on these, one can thus determine the limit strength, $\sigma = f(t)$, for a device that weakens during degradation under 37ºC, according to the degradation media.

Table 2 – Degradation rate of strength of PLA-PCL, PDO and PGA incubated in water, saline and PBS at 37ºC

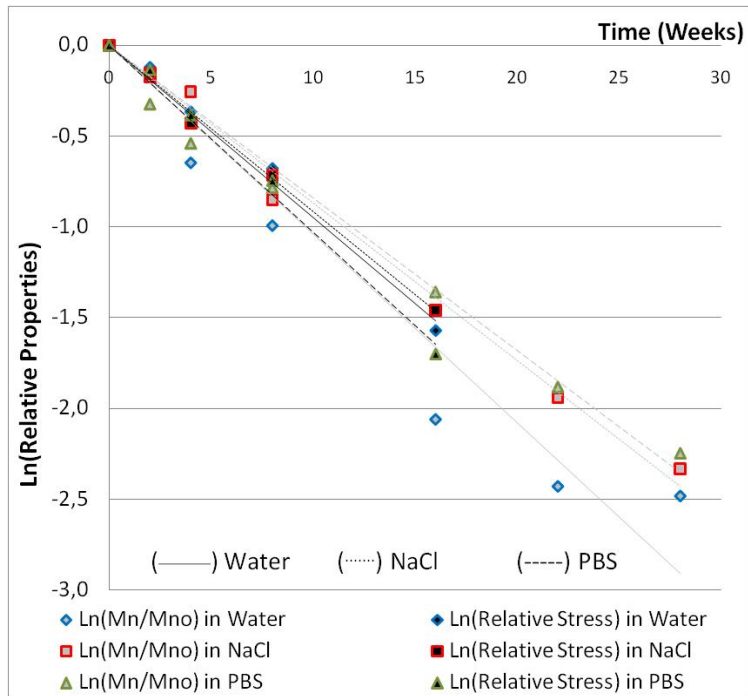| $\ln(\sigma/\sigma_o) = -u_s t$		u_s
	Water	0.092
PLA-PCL	NaCl	0.095
	PBS	0.103
	Water	1.481
PDO	NaCl	0.475
	PBS	0.483
	Water	0.848
PGA	NaCl	0.752
	PBS	0.797

Figure 6 - Relative molecular weigth (Mn/Mn$_o$) and relative tensile strength (σ/σ_o) evolutions, for PLA-PCL suture fibres of 400 µm, incubated in water, saline solution and PBS

CONCLUSIONS

Tensile strength evolution of ordinary biodegradable aliphatic polyesters, such as PLA, PGA, PCL, PDO and there combinations, can be determined along degradation time in fibers or other thin elements. This is possible since hydrolytic reaction is the limiting step of overall degradation process. Diffusion may be neglected in these cases, and hydrolysis may be considered to take place homogeneously within the sample volume. The degradation rate can be further used in the dimensioning of biodegradable devices, using a first order equation. From our results we also conclude, in agreement with [7] that tensile strength depends on molecular weight. However, Young modulus is independent of molecular weight.

In these cases when diffusion is neglected, the rule of mixtures can be further used to calculate the degradation rate of a composite of two or more biodegradable materials.

ACKNOWLEDGEMENTS

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