

Study of the high temperature HYDROLYSIS of POLY(EPSILON-CAPROLACTONE)

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Abstract

To study the hydrolytic degradation of poly(ϵ -caprolactone) (PCL) some samples were kept in water for some days and were weighed daily to determine the weight evolution. In order to accelerate the natural process of hydrolysis the samples were maintained in a heated thermal bath.

From this work it was possible to conclude that the hydrolysis of PCL occurs at high temperatures, around and slightly under its melting point, and that the hydrolysis rate is slightly smaller at 50°C than at 60°C.

Keywords: Polyester, Poly(epsilon-caprolactone), polymer hydrolysis, polymer degradation.

1 - Introduction

Poly(ϵ -caprolactone) (PCL) is a polyester with special and unique properties: it is biodegradable, unlike other saturated and unsaturated polyesters that don't suffer biological degradation; it is miscible with a wide variety of other polymeric materials; it crystallises very readily and finally it is non-toxic and of great permeability (Hiljanen, 1996; Mark, 1965).

PCL is a bioerodible polymer that degrades by hydrolysis with random chain scission in a process that is autocatalysed by the generation of carboxylic acid end groups. The degradation of PCL occurs in two stages: the first one involving a decrease in the molecular weight due to nonenzymatic, random, hydrolytic scission of ester cleavage, and the second one characterized by mass loss and loss of mechanical strength as well as a change in chain scission rate. The chemical erosion may be heterogeneous, occurring at the polymer surface, or homogeneous, causing degradation through the polymer matrix at a constant rate, and these two mechanisms can take place

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simultaneously (Malin, 1996).

Hydrolysable copolymers constitute a very important group of polymeric materials that have recently known an incredible increase in their possible applications. One of the most critical properties of these copolymers is their rate of degradation, that is strongly affected by the degree of crystallinity, the molecular weight and chemical composition. From the degradable polymers the aliphatic polyesters are the most used in medical applications, because they degrade by hydrolysis producing components that are resorbed by the body tissues with minimal reaction (Lofgren, 1994; Malin, 1996).

Due to its properties PCL has been largely used in medical applications, and it is also very appropriate for the production of various copolymers with mechanical properties varying from rigid to elastomeric. The elastomeric copolymers of PCL have good elongation characteristics, making them very useful for applications that require both elasticity and degradability (Karjalainen, 1996). Lately the hydrolysable and biocompatible copolymers of ϵ -caprolactone and L-lactide have been widely used in the medical field, in applications that include surgical sutures, temporary scaffolds for hard and soft tissue and implantable drug delivery devices (Karjalainen, 1996; Storey, 1994).

The biodegradability and lack of toxicity of PCL allows a controlled release of drugs from polymer devices implanted under the skin. When PCL is used in the form of a copolymer its melting point may be reduced to values under body temperature, which enhances its degradation rate (Fukuzaki, 1990; Pitt, 1987; Vion, 1986).

2 - Experimental

To study the degree of hydrolytic degradation of PCL in pure water at neutral pH, a set of samples was prepared and left in a thermal bath for some days to evaluate the weight evolution.

The hydrolysis process was studied at high temperature, close to the melting point of the polymer, and therefore the samples were kept in the thermal bath at 50°C and 60°C.

Material: The samples consisted of plastic tablets with 4*6*49mm, produced by extrusion from poly- ϵ -caprolactone commercialised under *Tone P-700 Polymer* (Union Carbide Co).

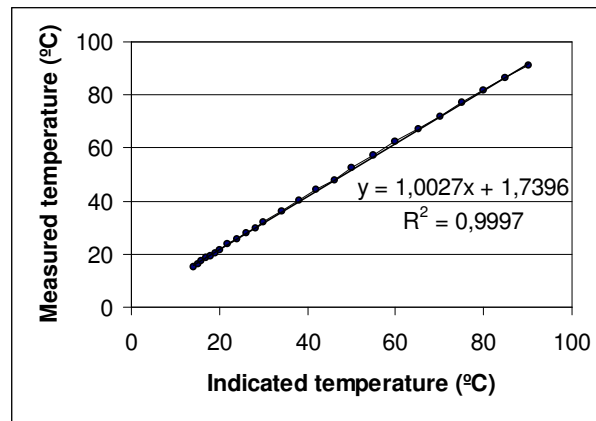
Equipment: Thermal bath SALVIS

2.1 - Calibration of the thermal bath

To test whether the thermal bath was working properly some temperature checkings were made by measuring the actual temperature of the bath and comparing it with the temperature indicated by the thermal equipment. As it was observed a discrepancy of about 2°C between the two values, a calibration of the thermal bath was carried out in the range of temperatures from 14°C to 90°C and the indicated and measured temperatures were registered. The speed was set to 3 strokes/min and to make the measurements of the bath temperature 3 different thermometers were used.

The resulting calibration curve is presented in Figure 1.

Figure 1 - Thermal bath calibration curve.



2.2 - Experimental procedure

In general terms the experimental procedure was as follows:

- Turn on the thermal bath to the desired temperature with a speed of 3 strokes/min.
- Fill 10 glass tubes with 10 ml of distilled water (pH=7), close them and put them in the bath.
- Weight the 10 pieces of polymeric material separately.
- When the bath and the water in the tubes reach the desired temperature the samples are put in the tubes.
- weight the samples daily.

The first experiment was carried out with the thermal bath temperature set to 60°C, which is a temperature near the melting point of the polymer. Five hours after having been put in water the polymeric tablets were melting and the samples were maintained in the bath at 60°C until the next day. After 24 hours the samples were solidified by cooling the water from the bath with ice, and then were taken out of the water and the excess of moisture was gently eliminated with a paper tissue, after which they were weighed. Finally, the samples were dried under vacuum at 50°C for another 24 hours and weighed again.

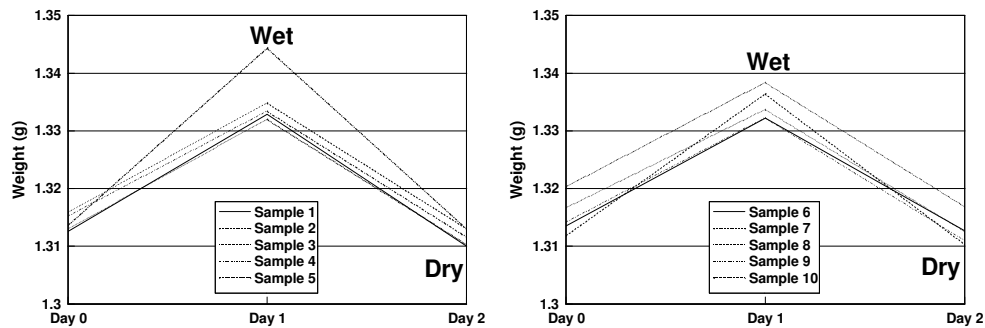
The second experiment was carried out at 50°C, also a high temperature but under the melting point of PCL, and the procedure was as described earlier in this section.

3 - Results and discussion

In figure 2 the results from the experiment at 60°C are presented and it is clear that the behaviour of all the samples is similar, showing an increase in weight from day 0 to day 1 and a decrease to a lesser value than the initial one from day 1 to day 2.

This increase in weight observed at first does not at all mean that the polymer tablets did not suffer hydrolysis. In fact, because they were weighed immediately after coming out of the bath and having just been superficially dried, this increase was most likely due to the water present inside the tablets. This hypothesis has later been proved to be true by drying the samples in the oven under vacuum for 24 hours at 50°C. During this drying period the retained water was removed by evaporation and the weight of the samples at the 2nd day was actually less than initially. Therefore, this experiment shows that there is a weight loss in the polymeric tablets, although the overall variation in weight is less than 1% to all samples (approximately 0.2 to 0.3%), leading to the conclusion that in some small degree the hydrolysis of the PCL occurs in the conditions tested.

Figure 2 – Evolution of weight of the PCL tablets in the experiment at 60 °C.



A second experiment was produced with the thermal bath temperature set to 50°C and was carried out for a longer period, 23 days, and the results are presented in Table I.

For better visualisation of weight variations along time, the data from table I was compiled in two graphics represented in figures 3 and 4, which correspond respectively to samples 1 to 5 and 6 to 10. By observing these two figures it is possible once more to establish a common behaviour, as the samples show periodical increases in weight around days 1-2 and again around days 6-7, to decrease to an approximately constant value after the 9th day.

The increase in weight of about 0.4% observed after 3 weeks in water (at the end of day 21) is due to the water retained in the PCL sample, and that is clearly proved by the weight values after drying, at the 22nd day, which show a decrease of 0.4% in relation to the initial values.

Table I - Weight of the polymeric tablets in the experiment at 50°C (g).

Time	Sample nº									
	1	2	3	4	5	6	7	8	9	10
Day 0(1)	1.3126	1.3260	1.3104	1.3187	1.3121	1.3110	1.3261	1.3210	1.3229	1.3265
Day 1(2)	1.3193	1.3334	1.3171	1.3269	1.3191	1.3180	1.3342	1.3288	1.3305	1.3336
Day 2	1.3187	1.3354	1.3174	1.3257	1.3210	1.3179	1.3333	1.3294	1.3301	1.3351
Day 6	1.3184	1.3323	1.3160	1.3257	1.3180	1.3172	1.3324	1.3295	1.3297	1.3330
Day 7	1.3189	1.3317	1.3172	1.3256	1.3180	1.3169	1.3340	1.3268	1.3286	1.3329
Day 8	1.3179	1.3333	1.3170	1.3244	1.3180	1.3175	1.3318	1.3269	1.3300	1.3352
Day 9	1.3177	1.3316	1.3159	1.3240	1.3174	1.3164	1.3316	1.3267	1.3287	1.3323
Day 10	1.3176	1.3313	1.3157	1.3239	1.3173	1.3164	1.3316	1.3267	1.3285	1.3317
Day 13	1.3174	1.3312	1.3154	1.3238	1.3170	1.3160	1.3313	1.3262	1.3280	1.3312
Day 15	1.3173	1.3312	1.3154	1.3238	1.3171	1.3161	1.3313	1.3263	1.3284	1.3313
Day 21	1.3174	1.3310	1.3152	1.3244	1.3172	1.3160	1.3311	1.3262	1.3282	1.3312
Day 22(3)	1.3066	1.3207	1.3053	1.3134	1.3065	1.3056	1.3206	1.3162	1.3179	1.3208
	Variation in weight (%) (4)									
WET	+0.366	+0.377	+0.366	+0.432	+0.389	+0.381	+0.377	+0.394	+0.401	+0.354
DRY	-0.457	-0.400	-0.389	-0.402	-0.427	-0.412	-0.415	-0.363	-0.378	-0.430

- (1) Before being put into water.
- (2) 24 hours after being in water.
- (3) After being in the oven under vacuum for 24 hours at 50°C.
- (4) Calculated relatively to the initial weight:

$$\text{Variation} = (\text{final weight} - \text{initial weight}) / (\text{initial weight}) * 100 \%$$

The final weight is considered at day 21 for WET and at day 22 for DRY.

Figure 3 – Evolution of weight variations in time (samples 1 to 5).

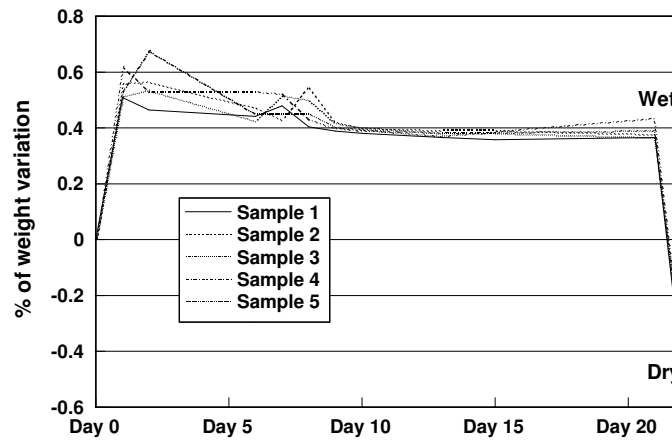
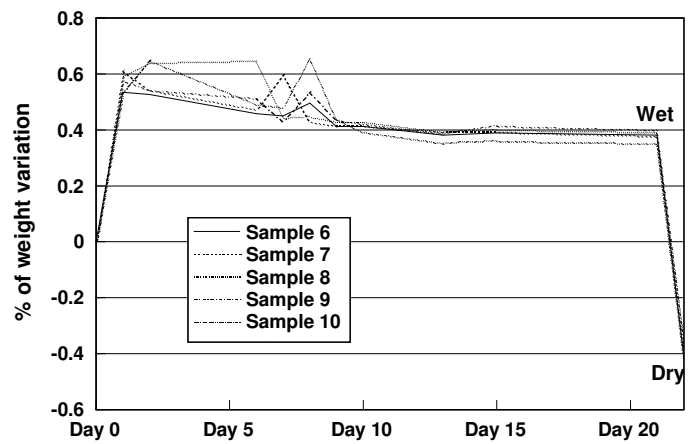


Figure 4 – Evolution of weight variations in time (samples 6 to 10).



4 - Conclusions

From this work it is possible to infer that the hydrolysis of poly(ϵ -caprolactone) occurs at high temperatures, around and slightly under its melting point, although the hydrolysis rate is naturally a little bit smaller at 50°C than at 60°C.

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