

Hydrolysis of Lactic Acid Based Poly(ester-urethane)s

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Abstract: The hydrolysis behaviour of lactic acid based poly(ester-urethane)s has been studied in a buffer solution of pH 7.00 at 37 and 55°C. Samples were prepared using a straight two step lactic acid polymerization process. The lactic acid was first polymerized by condensation with a low molecular weight by hydroxyl terminated telechelic prepolymer and the molecular weight then was increased with a chain extender such as a diisocyanate. In the hydrolysis study, the effect on the hydrolysis rate of different stereostructures (different amount of D-units in the polymer chain) and the length of the ester units were studied. The rate of hydrolysis was examined by various techniques including weighing (water absorption and weight loss), GPC (molecular weight and polydispersity), and DSC (thermal properties). GPC measurements showed that at 37°C the weight average molecular weight of the poly(ester-urethane)s started to decrease slowly during the first week of hydrolysis, but that at 55°C the weight average molecular weight decreased dramatically during the first week of hydrolysis. Significant mass loss occurred later at both temperatures. © 1998 Society of Chemical Industry

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INTRODUCTION

Poly(ester-urethane)s (PEUs) are polymers which contain low molecular weight polyester chains connected together by diisocyanates. The types and lengths of the polyester units so joined determine whether the final PEU will be rubbery or glassy at room temperature.¹ Furthermore, PEUs derived from long chain polyesters have been observed to hydrolyse to a greater extent than those manufactured from shorter chain polyesters.² Of the bonds present in PEUs, the most susceptible to hydrolysis is the ester, which reverts to carboxylic acid and alcohol. The acids produced in this reaction further catalyse the ester hydrolysis so that the autocatalysis reaction becomes prevalent.³ According to the literature, the hydrolysis of urethane bonds is one order of magnitude slower than that of ester bonds, so that its effect on the molecular weight decrease is practically negligible.^{1,3,4} PEUs have also been shown to be

susceptible to commercially available lipases and to purified esterase enzymes extracted from fungi.⁵ In addition, the suggestion that bacteria may play a significant role in the biodegradation and biodeterioration of PEUs has been made.⁶ Owen *et al.*⁷ found that the rate of weight loss of poly(D,L-lactic acid) PU compounds when shaken in a fungal culture increased when (i) the polyisocyanate content in the polyurethane was reduced, (ii) the molecular weight of the polyethylene glycol moiety of the polyol was increased and (iii) the lactic acid content in the polyol was increased. The hydrolysis studies^{1,3,4,8} have usually been carried out with commercial PEUs such as Estane 54600 (ester segments were made from adipic acid and 1,4-butanediol, methylenediphenylisocyanate (MDI) was used as the diisocyanate, and the chain extender was 1,4-butanediol) and the hydrolytic degradation is not a desired polymer property.

In our case, the prepolymers were synthesized from lactic acid^{9–11} and these prepolymer chains were joined together with aliphatic 1,6-hexamethylene diisocya-

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nate.¹²⁻¹⁴ The resulting PEUs are required for applications where these materials are composed after use. This kind of material is important, for example, in food packaging applications. Before composting it is important to clarify how these materials degrade upon hydrolysis. In an earlier study,¹⁵ we investigated how these PEUs biodegraded in the head-space test. In this test biodegradation was followed by measuring the resulting amount of carbon dioxide formed. It was not possible to measure the change in polymer properties. In the head-space study,¹⁵ we noticed that lactic acid based PEUs were stable at room temperature but they biodegraded at elevated temperatures. At 25°C the highest biodegradation percentage was only 0.6% after 63 days, indicating that these materials are not hydrolysable at room temperature. The hydrolysis temperatures 37°C and 55°C used in this paper were chosen because at these temperatures the polymer chains seemed to biodegrade within a reasonable time. The purpose has been to study how the properties of PEUs changed during the hydrolysis at elevated temperatures. The hydrolysis was followed by measuring the water absorption, weight loss and decrease in molecular weight.

In the PEUs tested, the polyester chains were synthesized by a straight polycondensation of L- or D,L-lactic acid, or a mixture of both, and the polyester chains were connected together using, 1,6-hexamethylene diisocyanate as a chain extender. Different PEUs were synthesized on a laboratory scale, and in the hydrolysis tests the effects of different stereostructures, the length of the polyester chains in the final PEU and the hydrolysis temperature were studied.

EXPERIMENTAL

Materials

PEUs were prepared and analysed as described in our earlier work.⁹⁻¹⁵ PEUs were polymerized by a two-step bulk polymerization process. The first step was the condensation polymerization of lactic acid with 1, 2 or 4 mol% of 1,4-butanediol, using Sn(II)octoate (0.05 wt%) as a catalyst to form a low molecular weight hydroxyl terminated prepolymer. A typical batch size was 6000 g of 88% aqueous solution of lactic acid. Different amounts of 1,4-butanediol were used to control the molecular weight of the prepolymer. The polymerization temperature was increased to 205°C and the pressure was decreased to 20 mbar in 8 h. Typically the condensation polymerization time was 15 h. The colour of the prepolymers was slightly yellow.

The second step was to link prepolymer molecules together with 1,6-hexamethylenediisocyanate to form high molecular weight PEU. Chain extension was started after the acid number of the prepolymer had dropped below unity. The polymerization temperature

was then decreased to 180°C and kept constant during chain extension. The amount of 1,6-hexamethylenediisocyanate was chosen so that the isocyanate: hydroxyl end group ratio was unity. The chain extension time was about 30 min. After polymerization, the polymer was pelletized, vacuum dried and analysed.

Polymer samples for hydrolysis were prepared by compression moulding (Fontijne TP 400) at 160°C. Test specimens (20 × 20 × 3 mm³) were cut from moulded plates with a saw.

Hydrolysis study

For each hydrolysis time, three weighed parallel test specimens were placed in test tubes immersed in 20 ml of phosphate buffer solution at pH 7.00 ± 0.01 at 37°C or 55°C. The buffer solution was changed every other week. The sample concentration was 0.025 ± 0.05 g ml⁻¹ at the beginning of the study. The gently mixed water baths (SALVIS SBK 25D) maintained the set temperature value with an accuracy of ±0.2°C. The test specimens were recovered from the test tubes at different intervals and weighed. Specimens were then vacuum dried for 6 days at 30°C and stored in a dessicator for further analysis.

Characterizations

Molecular weights (\bar{M}_n and \bar{M}_w) and polydispersity (\bar{M}_w/\bar{M}_n) were determined with respect to polystyrene standards by gel permeation chromatography. The Waters Associates system that was used was equipped with a Waters 700 Satellite visp injector, a Waters 510 HPLC solvent pump, four linear PL gel columns (10⁵ Å, 10⁴ Å, 10³ Å and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analysed at room temperature. Chloroform was used as eluent. The eluent was delivered at a flow rate of 1.0 ml min⁻¹. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 µl.

Differential scanning calorimetric (DSC) measurements were made on a PL Thermal Sciences DSC. The measurements were run from -50 to 200°C at a heating rate of 10°C min⁻¹. The glass transition temperatures were determined from the second heating period.

RESULTS AND DISCUSSION

Test materials

The detailed analysis of the prepolymers and PEUs has been described in our previous studies.⁹⁻¹⁵ The properties of the PEUs used in the hydrolysis tests are collected in Table 1. The GPC was calibrated with narrow

TABLE 1. Properties of poly(ester-urethane)s used in the hydrolysis study

| Polymer | Prepolymer | | | | | | Poly(ester-urethane) | | |
|---------|-----------------------------------------|-----------------------------------------|---------------|-----------------------------------------|-------------------|-------------------------------------|-----------------------------------------|-----------------------------------------|---------------|
| | \bar{M}_n^a (g mol ⁻¹) | \bar{M}_w^a (g mol ⁻¹) | T_g (°C) | \bar{M}_n^b (g mol ⁻¹) | Lactide (mol%) | D structures ^b (mol%) | \bar{M}_n^a (g mol ⁻¹) | \bar{M}_w^a (g mol ⁻¹) | T_g (°C) |
| 1 | 6 800 | 10 300 | 40 | 3 000 | 2.4 | 27.2 | 68 800 | 110 200 | 47 |
| 2 | 5 300 | 9 500 | 33 | 2 900 | 1.9 | 64.1 | 66 200 | 106 900 | 43 |
| 3 | 5 300 | 10 000 | 31 | 3 000 | 2.6 | 76.4 | 62 800 | 103 700 | 41 |
| 4 | 3 400 | 4 900 | 27 | 1 500 | 2.1 | 26.9 | 46 700 | 71 500 | 44 |
| 5 | 15 300 | 22 200 | 46 | 6 600 | 2.8 | 25.9 | 79 700 | 127 600 | 50 |

^a GPC.^b NMR.

polystyrene standards, and therefore the GPC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. The prepolymer data in Table 1 shows the properties of the polyester block, and the PEU data describe the properties of urethanes which are formed when the hydroxyl terminated ester blocks are joined together with urethane bonds. The prepolymer contained less than 2.8 mol% of lactide and less than 1 mol% of lactic acid monomer measured by ¹³C NMR, but the final PEU was lactide- and monomer-free.

Water absorption and weight loss

The water absorption was determined in order to evaluate the degree of swelling, which indicates the hydrophilicity of the polymer. Water absorption was calculated as the difference between the weight of the wet polymer sample after hydrolysis and the weight of the dried sample, divided by the weight of the dried polymer. Similarly, mass losses were calculated as the difference

between the initial weight of the polymer and the weight of the dried polymer, divided by the initial weight of the polymer.

The water absorption of PEUs as a function of hydrolysis time at 37°C and 55°C is presented in Figs 1 and 2. For all PEUs the water absorption increased throughout the hydrolysis period. At 37°C the water absorption of different samples after 80 days' hydrolysis varied from 50 to 200 wt%, while at 55°C and after 50 days' hydrolysis the corresponding values varied from 400 to 2500 wt%. At both temperatures, the PEUs which were synthesized from D,L-lactic acid (2 and 3) reached the highest water absorption values, and at the end of the hydrolysis period the samples were gel-like. The gelled sample form explains why these polymers could absorb so much water. There were no big differences in water absorption behaviour between any of the L-lactic acid based PEUs, despite the fact that they contained different molecular weight ester blocks. Furthermore, the water absorption of D,L-lactic acid polymers increased considerably during hydrolysis, whereas the

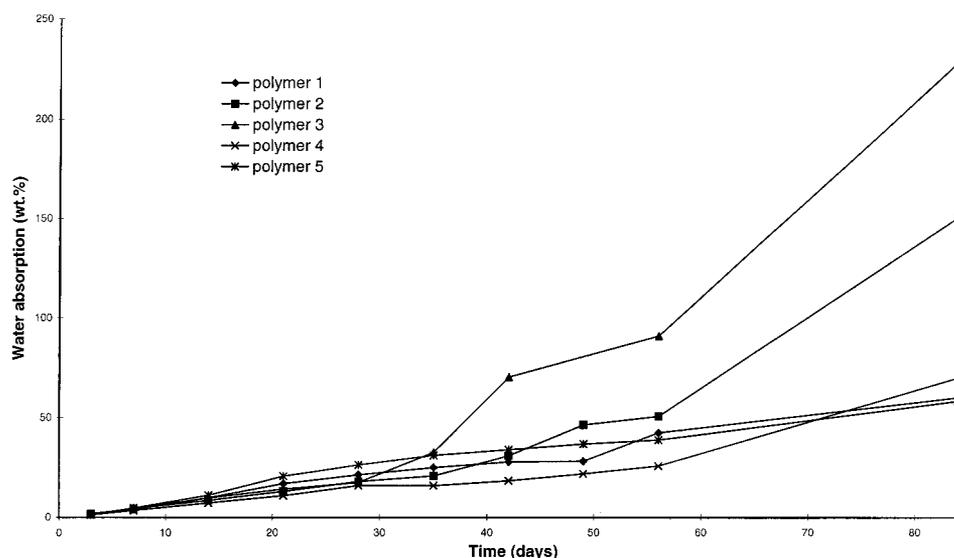


Fig. 1. Water absorption of poly(ester-urethane)s as a function of hydrolysis time at 37°C.

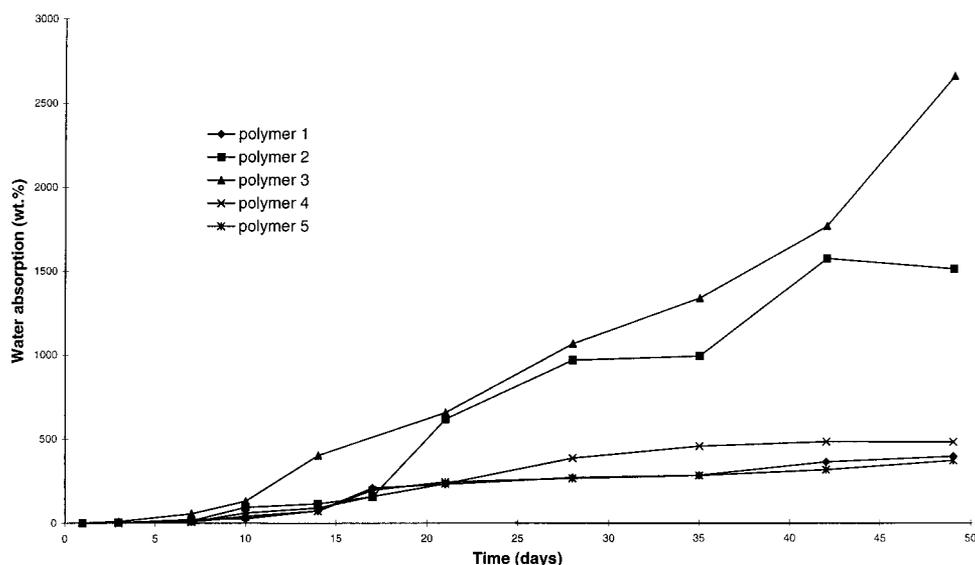


Fig. 2. Water absorption of poly(ester-urethane)s as a function of hydrolysis time at 55°C.

water absorption curves for L-lactic acid polymers were quite linear. All PEUs tested were amorphous but only D,L-lactic acid based polymers formed a gel at the end of the hydrolysis period.

The weight loss curves of the PEUs as a function of hydrolysis time at 37 and 55°C are presented in Figs 3 and 4. At 37°C, the weight loss started after 40 days' hydrolysis for all samples. The influence of the stereoisomerism on the weight loss is clear. The more D-lactic acid structures the PEUs contained, the faster the weight decreased during hydrolysis. For the PEU synthesized from pure D,L-lactic acid (polymer 3) the weight loss was especially fast after 40 days' hydrolysis. For L-lactic acid based PEUs the weight loss was almost linear after 40 days. The longer the ester block in the PEU, the slower the weight loss. At 55°C, the weight

loss started after 3 days' hydrolysis and the behaviour of the weight loss was similar to that at 37°C, except that the weight loss percentages were much bigger at 55°C. The D,L-lactic acid based PEU hydrolysed almost completely, while the long ester block L-lactic acid based PEU (polymer 5) lost 60% of its original weight after 50 days' hydrolysis.

The hydrolysis behaviour of the PEUs was different to that reported for polylactide.¹⁶⁻¹⁸ The PEUs did not degrade more slowly at the surface of the sample as did polylactides. At the beginning (1-3 days) of the hydrolysis there was a white layer at the surface of the samples but the centres of the samples were still harder than the surface. For L-lactic acid based PEUs the samples were almost powdered by the end of hydrolysis and there was no empty core structure during hydro-

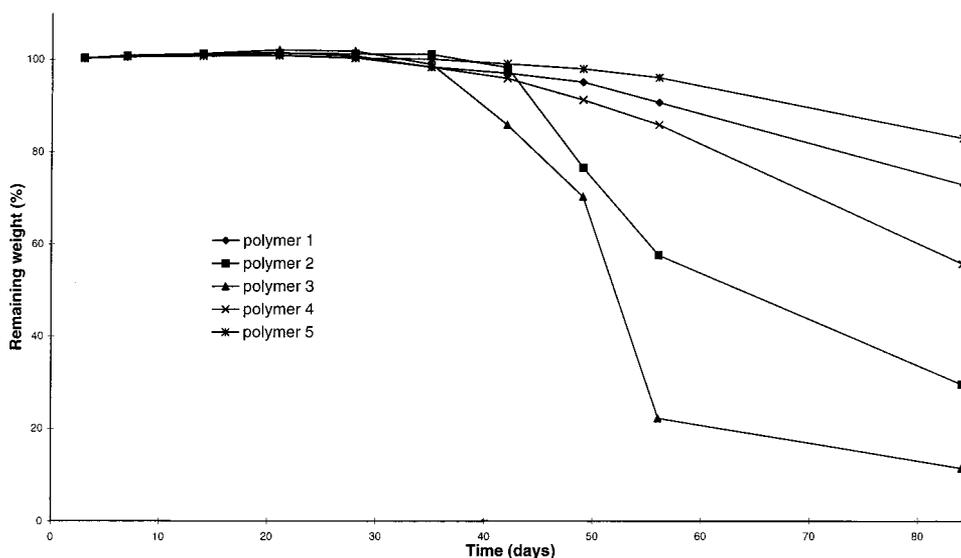


Fig. 3. Weight loss curves of poly(ester-urethane)s as a function of hydrolysis time at 37°C.

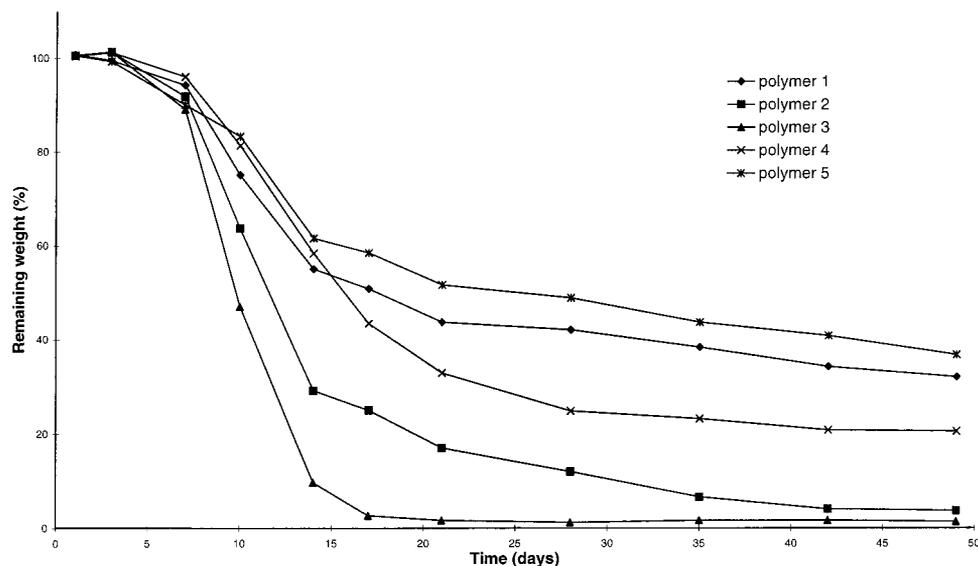


Fig. 4. Weight loss curves of poly(ester-urethane)s as a function of hydrolysis time at 55°C.

lysis, as mentioned in the literature for lactide-based polymers.^{16–18} D,L-Lactic acid samples softened smoothly and were gel-like at the end of hydrolysis.

Decrease in molecular weights

The most sensitive parameters for studying degradation effects are molecular weight and molecular weight distribution. According to the literature, the molecular weight has to be reduced substantially to permit mass loss through solubilization.¹⁹ A large decrease in molecular weight at the beginning of hydrolysis is generally assumed to be indicative of random scission of the polymeric chains.²⁰ The weight average molecular weight curves of PEUs tested at 37 and 55°C are presented in Figs 5 and 6.

As expected, the molecular weights of the PEUs decreased faster when the amount of D,L-lactic acid structures was increased. At 37°C, the degradation rate

can be controlled by the stereostructure and by the length of the ester block, but at 55°C the weight average molecular weight of all samples decreased considerably during the first 3 days. At 37°C, the molecular weight of the PEUs tested decreased slowly for L-lactic acid based polymers, but for D,L-lactic acid based polymers the decrease was much faster after 10 days' hydrolysis. The totally amorphous D,L-lactic acid polymers could not resist hydrolysis and therefore the molecular weight of these polymers decreased rapidly, while L-lactic acid polymers seemed to resist hydrolysis slightly better.

At 55°C, the molecular weight of all PEUs had already collapsed after 3 days' hydrolysis. This temperature is above the glass transition temperature of all the polymers but the hydrolysis still decreased the molecular weight of these polymers remarkably fast. At this temperature the hydrolysis mechanism is apparently random chain scission, because the decrease in molecular weight was so rapid.

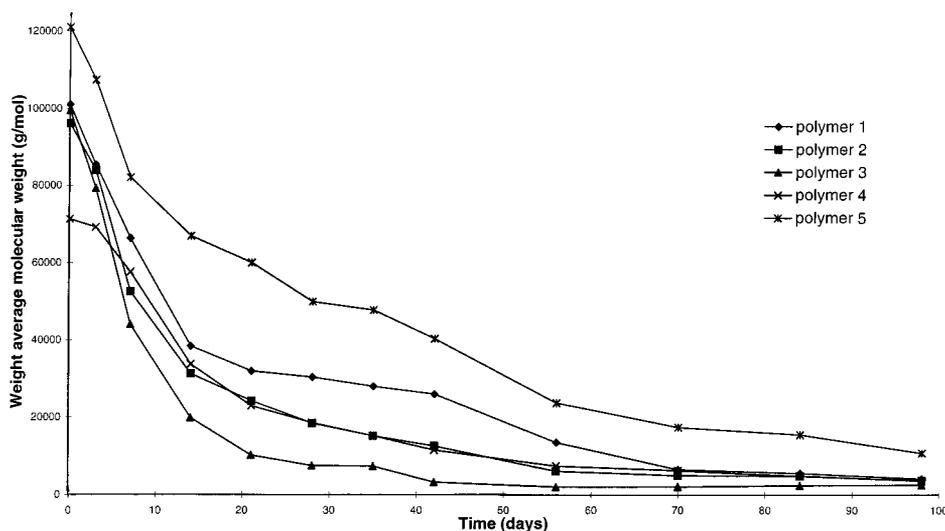


Fig. 5. Decrease in weight average molecular weight during hydrolysis at 37°C.

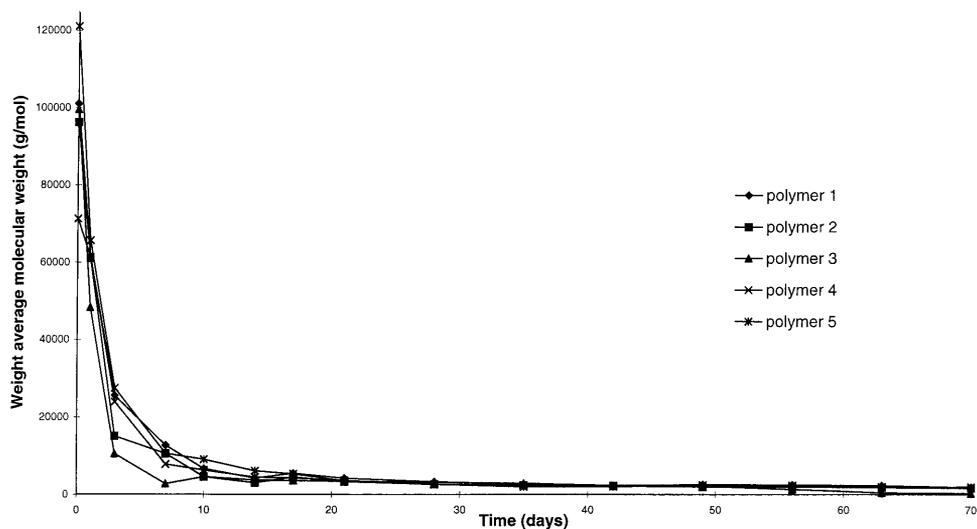


Fig. 6. Decrease in weight average molecular weight during hydrolysis at 55°C.

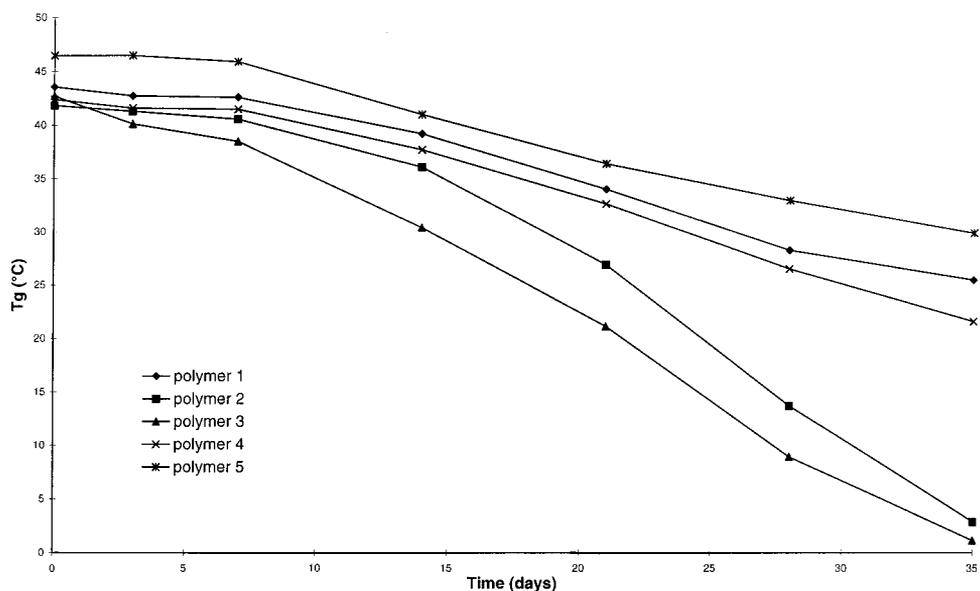


Fig. 7. Behaviour of the glass transition temperature at 37°C during 35 days' hydrolysis.

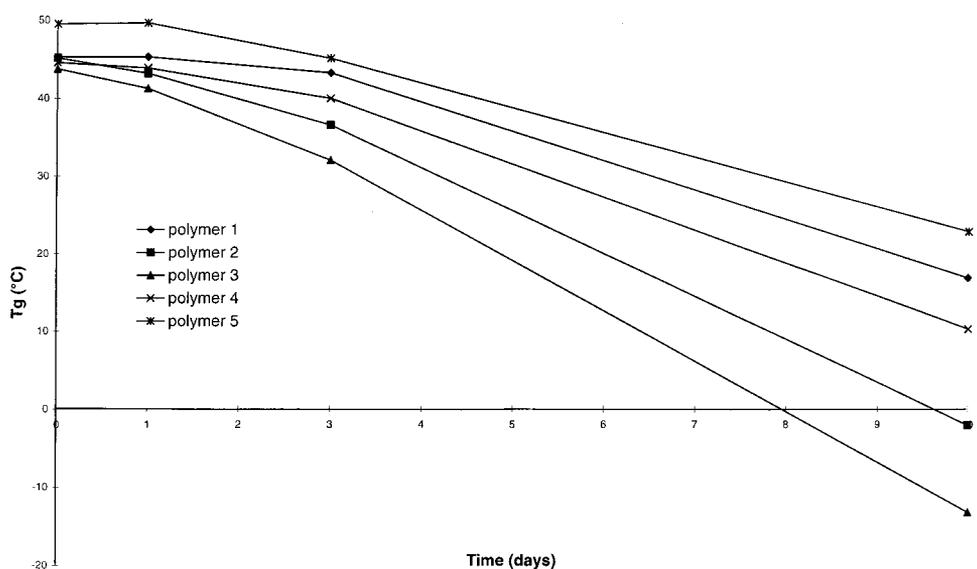


Fig. 8. Behaviour of the glass transition temperature at 55°C during 10 days' hydrolysis.

At both 37 and 55°C, the glass transition temperature of the PEUs decreased with decreasing weight average molecular weight. All glass transition temperatures decreased from the original value (over 40°C) to near zero or below zero during the hydrolysis period. All samples tested were amorphous and they did not crystallize during hydrolysis. Figure 7 shows how the glass transition temperatures decreased at 37°C during 35 days' hydrolysis and Fig. 8 how they decreased 55°C during 10 days hydrolysis.

The hydrolysis mechanism and a characterization of the hydrolysis products will be published later.

CONCLUSIONS

In this work, the hydrolysis of lactic acid based PEUs has been studied and the effect of temperature clearly shown. At 37°C, all the measured hydrolysis parameters (water absorption, weight loss and decrease of weight average molecular weight) can be controlled by the use of different stereostructures and by varying the length of the ester block in the final PEU. For example, at this temperature, the weight average molecular weight of D,L-lactic acid based PEU decreased from 103 700 to 3300 g mol⁻¹ in 42 days, while the weight average molecular weight of the PEU prepared with L-lactic acid decreased from 110 200 to 28 900 g mol⁻¹ over the same period. At 55°C, the weight loss and the decrease in weight average molecular weight were remarkably fast and the largest water absorption percentage was over 2500%. The results at 55°C show that these polymers can be composted with other biodegradable material and all of the polymer will degrade during the normal composting cycle. This kind of behaviour is essential if these materials are to be used as materials for food packaging applications. When our results are compared with the hydrolysis results for commercial PEUs there is one big difference. In our case, the hydrolysis rate is decreased when the length of the ester block is increased, while in the literature the opposite behaviour is reported. Furthermore, PEUs did not degrade more slowly at the surface of the test samples as did polylactides. The hydrolysis mechanism and the hydro-

lysis products require further study and the results will be published later.

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