Changes in Crystalline Morphology, Thermal, and Mechanical Properties with Hydrolytic Degradation of Immiscible Biodegradable PPDX/PCL Blends

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ABSTRACT: Immiscible blends of high molecular weight commercial poly(*p*-dioxanone) (PPDX) and poly(ε-caprolactone) (PCL) were prepared by melt mixing in a wide composition range. The materials were exposed to a hydrolysis medium (phosphate buffer kept at a constant pH of 7.2) at 37°C during 36 weeks. The change in weight of the samples as well as their thermal properties, morphology, spherulitic crystallization kinetics, and tensile properties were studied as a function of degradation time. As PCL does not experience weight loss during the entire degradation period explored here, weight loss was indicative of PPDX degradation only. The combined results of calorimetry, spherulitic texture, and spherulite growth kinetics allowed us to establish that the PPDX component in the blends experiences a much faster degradation rate than in neat PPDX. Such increase in degradation rate could be due to the larger surface area of PPDX component when it is dispersed in immiscible PCL. Nevertheless, the presence of PCL in the blends can extend the physical integrity of the samples in the degradation medium as well as their mechanical properties for longer periods of time as compared with neat PPDX. Therefore, the blends may be good candidates for replacing neat PPDX in specific applications requiring longer life time of the material. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3848–3858, 2008

Key words: immiscible blends; hydrolytic degradation; polyesters; poly(ε-caprolactone); poly(*p*-dioxanone)

INTRODUCTION

The study of biopolymer degradation constitutes one of the most interesting research fields in polymer science, as it is possible to predict the behavior of these materials based on their degradation kinetics to predict their life time and properties for specific applications.

Because of the presence of hydrolytically unstable bonds, polymers such as polyesters may degrade in a reasonable time span under physiological pH and temperature conditions (pH from 7 to 7.4 and a temperature of 37°C). One of the aspects to be considered when studying the hydrolytic degradation of polymers is their crystallinity and morphology. The morphological changes experienced by semicrystalline polymers as a consequence of the surrounding medium will to a great extent determine the final properties of the material.

It has been reported that the physical and chemical structure of polymers such as polylactic acid (PLA), polyglycolic acid (PGA), PGA/PLA copolymers,[1–4] and poly(*p*-dioxanone) (PPDX)[5–7] determines their *in vivo* as well as their *in vitro* degradation. The degradation seems to depend on several intrinsic and extrinsic factors such as molecular weight, stereocomposition, the presence of residual monomer, or catalyst, among others; however, a clear relationship has not been established between these factors and polymer morphology, medium temperature, pH, and the degradation process.[8–10]

Degradation by hydrolysis generally produces low molecular weight molecules which would sooner or later dissolve in the hydrolysis medium and would at some point be absorbed by the human body (if the experiment is carried out *in vivo*).[4,6]

Recent studies on PPDX hydrolysis have shown that the degradation rate of this material strongly depends on its degree of crystallinity, because hydrolysis is faster in the amorphous regions of this semicrystalline material.[5,11]

The hydrolytic degradation of poly(ε-caprolactone) (PCL) is very slow and displays a weak dependence

on conditions such as the temperature or acidity of the medium.[12,13] On the other hand, in PPDX hydrolytic degradation studies, Sabino et al. and others have found that the pH of the medium changes as hydrolysis progresses.[5] Chain breakdown produces low molecular weight acid species which, when dissolved in the medium, reduce its pH and can catalyze the degradation process, resulting in a substantial decrease of the molecular weight.

We have recently shown that blends of PPDX and PCL are immiscible in the entire composition range examined (the materials were exactly the same as those employed in this work), as DSC data showed no change in relevant thermal transitions on blending and Scanning Electron Microscopy revealed a very clear two phase morphology with poor adhesion between the PCL and the PPDX phases.[10,14]

In this work, we have added a more stable polyester like PCL to PPDX with the aim to tune its lifetime under hydrolysis for potential biomedical applications. We have studied how the morphology, thermal, and mechanical properties change as a function of degradation time in selected blend compositions.

EXPERIMENTAL

Materials

The polymers employed in this study were as follows: Poly(p-dioxanone) (PPDX) with a viscosity average molecular weight (M_v) of 70 kg/mol purchased from Johnson and Johnson (Somerville, NJ) in the form of monofilaments (Ethicon) and a glass transition temperature (T_g) of -9°C,[5] and a poly(ε-caprolactone) (PCL) with a number average molecular weight (M_n) of 120 kg/mol supplied by Union Carbide, in the form of pellets, its T_g is around -60°C.[14]

Blend extrusion and molding of cylindrical pins

PPDX/PCL blends of 100/0, 60/40, 47/53, 40/60, and 0/100 were prepared using an Atlas-LME miniextruder at a working temperature of 130°C at the extruder head and the screw and a 30 rpm speed.

Cylindrical pins with a length of about 3 ± 0.5 cm and a diameter of about 1.5 ± 0.5 mm were obtained by molding the materials in a compression-transfer molding equipment.

Hydrolytic degradation of the blends

Sample pins obtained by compression-transfer molding were hydrolyzed in a time interval of 0–36 weeks in 15 mL phosphate buffer solution (Na = 0.157M, K = 0.00445M, PO$_4$ = 0.0119M) at pH = 7.4

determined with a pH-meter (ORION, model 420A) and within a thermostatically controlled bath (Julabo-P) at 37°C (i.e., approximate human body conditions reproduced in vitro). The pH was kept constant by replacing the buffer solution weekly with a fresh one at pH = 7.4.

The progress of the hydrolytic degradation was studied by the extraction of 10 pins per blend at Weeks 4, 6, 10, 26, and 36. Weight loss analysis for each hydrolyzed sample was carried out as follows: once the sample was removed from the hydrolysis medium, it was left to dry in a vacuum oven for 5 days to extract the maximum possible amount of water; the material was then weighted (until a constant weight was obtained); then, the weight loss was calculated for each sample/week of hydrolysis.

Degraded and nondegraded samples were characterized by thermal and tensile analysis, as well as by optical microscopy as indicated later.

### Differential scanning calorimetry

Calorimetric analysis were carried out in a Perkin–Elmer DSC-7 under an inert atmosphere (ultra-high purity N$_2$) and using aluminum pans containing 10.0 ± 0.1 mg of sample. The equipment was calibrated with indium and tin standards. Differential scanning calorimetry (DSC) cooling and heating scans were performed at 10°C/min in a temperature range of -20 to 130°C.

Polarized light optical microscopy

Polarized light optical microscopy (POM) was employed for the morphological observation of spherulitic superstructural texture and for the measurement of spherulitic growth rate of each sample by using a Zeiss MC-80 Polarized Light Optical Microscope equipped with a Linkam TP-91 hot stage and a Nikon Coolpix 990 Digital Camera. A thin film was melted at 130°C for 3 min to erase previous thermal history; then, it was cooled at 90°C/min until a crystallization temperature (T_c) was reached in the range of 40–90°C. To enhance contrast a λ plate was placed in between the crossed polarizers.

Tensile properties

Mechanical properties of the degraded and nondegraded pins were evaluated by an uniaxial tensile test carried out in a Vitrodyne V1000 Tensile Testing Apparatus, using a 10 kg cell and a crosshead speed of 0.5 mm/s. Ten specimens were tested per sample.
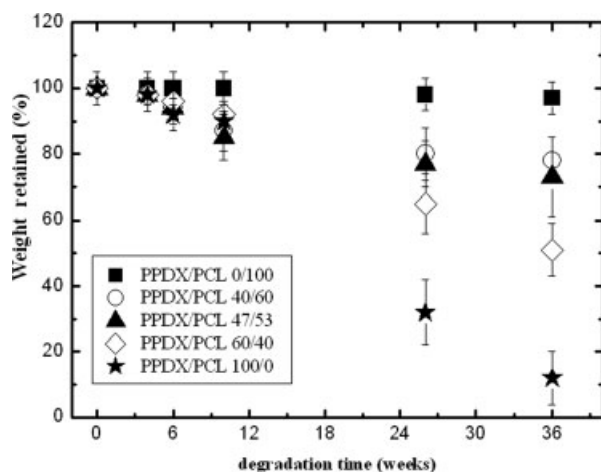
Figure 1 Weight change (%) as a function of exposure time to the hydrolysis medium for PPDX/PCL blends.

RESULTS AND DISCUSSION

Weight loss

To study the behavior of PPDX/PCL in the degradation medium, we evaluated the weight loss of the materials for different periods of time. Figure 1 shows the percentage of weight retained as a function of degradation time for the PPDX/PCL blends. During the first weeks of hydrolysis, neat PPDX samples did not show a significant weight loss; after having been 10 weeks in the degradation medium, they showed an approximate weight loss of 10%. At times larger than 10 weeks, weight loss increased rapidly in such a way that after 36 weeks of hydrolysis the neat PPDX weight loss reached 89%.

Although studying the degradation of PPDX, Sabino et al.[5,11,15] found a weight change of 25% after 10 weeks of hydrolysis in a medium whose pH was 7.4 at the beginning of the experiment; however, the buffer was not renewed during hydrolysis. This weight loss value for 10 weeks exposure is much higher for PPDX than the one obtained here (even though the samples had approximately equal molecular weights), as the pH changed from 7.4 at week 0 to 5.64 after 10 weeks. Similar results were reported by Lin et al.[6] In this work, the pH used to hydrolyze the samples was kept constant at 7.4 by periodic replacement of the hydrolysis medium, thus limiting the accumulation of acid degradation products that might catalyze the hydrolysis. Therefore, in view of this difference in pH over time, the weight loss values (for the same neat PPDX polymer) obtained here (Fig. 1) were significantly lower than those obtained by Sabino et al.[5,11,15] for the same exposure time to the hydrolysis medium.

During the first weeks of exposure, weight loss was low, because only the amorphous regions had been attacked. Once a great portion of this region

has been hydrolyzed and the molecules bonding it with the crystalline region (i.e., tie chains) have been degraded, the medium will diffuse into the crystals. This will produce the breakdown of bonds in that region and will eventually result in an abrupt weight loss at much longer degradation times (until the 36 weeks tested),[11,16,17] especially, in the case of PPDX rich blends, which is the material that suffers most of the degradation in view of its faster hydrolysis rate.

Neat PCL pins showed no relevant changes in their weight or their mechanical properties (as will be discussed later) when exposed to the hydrolysis medium under the same experimental conditions than pins made with neat PPDX and its blends. These results indicate that PPDX is the only component of the blends which is degrading and it would mean that the higher the amount of PPDX in the blend, the more material is being hydrolyzed. This results in a higher weight loss for the same degradation time in the case of the blends with a higher PPDX content.

However, adding PCL to PPDX improved the degradation stability of the material as a whole, as the PCL component did not degrade and kept its structural integrity. The blends showed more stable properties and a better structural stability than PPDX homopolymer. Pins of PPDX/PCL blends maintained their physical structure regardless of the blend composition during the whole hydrolysis period tested (36 weeks). As a result, mechanical properties could be tested throughout the whole experimental period. In contrast, neat PPDX pins exhibit dramatic deterioration of their mechanical integrity after 10 weeks exposure to the hydrolysis medium.

Table I shows the retained weight experimental values obtained for the 47/53 PPDX/PCL blend tested and their corresponding calculated values derived assuming that only PPDX degrades in the blend (obtained from the data for the homopolymer). With these results we intend to identify

TABLE I
Calculated and Experimental Retained Weight Percentage (%) for PPDX/PCL Blends at Different Exposure Times to the Hydrolysis Medium

	Percentage of PPDX		
	100	47	
Weeks	Exp.	Exp.	Calc.
4	99.2	98.0	99.6
6	98.7	94.2	99.4
10	91.0	86.3	95.8
26	33.0	76.0	68.5
36	11.0	71.0	58.2
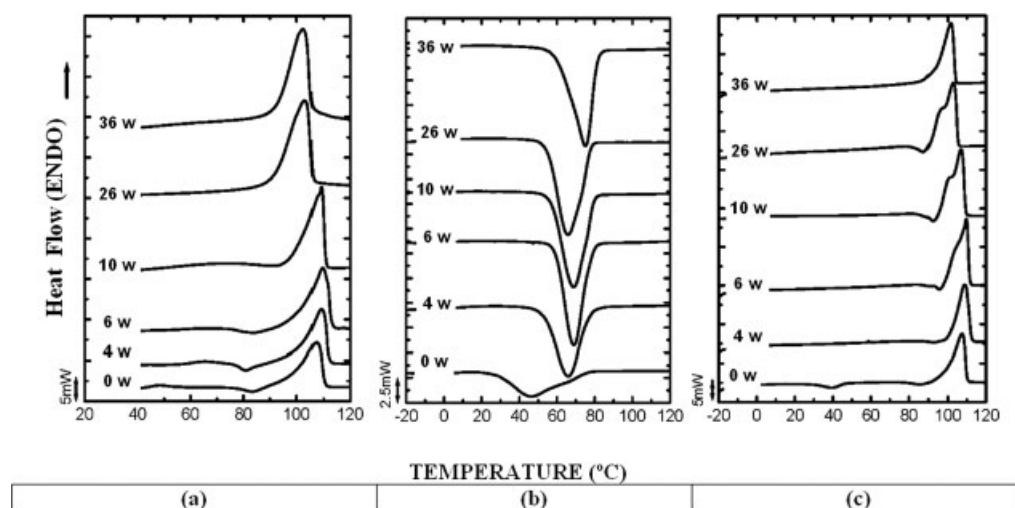
Figure 2 DSC scans at 10°C/min for PPDX homopolymer at different exposure times to the hydrolysis medium. (a) First heating, (b) cooling, and (c) second heating.

whether or not the weight loss only depends on the PPDX content in the blends.

Analyzing these results (but without considering the DSC and POM results that will be discussed later), we can observe that during the first 10 weeks of hydrolysis, weight retention percentages of the PPDX fraction (for both 100% PPDX and 47% PPDX) are more or less the same or slightly lower than the calculated values expected for the blends. This might be explained by the fact that there is a pronounced phase separation between the components and therefore a large interfacial area is created that increases the amount of exposed material to the attack of the hydrolysis medium. After 10 weeks of hydrolysis, the behavior apparently changes, i.e., the experimental values indicated that samples have lost less weight than expected when they are compared with their calculated values (higher weight retention). As a result, it might be said that at this stage of hydrolysis, the PCL could be contributing to prevent the diffusion of the lower molecular weight material to the hydrolytic medium (as one should not necessarily directly equate lack of weight loss with no degradation, especially at long exposure times).

Results shown by PPDX/PCL blends at this stage (where only weight lost is being considered) would seem to agree with the results found for PPDX-*b*-PCL diblock copolymers studied by Albuerne and coworkers[18,19] (without forgetting that in copolymers, PCL is covalently bonded to PPDX).

As the results of the following sections will show, in the case of PPDX/PCL immiscible two phase blends studied here, PPDX is not in fact protected by PCL but instead, because it is dispersed with a larger surface area within the blends (as compared with the bulk material) the material degrades faster in the blends than in the bulk, only that PCL pre-

vents the degradation products from migrating to the hydrolysis medium and therefore the degradation cannot be determined by weight loss measurements. It must be remembered that weight loss can only occur when the degradation products are of sufficiently low molecular weight to be able to dissolve in the degradation medium and in the case of the blends, they have to percolate through the material that contains hydrophobic PCL regions.

Thermal analysis

Figures 2 and 3 show DSC scans for the PPDX homopolymer and the 47/53 PPDX/PCL blend, which were chosen to compare the effects of different hydrolysis times. For each of the materials, the first heating scan is presented, followed by the subsequent cooling after erasing the thermal history for 3 min at 130°C, and then followed by the subsequent second heating scan.

DSC first heating scans show that, for all the samples, T_m values for PPDX (plotted in Fig. 4 as a function of degradation time) increased slightly during the first weeks of hydrolysis and then decreased with exposure time to the hydrolysis medium. Previous PPDX homopolymer degradation studies[17,20–23] have reported that during hydrolysis T_m of the material tends to decrease with hydrolysis time, whereas the heat of fusion (ΔH_m) tends to increase (a result also observed here, see Fig. 5 later); this behavior is associated with the loss of entanglements in the amorphous region and the successive incorporation of these chains to new crystalline regions. This process is known as "cleavage-induced crystallization."[17–19] Eventually, as degradation advances, more and more crystalline regions will be attacked; one would expect that eventually ΔH_m would
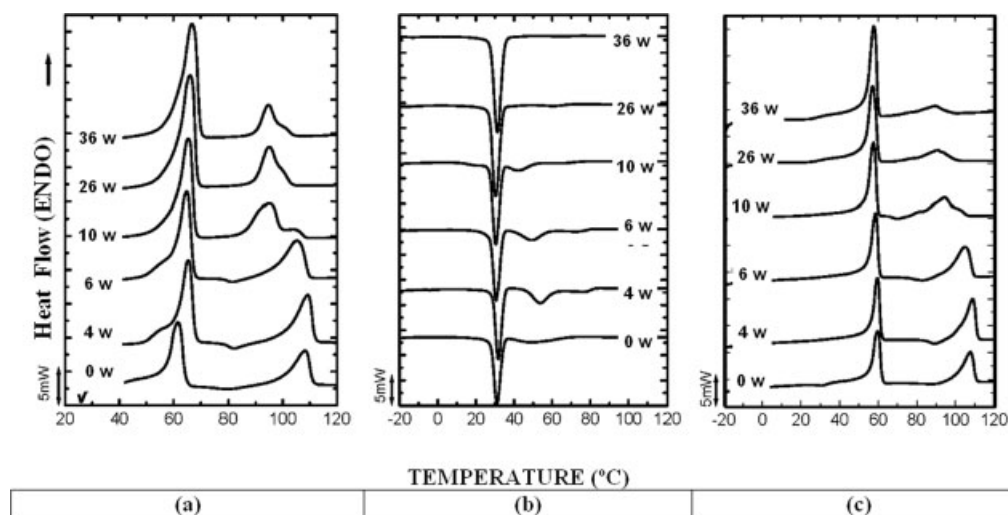
Figure 3 DSC scans at 10°C/min for the 47/53 PPDX/PCL blends carried out at different exposure times to the hydrolysis medium. (a) First heating, (b) cooling, and (c) second heating.

decrease, although this has not been observed for PPDX homopolymer, perhaps, because longer exposure times are needed. Thus, the results shown for neat PPDX in Figures 4 and 5 (decrease of T_m and increase of ΔH_m of PPDX) indicate that the polymer shows clear signs of cleavage induced crystallization and hydrolytic degradation.

In the same Figure 4, T_m of PCL showed a slight and steady increase with degradation time for all samples. This is due to annealing of PCL crystals being favored at the temperature employed during the duration of the experiment (37°C). As can be seen, during the second heating (Fig. 3) this effect is no longer seen and the T_m of the PCL stayed relatively constant throughout the whole degradation period studied and all the samples exhibited a similar behavior. This experimental observation suggests that PCL is not affected by the degradation during the whole period studied. Thus, the results suggest that only the PPDX within the blends is attacked by the aqueous medium. A similar behavior as the one shown by the T_m of the components of the materials studied herein was found by Albuerne et al.[18,19] when studying PPDX-b-PCL copolymers and by Sabino et al.[17] when studying the degradation of PPDX pins.

Figure 5 shows the change of the enthalpy of fusion (ΔH_m) as degradation proceeds. As stated earlier, for PPDX, ΔH_m increased as the hydrolytic degradation went on, whereas for the PPDX component of the blends an increase was observed during the early stages of hydrolysis, but after Week 10, this parameter decreased.

Unlike what can be seen in Table I (which includes global PCL and PPDX weights), DSC analysis (which allows to separate the behavior of each phase) suggests that the PPDX in the blends is

degrading faster than the homopolymer, as both T_m and ΔH_m values are lower for the PPDX component in the blends than for neat PPDX (Figs. 4 and 5). This would indicate that more advance stages of the second step of hydrolysis (the second step being the attack of the crystalline regions), where a decrease in crystallinity is expected (i.e., when crystals are massively attacked and their depletion rate is faster than any possible cleavage induced recrystallization), has started for the PPDX contained within the blends. This behavior can be attributed to the larger surface area of PPDX in the blends (as compared with neat PPDX) which enhances exposure to the degrading medium. Low molecular weight species formed may not diffuse or may have difficulty in diffusing to the hydrolysis medium because of the presence of
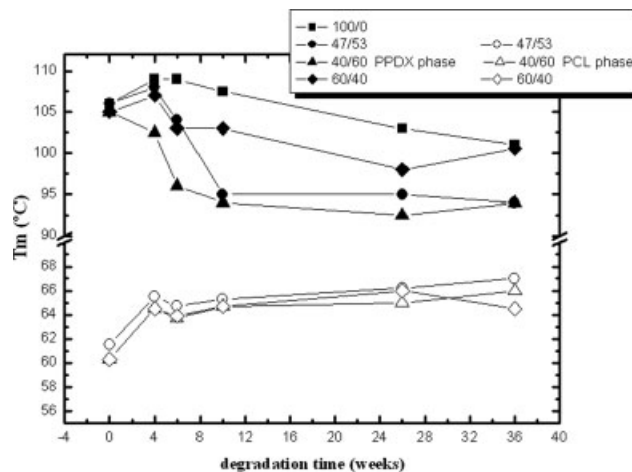
Figure 4 Variation of the melting temperature (T_m) for the PPDX (filled symbols) and the PCL fractions (empty symbols) in PPDX/PCL blends, obtained from the DSC scans corresponding to the first heating of samples exposed to the hydrolysis medium at the times indicated.
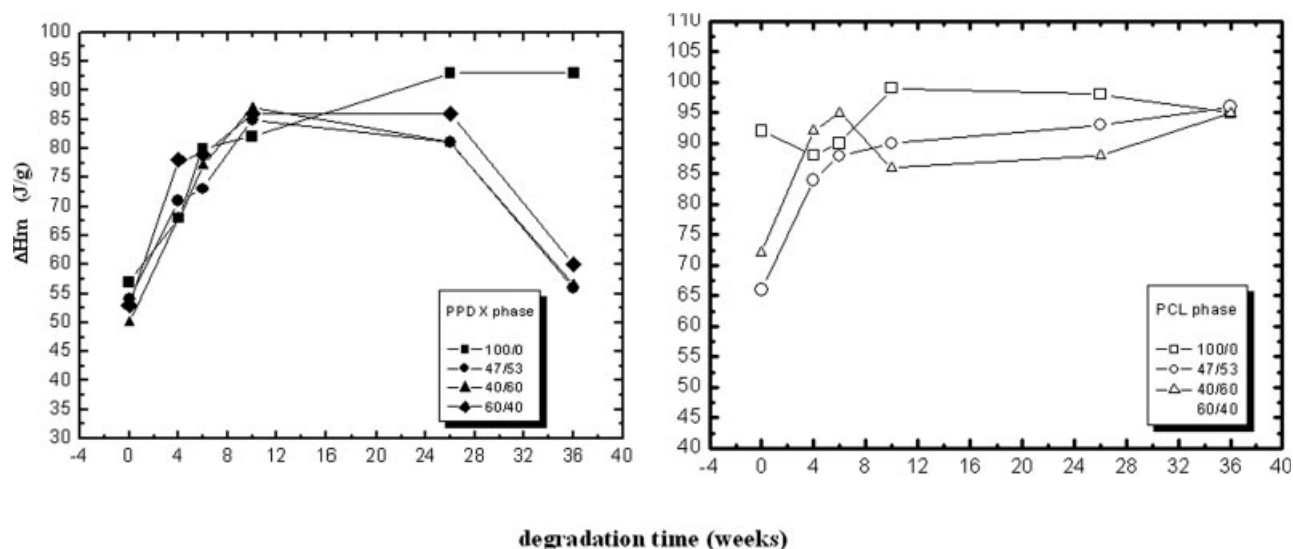
Figure 5 Variation of the enthalpy of fusion ΔH_m of the PPDX and the PCL fractions in PPDX/PCL blends. Values were obtained from the DSC scans corresponding to the first heating of samples exposed to the hydrolysis medium at the times indicated.

hydrolytically stable and hydrophobic PCL. Thus, such low molecular weight species may accumulate at the interphase and, given their acid nature, they might catalyze the degradation in a localized manner in specific zones of the sample. As a result, numerous chain scissions continue to occur in the PPDX fraction. Thus, pins made with blends kept their physical integrity, because the PCL phase (almost unaffected by hydrolysis) managed to support this system structurally and mechanically, whereas in the inside the PPDX fraction was highly degraded.

DSC cooling scans show that the crystallization exotherm of neat PPDX becomes narrower and shifts to higher T_c as the hydrolytic degradation proceeds and its enthalpy of crystallization, ΔH_c, increases with the degradation time. This indicates that hydrolysis is favoring the crystallization of the material (i.e., cleavage induced crystallization). This effect cannot be evidenced in the cooling scans for the blends, because the crystallization exotherms for PPDX and PCL tend to overlap. Please refer to Figures 2(b) and 3(b).

Several characteristic transitions can be observed in the second heating scans [Figs. 2(c) and 3(c)] for both homopolymers, which are of considerable interest. When the DSC scans of the neat PPDX are amplified (results not shown), the glass transition temperature (T_g) can be observed. As the degradation time increases, the T_g of PPDX shifts to lower temperatures (changing from about $-7°C$ to $-11°C$ after 10 weeks of degradation). This may be attributed to the decrease in the molecular weight which is preferably occurring in the PPDX phase. It is difficult to evaluate this transition clearly in the case of

the blends, but the few measurements made indicate a similar trend to the one shown by the homopolymer.

Values for the melting temperature (T_m) and enthalpy of fusion (ΔH_m) of neat PPDX and the PPDX fraction in the blends [Figs. 2(c) and 3(c)], show similar trends as those observed during the first heating before erasing the thermal history, and therefore can be explained using the same considerations pointed out earlier.

Polarized light optical microscopy (POM)

In the case of the hydrolytically degraded PPDX/PCL blends, spherulitic growth was monitored only for the PPDX fraction, because the crystallization of the PCL component was experimentally hard to observe without the interference of the previously crystallized PPDX phase. We also studied the spherulitic growth for the PPDX homopolymer after different degradation times.

Figure 6 shows a sequence of micrographs of spherulitic texture for neat PPDX at different crystallization temperatures (T_c) and different degradation times (weeks). As can be seen, the characteristic shape of PPDX spherulites changed with crystallization temperature and degradation time.

Optical microscopy observations revealed that neat PPDX crystallizes in the form of spherulites whose morphology will depend on the degree of supercooling (ΔT) used during the isothermal crystallization. At high supercooling, spherulites with Maltese cross and simple banding were observed; at intermediate supercooling, spherulites showed a clear Maltese extinction pattern and double banding;
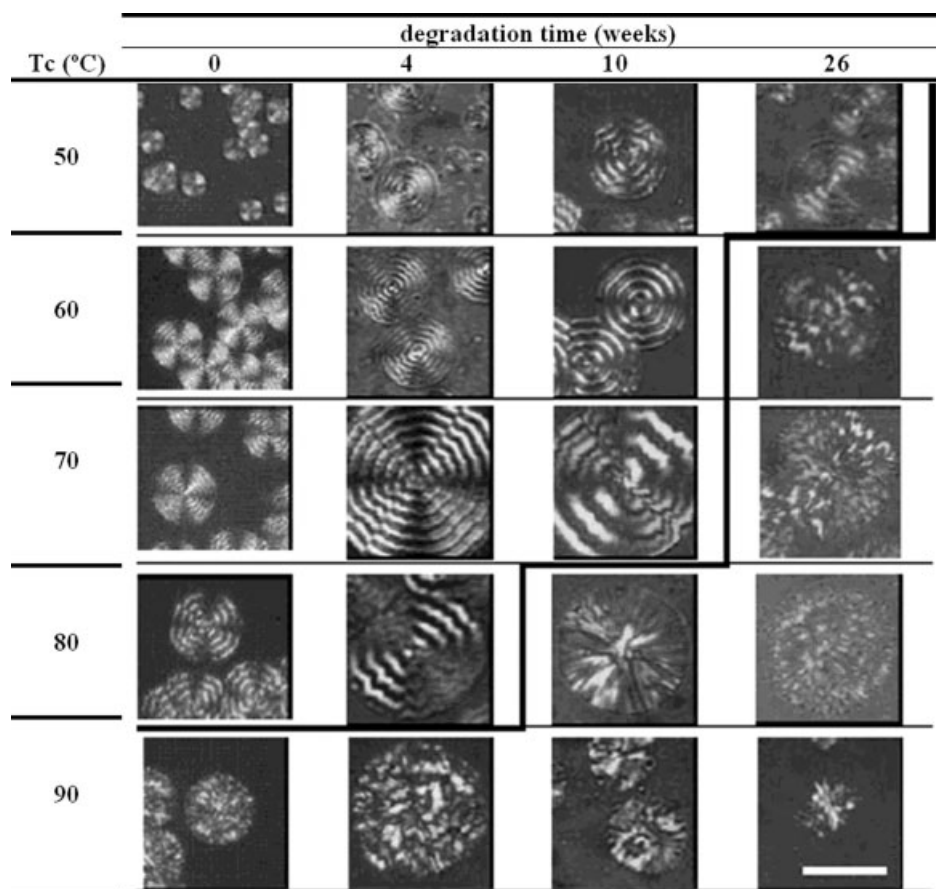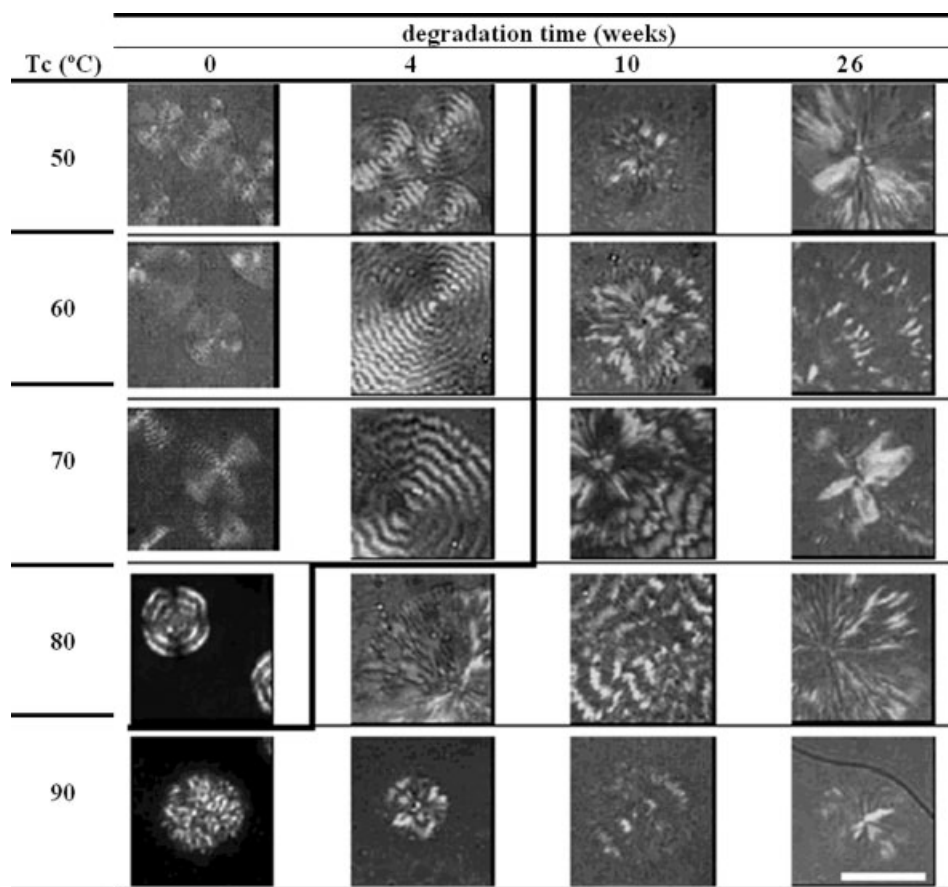
Figure 6 Spherulitic morphology obtained by POM at various crystallization temperatures for PPDX (or 100/0 PPDX/PCL blend) after exposure to the hydrolysis medium at the times indicated. The scale mark corresponds to 50 μm and the dark internal line separates the defined banding from the irregular or diffuse banding morphologies (which appears in the more degraded samples).

and, at low supercooling, spherulites exhibited irregular banding without Maltese cross extinction pattern. Similar effects were shown by PPDX spherulites from neat material and by those of the PPDX/PCL blends studied.

As the degradation time increased, we observed how the morphology of the spherulites changed. At the same T_c, spacing between banding tended to increase with degradation (please see the sequence of micrographs of degraded PPDX crystallized at 50°C in Fig. 6); whereas in other cases, the banding effect disappeared after 4 and 10 weeks of degradation for samples crystallized at 80 and at 60–70°C. The degradation process, which affects the polymer chains by producing random chain scissions, also generates changes in the spherulitic morphology. In general, micrographs seem to indicate that to observe similar spherulitic structures in degraded and nondegraded samples, it is necessary to compare nondegraded samples (crystallized at a given T_c1) to its degraded counterpart crystallized at lower T_c (at $T_c < T_c1$).

This shift of the morphology as a function of crystallization temperature as the degradation proceeds is related to the molecular weight of the samples. As degradation increases, the melting temperature of the crystals tends to decrease (see DSC results discussed earlier). This would mean that when carrying out the tests at the same T_c, the supercooling of the degraded sample would be smaller with respect to its nondegraded counterpart and the spherulitic texture depends on supercooling.

POM results clearly show that PPDX seems to be degrading faster in the blend than in the neat material. The comparison of the spherulites obtained at different crystallization temperatures and degradation times indicates that PPDX in the blends looses its ability to crystallize in the form of spherulites with a well-defined banding pattern at high temperatures at lower hydrolysis times than the neat material (see the internal dark line shown on Figs. 6 and 7); this can be directly related to the loss or decrease in molecular weight as a result of the hydrolytic attack. The PPDX spherulitic texture is a good

Figure 7 Spherulitic morphology obtained by POM at various crystallization temperatures for a 47/53 PPDX/PCL blend after exposure to the hydrolysis medium at the times indicated. The scale mark corresponds to 50 μm and the dark internal line separates the defined banding from the irregular or diffuse banding morphologies (which appears in the more degraded samples).

indication of the degradation of the material since it is highly dependent on the molecular weight.

Figure 8 shows a plot of the spherulitic growth rate (G) determined by POM versus the isothermal crystallization temperature T_c at different degradation times for neat PPDX and for PPDX within one representative blend composition.

Figures 8 presents two evidences indicating that PPDX in the blend is degrading more than neat PPDX. The first one is related to the dependence of the G versus T_c curve on exposure time to the hydrolysis medium. Figure 8(top) shows that as exposure time increases (and therefore degradation proceeds[17,19]) the growth rate first increases, then reaches a maximum at 10 weeks and then decreases at 26 weeks. This behavior replicates the molecular weight dependence of the spherulitic growth rate (at constant T_c) that normally increases as molecular weight decreases but goes through a maximum since when the chains are too short they have problems for nucleation and growth at equivalent T_c values. Figure 8(bottom) shows that for the PPDX within the 47/53 PPDX/PCL blend this maximum in

growth rate is already achieved at 6 weeks exposure time (compare data at 60°C for instance), thereby indicating that degradation is faster for the PPDX component in the blend as compared with neat PPDX.

The second evidence that indicates faster degradation for the PPDX in the blend as compared with neat PPDX is related to the changes experienced by the shape of the G versus T_c curve. The curves are all roughly symmetrical with a maximum around 60°C for neat PPDX (Fig. 8, top) and they turned asymmetrical with the maximum shifted to lower T_c values in the blends with more than 4 weeks exposure to the hydrolysis medium. The typical bell shape curve (for G versus T_c) of neat undegraded PPDX is characteristic of many semicrystalline polymers. The right hand side is dominated by secondary nucleation (whose thermodynamic driving force increases with supercooling) whereas diffusion plays an increasingly dominant role on the left hand side of the curve as temperature is reduced and viscosity in the melt becomes very large, these two competing effects cause a maximum in G located somewhere in
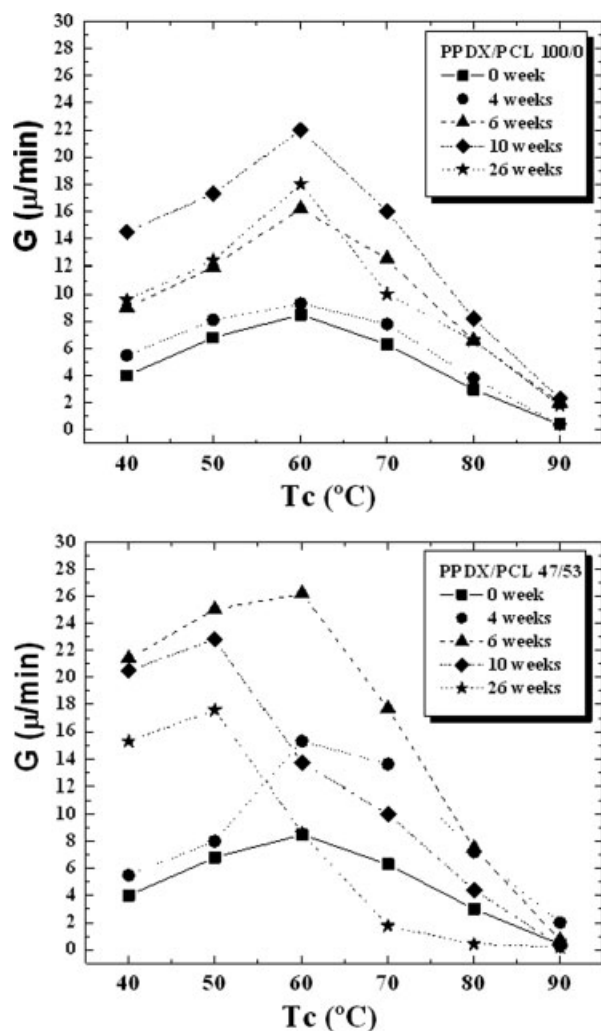
Figure 8 Spherulitic growth rate (*G*) of the PPDX homopolymer and the PPDX fraction in 47/53 PPDX/PCL blends as a function of the isothermal crystallization temperature (T_c) at different hydrolytic exposure times (0, 4, 6, 10, and 26 weeks).

between T_g and T_m. As hydrolysis proceeds, the crystallization rate increases at the lower crystallization temperatures because of enhanced diffusion (left side of the curve). Lower molecular weight species may diffuse faster at lower temperatures, thus shifting the curve to lower crystallization temperatures.

If we plot the spherulitic growth rate at selected constant crystallization temperatures as a function of degradation time, as shown in Figure 9, once again evidences indicating that the PPDX component in the blend is degrading faster than neat PPDX homopolymer are obtained. As can be seen, and explained above, the peak in *G* with degradation time is associated with extensive degradation, enhanced chain diffusion and a shift in the *G* versus T_c curve to lower temperatures. The relative values of *G* at each T_c are also related to molecular weight as they depend on

the capacity of the chains to crystallize. It is clear from both curves shown in Figure 9 for two selected T_c values that the PPDX in the blend degrades faster than neat PPDX, as the values of *G* are larger and the time at which *G* peaks is lower for the PPDX component in the blend.

Mechanical properties

As polymers degrade hydrolytically their mechanical properties will deteriorate. In the case of bioabsorbable implants, the decrease of elastic modulus is particularly important, as it usually determines the application of the implant and its lifetime.

Figure 10 shows the values of the elastic modulus (*E*) for the samples as a function of hydrolysis time.

The Young modulus (*E*) obtained for the nondegraded neat PPDX was 422 ± 45 MPa, which is close with the value reported by Pezzin et al.[24,25] who found an elastic modulus of 584 ± 45 MPa for the
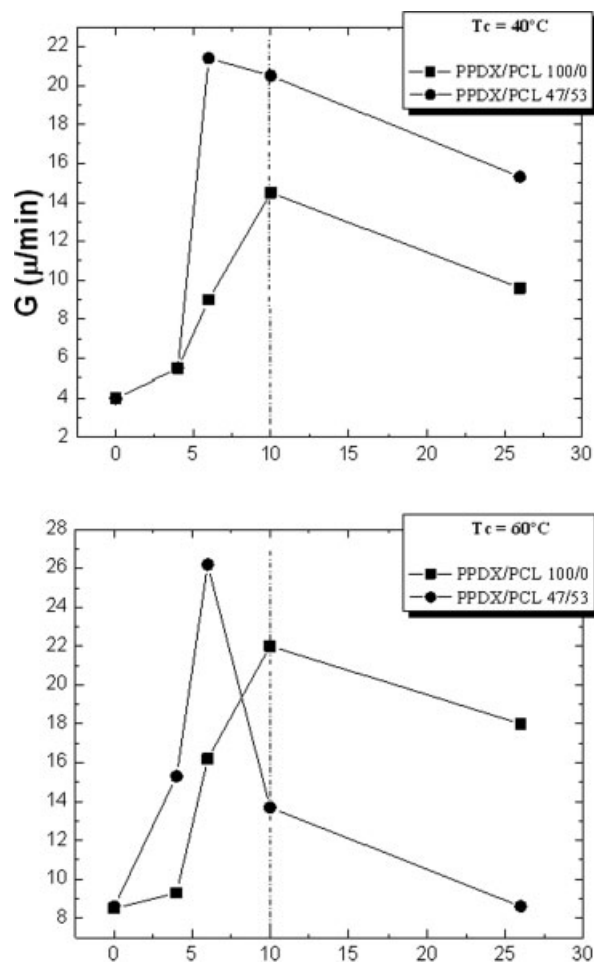
Figure 9 Spherulitic growth rate (*G*) of the PPDX homopolymer and the PPDX fraction in 47/53 PPDX/PCL blends as a function of exposure time to the hydrolysis medium at two different crystallization temperatures (40°C and 60°C).
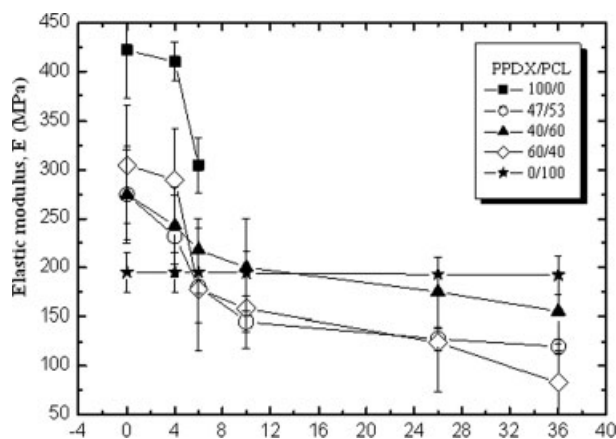
Figure 10 Change of the tensile modulus (E) versus exposure time to the hydrolysis medium obtained for PPDX homopolymer and different PPDX/PCL blends in tensile tests.

neat PPDX before degradation. For neat PCL we obtained a Young modulus of 193 ± 18 MPa, which is consistent with previously reported values, e.g., in the PP/PCL blends study by Gouveia and coworkers.[26] who found a value of 220 ± 20 MPa for neat PCL; other researches had reported also some mechanical properties for PCL.[27]

Mechanical properties of neat PPDX could only be studied until week 6 of hydrolysis; after that, pins were too brittle to be handled and placed in the testing machine without breaking. Similar results were reported by Sabino et al.[28] when studying the hydrolytic degradation of PPDX filaments. However, the mechanical properties of PPDX/PCL blends could be studied over the entire degradation period employed here (36 weeks) because they kept their mechanical integrity and stability.

It can be seen that as degradation proceeds, the elastic modulus decreases for all the materials studied (both homopolymers and blends). It has been qualitatively shown that the drop of the elastic modulus of polymers as a function of their hydrolytic degradation time is caused by a set of factors such as the decrease in the molecular weight and the weight loss,[5,18,19,28] among others.

Specifically in this study, we found that the decrease in the elastic modulus tended to be gradual for the first degradation times evaluated (from 0 to 4 weeks). At intermediate degradation times (4 to 8 weeks), this decrease was much more drastic. Finally, the elastic modulus seemed to stabilize decreasing only slightly as degradation progressed (weeks 10 to 36).

The previous results indicate that there might be an initial degradation stage during which the elastic modulus does not change significantly, because the soluble low molecular weight fragments have not

yet been produced, chain breakdown is random and mainly occurs in the amorphous regions. The fact that materials preserve their properties during this stage is relevant for the practical application of the material, because it would mean that the implant would show a good performance while the recovering tissue consolidates (bone tissue, for example).

CONCLUSIONS

The degradation of PPDX/PCL blends is a very complex function of the composition and phase dispersion. Our results indicate that both neat PCL and the PCL component in the blends experience minimum degradation, as expected, during the relatively short duration of our experiments (36 weeks of exposure to the hydrolysis medium). Both PPDX homopolymer and the PPDX phase within PPDX/PCL blends degrade extensively as judged by weight loss measurements, DSC, POM, and mechanical properties. However, PPDX degrades much faster when it is dispersed in the PPDX/PCL blends as compared with the bulk state. Evidences include the following: (1) the reduction in enthalpy of fusion at longer degradation times for the PPDX in the blend which was never observed for neat PPDX, (2) the change in spherulitic texture observed, and (3) the changes in spherulitic crystallization rate as a function of isothermal crystallization temperature.

Nevertheless, because the PCL is stable during the exposure times explored in this work, the mechanical properties of the blends can be considered better than neat PPDX for exposure times longer than 10 weeks, a fact that may be interesting for specific applications requiring slower degradation kinetics than neat PPDX, albeit with different mechanical resistance.

References

1. Maurus, P. B.; Kaeding, C. C. Oper Tech Sports Med 2004, 12, 158.
2. Schitz, J.; Hollinger, J. O. Clinic Orthop Relat Res 1988, 237, 245.
3. Ray, J. A.; Doddi, N.; Regula, D.; Williams, J. A.; Melveger, A. Surg Gynec Obst 1981, 153, 497.
4. Roman, S. J Rev Plast Mod 1990, 413, 689.
5. Sabino, M. A.; Gonzalez, S.; Feijoo, J. L.; Márquez, L. Polym Degrad Stab 2000, 69, 209.
6. Lin, L. H.; Chu, C.; Grubb, D. J Biomed Mater Res 1993, 27, 153.
7. Bellerger, V.; Ganem, M.; Mortaigne, B.; Verdu, J. Polym Degrad Stab 1995, 49, 91.
8. Hyon, S. H.; Jamshidi, K.; Ikada, Y. Polym Int 1998, 46, 196.
9. Anderson, J.; Hiltner, A.; Wiggins, M.; Schubert, M.; Collier, T.; Kao, W. J.; Mathur, A. Polym Int 1998, 46, 163.
10. Sabino, M. A. Polym Degrad Stab 2007, 92, 986.
11. Sabino, M. A.; Feijoo, J. L.; Müller, A. J. Polym Degrad Stab 2001, 73, 541.

12. Akira, I.; Yutaka, T. Polym Degrad Stab 1994, 45, 205.
13. Latere, D. J.; Lecomte, P.; Dubois, P. H.; Jèrôme, R. Macromolecules 2003, 36, 2609.
14. Brito, Y.; Sabino, M. A.; Ronca, G.; Albuerne, J.; Müller, A. J. Rev Latinoamericana de Metalurgia y Materiales 2006, 26, 61.
15. Sabino, M. A.; Márquez, L.; Feijoo, J. L. Rev Téc Ing Univ Zulia 1998, 21, 170.
16. Chu, C. J Appl. Polym Sci 1981, 26, 1727.
17. Sabino, M. A.; Albuerne, J.; Müller, A. J.; Brisson, J.; Prud'homme, R. Biomacromolecules 2004, 5, 358.
18. Müller, A. J.; Albuerne, J.; Márquez, L.; Raquez, J. M.; Degée, P. H.; Dubois, P. H.; Hobbs, J.; Hamley, I. W. Faraday Discuss 2005, 128, 231.
19. Albuerne, J.; Márquez, L.; Müller, A. J.; Raquez, J. M.; Degrée, P. H.; Dubois, P. H.; Castelletto, V.; Hamley, I. W. Macromolecules 2003, 36, 1633.
20. Tomihata, K.; Suzuki, M.; Ikada, Y. J Biomed Mater Res (Appl Biomater) 2001, 58, 511.
21. Yang, K.; Wang, X.; Wang, Y.; Wu, B.; Jin, Y.; Yang, B. Eur Polym J 2003, 39, 1567.
22. Jitendra, K.; Pandey, K.; Reddy, R. A.; Pratheep, K.; Singh, R. P. Polym Degrad Stab 2005, 88, 234.
23. Wu, C.; Gan, Z. Polymer 1998, 39, 4429.
24. Pezzin, A.; Van Ekenstein, A. G.; Duek, E. A. R. Polymer 2001, 42, 8303.
25. Pezzin, A.; Duek, E. Polym Degrad Stab 2002, 78, 405.
26. Balsamo, V.; Gouveia, L. M. J Polym Sci Part B: Polym Phys 2007, 45, 1365.
27. Chrissafis, K.; Antoniadis, G.; Paraskevopoulos, K. M.; Vassiliou, A.; Bikiaris, D. N. Compos Sci Technol 2007, 67, 2165.
28. Sabino, M. A.; Sabater, L.; Ronca, G.; Müller, A. J Polym Bull 2002, 48, 291.