Comparison of the Hydrolytic Degradation and Deformation Properties of a PLLA−Lauric Acid Based Family of Biomaterials

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Received October 5, 2005; Revised Manuscript Received November 9, 2005

Addition of lauric acid to PLLA results in a significantly increased rate of hydrolytic degradation, with the time-to-loss of tensile strength directly related to the concentration of lauric acid. In this study, the hydrolytic degradation profiles of four materials were studied: amorphous PLLA, amorphous PLLA containing 1.8 wt % lauric acid, amorphous PLLA containing 4.5 wt % lauric acid, and pre-crystallized PLLA containing 1.8 wt % lauric acid. Hydrolytic degradation was monitored through mass profiles, molecular weight profiles, crystallinity and the development of mechanical properties and deformation mechanisms (through simultaneous small-angle X-ray scattering and tensile testing), and a "phase diagram" of properties suggested. The key factor in determining the development of properties was found to be the time at which crystallization occurred in relation to the loss of molecular weight, with the two factors most affecting this being the lauric acid content and the pre-degradation annealing treatment.

Introduction

Poly(L-lactide) (PLLA) is a polymer that has been successfully used in medical devices for a number of years, due to both its resorption properties through hydrolysis and its good biocompatibility. The hydrolytic degradation time of PLLA is long, however, with degradation often taking several years or more.[1,2] As such, poly(lactide) is more often studied in the form of a copolymer or blend, by copolymerizing L-lactic acid with D-lactic acid, glycolic acid, or both, and/or blending of the homo- or copolymers. This has resulted in a whole family of resorbable polymers with a large range of both mechanical properties and hydrolytic degradation times; however, the relationship between composition and properties is complex. Due to the nature of the different monomers that form the polymer, some of these materials are intrinsically crystalline, some intrinsically amorphous, whereas some crystallize on hydrolytic degradation and some remain amorphous throughout. This has meant that each composition of polymer must be understood as an individual material, making prediction of properties, and hence medical device design, difficult.[3−8]

In a previous paper by these authors, a new PLLA-based material was introduced, namely PLLA containing 4.5 wt % lauric acid (PLLA4.5).[9] This material had previously been patented[10] and showed significantly enhanced hydrolytic degradation properties due to the catalyzing effect of the lauric acid on the hydrolysis reaction, with no leaching of the lauric acid. Although the degradation time in this case was not particularly medically relevant, with loss of tensile strength occurring in a matter of days, this paper demonstrated the dramatic effect of a high concentration of lauric acid in PLLA (near to the solubility limit of lauric acid in PLLA, beyond which precipitation of the lauric acid occurs) and presented the concept of the use of lauric acid concentration as a method for controlling hydrolytic degradation rate. This paper also demonstrated the influence of developing crystallinity on the deformation mechanism of the materials, whereas a further paper on PLLA by the same authors introduced the effect of annealing on the deformation mechanism.[11]

The immediate advantage of the PLLA−lauric acid family of materials over copolymers or blends is the direct relationship between lauric acid concentration and hydrolytic degradation time, meaning that prediction of degradation rates for device design is significantly easier. The mechanical properties of the materials at all stages of hydrolytic degradation are also of key importance in the design of load-bearing medical devices. On further investigation however, the way in which the mechanical properties develop with degradation was also found to be dependent on the concentration of lauric acid, and this will be one of the concepts introduced here.

In this paper, three compositions of the PLLA−lauric acid materials will be compared: PLLA, PLLA containing 1.8 wt % lauric acid (PLLA1.8), and PLLA containing 4.5 wt % lauric acid (PLLA4.5). The effect of the induced microstructure will also be studied by comparing the hydrolytic degradation properties of the amorphous and crystallized material at one composition. Previous studies by other authors have shown that PLLA crystallizes with spherulitic morhphology when crystallized either from the melt or from the glassy state.[12,13] This has also been found to be the case for PLLA containing lauric acid (data not shown). By comparison of mass profiles, crystallinity, molecular weight, mechanical properties, and deformation mechanism, the relationship between these parameters will be demonstrated and a "phase diagram" of properties drawn.

Experimental Method

PLLA was purchased from Purac and 99.5% pure lauric acid from Aldrich. For PLLA1.8 and PLLA4.5, PLLA and lauric acid were dry blended in the correct weight ratio and then solution blended with chloroform. After complete dissolution, the solution was cast and dried, before compression moulding, and the lauric acid content was determined using gas chromatography.

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10.1021/bm050746v CCC: $33.50
Published on Web 01/10/2006

All samples were formed by compression moulding into stainless steel moulds to form rectangular bars and then quenching in ice−water. These bars were then machined and cut to form specimens 10 × 20 × 0.6 mm with semicircular cut-outs 3 mm in radius, halfway along the long edge. This nonstandard tensile test bar was used for simultaneous small-angle X-ray scattering (SAXS) and tensile testing to ensure deformation occurred in the center of the sample where the X-ray beam was focused and has been discussed by other authors.[14]

Four types of samples were prepared: amorphous PLLA (PLLAa), amorphous PLLA4.5 (PLLA4.5a), amorphous PLLA1.8 (PLLA1.8a), and annealed PLLA1.8 (PLLA1.8x). The latter was prepared by annealing the quenched rectangular bars, prior to machining, in an oven on a preheated copper block at 110 °C for 5 min (at which time complete crystallization had occurred as determined by DSC experiments, data not shown). Samples were weighed, then degraded in pH 7.4 phosphate buffer solution at 37 °C, for in vitro modeling of biological conditions.[15] At set time-points, samples were removed from the solution, excess water was removed, and the samples were weighed. Simultaneous SAXS and tensile testing was then performed on station 16.1 of the Synchrotron Radiation Source at the CLRC Daresbury Laboratory using a two-dimensional "RAPID" detector calibrated using wet rat-tail collagen, and a miniature materials tester (MINIMAT). Radiation of wavelength 1.4 Å was used along with a sample-to-detector distance of 5 m giving a q-range of 0.06−0.85 nm^{-1}. Due to the different experimental sessions at which this data was collected, different deformation rates were used for the different materials (PLLAa and PLLA4.5a deformed at 0.2 mm min^{-1}, PLLA1.8a and PLLA1.8x deformed at 0.05 mm min^{-1}). Ideally for comparison of tensile data, the same deformation rate would be used; however, this deviation was unavoidable due to the time constraints of synchrotron radiation experiments. Further data (not shown) suggested that, although this change in deformation rate had some effect on the load-displacement curves, it did not significantly affect the deformation mechanism. After SAXS experiments, samples were dried under vacuum at room temperature for several weeks before weighing.

Crystallinity was determined using wide-angle X-ray scattering (WAXS) by fitting of the amorphous halo (determined from a fully amorphous sample) and determining the percentage of the total scattering caused by the crystalline material. WAXS experiments were carried out on a Philips vertical diffractometer with a long fine focus X-ray source and a curved graphite monochromator and PANanalytical X'Pert data collection software. Molecular weight was then determined using gel permeation chromatography. Samples (in duplicate) were dissolved in chloroform and filtered through 0.45 μm Nylon filters prior to analysis, and calibration was carried out versus polystyrene calibrants supplied by Polymerlabs. The parameter chosen for discussion was M_n, the number average molecular weight, since this was deemed to be the parameter most relevant to the mechanical properties.[16]

Results

Figure 1 shows the mass changes that were monitored throughout hydrolytic degradation. Water up-take (WU) and mass loss (ML) were defined by eqs 1 and 2, respectively, where m_i was the initial dry mass, m_w was the wet mass after degradation, and m_d was the mass on drying after degradation

$$\mathrm{WU} = \frac{(m_w - m_d)}{m_i} \times 100\% \quad (1)$$

$$\mathrm{ML} = \frac{(m_d - m_i)}{m_i} \times 100\% \quad (2)$$

The water up-take equation (eq 1) gives the amount of solvent that was lost on drying the sample, taking account of any changes in sample mass due to degradation, whereas this mass loss is itself defined by eq 2.

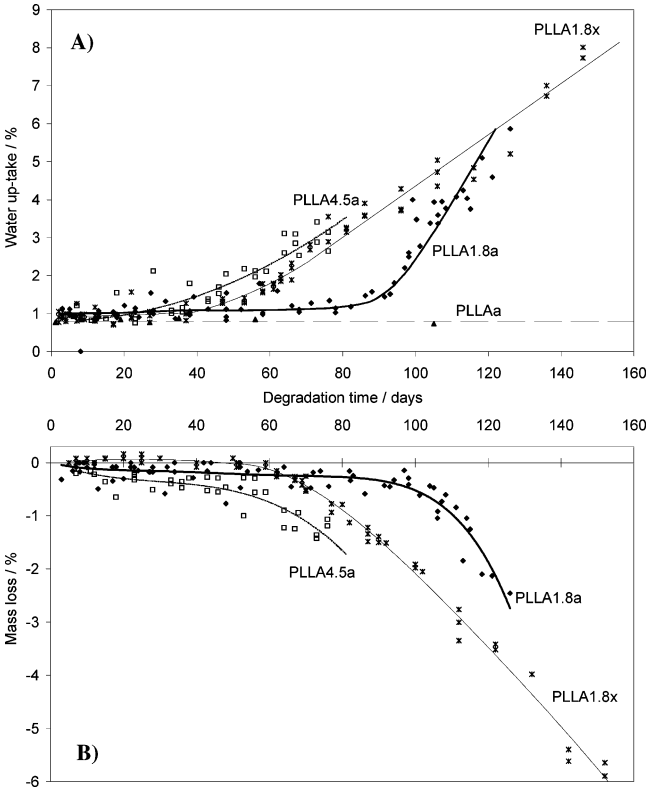

Figure 1. (A) Water up-take profiles and (B) mass-loss profiles for ▲, PLLAa; ◆, PLLA1.8a; □, PLLA4.5a; ∗, PLLA1.8x.

All of the materials quickly absorbed approximately 1 wt % water (within the first day), at which point water up-take stabilized. PLLA4.5a was the first to show a further increase in water up-take at approximately 30 days, which was shortly followed by the onset of mass loss. PLLA1.8x showed very similar water up-take and mass loss profiles to PLLA4.5a, although the time to the onset of these changes was slightly later: approximately 40 days for water-uptake and 50 days for mass loss. The profiles for PLLA1.8a were significantly different, with the increase in water up-take not occurring until approximately 90 days and increasing much more quickly than seen for the other materials. The mass loss profile followed a similar trend, with no mass loss until approximately 100 days, but with severe mass loss after this time. The rise in water up-take appeared to slightly precede the rise in mass loss in all samples. PLLAa showed no increase in water uptake (after the initial stabilization at 1 wt %) and no mass loss for the duration of the experiment.

The development of crystallinity with hydrolytic degradation is shown in Figure 2. An increase in crystallinity can, of course, result from either crystallization of amorphous material within the bulk or loss of amorphous material due to degradation. The time scales of the mass loss curves in Figure 1b indicate that for these samples the majority of the changes seen for each sample are the result of crystallization not loss of amorphous material, since in all cases crystallization had occurred prior to any mass loss. There does not appear to be any direct relationship between crystallinity and water up-take or mass loss in general. The crystallinity of PLLA1.8x was at all times greater than for the other samples, whereas the water up-take and mass loss profiles of PLLA1.8x are intermediate between PLLA4.5a

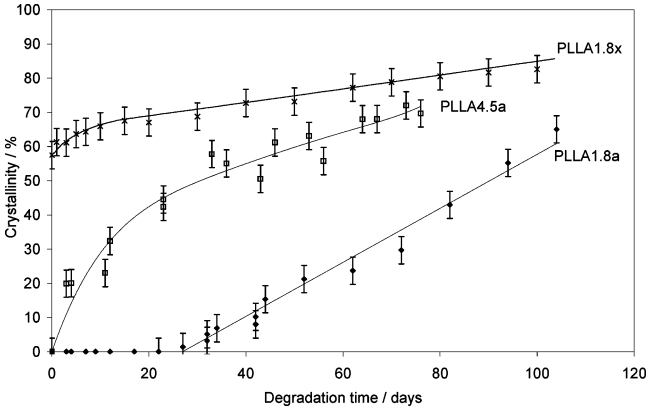

Figure 2. Development of crystallinity with hydrolytic degradation for ◆, PLLA1.8a; □, PLLA4.5a; ∗, PLLA1.8x. PLLAa (not shown) showed approximately 1% crystallinity after 8 months.

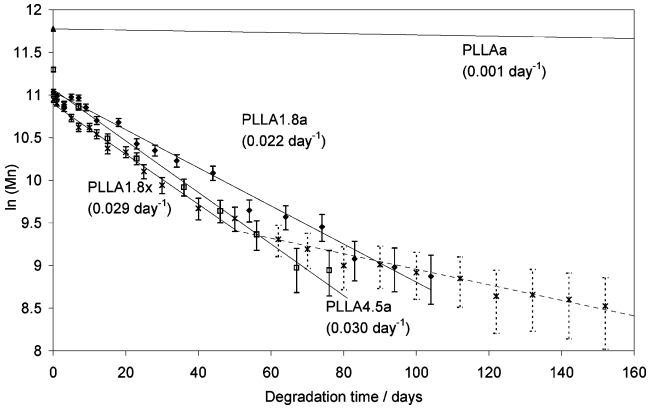

Figure 3. Loss of molecular weight with hydrolytic degradation ▲, PLLAa; ◆, PLLA1.8a; □, PLLA4.5a; ∗, PLLA1.8x.

and PLLA1.8a. However, in both PLLA4.5a and PLLA1.8a, water up-take began at a crystallinity of approximately 40−50%, whereas mass loss began at a crystallinity of approximately 50−60%.

PLLAa, PLLA1.8a, and PLLA4.5a were all initially amorphous; however, on immersion in solution, the behavior of these materials was very different. On immersion, PLLA4.5a immediately began to crystallize, with crystallinity rising sharply for the first 20 days and then continuing to rise but at a slower rate for the duration of the experiment (80 days in total). PLLA1.8a showed no increase in crystallinity for the first 25 days, but after 25 days, the crystallinity increased linearly for the duration of the experiment (100 days in total), whereas PLLAa developed only about 1% crystallinity after 8 months of hydrolytic degradation. PLLA1.8x had an initial crystallinity of approximately 58%, but in a manner similar to PLLA4.5a, the crystallinity increased sharply for a short period (10−15 days) and then continued to increase but at a slower rate.

Addition of lauric acid to PLLA resulted in a slight drop in molecular weight due to the extra processing required; however, all samples containing lauric acid had similar molecular weights. Plots of ln(M_n) vs hydrolytic degradation time are shown in Figure 3, and their initial linearity is consistent with the accepted degradation mechanism of aliphatic polyesters: hydrolysis of the ester groups in which the resulting end groups further catalyze the reaction.[4,17] For such a process, the rate equation is given by eqs 3 and 4 and simplifies to eq 5, where [COOH], [H_2O], and [E] are the concentrations of the carboxyl end groups, water, and the ester, respectively, and the effective rate constant $k' = k[H_2O][E]$

$$d[COOH]/dt = k[COOH][H_2O][E] \quad (3)$$

$$[COOH] = [COOH]_0 \exp(-k't) \quad (4)$$

$$M_n = M_n^0 \exp(-k't) \quad (5)$$

A plot of ln(M_n) vs time (days) should thus be linear, with the gradient representing the rate constant, i.e., the percentage of remaining ester groups "cut" each day. From Figure 3, the PLLA experienced hydrolytic degradation with a rate constant of approximately 0.001 ± 0.002 day^{-1}, slightly lower, but of similar order of magnitude to that found by other authors (0.0027 day^{-1} by Tsuji et al.,[18] and 0.00672 $days^{-1}$ by Cha et al.[19]). PLLA1.8a had the next fastest rate constant at 0.022 ± 0.001 day^{-1}, approximately 20 times faster than PLLAa, whereas PLLA1.8x and PLLA4.5a had very similar rate constants at approximately 0.029 ± 0.001 and 0.030 ± 0.002 day^{-1} respectively. A change in gradient was seen for PLLA1.8x at approximately 50 days, corresponding to the time at which mass loss began (Figure 1b). Beyond this time, short degradation products were able to diffuse out of the sample into the buffer solution and were not included in the molecular weight measurements, skewing the results toward higher values. It is possible that this also happened to some extent in PLLA4.5a and PLLA1.8a, since in both cases mass loss began within the duration of the experiment; however, this effect was not significant within the given time, and more readings at longer degradation times would be needed to determine both the time and magnitude of any gradient change. A discussion of the validity of the linearity of these graphs is given later in the discussion section.

Figure 4 shows the tensile test data for the four sample-types at different stages of hydrolytic degradation, and their associated SAXS patterns just after yield (displacement at time of data collection given by each pattern in mm). Due to the shape of the tensile bars required for SAXS data collection, only load-displacement data may be presented. The degradation times shown were chosen to represent material that was "undegraded", "hydrated", with "mild degradation", and "severe degradation". Hydrated corresponded to 1 day in solution (except for PLLAa when 10 days was used), whereas "mild degradation" corresponded to PLLAa, 8 months; PLLA1.8a, 22 days; PLLA4.5a, 4 days; PLLA1.8x, 3 days.

Throughout the hydrolytic degradation of PLLAa (up to 8 months), all samples failed in a ductile manner (post-yield), and plastic deformation occurred by crazing, as demonstrated by the characteristic "lobe and spike" SAXS pattern. This pattern is the result of diffraction from the craze fibrils and reflection from the craze planes and has been discussed in detail by other authors.[20,21] No data was available for severe hydrolytic degradation of PLLAa due to the extremely long degradation times required; however, it is expected from literature that the PLLA would eventually become brittle (fail prior to yielding).[7,22] For PLLA1.8a, all samples up to 42 days of hydrolytic degradation deformed post-yield by crazing, although the elongation at break was considerably increased between 1 and 22 days, compared to the undegraded material. At 32 days, the elongation at break was reduced (data not shown), and beyond 42 days, samples failed in a brittle manner with no development of the SAXS pattern. Dry PLLA4.5a also deformed post-yield by crazing, and hydration again resulted in an increase in the elongation at break (no SAXS data available). After 4 days of

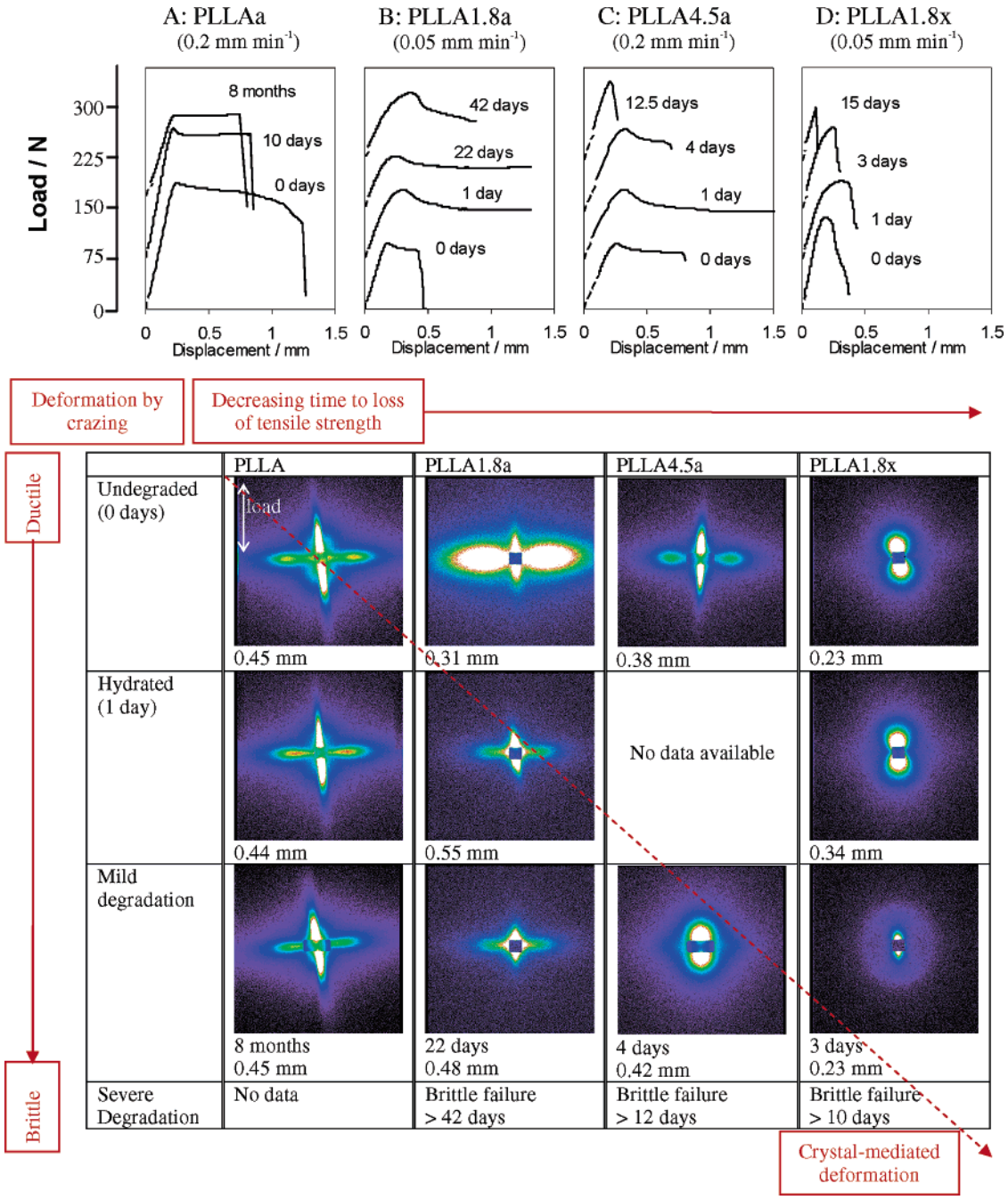

Figure 4. Load-displacement tensile curves and "phase diagram" of deformation properties showing SAXS patterns just after yield. Each load-displacement plot is shifted vertically by 75 N in the load direction, in relation to the previous plot, for clarity. All data is shown with the same load scale and the deformation rate shown.

hydrolytic degradation, the elongation at break was reduced, and the post-yield deformation mechanism had changed to one of crystal-mediated deformation. This was evident from the SAXS pattern which showed a characteristic "lemon and peanut" shape, discussed by other authors,[23] which resulted from deformation through a combination of cavitation and fibrillated shear.[24]

Beyond 12 days, PLLA4.5a failed in a brittle manner. Undegraded PLLA1.8x deformed post-yield through crystal-mediated deformation, again through cavitation and fibrillated shear, although failure occurred very shortly after yield. On hydration, the elongation at break was slightly increased, and the deformation mechanism remained unchanged. By 3 days of hydrolytic degradation, the elongation at break was reduced and development of the SAXS pattern was restricted, suggesting failure occurred after less "local" plastic deformation. Beyond 10 days, PLLA1.8x failed in a brittle manner.

Discussion

The results presented in this paper demonstrate the severe effect lauric acid had on the hydrolytic degradation properties of PLLA, when blended into the material. The two "extreme" samples in this series were PLLAa and PLLA1.8x, which showed very different properties, whereas PLLA1.8a and PLLA4.5a showed behavior somewhat intermediate between the two. This concept is represented in Figure 4 in the order of the table columns, to create a form of "phase diagram" of properties, though it should be noted that this is intended as a guide to understanding the properties rather than as a rigid phenomenon.

PLLAa. PLLAa showed no significant signs of hydrolytic degradation and only very mild crystallization (approximately 1 wt %) after 8 months in the degradation solution, and the post-yield deformation mechanism remained consistently that of crazing. Further experimentation would be required to determine any further transitions in properties beyond this time.

PLLA1.8a. The trend in behavior of PLLA1.8a was similar to that of PLLA, with a relatively long period of stable water content and no mass loss, during which time the crystallinity remained negligible and the post-yield deformation mechanism remained one of crazing. The main differences lay in the rate of hydrolysis, with PLLA1.8a degrading approximately 20 times faster than PLLAa, and in the elongation at break of the hydrated material; the elongation at break of PLLAa was relatively unaffected by hydration, whereas the elongation at break of PLLA1.8a was significantly increased on hydration, possibly due to the combined plasticising effects of the lauric acid and the absorbed water.

Once water was absorbed into the polymer, chain scission began, gradually increasing the chain mobility. The plasticising effect of the lauric acid however was not significant enough to allow crystallization to occur at this time. At approximately 25 days, the chain length was sufficiently reduced for crystallization to occur. It is likely that since this crystallization occurred in the partially degraded polymer, a large number of chain ends were excluded into the amorphous regions resulting in very defective intercrystallite regions. Furthermore, each chain would only pass through a limited number of crystals due to its short length resulting in few tie-chains. This poorly connected crystalline structure would be less able to support an applied load and this would explain why the failure mechanism very quickly changed to that of brittle failure.

Water up-take and mass loss began a considerable time after crystallization. It is possible that the early crystallization of the polymer pinned low molecular weight material into the bulk, which otherwise might have been of sufficiently low molecular weight to be released. Once the mass loss occurred, it was probably occurring from within the constrained amorphous regions between crystallites, where water absorption would be high both due to the "defective" structure[22] and due to the high concentration of hydrophilic chain ends. This may explain why once mass loss began, it proceeded rapidly. It should also be noted, however, that some mass loss may be due to surface erosion of the sample, rather than to diffusion of low molecular materials from the bulk; however, the dimensions of the samples were not significantly reduced on completion of the experiments.

PLLA4.5a. PLLA4.5a again showed behavior initially similar to that of PLLAa, with post-yield deformation by crazing. On hydration however, crystallization began immediately, possibly due to the added plasticising effect of the greater concentration of lauric acid, compared with PLLA1.8a. Within 4 days, the post-yield deformation mechanism had changed to that of crystal-mediated deformation, a mechanism not seen for PLLA1.8a. Although the hydrolytic degradation rate of PLLA4.5a was somewhat faster than that of PLLA1.8a (due to the greater amount of acid catalyst present), since crystallization occurred very early on in the hydrolytic degradation, the crystalline structure is likely to have formed from a higher molecular weight polymer. This suggests that the crystalline structure was relatively strong, with few chain ends (so with less "defective" amorphous regions) and with each chain passing through a large number of crystals (meaning a large number of tie-chains). This crystalline structure was sufficiently strong that it was able to plastically deform on application of a load (unlike the brittle failure seen in PLLA1.8a), resulting in the "lemon and peanut" SAXS pattern of crystal-mediated deformation. Again, as with PLLA1.8a, mass loss began after considerable crystallization occurred, and this is again likely to be due to the pinning effect of the crystallization preventing mass loss.

PLLA1.8x. PLLA1.8x was crystallized prior to hydrolytic degradation, at 110 °C for 5 min, at which time complete crystallization had occurred, resulting in a spherulitic morphology. Since the PLLA1.8x was crystallized prior to degradation, the crystals formed in the maximum possible molecular weight material, probably meaning that there were few chain ends and that each chain passed through many crystals. The crystalline structure was therefore sufficiently strong that it could deform on application of a load, and the deformation mechanism was that of crystal-mediated deformation through cavitation and fibrillated shear. Despite this, the elongation at break of PLLA1.8x was low, suggesting that, although the applied load was initially supported, the rigidity of the structure was such that it was unable to support extended deformation.

The degradation mechanism for crystallized (spherulitic) PLLA has been discussed by other authors,[18,25] but in general, degradation can be considered to occur preferentially in the amorphous regions of the sample. This is considered to be due to both the greater ease of water penetration into the amorphous regions over the crystalline regions and the more hydrophilic nature of these amorphous regions due to exclusion of hydrophilic chain ends from the crystals. These restricted amorphous regions between crystallites also degrade faster than the "free amorphous" material in a fully amorphous sample due to the more "defective" structure of these regions allowing greater water penetration.[22]

The hydrolytic degradation rate constants for PLLA4.5a and PLLA1.8x were similar; however, this value represents an average value for the whole sample (both amorphous and crystalline phases), whereas in the semicrystalline material, chain scission occurred preferentially in the amorphous regions due to exclusion of water from the crystallites.[25] This meant that in initially amorphous PLLA4.5a chain scission was initially occurring throughout the whole sample, whereas for crystalline PLLA1.8x, it was confined to the amorphous region, so that, although the average rates were similar, the local rate of chain scission in the amorphous regions of PLLA1.8x was likely to be much higher. This may have been due to concentration of the (catalyzing) lauric acid into the amorphous regions due to exclusion from the crystals during crystallization of PLLA1.8x. Another possible cause is the more defective inter-crystallite amorphous regions of PLLA1.8x, compared with the free-amorphous material of PLLA4.5a,[22] resulting in more water penetration into the amorphous regions of the PLLA1.8x and hence faster hydrolysis.

The fact that the molecular weights plotted in Figure 3 remain approximately linear throughout the early stages of degradation does not immediately relate crystallinity profiles for those samples. Since PLLA 4.5a and PLLA1.8x both increased in crystallinity throughout this period, a reduction of the percentage of amorphous material present, combined with preferential degradation of the amorphous regions, would both be factors that would lead to slowing of the loss of molecular weight. However as discussed above, the competing factors of increasing "defectiveness" of these amorphous regions as the crystallinity increases and exclusion of hydrophilic chain ends into the amorphous regions would both act to increase the rate of loss of molecular weight within the amorphous regions. Since the molecular weights presented are averages for the whole sample,

these factors appear to balance, maintaining the approximate linearity of the graphs.

This faster hydrolysis of the amorphous regions of PLLA1.8x compared with those of PLLA1.8a would contribute to the earlier onset of mass loss in PLLA1.8x (Figure 1b). This would complement the effects of ongoing crystallization, whereby PLLA1.8a is able to crystallize and pin oligomers which might otherwise dissolve, a process which will be much less widespread in the already mature crystalline structure of PLLA1.8x. The faster hydrolysis of the amorphous regions of PLLA1.8x may also have been the factor allowing crystallization of the amorphous regions to occur from the onset of hydrolytic degradation (without the lag-time seen in PLLA1.8a). The combination of these factors meant that within 3 days of degradation the scission of "tie-chains" that held the crystals together, and embrittlement by crystallization, was sufficiently great to result in failure of the samples after only a small amount of deformation (as seen from the less developed SAXS pattern at failure). For PLLA1.8x after 3 days of degradation, far less SAXS development occurred than in PLLA4.5a after 4 days, despite the similar "average" molecular weight (but admittedly much lower crystallinity).

In summary, Figure 4 is suggestive of a "phase diagram" of properties, with the time to loss of tensile strength decreasing from left to right, a transition from crazing to crystal-mediated deformation from top-left to bottom-right, and a transition from ductile to brittle failure from top to bottom. The key factor in determining the development of the mechanical behavior of the materials appeared to be the molecular weight at which crystallization occurred, with high molecular weight crystals able to deform (although not necessarily able to maintain extended deformation), and low molecular weight crystals resulting in brittle failure. The two factors that most obviously affected this were the amount of plasticizer present (possibly since more lauric acid allowed crystallization to occur earlier) and the processing conditions (annealing prior to hydrolytic degradation affecting the polymer molecular weight of the crystals present).

This "phase diagram" should not be considered in the conventional sense as allowing the ideal material to be picked off the graph but should be considered in terms of allowing trends in properties to be viewed and their importance weighed. On first appearance, factors such as lauric acid content appear dominating, and one might argue that they should be kept low, keeping the hydrolytic degradation time in months and maintaining good mechanical properties. However, this would lead to a sudden change in mechanical properties at a sudden "crystallisation point". Also on first appearances, crystallization would appear to need to occur in the high molecular weight materials to prevent a sudden change in mechanical properties. However, this structure is then not necessarily able to *maintain* that deformation and may lead to a low elongation at break. Some compromise of properties must obviously be made, but other factors may also be introduced to improve these properties. For example, the use of a plasticizer (which does not affect the hydrolytic degradation process through catalysis) in the low lauric acid material may allow for the desired degradation time but also allow a transition of crystal-mediated deformation while allowing that deformation to be maintained at greater elongation. In terms of medical device applications, none of the materials studied herein are perfect; however, the "mapping" of the different behaviors of all these materials does allow for some discussion of the potential advantages and disadvantages of the properties noted.

Conclusions

Addition of lauric acid to PLLA has previously been shown to result in acceleration of the hydrolytic degradation processes, with the time to loss of tensile strength directly related to the lauric acid content.[10] This paper demonstrated that the development of mechanical properties is also affected by the lauric acid content, with a key factor being the time at which crystallization begins in relation to the loss of molecular weight. With low lauric acid content, a lag-time to the onset of crystallization occurs, possibly resulting in a low molecular weight crystal structure that fails in a brittle manner. A high concentration of lauric acid plasticizes the material, resulting in early crystallization, suggestive of a crystalline structure that was able to plastically deform. Pre-crystallization of the material prior to hydrolytic degradation also results in a high molecular weight structure that is able to deform, but possibly due to the rigidity of this structure, deformation cannot be maintained, resulting in a low elongation at break.

Acknowledgment. The authors thank the EPSRC, Smith and Nephew, and CCLRC for funding this research and Antony Gleeson, Peter Laity, Sharlene Freeburn, and Anousha Kamvari for assistance with synchrotron radiation experiments.

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BM050746V