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# DEGRADATION OF ALIPHATIC POLYESTERS IN THE PRESENCE OF INORGANIC FILLERS\*

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**ABSTRACT:** Aliphatic polyesters are melt mixed with bioactive fillers and converted into sheets in order to compare their degradation behavior in a phosphate buffer saline (PBS) solution as a function of processing method, polymer type, and crystallinity and type of filler. The samples are tested for weight changes, pH, intrinsic viscosity (IV), and thermal and mechanical property changes as a function of time. The study establishes that although the fillers appear to enhance the polymer degradation, they also have an effect on crystallinity after several immersion periods. Intrinsic viscosity measurements show degradation in the form of molecular weight reduction even after short periods of immersion.

**KEY WORDS:** Degradation, biodegradable polymers, aliphatic polyesters, polylactic acid, polycaprolactone, poly(1,4-butylene adipate-co-1,4-butylene succinate), crystallinity, intrinsic viscosity, elongation, pH, tensile stress.

## INTRODUCTION

**I**N ORDER TO address the growing demand for materials with controlled degradation characteristics and desirable mechanical properties, a number of studies have been conducted on synthetic biodegradable polymers [1–6]. Synthetic aliphatic polyesters cover a broad area in the field of biodegradable materials. Some of the most common commercially available aliphatic polyesters include polyglycolic acid, polylactic acid, poly- $\epsilon$ -caprolactone, polybutylene succinate, and

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Figures 1–13 appear in color online: <http://jpf.sagepub.com>

polybutylene adipate, as well as blends and copolymers of the above. All the aforementioned polymers have been studied for degradation rates to variable degrees, and results have been reported regarding their usage in biomedical and packaging films, as well as their properties and characteristics [2–5].

In many cases, these materials need to be reinforced with organic or inorganic fillers that consequently lead to a significant modification of their properties. In addition, different processing conditions have different effects on the characteristics of the final material. Specifically, in the case of biomedical materials for *in vivo* applications, solvents should be avoided, and conventional thermoplastic melt processing techniques should rather be used. It is known that for thermoplastic materials, physical and mechanical properties are strongly dependent on the amount and the type of crystallization resulting from processing [7]. This study is part of a broader effort to determine the effects of different fillers and processing conditions on the degradation characteristics of the final product. Several aliphatic polyesters such as polycaprolactone, different grades of polylactic acid and butylene adipate-co-butylene succinate copolyester have been tested for weight changes, pH, intrinsic viscosity (IV), and thermal changes during several degradation periods in a phosphate buffer saline (PBS) solution. For aliphatic polyesters, degradation is known to take place through hydrolytic scission of the ester group [8]. For different applications, a different degradation behavior is desired. For example, in the case of biomaterials used for drug release, high rates of mass losses are desirable. However, for certain tissue engineering implants, strength loss and healing rate need to be coordinated so that the implant can support loading during the healing period of the tissue [9]. The factors that affect mechanical performance are monomer selection, process conditions, and the presence of additives. These factors, in turn, influence polymer hydrophilicity, crystallinity, melt and glass transition temperatures, molecular weight, and molecular weight distribution.

This is the main reason why it is essential to follow not only weight changes, but also mechanical property and crystallinity changes during degradation.

In this study, the degradation behavior of biodegradable polymers (both amorphous and semicrystalline), with emphasis on the effects of fillers with different structures, in a PBS solution was investigated through intrinsic viscosity measurements. Fillers included surface reactive inorganic compounds, salts, and glasses that have structural compatibility to the mineral phase of the human bone, specifically,

specialty glasses containing  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{P}_2\text{O}_5$  at specific ratios and a calcium silicate. The effects of processing conditions and type of filler on crystallinity, water uptake ability, and mechanical properties were explored.

## Degradation Mechanisms

In order to have a better understanding of the effect of fillers and processing conditions on the degradation of the composite, it is essential to review the mechanisms and the factors that could affect the polymer degradation.

Aliphatic polyesters decompose through hydrolytic degradation. When in aqueous media, degradation occurs through cleavage of the ester bond [1,10]. Although a number of studies have been conducted on the synthesis and degradation of these materials, the role of the low molecular weight fragments in the degradation process is still unknown. Schliecker et al. [1] suggested that the hydrolytic degradation process could be affected by four parameters specifically, the rate constant, the amount of water that has been absorbed, the diffusion coefficient of the chain fragments, and the solubility of the degradation byproducts in the aqueous media.

The degradation of a polymer matrix could proceed through the following mechanisms: (i) surface or heterogeneous and (ii) bulk or homogeneous erosion [10]. In the first case (1), water is being absorbed by the polymer and hydrolytic ester cleavage occurs at the surface of the polymer matrix. This generates chain fragments that have acidic end groups. Initially, polymer degradation is faster than water intrusion into the polymer bulk which results into degradation mainly in the outermost and not in the inner part of the matrix. The decrease in molecular weight, along with an increase in the polydispersity,  $M_w/M_n$ , and polymer mass loss occur. After a short time, water diffusion is relatively rapid in comparison to polymer degradation. Reaction/diffusion phenomena, that involve water soluble low molecular weight degradation products at the surface and the inner part of the polymer, govern polymer degradation [1]. In small size medical devices, soluble oligomers can escape before the devices are totally degraded. In contrast, in large size devices, only soluble oligomers that are located close to the outer surface can escape, whereas the ones inside the device remain entrapped as a result of their relatively small diffusion coefficients. Consequently, carboxyl end groups are more concentrated in the center, and the degradation rate increases due to autocatalysis of ester hydrolysis by the carboxyl groups [1,10].

In the second case of homogeneous erosion, polymers degrade slowly and water diffusion into the system is faster than polymer degradation. As a result, the whole system hydrates rapidly and when the polymers change into oligomers, they are cleaved throughout. It is essential to note that degradable polymers can erode via both pathways depending on the erosion conditions, the geometry of the samples, and the hydrophilic/hydrophobic characteristics of the polymer [4,10].

In the case of amorphous polylactic acid, material degradation proceeds through heterogeneous erosion and takes place faster in the inner part than at the surface due to the autocatalysis phenomena. On the contrary, the degradation of semi-crystalline polylactic acid proceeds in a more complex way. Initially, the degradation proceeds through the amorphous regions, since they have higher water uptake ability than the crystalline ones. The degraded fragments diffuse and then recrystallize. The degree of crystallinity could increase along with degradation. After the major part of the amorphous area degrades, hydrolysis proceeds from the edge to the center of the crystalline domains [6,10].

Polycaprolactone is also a semi-crystalline aliphatic polyester but with higher crystallinity and hydrophobicity than polylactic acid, and as a result, it exhibits a different degradation behavior. The hydrophobicity of polycaprolactone could lead to a surface erosion/degradation behavior as Xu et al. [4] illustrated in their study of hydrophobic polyesters. Polycaprolactone has lower degradation rates than polylactic acid, but being highly compatible with osteoblasts is used for long-term implant applications [6].

## EXPERIMENTAL

### Materials

Poly- $\epsilon$ -caprolactone, PCL, (TONE 767) (CAS No. 24980-41-4) was supplied from Dow Chemicals. Poly(L-lactic acid), PLLA, (trade name Biomer L9000) (CAS No. 26680-10-4) was purchased from Biomer. Amorphous polylactic acid, PLA, (trade name PLA 4060D) was purchased from Nature Works LLC. Poly(1,4-butylene adipate-co-1,4-butylene succinate), PST, extended with 1,6-diisocyanatohexane, a biodegradable thermoplastic copolyester (CAS No. 119553672) was obtained from Sigma-Aldrich. Calcium silicate CS (CAS No. 1344-95-2) filler with a density of 2.9 g/cc, was also obtained from Sigma-Aldrich. The bioactive glass BG45S5 flakes, with a particle size of 90–212  $\mu\text{m}$  and

a density of about 2.5 g/cc, were purchased from Mo-Sci Health Care L.L.C.

**Processing**

Designation of polymer and composite samples produced by different processing methods is shown in Table 1.

*Melt Mixing*

PCL was ground to a fine powder under liquid nitrogen and then premixed with powdered fillers at a 7:3 polymer:filler weight ratio, before feeding the mixture in a co-rotating 15 mm twin screw extruder (APV MP-2015) at 80°C. PCL alone was also fed in the twin screw extruder in order to obtain a control sample. In addition, PST and PLLA were processed in the extruder at 130 and 200°C, respectively.

PLA was similarly mixed with the fillers in a Brabender plasticorder PL2000 at 190°C.

*Compression Molding*

Composite samples and extruded unfilled polymers were compression molded in a PHI press at their processing temperatures using a 44 kN force for 5 min to form standard test disc specimens with a nominal thickness of 0.75 mm and a diameter ranging from 20 to 33 mm.

**Table 1. Designation of materials.**

Polymer name/sample designation	wt% Filler	Processing method
Poly(1,4-butylene adipate-co-1,4-butylene succinate)/PST CM	–	Compression molding
Poly(1,4-butylene adipate-co-1,4-butylene succinate)/PST EXT	–	Extrusion
Poly(L-lactic acid)/PLLA CM	–	Compression molding
Poly(L-lactic acid)/PLLA EXT	–	Extrusion
Poly-ε-caprolactone/PCL CM	–	Compression molding
Poly-ε-caprolactone/PCL EXT	–	Extrusion
Poly-ε-caprolactone/PCL CS	30% Calcium silicate	Extrusion
Poly-ε-caprolactone/PCL BG	30% Bioglass 45S5	Extrusion
Poly(lactic acid)/PLA CM	–	Compression molding
Poly(lactic acid)/PLA	–	Brabender plasticorder
Poly(lactic acid)/PLA-CS	30% Calcium silicate	Brabender plasticorder
Poly(lactic acid)/PLA-BG	30% Bioglass 45S5	Brabender plasticorder

Polymer pellets were also compression molded in order to obtain samples for the degradation studies in the PBS solution.

### *Film Extrusion*

PCL and PLA pellets were predried and extruded through a Brabender single screw extruder ( $D = 1.9$  cm and  $L/D = 15$ ), equipped with a 10 cm wide flat sheet die to obtain film samples for mechanical testing.

## **Testing and Characterization**

### *Degradation Study*

Degradation behavior was followed by immersing duplicate specimens in a PBS solution with a pH of 7.4 at 37°C. The composition of the PBS aqueous solution is 1.38 mM NaCl, 1.15 mM Na<sub>2</sub>HPO<sub>4</sub>, 1.2 mM KH<sub>2</sub>PO<sub>4</sub>, and 2.7 mM KCl. The PBS solution is a buffer solution that is commonly used by researchers for hydrolytic degradation and controlled release experiments *in vitro*. At predetermined immersion periods, the specimens were removed from the solution, and after wiping the excess, they were weighed. pH measurements were also made at these times. When the test was completed, the specimens were washed with distilled water and dried under vacuum at room temperature, for further characterization.

### *Intrinsic Viscosity Measurements*

The intrinsic viscosity of 1% w/v solutions of PCL in methylene chloride and PLLA, PLA, and PST in chloroform, before and after several immersion periods in PBS, was measured at 25°C in a constant temperature bath using an Ubbelohde viscometer (Kannon K879). The solvents were filtered 3 times using disposable Teflon filters.

### *Differential Scanning Calorimetry (DSC) Analysis*

Information on glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), cold crystallization temperature ( $T_{cc}$ ), as well as heat of fusion ( $\Delta H$ ) and % crystallinity was obtained by using differential scanning calorimetry, DSC (TA Instruments, QA100). For all samples, heating and cooling rates were 20°C/min.

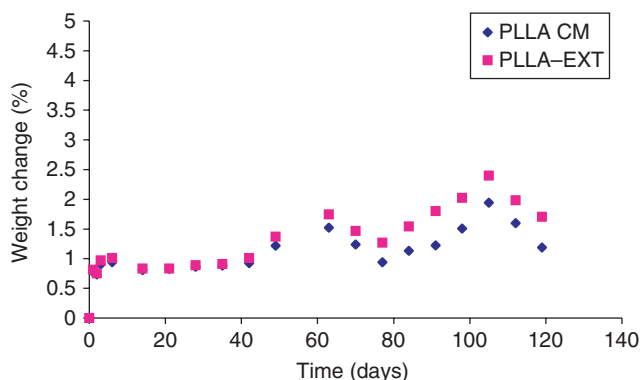
### Mechanical Properties Testing

Tensile stress at yield and break and elongation at yield and break of PLA shaped films (Type 5) were measured by a Tinius-Olsen (Lo Cap Universal) testing machine as per ASTM method D882. The speed of the test was 12.7 mm/min.

## RESULTS AND DISCUSSION

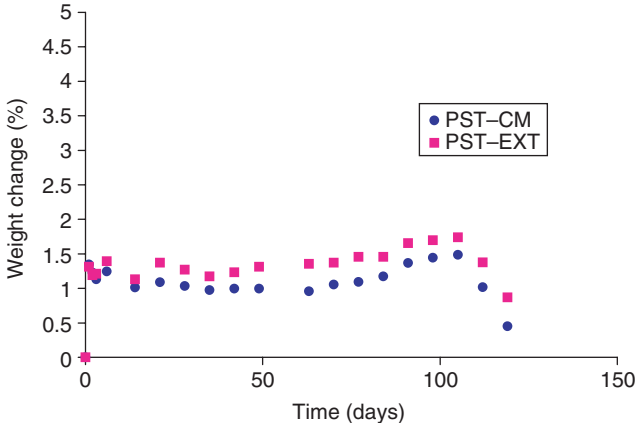
Aliphatic polyesters are known to degrade through hydrolysis. In the case of polylactic acid resins, degradation takes place in the bulk of the material and does not start from its surface. The cleavage of the ester bond that happens through hydrolysis proceeds preferentially in the amorphous regions, and as a result, crystallinity increases. For this reason, the hydrolysis rate is higher in the amorphous PLA polymer rather than in the semicrystalline PLLA. The chain cleavage leads to formation of lactic acid oligomers, which result in an increase of carboxylic groups that then catalyze the degradation reaction [8]. PCL and PST have similar degradation behavior to that of polylactic acid [3,11].

Figures 1–5 represent percentage weight changes of the different polymer and composite samples as a function of time. Figures 1 and 2 show that for both PLLA and PST polymers, extruded samples show slightly higher water uptake than compression molded samples, although only slight differences were observed for up to 120 days. This will lead to a faster degradation rate for the extruded samples, since

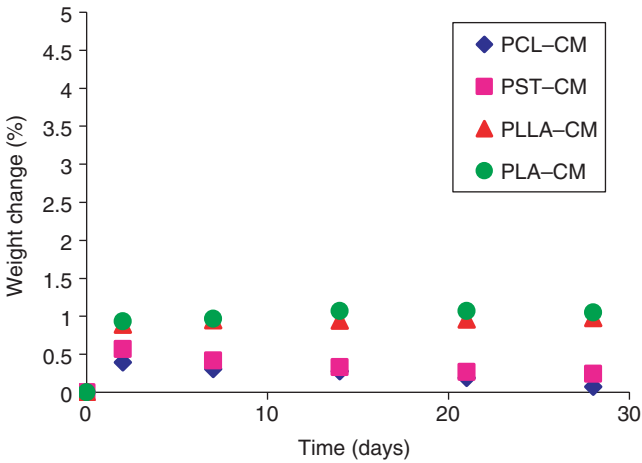


**Figure 1.** Percentage weight change vs time for PLLA CM and PLLA EXT.



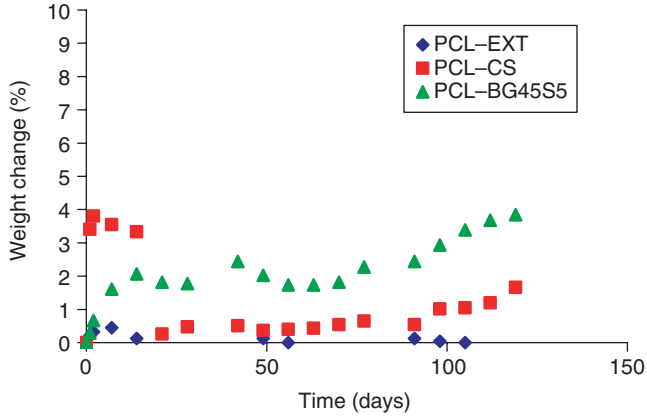


**Figure 2.** Percentage weight change vs time for PST CM and PST EXT.

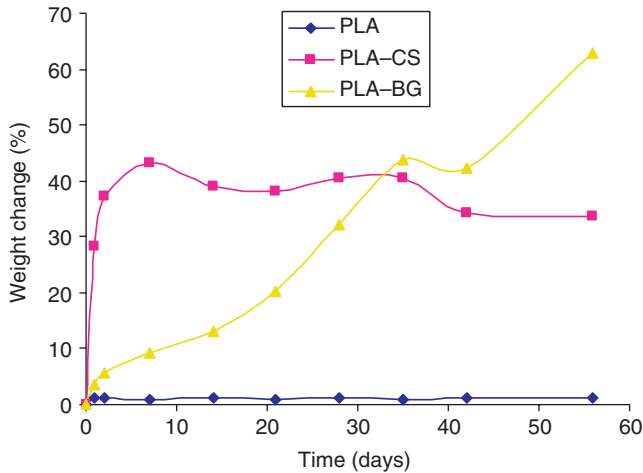


**Figure 3.** Percentage weight change vs time for PCL, PST, PLLA, and PLA compression molded specimens.

the additional processing step may have lowered the molecular weight of the sample. Molecular weight and crystallinity are important factors affecting the degradation characteristics of any biodegradable polymer. The lower the molecular weight and the crystallinity, the faster the degradation. Figure 3 shows slight changes in the degradation behavior of all aliphatic polyesters used in this study over the first 30-day period with the amorphous PLA appearing to have a faster degradation rate. Figure 4 shows the effect of the presence of the filler on the degradation



**Figure 4.** Percentage weight change vs time for PCL-EXT and its composites. Samples were prepared by extrusion mixing (see Table 1).

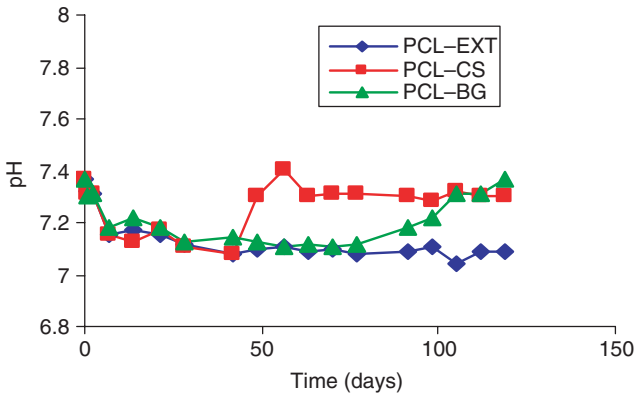


**Figure 5.** Percentage weight change vs time for PLA and its composites. Samples were prepared by batch mixing (see Table 1).

of PCL. Although the fillers appear to enhance the degradation behavior of PCL, the degree of swelling in all cases remains low (only at about 5%) even after a period of 120 days. This was expected for a semicrystalline polymer as PCL, since crystalline regions have the tendency to retard water ingress. Variations in percentage weight change for PCL-CS from 0 to 14 days may be due to sample imperfections, such as cracks that allowed fast water absorption initially, followed by removal of CS particles to the solution during

continuous immersion. Figure 5 similarly shows the effect of the fillers on the degradation behavior of the PLA. In this case, the degree of swelling is much higher (reaches about 60%) in the case of the PLA–BG composite. This confirms not only that PLA, being an amorphous polyester, has a faster degradation rate but also the effect of each filler on a given polymer. Both CS and Bioglass 45S5 enhance the degree of swelling and consequently the rate of degradation. Calcium silicate composites appear to have reached a plateau of swelling after an initial immersion period, whereas in the case of Bioglass 45S5 the degree of swelling continues to increase. Such differences may be attributed to the fact that the fillers' shape and size could influence water diffusion rates.

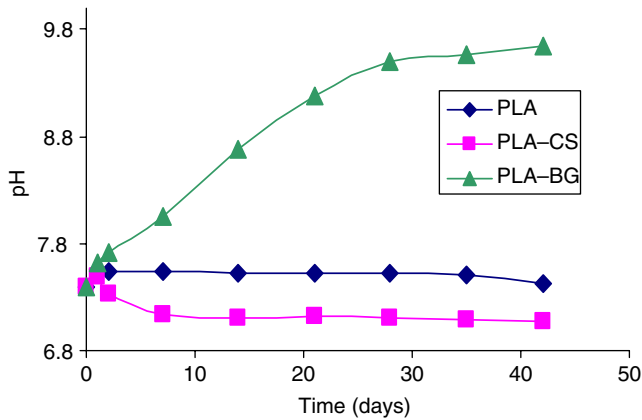
Figures 6 and 7 represent the pH change of the PBS buffer with respect to time for PCL and PLA polymers and composites. Figure 6 confirms the anticipated neutralization ability of the fillers. In Figure 7, the pH results for the PLA degradation are slightly different. In the case of CS composites, one can observe a decrease in the pH values. This could be due to oligomers that have diffused out of the sample to the PBS solution, although such an explanation may not be valid for the behavior of oligomers and filler particles in human blood plasma, since degradation products and filler particles may not always be associated. Calcium silicate particles, that tend to form aggregates, will eventually pass to the solution and could have a neutralizing effect over a longer time period. Bioglass 45S5 behaves in a different way. There was a significant increase in the pH of the PBS solution. This could be attributed to the reactivity and dissolution characteristics of the glass grade used. Specifically, Bioglass 45S5 flakey particles are free flowing



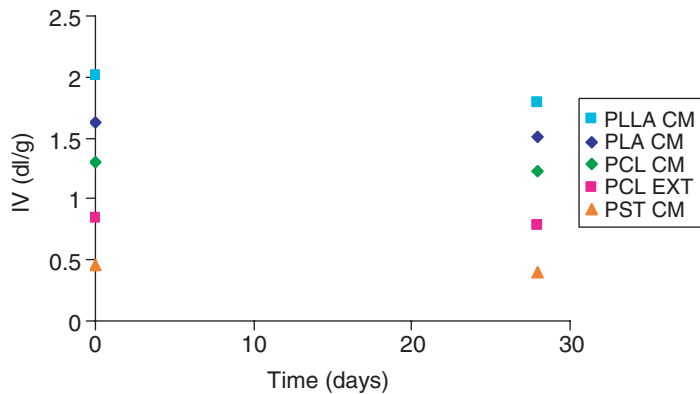
**Figure 6.** pH change vs time for PCL–EXT and its composites. All samples were prepared by extrusion mixing (see Table 1).

(non-agglomerating) and according to supplier’s data have a decay rate of  $150 \mu\text{g}/\text{cm}^2/\text{day}$ . They dissolve faster and the released ions make the surrounding degradation environment more alkaline. It is essential for biomaterials used for *in vivo* applications to maintain a neutral pH, since this would minimize inflammation effects from the acidic degradation fragments of certain polyesters.

The IV of the unfilled samples, before and after immersion, was calculated using the Solomon–Ciuta equation [12] for a single point measurement. Results are shown in Figures 8 and 9. Although no weight



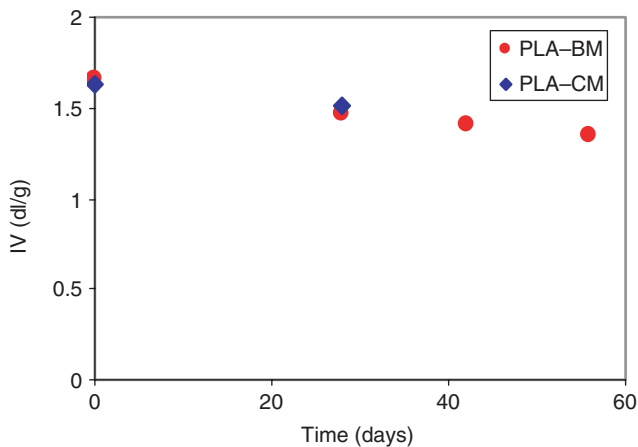
**Figure 7.** pH change vs time for PLA and its composites. All samples were prepared by batch mixer (see Table 1).



**Figure 8.** Intrinsic viscosity measurements for polyesters as a function of immersion time. The designation CM and EXT denote compression molded and extruded samples, respectively.

losses were shown, there was already an onset of degradation confirmed by the reduction in intrinsic viscosity (which corresponds, in turn, to reduction in MW) after immersion. In addition, in Figure 8, the extruded PCL samples appear to have a lower IV, which confirms once more, that thermal degradation of PCL occurred during extrusion. Figure 9 shows the reduction in IV in the PLA samples that have been prepared by mixing in a Brabender plasticorder and merely batch mixed before compression molding. Both samples had similar IV changes with time up to 28 days, hence IV measurements for the batch mixed sample were discontinued after 28 days.

Tables 2–4 represent thermal data obtained by DSC experiments for PCL, PLA, and PST. The percentage crystallinity was calculated from  $(\Delta H_f - \Delta H_{cc})/\Delta H_{pf}$ , where  $\Delta H_f$  is the heat of fusion,  $\Delta H_{cc}$  is the heat of cold crystallization, and  $\Delta H_{pf}$  is the heat of fusion for a perfect crystal [13]. For PLA, PCL, and PST the values for  $\Delta H_{pf}$  are 93.1 [14], 139.5 [15], and 122.75 J/g [3] (assuming a 50/50 comonomer content), respectively. In the case of unfilled PCL (Table 2), the method of processing appears to affect crystallinity, since the extruded samples show higher percentage of crystallinity than the compression molded ones. In addition, the composite that contains Bioglass 45S5 exhibits a higher crystallinity. In the case of PLA it is interesting to note that the Bioglass 45S5 decreases somewhat the  $T_g$  of the composite after immersion, whereas CS does not (second heating); however, after the second heating, immersion does not appear to affect the  $T_g$ . The  $T_g$  for



**Figure 9.** Intrinsic viscosity measurements for PLA under different processing methods as a function of immersion time. PLA BM and PLA CM correspond to batch mixer and compression molded samples, respectively.

PLA alone appears to increase with immersion time during the first heating. The differences in composites containing Bioglass 45S5 could be the result of the glass reactivity. Bioglass 45S5 has a decay rate of  $150 \mu\text{g}/\text{cm}^2/\text{day}$ , and its composition changes as a function of

**Table 2. Thermal data for PCL and its composites.**

Sample description	Second heating		
	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_f$ (J/g)	% Crystallinity
PCL CM	57.2	51.1	36.6
PCL CM 28 days PBS	59.0	50.3	36.0
PCL extrusion	60.1	47.3	33.9
PCL extrusion 28 days PBS	59.0	59.2	42.4
PCL extrusion 378 days PBS	60.5	65.7	47.1
PCL BG	59.8	77.3	55.4
PCL BG 28 days PBS	60.9	79.1	56.7
PCL BG extrusion 378 days PBS	59.6	92.3	66.2
PCL CS	58.7	60.1	43.1
PCL CS 28 days PBS	58.3	62.1	44.5
PCL CS 378 days PBS	59.8	67.7	48.5

**Table 3. Thermal data for PLA and its composites.**

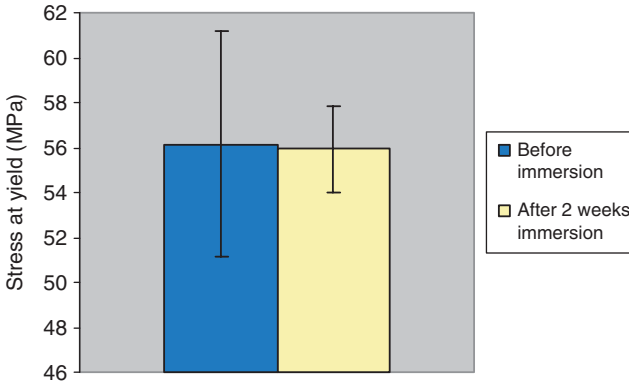
Sample description	First heating	Second heating
	$T_g$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )
PLA before immersion	63.5	61.9
PLA 28 days PBS	66.6	62.0
PLA 56 days PBS	67.3	62.3
PLA BG before immersion	60.3	59.6
PLA BG 28 days PBS	54.9	57.1
PLA BG 56 days PBS	57.3	57.4
PLA CS before immersion	61.2	59.8
PLA CS 28 days PBS	61.6	61.4
PLA CS 56 days PBS	62.7	61.9

**Table 4. Thermal data for PST before and after 28 days immersion.**

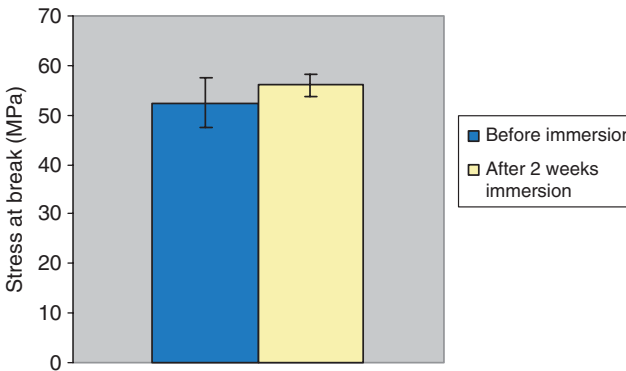
Sample description	First heating					Second heating				
	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_f$ (J/g)	$T_{cc}$ ( $^{\circ}\text{C}$ )	$\Delta H_{cc}$ (J/g)	% Crystallinity	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_f$ (J/g)	$T_{cc}$ ( $^{\circ}\text{C}$ )	$\Delta H_{cc}$ (J/g)	% Crystallinity
PST CM	99.8	58.5	73.6	4.2	44.5	98.4	48.6	76.7	5.8	34.8
PST-CM 28 days PBS	100.2	45.4	77.5	3.9	33.9	99.8	45.7	76.8	4.7	33.4

immersion time. This could possibly explain the changes in thermal data for both PLA and PCL composites filled with Bioglass 45S5. For PST compression molded films, at the second heating, there are only slight differences in the  $T_m$  and the percentage of crystallinity before and after 28 days immersion.

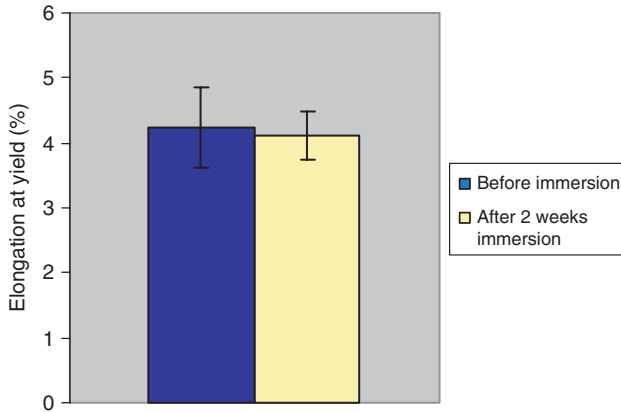
Figures 10–13 show the results of tensile properties of PLA as a function of hydrolytic degradation time. Elongation at break for PLA decreases as early as 2 weeks of immersion in the PBS (Figure 13), whereas the other properties are less sensitive to immersion in PBS for the same time period. Longer term immersion experiments are in progress. The mechanical properties are dependent on the amount and the type of crystalline regions developed after processing [7], as well as



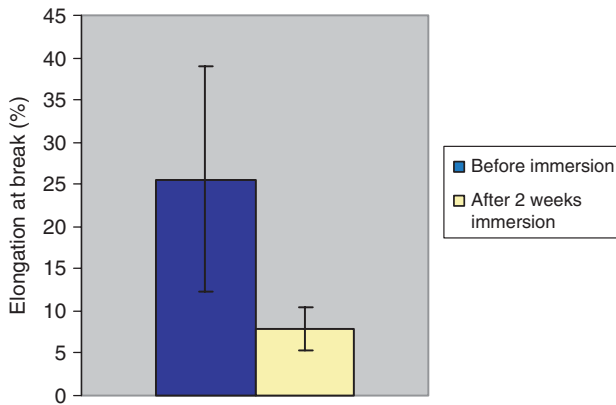
**Figure 10.** Stress at yield for PLA before and after 2 weeks immersion.



**Figure 11.** Stress at break for PLA before and after 2 weeks immersion.



**Figure 12.** Percentage elongation at yield for PLA before and after 2 weeks immersion.



**Figure 13.** Percentage elongation at break for PLA before and after 2 weeks immersion.

during immersion time. It does not appear that these changes are related to changes in  $T_g$  after immersion, since, as per Table 3 (second heating), these differences do not appear to be significant even after 56 days. Molecular weight reductions, as shown earlier from IV measurements, appear to affect much more the percentage elongation at break than the other mechanical properties.

## CONCLUSIONS

The aim of this study was to determine the effects of polymer crystallinity, fillers, and processing methods on the degradation of



aliphatic polyesters. Hydrolysis rate was higher in amorphous polymers such as PLA, since the cleavage of the ester bond proceeds faster through the amorphous regions. The CS and Bioglass 45S5 fillers appeared to enhance the degradation behavior for both PCL and PLA. The pH changes, during hydrolytic degradation, depend not only on the polymer used, but also on the filler. The Bioglass due to its reactivity results in significant pH increase in the case of PLA, but not in the case of PCL. Intrinsic viscosity measurements for the unfilled polyesters show a decrease in viscosity as immersion time increases. As a result, although MW decreases even after a short period of time, weight changes do not confirm such an effect. Thermal data showed crystallinity increased with immersion time in all samples, although crystallinity appeared to increase more in extruded versus compression molded samples. Bioglass 45S5 appears to affect the crystallinity of PCL more than the CS. In the case of PLA, Bioglass 45S5 decreases the  $T_g$  of the composite as immersion time increases. Mechanical testing showed a significant decrease of elongation at break for PLA after a short 2 week immersion period.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Schliecker, G., Schmidt, C., Fuchs, S. and Kissel, T. (2003). Characterization of a Homologous Series of D,L-lactic Acid Oligomers a Mechanistic Study on the Degradation Kinetics in vitro, *Biomaterials*, **24**(11): 3835–3844.
2. Tserki, V., Matzinos, P., Pavlidou, E., Vachliotis, D. and Panayiotou, C. (2006). Biodegradable Aliphatic Polyesters. Part I. Properties and Biodegradation of Poly(butylenes succinate-co-butylene adipate), *Polymer Degradation and Stability*, **91**(2): 367–376.
3. Tserki, V., Matzinos, P., Pavlidou, E. and Panayiotou, C. (2006). Biodegradable Aliphatic Polyesters. Part II. Synthesis and Characterization of Chain Extended Poly(butylene succinate-co-butylene adipate), *Polymer Degradation and Stability*, **91**(2): 377–384.
4. Xu, X.-J., Sy, J.C. and Shastri, V.P. (2006). Towards Developing Surface Eroding Poly( $\alpha$ -hydroxy acids), *Biomaterials*, **27**(15): 3021–3030.

5. Qian, Z., Li, S., He, Y., Zhang, H. and Liu, X. (2004). Hydrolytic Degradation Study of Biodegradable Polyesteramide Copolymers Based on  $\epsilon$ -Caprolactone and 11-aminoundecanoic Acid, *Biomaterials*, **25**(11): 1975–1981.
6. Mano, J.F., Sousa, R.A., Boesel, L.F., Neves, N.M. and Reis, R.L. (2004). Bioinert, Biodegradable and Injectable Matrix Composites for Hard Tissue Replacement: State of the Art and Recent Developments, *Composite Science and Technology*, **64**(6): 789–817.
7. Sarasua, J.R., Arraiza, A.L., Balerdi, P. and Maiza, A. (2005). Crystallinity and Mechanical Properties of Optically Pure Poly lactides and Their Blends, *Polymer Engineering and Science*, **45**(5): 745–753.
8. Paul, M.A., Delcourt, C., Alexandre, M., Degee, P., Monteverde, F. and Dubois, P. (2005). Poly lactide/Montmorillonite Nanocomposites: Study of the Hydrolytic Degradation, *Polymer Degradation and Stability*, **87**(3): 535–542.
9. Renouf-Glauser, A.C., Rose, J., Farrar, D.F. and Cameron, R.E. (2005). The Effect of Crystallinity on the Deformation Mechanism and Bulk Mechanical Properties of PLLA, *Biomaterials*, **26**(29): 5771–5782.
10. Proikakis, C.S., Mamouzelos, N.J., Tarantili, P.A. and Andreopoulos, A.G. (2006). Swelling and Hydrolytic Degradation of Poly(D,L-lactic acid) in Aqueous Solutions, *Polymer Degradation and Stability*, **91**(3): 614–619.
11. Chen, C.-C., Chueh, J.-Y., Tseng, H., Huang, H.-M. and Lee, S.-Y. (2003). Preparation and Characterization of Biodegradable PLA Polymeric Blends, *Biomaterials*, **24**(7): 1167–1173.
12. Xanthos, M., Young, M.-Y., Karayannidis, G.P. and Bikiaris, D.N. (2001). Reactive Modification of Polyethylene Terephthalate with Polyepoxides, *Polymer Engineering and Science*, **41**(4): 643–655.
13. Xanthos, M., Yilmazer, U., Dey, S.K. and Quintans, J. (2000). Melt Viscoelasticity of Polyethylene Terephthalate Resins for Low Density Extrusion Foaming, *Polymer Engineering and Science*, **40**(3): 554–566.
14. Shinoda, H., Asou, Y., Kashima, T., Kato, T., Tseng, Y. and Yagi, T. (2003). Amphiphilic Biodegradable Copolymer, Poly(aspartic acid-co-lactide): Acceleration of Degradation Rate and Improvement of Thermal Stability for Poly(lactic acid), Poly(butylene succinate) and Poly(caprolactone), *Polymer Degradation and Stability*, **80**(2): 241–250.
15. Seretoudi, G., Bikiaris, D. and Panayiotou, C. (2002). Synthesis, Characterization and Biodegradability of Poly(ethylene succinate)/poly( $\epsilon$ -caprolactone Block Copolymers, *Polymer*, **43**(20): 5404–5415.

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