Biodegradation and thermal decomposition of poly(lactic acid)-based materials reinforced by hydrophilic fillers

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ABSTRACT

The effect of hydrophilic fillers (starch and wood-flour) on the degradation and decomposition of poly(lactic acid) (PLA) based materials was investigated. Biodegradation was evaluated by composting under controlled conditions in accordance with AS ISO 14855. Thermal decomposition was studied by thermogravimetry (TGA). Morphological variations during biodegradation were investigated by SEM examination. It was found that biodegradation rates of PLA/starch blends and PLA/wood-flour composites were lower than that of pure cellulose but higher than that of pure PLA. The biodegradation rate was increased from about 60% to 80% when the starch content was increased from 10% to 40% after 80 days. Both starch and wood-flour accelerated thermal decomposition of PLA, and starch exhibited a relatively stronger affect then wood-flour. The decomposition temperature of PLA was decreased about 40 °C when the filler content was increased to 40%. Small polar molecules released during thermal decomposition of starch and wood-flour were attributed to the thermal decomposition behaviours of the PLA based blends and composites and their role is further discussed in this paper.

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1. Introduction

Blending and composite formation techniques are particularly important in the development of new biodegradable materials, as most raw materials are either of poor quality or very expensive. Poly(lactic acid) (PLA) blended with starch or reinforced by cellulose are two promising techniques for developing biodegradable polymer materials, since both starch and cellulose are commercially available and are derived from renewable resources [1–7]. Since hydrophobic aliphatic polyester PLA and hydrophilic starches are thermodynamically immiscible, which would generally lead to poor adhesion between the two components, hence poor performance, various compatibilisers and additives have been developed to improve the interfacial adhesion between PLA and starch [1].

Biodegradation of PLA has been extensively studied and widely reported [8–13]. The effect of additives on the biodegradation of PLA has attracted great interest recently [14–18]. Nieddu et al. [16] studied the effect of nano-clay on the biodegradation and found

that the clay accelerated the biodegradation of PLA. Ginebra et al. [17] found that incorporation of phosphate glass particles into PLA significantly accelerated its degradation and induced the formation of calcium phosphate precipitates at the composite surface. Recently, Wu [18] studied the biodegradability of PLA and PLA/starch blends through encapsulating the cells of an indigenous PSB strain (Bacillus sp. PG01), and found that starch accelerated the biodegradation of PLA. Thermal degradation of PLA and its blends or composites have also been widely reported [19–25]. Zhou and Xanthos [22] reported that due to better filler dispersion in the polymer matrix, the thermal degradation rate constants of the nanocomposites are significantly lower than those of the unfilled polymers and their microcomposites under air. Thermal gravimetric analysis also showed that the addition of the two types of epoxycyclohexyl increased the decomposition temperature and activation energy, consequently retarding the thermal degradation of PLA/PBSA [23]. Wang et al. [24] reported a new decomposition temperature for the crosslinked blends of PLA/starch, and suggested that branched and crosslinked macromolecules were formed during reactive extrusion. The effect of starch on the degradation of polyolefins has also been widely reported [25,26]

In this work, the effect of hydrophilic fillers (starch and cellulose) on the biodegradation and thermal decomposition of PLA based materials was studied. Biodegradation was evaluated by

composting under controlled conditions (AS ISO 14855). Morphology variations during biodegradation were characterised by SEM examination. Thermal decomposition was investigated by thermogravimetry (TGA) in air.

2. Experimental

2.1. Materials

A commercially available poly(lactic acid) (PLA 7000D from NatureWorks), a high-amylose cornstarch (supplied by Penford, Australia) with particular size about 20 μm, and a wood-flour (AWF 2010, American Wood Fibers) with particular size about 500 μm were used in the experimental work. Prior to compounding, the PLA pellets were dried in air for 24 h at 70 °C in a desiccated oven. Starch and wood-flour were dried overnight at 130 °C in a desiccated oven.

2.2. Sample preparation

The materials were compounded using a twin-screw extruder (Theysohn, TSK030-40D) with a screw diameter of 30 mm and a length/diameter ratio of 40. The highest temperature in the extruder barrel was 190 °C. The specimens used for degradation testing were cut from impact specimen prepared by an injection moulder (Battenfield, 800-315 CDC) with an injection temperature of 200 °C.

2.3. Biodegradation evaluation

Mature compost samples (aged approximately 2–3 months) were collected from a commercial composting facility (NRS Victoria, Australia). The compost was sieved through a sieve of 10 mm aperture and any glass or stone pieces were manually removed to obtain a homogeneous mix prior to testing. A standard protocol was followed to determine pH and dry weight of the compost and (AS ISO 14855). Specimens were cut from injected moulded samples (3 mm thickness, 10 × 20 mm) and mixed with the compost samples (pH 8.4); (dry weight 46.4%) in a vessel according to a standard procedure outlined in AS ISO 14855. Cellulose was used as a reference substrate. Three replicates of each sample type were set up and biodegradation testing was conducted in a NATA certified respirometric unit for a period of 85 days. During the course of this testing, carbon dioxide evolved from each composting vessel at intermediate time intervals was measured using an infra-red analyser and percentage biodegradation was calculated as given in AS ISO 14855.

2.4. Thermal decomposition evaluation

A Pyris-1 TGA apparatus was used to study the thermal decomposition of samples heated to 650 °C at a rate of 20 °C/min in air condition.

2.5. Morphological examination

A Phillips XL-30 FEGSEM was used to examine the morphologies of biodegraded surfaces of the various materials, with imaging performed in high-vacuum mode at an accelerating voltage of 5 kV. All the surfaces were coated with iridium prior to examination.

3. Results and discussions

Fig. 1 shows the biodegradability evaluated by the amount of CO_2 collected during biodegradation in composting testing. It was observed that the positive reference, cellulose started to degrade immediately and its degree of biodegradation is more than 70% in
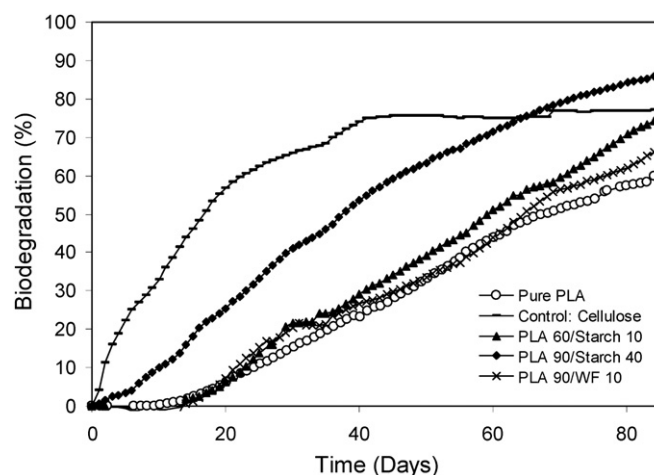

Fig. 1. Rate of biodegradation of PLA/starch, PLA/wood-flour and cellulose samples under aerobic composting conditions.

40 days. These results validate the biodegradability test conducted in this study as according to AS ISO 14855, the % biodegradability of reference material should be 70% after 45 days. Test sample PLA60/starch40, with relatively higher starch content (40%) also initiated biodegradation immediately and it achieved approx 50% biodegradation in 40 days and more than 80% after 80 days. In contrast, biodegradation of PLA90/starch10, containing lower starch content (10%) was initiated after a lag phase of about 15 days. Its rate of biodegradation was relatively slower as compared to PLA60/starch40, although it achieved approx 60% biodegradability after 80 days. Similar phenomenon of accelerated biodegradation by starch has been observed by Wu [18]. It was found that the rate of weight loss for the PLA/starch blends was higher as compared to that of pure PLA, after encapsulating bacterium in these two test materials for 60 days. Decrease in molecular weight and intrinsic viscosity were also reported higher for the PLA/starch blends.

The degradation of PLA/wood-flour composite was also evaluated. A lag phase of about 15 days, similar to that observed for PLA 90/starch 10 samples, was observed and the degree of biodegradability was approx 50% after 80 days. Liu et al. [19] has reported higher degradation rate of PLA after adding sugar beet pulp (SBP). SBP weight loss was clearly seen for all samples and a greater SBP weight loss was measured for composites with higher SBP content. It was considered that the organic acids generated by SBP digestion by microbes reduce the pH value in the microenvironments, which accelerates PLA hydrolysis. In this work a decrease in pH (from about 8.4 to 6.0) was also detected following biodegradation.

Fig. 2 shows SEM morphologies of the specimens of the blends and composites after partial biodegradation in composting testing. The images indicate that the biodegradation process started from the phase of the hydrophilic fillers. There are no obvious particles of starch granules or wood-flour which could be clearly identified on the surface. The poor interface between PLA and the fillers may have created a new surface for water penetration and bacteria growth. The results indicate that natural fillers, such as wood-flour form a network, which facilitates water ingress into the PLA matrix more rapidly as well as bacterial growth, which leads to the gradual degradation of the PLA matrix.

Fig. 3 shows the thermal decomposition of PLA/starch blends evaluated by TGA. The curves of derivative weight are shown in the left bottom, which represents the decomposition stages as peaks. It can be seen that there are three steps in the thermogravimetric (TG)
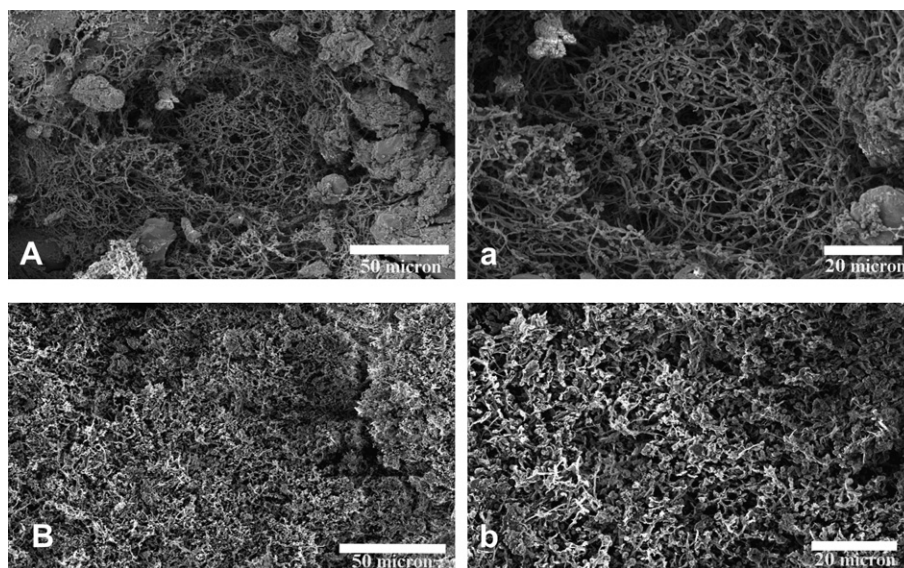
Fig. 2. SEM morphologies of the specimen after partial biodegradation in composting testing (A and a are PLA 90/starch 10 blend; B and b are PLA 90/WF 10 composite).

curve of pure starch: the first one observed up to 150 °C is related to the loss of absorbed and bound water. In the second step, the weight loss from about 20% to 87% is due to the thermal decomposition of the PLA polymer chains. The third step presents the carbon burning at about 450 °C as reported previously in the literature [29,30]. Correspondingly, there are three peaks in derivative thermogravimetric (DTG) curves: one is due to dehydration, second is due to decomposition of starch and third is the carbon burning. There are two stages of decomposition for PLA: one is decomposition and another one is carbon burning. It is seen that the decomposition temperature of starch is lower than that of PLA. The decomposition temperatures of the PLA decreased gradually with increasing starch content.

Fig. 4 shows the thermal decomposition of PLA/wood-flour composites measured by TGA. Similar to starch, the processes of dehydration and carbon burning can be clearly observed at about 150 and 450 °C, respectively. It was noted that a "shoulder" occurred from 250 °C to 350 °C and a large decomposition peak for the pure wood-flour. Previous studies [27,28] have shown that the "shoulder" peak can be attributed to decomposition of hemicellulose and slower decomposition of lignin, and the large

degradation at about 400 °C can be attributed to the degradation of cellulose. The decomposition temperature of wood-flour is lower than that of PLA. The decomposition temperatures of PLA/wood composites gradually decreased with increasing wood-flour content.

Fig. 5 shows a plot of filler content vs. decomposition temperature for PLA/starch blends and PLA/wood-flour composites. It is seen that the decomposition temperatures of PLA/starch blends are lower than that of PLA/wood-flour composites. It has been noted that the decomposition temperature of starch (322 °C) is lower than that of wood-flour (355 °C). When starch decomposes it produces some small polar molecules, and it has previously been reported [29–33] that various gaseous emissions such as CO, CO_2, H_2O, CH_4, C_2H_4 and CH_2O could be detected by FTIR. It is highly likely these molecules could break down the polyester chain of the PLA in a similar fashion to break down by hydrolysis, resulting in a decrease in the decomposition temperature of PLA. The lower decomposition temperature of starch as compared to wood-flour could be used to explain the lower decomposition temperature of PLA in the blends with starch.
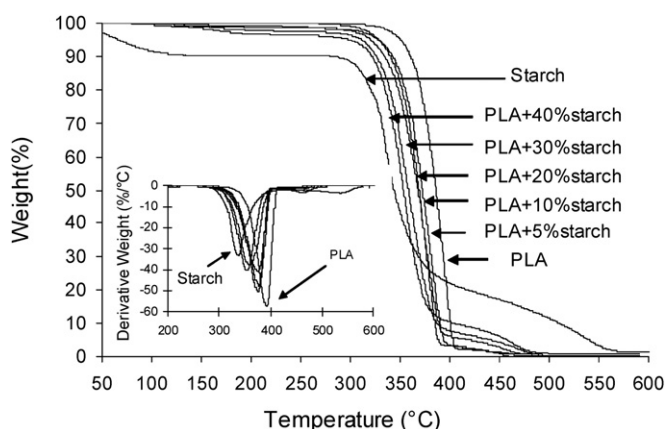

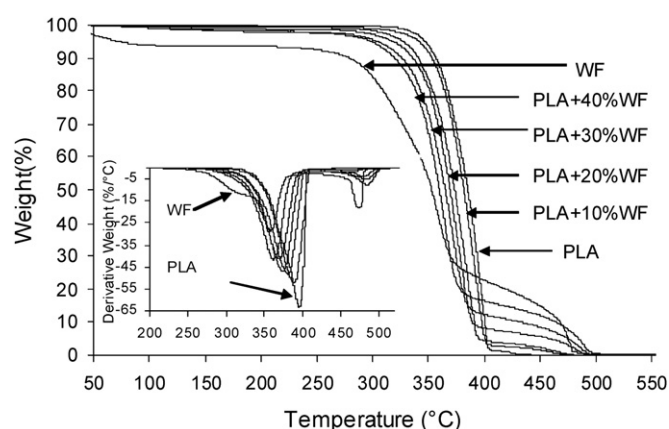**Fig. 3.** Thermal decomposition of PLA/starch blends evaluated by TGA at a heating rate of 20 °C/min.

Fig. 4. Thermal decomposition of PLA/wood-flour composites evaluated by TGA at a heating rate of 20 °C/min.
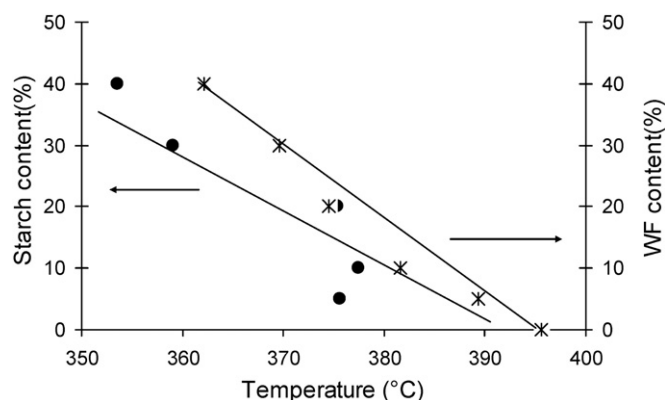
Fig. 5. A plot of filler content vs. decomposition temperature for PLA/starch blends and PLA/wood-flour composites.

4. Conclusions

The effect of hydrophilic fillers (starch and wood-flour) on the degradation and decomposition of PLA based materials was studied. Biodegradation was evaluated by composting testing. Thermal decomposition was studied by TGA. It was found that degradation rates of both, PLA/starch blends and PLA/wood-flour composites, were lower than that of pure cellulose but higher than pure PLA. The biodegradation rate was increased from about 60% to 80% when the starch content was increased from 10% to 40% after 80 days. On the other hand, both starch and wood-flour accelerated the thermal decomposition of PLA, and starch exhibited a greater impact than wood flour. When the starch content increased from 0 to 40% the decomposition peak of PLA decreased from about 397 °C to 352 °C, while when the wood-flour content increased from 0 to 40% the decomposition peak of PLA decreased to about 362 °C. Small polar molecules may have been produced during decomposition of starch and wood-flour. These molecules can break down polyester chains in PLA similar to moisture, resulting in a decrease in the decomposition temperature of PLA. The lower decomposition temperature of starch (322 °C) compared to the wood-flour (355 °C) could be used to explain the lower decomposition temperature of PLA in the blends with starch.

Acknowledgments

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