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Development of a green material for horticulture

Abstract: Poly(lactic acid) (PLA), used as a matrix, was mixed with wood fibers, coffee grounds, fertilizer and a foaming agent to develop an ecofriendly material to be used in horticulture. For this application materials should have mechanical properties similar to PLA, increased biodegradability and a lower price than currently used materials. The new materials were prepared by melt processing in an internal mixer at 190°C and were characterized by several techniques. The mechanical properties of the biocomposites, measured by flexural tests, were similar to neat PLA, even with a reduction of 40 wt% of polymer. Biodegradation assessment by composting tests in an aerobic environment demonstrated that the green materials exhibited higher biodegradability than PLA. Biocomposites containing wood fibers and fertilizer were revealed to be the most suitable for horticulture application, as these can combine mechanical properties, biodegradability and fertilizer release. Moreover, this green material has two main advantages: it can be prepared using materials from natural resources, and it does not generate any residue after use.

Keywords: agriculture; biodegradation; coffee grounds; foaming agent; poly(lactic acid); wood fibers.

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1 Introduction

In the horticulture industry the disposal of plastic containers used in greenhouses and nursery crops is an ongoing practical issue. It is particularly critical in the annual and perennial bedding plant markets. As a result of large-scale small plants production, the need for disposal of used plastic containers grows annually [1]. Generally not reusable, plastic containers are disposed after plants are transferred into the ground. Developed to ensure reliable consumer packaging, transportation and used sometimes as a marketing product, as well as propagation and production receptacle, plastic containers are strong and can have any size, shape and color [2]. Nevertheless, they have two main drawbacks; first, roots tend to circle the outer perimeter of the root ball once contact is made with the container, which can reduce growth and survival of plants after transplantation [3, 4]; second, most of the containers are not biodegradable, thus contributing to large waste quantities.

Aiming to overcome waste production, numerous attempts have been made to develop biodegradable materials that can be buried directly into the soil. Peat, paper and coir fiber are the most common nonplastic materials used to prepare biodegradable containers [5–7]. However, according to Evans and Hensley [1], these containers are more expensive than the plastic ones and can easily break or tear when wet. To overcome these disadvantages, the horticulture industry has started to study other biodegradable and compostable biopolymers derived from raw materials, such as starch (corn, rice hulls and wheat, among others), cellulose, soy protein and lactic acid [8]. Nonetheless, when compared to conventional polymers, biopolymers have some drawbacks, such as poor mechanical and barrier properties, processability and thermal stability, which limit their industrial application. Recently biocomposites have proven to be a promising option to improve the properties of biopolymers [9]. Prepared by a combination of polymers coming from natural resources (biopolymers) and fillers (e.g., natural or modified clays or lignocellulose fibers), biocomposites combine the intrinsic properties of natural polymers and fillers. Then, these environmental-friendly materials open a wide range of applications for biodegradable polymers with potential objectives for horticulture [10].

Our research group investigated the development of new environmental ecofriendly materials, such as copolymers of biodegradable/conventional polymers and nanocomposites of poly(lactic acid) (PLA) containing organoclays [11, 12]. Therefore, using existing knowledge, the main objective of this work was to develop a green material to be used in horticulture. Then, PLA, used as matrix, was mixed with different amounts of wood fibers, coffee grounds, foaming agent and fertilizer. The obtained biocomposites were characterized by mechanical tests,

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and their biodegradability was assessed in the aerobic environment in compost. Gel permeation chromatography (GPC) was performed before and after biodegradation in order to assess changes in PLA molecular weight.

2 Materials and methods

2.1 Materials

The commercial PLA grade (3251D) was acquired by NatureWorks LLC (Georgetown, CT, USA). Coffee grounds and wood fibers dried and used without further treatment were supplied by local producers. Inorganic fertilizer, *Nitrolusal 20.5* composed of 12% N, 12% P_2O_5, 17%, K_2O and 2% MgO was supplied by ADP Fertilizantes (Alverca Do Ribatejo, Portugal) and used as a powder. The foaming agent, azodicarbonamide, powder, was used as received and was provided by Acros Organics (Geel, Belgium).

2.2 Sample preparation

PLA, coffee grounds, wood fibers and fertilizer were dried at 105°C under vacuum for at least 24 h in order to remove the moisture. All materials were prepared by melt mixing at 190°C in a Haake Rheocord 90 batch mixer (volume 60 cm^3), equipped with two rotors running in a counter-rotating way at a speed of 80 rpm. The following procedure was adopted to prepare the different materials, a specific amount of PLA was introduced into the hot mixer, and after melting the respective additives were added in order to obtain the compositions Table 1. The total sample was removed after 10 min of mixing.

PLA was also processed under the same conditions and was called sample A.

Sample E resulted from the crushed sample removed from the internal mixer blended with a foaming agent and placed in a hot press at 190°C.

Table 1 Samples composition.

Sample	PLA (%)	Coffee grounds (%)	Wood fibers (%)	Fertilizer (%)	Expander (%)
A	100	0	0	0	0
B	90	0	0	10	0
C	60	30	0	10	0
D	60	0	30	10	0
E	60	0	30	8	2

For all the previous prepared compositions, rectangular specimen samples for mechanical and biodegradation characterization were prepared in a hot press at 190°C under 20 tons for 15 min.

2.3 Characterization

2.3.1 Density

The density of the PLA and prepared materials were measured using the Archimedes impulsion method for solids, as in the ASTM D 782-00 standard. The samples, parallelepipeds with area of ±4 cm^2, were weighed with a SCALTEC SBC31 (Scaltec Corp., Dania, FL, USA) with a kit for density determination SDK01. The immersion liquids were isopropanol and water.

2.3.2 Gel permeation chromatography

Gel permeation chromatography was used to assess the molecular weight of the prepared compositions as collected from the mixer (with exception of sample E) and after composting. Solutions were prepared in THF (99.9%) and prefiltered on filter plate (hydrophobic polytetrafluoroethylene, 0.45 mm pore size) before injection. A Waters Alliance GPC Model 2695, equipped with 3 PLgel Mixed-B columns (inner diameter=7.5 mm, length=30 mm and particle size=10 mm) and a Waters 2410 Differential Refractometer as detector, were used for the determination. THF was used as eluent with a flow rate of 1 ml/min, and the temperatures were 25°C and 35°C at the injector and detector, respectively.

2.3.3 Mechanical properties

The flexural properties of processed PLA and biocomposites were measured using an Instron 4505. The flexion experiments were performed according to ASTM D 790-03, with a deformation rate of 2 mm/min at room temperature under a relative humidity of 45%. The samples tested have a length of 5 cm, width of 2.5 cm and a thickness of 0.1 cm. A minimum of five specimens was tested for each material.

2.4 Biodegradability

Biodegradation in compost was performed at 40°C using compression molded (25×25×0.125 mm) samples. Samples were placed in a composting medium made of soil, activated sludges from wastewater treatment, straw and animal manure. The composting medium was kept in a relative humidity of approximately 50–70%. Around 20 samples of each material were vertically buried at 6–8 cm depth to guarantee aerobic degradation conditions at a horizontal distance of 5–6 cm between samples according to Fukushima [13]. At selected times (every 3 weeks), samples were collected, cleaned and dried at room temperature until constant weight was reached. Based on the sample weight before and after composting, the average percentage of residual mass for each material was calculated.

3 Results and discussion

The torque evolution, along with mixing time during PLA processing and biocomposites preparation, are shown in Figure 1. The first peak is associated to PLA melting followed by the addition of the fillers, which in all cases increase the torque values. This increase was due to the presence of inorganic particles that did not melt at the mixing temperature, resulting in an increase of viscosity and consequently higher torque.

The density values of the biocomposites are presented in Table 2. As expected, with the exception of the biocomposite prepared with a foaming agent, which has a cellular structure, all exhibited higher density than PLA.

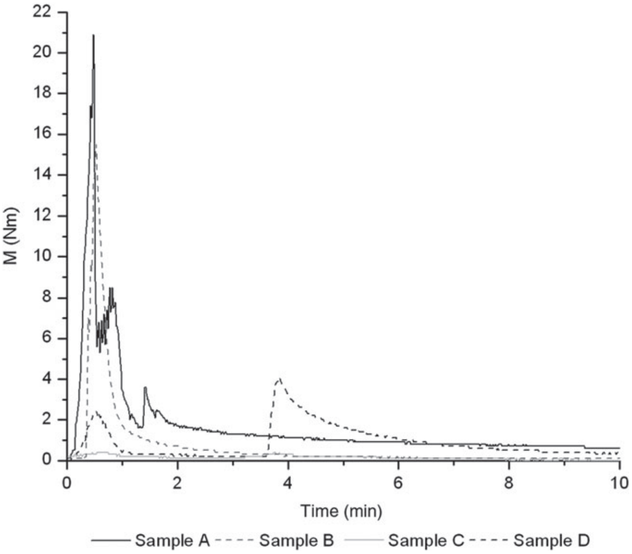

Figure 1 Torque evolution during biocomposites preparation.

Table 2 Density values of PLA and biocomposites.

Sample	A	B	C	D	E
Density	1.24±0.02	1.30±0.02	1.32±0.01	1.34±0.01	0.88±0.03

The initial molecular weight distribution of PLA, processed PLA and biocomposites are depicted in Figure 2. The results show that the curves of PLA and processed PLA almost overlap, indicating a very slight degradation of PLA during processing, which can be attributed to hydrolysis reaction under the processing conditions used. In contrast, all biocomposites exhibit a shift to the higher retention time, which can be associated with pronounced decrease in molecular weight due to chain scission. A similar molecular weight decreased was observed with coffee grounds and wood fibers. This can be related to a small amount of residual moisture contained in both compounds, which triggered the PLA chain scission through hydrolysis at the high processing temperature. Similar results were obtained by Pilla and colleagues [14]. Moreover, coffee grounds (sample C) present a second peak at higher retention time, which could be related to the presence of lower molecular weight molecules group due to the presence of some substances in the coffee residues [15]. Regarding sample E, the containing foaming agent had two processing cycles (melt mixing and foaming agent addition and compression molding), which affected PLA chains scission, resulting in a higher level of degradation. Although a molecular weight decrease was observed for all green composites, a unimodal distribution was kept.

The relative flexural properties of PLA and biocomposites are shown in Figure 3. The addition of other particles to PLA had a slight influence on its modulus and strength flexural properties. Sample B (PLA/fertilizer, 90/10, w/w), had a slightly higher modulus and strength

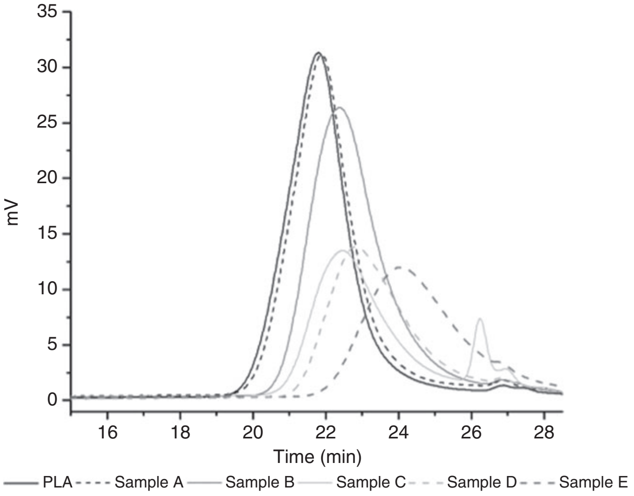

Figure 2 Molecular weight distribution of pristine PLA, processed PLA and biocomposites after synthesis.

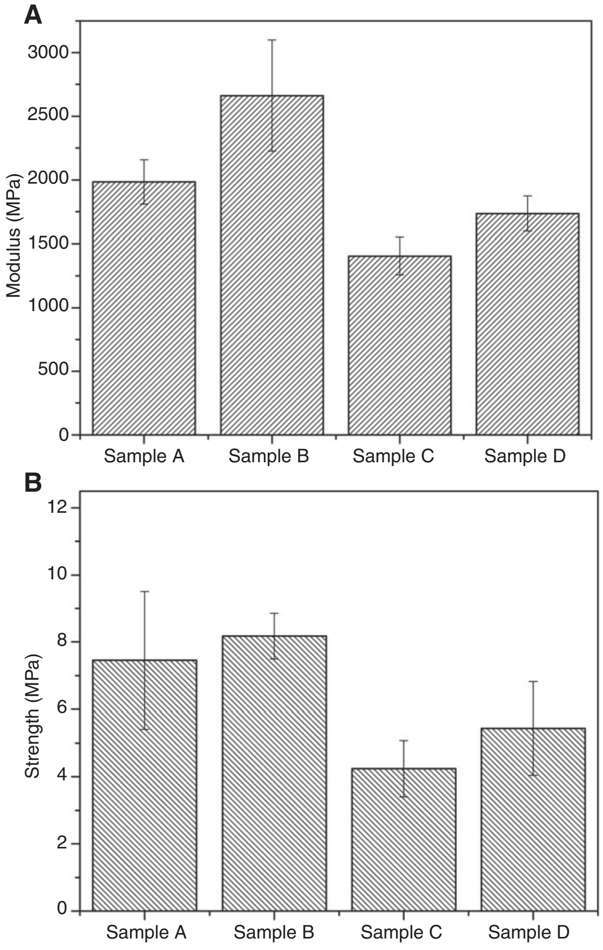

Figure 3 Flexural properties of PLA and prepared biocomposites.

than PLA, which might be associated to the good dispersion of small size particles. It is known that the restrains of the polymer chains movement increases the stiffness [16]. Conversely, samples C (PLA/coffee grounds/fertilizer, 60/30/10, w/w/w) and D (PLA/wood fibers/fertilizer, 60/30/10, w/w/) present a small decrease of PLA mechanical properties. Between these two composites, and taking into account the error associated with the measurements, sample D exhibits properties quite similar to PLA. The difference between PLA and these two samples can be due to both the relative amount of PLA/filler and the poor interfacial adhesion. Because wood fibers are normally used as thermoplastic reinforcement [17], one would expect to obtain better mechanical properties for sample D, as shown in various published results [18–22]. The explanation for results obtained in the present work is the absence of fiber treatment or the addition of compatibilizers to enhance the interfacial interactions. Green composite containing foaming agent is too brittle; it breaks almost immediately when the force is applied. For this reason its flexural properties are not present in Figure 3.

During PLA biodegradation, chemical hydrolysis is the primary driving force toward degradation and involves water absorption and ester chains cleavage forming oligomers. The latter are mineralized by the microorganisms, which generate carbon dioxide under aerobic conditions and methane under anaerobic conditions [11, 23]. Figure 4 presents real pictures of PLA and biocomposites after 3 and 12 weeks of biodegradation in compost (2.2 and

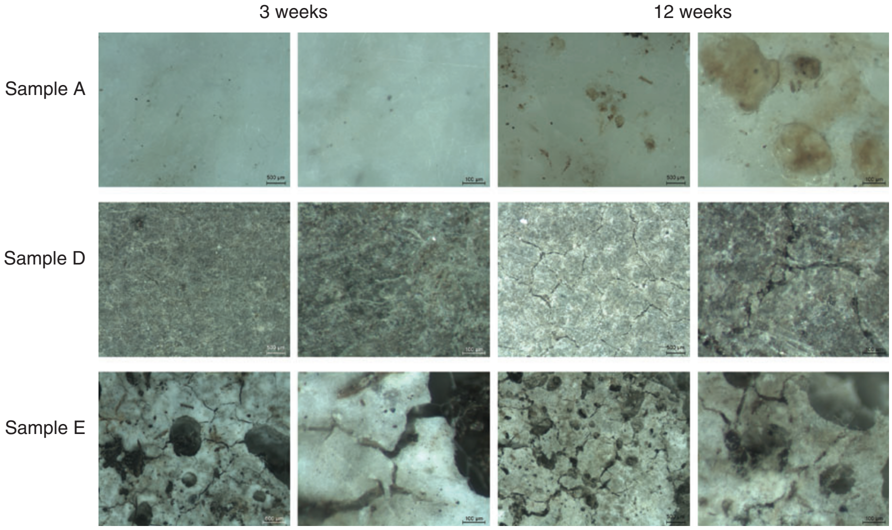

Figure 4 Surface pictures of PLA and biocomposites after 3 and 12 weeks in compost.

13.2 magnifications). It is clear that among all analyzed samples, only PLA samples were still intact after 12 weeks. Moreover, some areas of PLA showed a whitening aspect, which can be a signal that the process of hydrolytic degradation has already started. Hydrolysis induces a change in the refraction index as a consequence of water absorption and/or presence of products formed by the hydrolytic process [11, 13]. In contrast, samples D and E depicted a much more extensive degradation, characterized by a fractured surface. It is possible to observe the loss of polymeric material as a result of bacterial activity. The faster appearance of visual signs of degradation in biocomposites when compared to PLA is in the sample that contains wood fibers; it seems that a catalytic effect on hydrolysis of the ester groups of PLA occurs.

Figure 5 depicts PLA weight loss profiles of the developed materials in tandem to composting times. During the 12 weeks in compost, the samples showed different degradation behavior. The presence of wood fibers and foaming agent (samples D and E) enhanced the PLA degradation, and consequently these exhibited higher weight loss. This is associated with the higher level of wood water absorption capability that catalyses the ester chain cleavage. Furthermore, the cellular structure created by the foaming agent accelerated the moisture diffusion through the samples. In contrast, PLA with fertilizer and coffee grounds (samples B and C) exhibited a slower degradation rate. This was due to the resistance in water uptake and diffusion through the biocomposites and to the lower capability, in the case of fertilizer, to retain moisture. Moreover, roasted coffee grounds have antibacterial properties against a range of Gram-positive and Gram-negative bacteria [24, 25]. Then, the degradation observed in sample C was mainly provoked by moisture, which justifies the lowest degree of degradation detected. PLA (sample A) weight loss was not significant during the composting time period.

To evaluate the extent of degradation of PLA and biocomposites in compost, the collected samples were analysed by GPC (Figure 6). PLA and biocomposite curves shifted to lower molecular weight (higher retention time), which indicates that chain scission of the long molecules occurred, and smaller ones were formed. Moreover, the unimodal initial distribution became bimodal in the case of samples B, D and E, indicating the presence of different types of molecules with lower molecular weight. In agreement with the weight loss shown in Figure 5, samples D and E presented higher molecular weight reduction. Moreover, it is clear that the long molecules disappear due to intensive chain scission, and a peak due to smaller molecules appeared. In the case of a biocomposite containing coffee grounds (sample C), molecular weight remained almost the same as a result of the antibacterial activity of ground coffee, as explained previously. However, the last peak corresponding to coffee residues almost disappears, maybe by dissolution, indicating the output of these during composting. Similar results were obtained by Araújo and colleagues [11], in which organo-nanoclays in PLA matrix were dispersed.

These results demonstrate that, with exception of ground coffee, green composites present enhanced biodegradability in compost rather than neat PLA. Moreover,

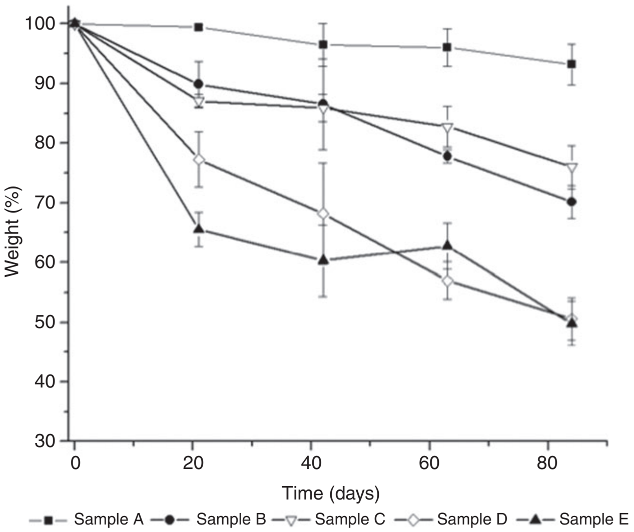

Figure 5 Weight loss of processed PLA and biocomposites during 12 weeks of degradation in compost at 40°C.

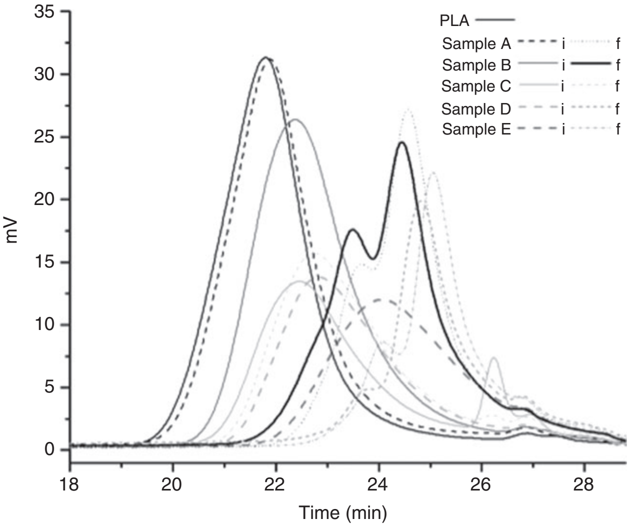

Figure 6 Molecular weight distribution of initial and degraded samples after 12 weeks in compost at 40°C.

no significant difference could be noticed between samples D and E, which means that sample D would be easier to prepare and has the required behavior.

4 Conclusion

The viability of PLA biocomposites to be used as green biodegradable materials for horticulture application was investigated. PLA was mixed with wood fibers, coffee grounds, fertilizer and a foaming agent to develop a green material with good mechanical properties, high biodegradability and the ability to release fertilizer.

The results obtained demonstrate that our aim was achieved; the biocomposites with wood fibers and fertilizer accomplish all the requirements.

The new material containing wood fibers revealed to be the most suitable for horticulture application, because it fulfills mechanical and biodegradable requirements. Moreover, this green material has two main advantages: it can be prepared using materials from natural resources, and it does not generate any residue after use.

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