INFLUENCE OF INCORPORATION AND GRANULOMETRY OF POST-CONSUMPTION YERBA MATE ON THE DEGRADABILITY OF POLY(LACTIC ACID): NATURAL WEATHERING AND COMPOSTING

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Abstract - Poly(lactic acid) (PLA), a biodegradable polymer produced from renewable sources, was used as a matrix for a composite reinforced with commercial Yerba mate (YM) in leaf (YL) and powder (YP) forms. PLA/YM composites in the mass ratio 70/30 were produced through injection, seeking to study the influence of the incorporation of vegetal fibers on their degradation rate when subjected to natural weathering and composting. At the end of the tests, the composites showed a more significant loss of mass than pure PLA, indicating that the incorporation of YM facilitated hydrolytic degradation and biodegradation. The samples showed a greater loss of mass when composted than when weathered. The natural weathering caused significant color changes in the composites. The PLA/YL composite demonstrated the greatest degradation capacity along with the greatest loss of mass. In addition, it showed surface cracks, which resulted from environmental stress-cracking.

Keywords: *Poly(lactic acid); Yerba mate; biodegradation; natural weathering; composting*

Introduction

Seeking for an ecological alternative to material waste and consumption of non-renewable resources, studies on polymers with degradability characteristics have gained space in recent decades. Among these, poly(lactic acid) (PLA) stands out for having easy processability and being produced through corn or sugar cane fermentation [1]. The incorporation of vegetal fibers into the polymeric matrix contributes to the modification of the material's properties and may also influence its degradation rate. The use of residues from agribusiness and food industry as a source of vegetal fibers provides an alternative use for a material that would be discarded [2].

Yerba mate (*Ilex paraguariensis*), a plant of great importance in the economy of the southern states of Brazil, is consumed in the form of *chimarrão* and generates a post-consumption residue that has not found viable alternatives for reuse yet [3, 4]. Thus, this study investigates the feasibility of incorporating commercial Yerba mate residue, in leaf (YL) and powder (YP) forms, in PLA/Yerba mate composites. In order to study the susceptibility to degradation after disposal, the samples (PLA, PLA/YP and PLA/YF) were evaluated when exposed to an external natural environment and when buried in composted soil.

Experimental

Materials

Poly(lactic acid) (PLA) (Ingeo™ Biopolymer 6260D, CAS#9051-89-2) was supplied by NatureWorks (USA). Yerba mate (*Ilex paraguariensis*) residue (YM) was simulated using commercial Yerba mate from the brands Nutrimate (batch number 1411 / powder form) (YP) and Madrugada (batch number 0219A1 / leaf form) (YL).

Preparation of the samples

Samples of YP and YL were kept in water for 2 h at an initial temperature of 80 °C in order to simulate the Yerba mate post consumption residue. The excess liquid was removed with filter paper and dried in an oven at 60 °C for 24 h. After the drying step, YM samples were blended with PLA using a twin-screw lab mixer with a length/diameter ratio of 25. The samples were processed at 190 °C for 6 minutes, with a rotation speed of 50 rpm. Two formulations of polymeric mixtures were prepared in the weight ratio 70/30 m/m for PLA/YP and PLA/YL. Pure PLA was also submitted to the same processing as a reference. Afterwards, the material obtained was ground in a knife mill and injected in order to produce samples based on the ASTM D3641-12 standard. The processing was carried out at an injection temperature of 190 °C using 60 °C for the mold temperature, under an injection pressure of 500 bar and a holding pressure of 350 bar. The heating time was 3 minutes, adopting 20 seconds for injection, 10 seconds for holding and 2 minutes for cooling.

Natural weathering and composting

Five injected samples from each formulation were exposed to natural weathering from October 17, 2019 to November 14, 2019 on platforms built with an angle of 45° to the ground, in Porto Alegre, RS (Brazil), 30°04'23.9"S 51°06'52.2"W. During the test period, the metereological data in the city of Porto Alegre were recorded daily.

The compost degradation started on April 26, 2019, by burying two injected samples for each composition in containers with soil fertilized with organic compounds (humus). The pH index was controlled weekly with indicator strips. At the end of the first month, one sample of each formulation was removed from the soil, dried and weighed on a precision scale. The same process was replicated two months after the start of the test and the analysis was concluded on June 25, 2019. The loss of mass for both tests was calculated according to Eq. 1, where m_i and m_f are equivalent to the initial and final masses of the samples, respectively.

$$\text{Loss of mass } (\%) = \frac{m_i - m_f}{m_i} \times 100 \tag{1}$$

Characterization

The surface of the samples corresponding to initial time (t_0), composted and exposed to weathering were analyzed by scanning electron microscopy in 200x. The color changes suffered after degradation tests were detected by a spectrophotometer through CIELab color space system.

Results and Discussion

From Fig. 1 it is possible to compare the visual aspects of pure PLA, PLA/YL and PLA/YP composites in t_0 and after degradation tests. It is observed that the pure polymer did not undergo significant visual transformations after the tests, while the composites showed discolorations and surface defects.
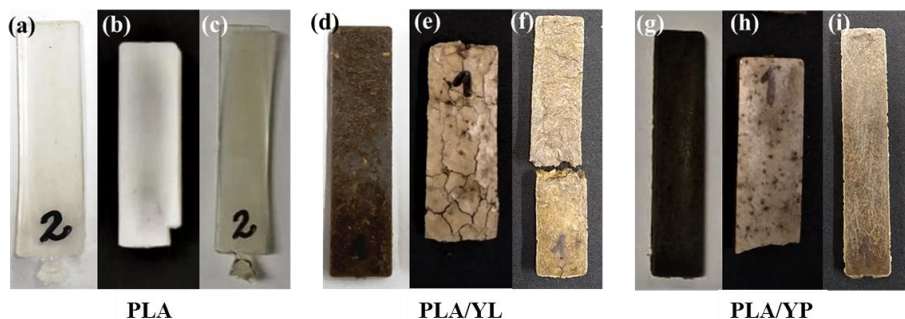

Figure 1 – Visual comparison between the samples: (a) PLA at t_0; (b) PLA after natural weathering; (c) PLA after composting; (d) PLA/YL at t_0; (e) PLA/YL after natural weathering; (f) PLA/YL after composting; (g) PLA/YP at t_0; (h) PLA/YP after natural weathering; (i) PLA/YP after composting.

Fig. 2 shows the percentage of remaining mass of the samples as a function of time. Except for pure PLA, both composites underwent gradual degradation, especially those that were incorporated with Yerba mate as leaves (PLA/YL). All composite formulations showed greater mass loss when composted than when naturally aged.

Although PLA is a biodegradable polymer, its decomposition by composting is very slow. However, vegetal compounds are easily degraded by microorganisms when buried in the soil [5]. In this sense, the incorporation of Yerba mate may be responsible for increasing the rate of degradation of the material, since the addition of vegetal fibers can facilitate the hydrolysis process. This leads to the formation of small monomers and short chain oligomers that are available to microorganisms, resulting in a higher rate of decomposition [6, 7]. The hydrolytic degradation of PLA produces lactic acid, which along with the hydrolysis of the vegetal fiber leads to a pH decrease of the composted soil: from 6.0, at the beginning of the test, to 5.0 at the end.
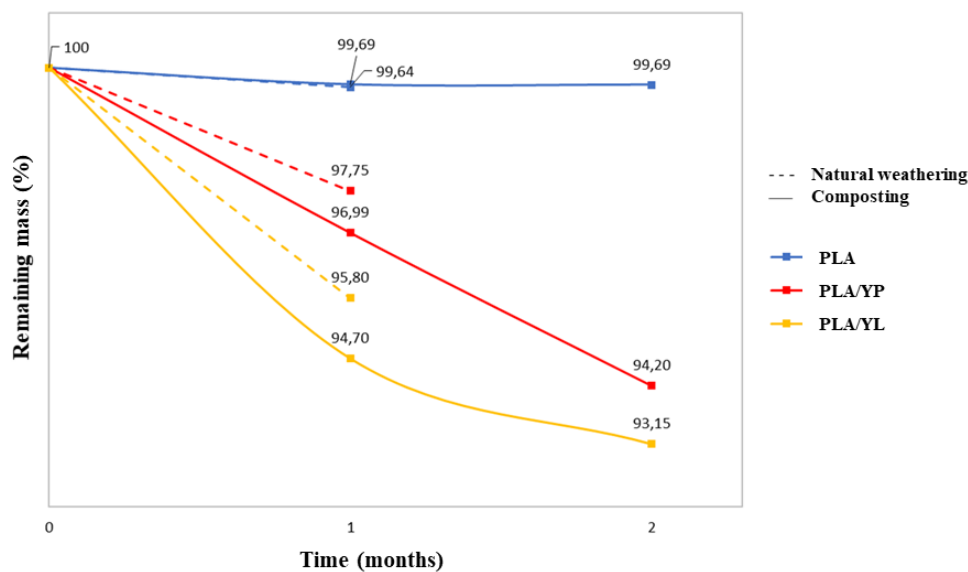

Figure 2 – Mass loss as a function of weathering time (dashed line) and composting time (continuous line) for pure PLA (blue line), PLA/ YP (red line) and PLA/YL (yellow line).

Fig. 3 shows a morphological comparison by scanning electron microscopy (SEM) between the polymer and the composites in initial time (t_0) and after biological degradation tests. It is observed that when pure PLA is exposed to weathering and composting (Fig. 3-b and Fig. 3-c) it shows some loose fragments and points of superficial erosion in comparison to the smooth surface in t_0 (Fig. 3-a).

Initially, the two composite formulations samples have a rough surface (Fig. 3-d and Fig. 3-g), but develop cracks and voids attributed to Yerba mate decomposition during the degradation tests. Surface erosion is more critical in PLA/YL, which shows clear degradation cracks after the test periods (Fig. 3-e and Fig. 3-f). In fact, in addition to presenting the most evident mass loss in both degradation tests, samples reinforced with Yerba mate in leaf form (YL) were also more brittle during composting. This greater degradation capacity may be related to a weak interfacial adhesion between polymer matrix and reinforcement, a factor that would increase the surface contact area of the vegetal fiber, facilitating its decomposition during exposure to microorganisms present in the soil [5].

The morphology of PLA/YP composite shows less apparent erosion (Fig. 3-h and Fig. 3-i), suggesting that the encapsulation of YM powder in the polymeric matrix was better performed, thus hindering water permeability and hydrolytic degradation [8]. Most evident cracks were seen in

composting test, indicating that hydrolytic degradation was favored by the presence of fibers, which confirms the greater mass loss found in this condition (Fig. 2).
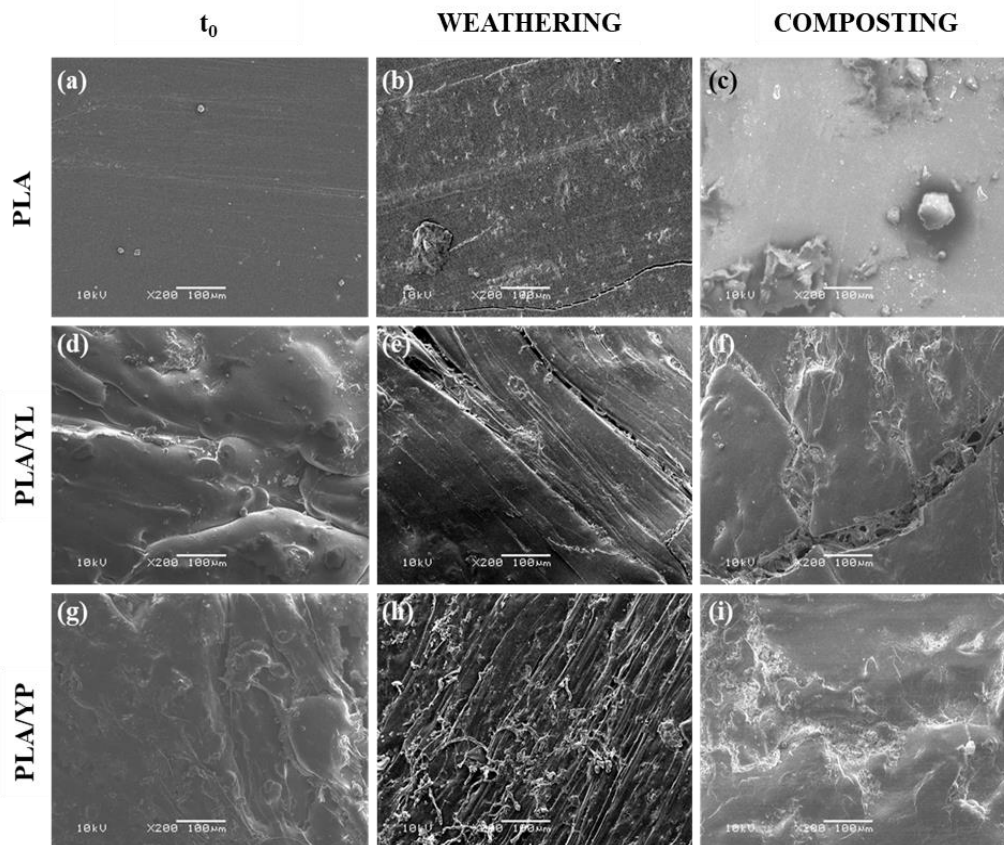

Figure 3 – SEM micrographs in t_0 and after natural weathering and composting tests for pure PLA, PLA/ YL and PLA/YP composites.

The color changes undergone by the samples are described in Table 1. Regarding t_0, it is noticeable that the weathering test caused an intense increase in L* parameter of the composites, which refers to luminosity. It is interesting to mention that, during the test period, high values of relative humidity were observed (around 70%). There was also a high rate of UV radiation, which reached values classified as extreme in some days of control.

Table 1 – Result of the analysis of luminosity (L*), two color channels (a* and b*) and glow (g) for PLA, PLA/YL and PLA/YP in t_0 and after natural weathering and composting tests.

Sample	L*	a*	b*	g
PLA (t_0)	63,67 ± 0,27	-1,13 ± 0,07	2,62 ± 0,14	24,21 ± 0,64
PLA (weathering)	64,96 ± 0,14	-0,81 ± 0,21	5,06 ± 0,85	19,11 ± 0,69
PLA (composting)	65,63 ± 0,78	-1,24 ± 0,67	2,10 ± 0,27	19,92 ± 0,14
PLA/YL (t_0)	31,43 ± 0,35	3,77 ± 0,21	7,29 ± 0,34	9,09 ± 0,22
PLA/YL (weathering)	54,14 ± 0,63	4,63 ± 0,78	14,17 ± 0,42	3,23 ± 0,31
PLA/YL (composting)	34,84 ± 0,73	3,96 ± 0,42	9,18 ± 0,69	3,26 ± 0,20
PLA/YP (t_0)	29,21 ± 0,46	2,86 ± 0,83	4,01 ± 0,85	9,02 ± 0,22
PLA/YP (weathering)	50,47 ± 0,73	3,73 ± 0,12	11,11 ± 0,20	3,72 ± 0,08
PLA/YP (composting)	37,03 ± 0,39	2,18 ± 0,64	5,29 ± 0,31	3,39 ± 0,87

The discoloration of composites takes place due to photo-oxidation promoted by UV radiation. This occurs because oxygen is used before it can diffuse into the material, causing a degradation

concentrated close to the surface. The formation of oxidation gradients causes density gradients paired with the breaking of the polymer chains, observed through the molecular weight reduction, causes the initiation and propagation of cracks. These superficial cracks cause the diffusion of the light, leading to the discoloration of the material [9]. This can be seen in morphological analysis of PLA/YL, which has a higher L* value and also a greater number of surface defects after the weathering test.

The negative values of the a* channel, which corresponds to the green-red color spectrum, obtained for pure PLA in all situations indicate that these samples have a greater tendency to achieve a greener aspect. No significant difference was observed in this parameter after the tests. On the other hand, parameter b*, which describes the blue-yellow color spectrum, has a significant increase after exposure to weathering. In fact, the photo-yellowing phenomenon is more evident in composites since the lignin degradation leads to the formation of chromophor groups, which increase the absorption of ultraviolet radiation. Therefore, the tendency to yellow is characteristic of the formation of hydroperoxide radicals [10, 11].

A decrease in the glowing (g) of all samples was observed after the weathering test, which is also associated with the degradative process that occurs due to the breaking of molecular chains [12]. Besides morphological alterations, no other remarkable changes were observed when comparing t_0 to the samples submitted to composting.

Conclusions

Biodegradable composites of PLA/YM in a 70/30 ratio with two different particle sizes, powder (YP) and leaf (YL), were developed. Both composites showed a loss of mass superior to the pure polymer when subjected to natural weathering and composting tests. Among these, composting was the test responsible for the greatest loss of mass in percentage. By SEM analysis, it was observed that the morphology of the polymeric matrix did not undergo considerable transformations after the degradation tests. However, the composites developed cracks and cavities. The natural weathering test caused an intense increase in the luminosity parameter and yellow tendency of the composites, as well as decreasing their brightness. It was found that PLA/YL corresponds to the formulation with the greatest deterioration capacity, showing the greatest loss of mass in degradation tests, along with more evident superficial cracks.

Acknowledgements

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