POLY(LACTIC ACID) / YERBA MATE COMPOSITES: INFLUENCE OF GRANULOMETRY ON THERMAL AND MECHANICAL PROPERTIES

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Abstract - Since the production of composites requires intense heat, this study was carried out to evaluate the thermal stability of Poly(lactic acid) (PLA) matrix composites reinforced with Yerba mate fiber (YM). The samples were also compared to the pure polymer for impact resistance, aiming to future applications in rigid biodegradable packaging. Composites in the mass ratio 70/30 were produced by injection using two YM granulometries: leaf (YL) and powder (YP). The samples were characterized by DSC/TGA and by Izod impact test. The composites showed crystallinity and impact strength reduction while PLA showed greater thermal stability. No significant difference was detected in thermal stability when comparing the two YM granulometries, although PLA/YP showed severe reduction in crystallinity content. PLA/YL presented significantly reduced impact resistance, which could be related to poor interfacial adhesion between matrix and reinforcement.

Keywords: *Poly(lactic acid); Yerba mate; biocomposite; thermal analysis; impact resistance*

Introduction

In the interest of lowering the environmental cost, the influence of incorporating vegetal fibers in polymeric matrices for the production of biocomposites has been studied in the last decades. Besides offering a renewable factor and low abrasiveness during processing, lignocellulosic materials are easily disposable and non-toxic [1]. As a polymeric matrix, the use of Poly(lactic acid) (PLA) is an interesting alternative, since it is easily processed and is also biodegradable. As the main factor for a lower environmental impact, PLA is produced from renewable sources, such as the fermentation of corn or sugar cane [2].

Yerba mate (*Ilex paraguariensis*), a plant of great importance to the economy of the southern states of Brazil, was studied as means of PLA reinforcement. The average consumption of processed Yerba mate in Rio Grande do Sul state is around 70,000 tons per year [3], representing one of the most important socio-economic cycles in southern Brazil, since it is mostly produced by small businesses [4]. While keeping the interest in a circular economy and considering that the disposal of post-consumer Yerba mate has not found viable alternatives for reuse yet [5], this study proposes the incorporation of Yerba mate waste in composites of PLA/YM, in leaf (YL) and powder (YP) forms, evaluating their thermal properties and impact resistance.

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) (YP), and Madrugada (batch number 0219A1 / leaves) (YL).

Preparation of YM 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.

Processing and characterization
After the drying step, YM samples were blended with the polymer using a lab mixer. Two formulations of polymeric mixtures were prepared in the weight ratio 70/30% for PLA/YP and PLA/YL. Pure PLA was also submitted to the same processing as a reference. The samples were ground in a knife mill and were conducted to DSC and TGA thermal analysis along with commercial YP. Five remaining samples from each formulation (PLA, PLA/YP and PLA/YL) were injected for Izod impact test. The fracture surface of the samples submitted to the impact test were analyzed by scanning electron microscopy in 200x and 400x.

Results and Discussion
The thermal decomposition of Yerba mate takes place in six stages, which are indicated in the thermogravimetric analysis presented in Fig. 1. By DTG, it is possible to observe that the sharpest peak occurs around 330 °C, which is related to the largest drop in the TGA curve, corresponding to the most intense mass loss (32.6% in the step 4). In vegetal fibers, this event refers to the disintegration of cellulose, occurring at temperatures around 200 °C ~ 330 °C [6].
The first stage of thermal decomposition occurs around 80 °C and is related to the vaporization of moisture from the vegetal fiber. The next two steps correspond to the degradation of pectins and hemicelulose [6]. The two peaks appearing at 460 °C and 700 °C (steps 5 and 6) are possibly related to the decomposition of lignin with different molar masses, since this occurs in a wide range of temperatures (between 100 °C ~ 900 °C) [7]. Apart from the high kinetic degradation of cellulose the other steps occur slowly, as seen by the lower curvature of DTG peaks. The residue that remains at the end of the process (~5% in mass), is usually composed of aromatic rings, whose ashes are stable above 600 °C under a nitrogen atmosphere [7, 8].
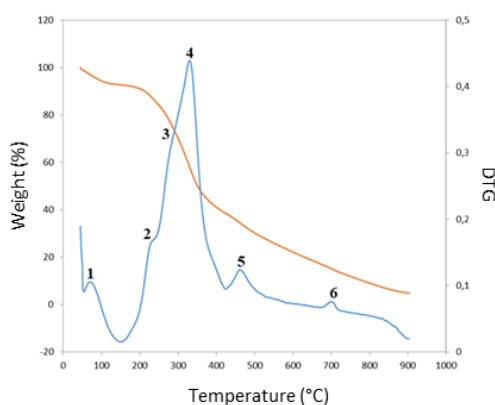

Figure 1 – Superposition of Yerba mate curves of TGA (in orange) and DTG (in blue), identifying the main stages of thermal decomposition.

Since the degradation of pure PLA occurs in just one step (~355 °C), the incorporation of vegetal fiber adds stages related to the elimination of organic compounds (Fig. 2-a). The profile of both composites TGA/DTG curves is similar, suggesting that the fiber particle size did not play a considerable role in the thermal stability of the matrix. Among the four samples, YM is the first material to suffer degradation under the influence of temperature. However, its decomposition is slower due to the high content of lignocellulosic components [5].
The DTG comparison (Fig. 2-b) shows four detectable steps of thermal decomposition for the composites. The first event takes place at 172 °C and concerns the elimination of water and

extractives. The decomposition temperature of pure polymer is in the same range as cellulose decomposition and represents an intense mass loss. Therefore, it is not possible to individually visualize the cellulose peak in the degradation of the composites. Information on the content of constituents released in each step of thermal decomposition is specified in Table 1.
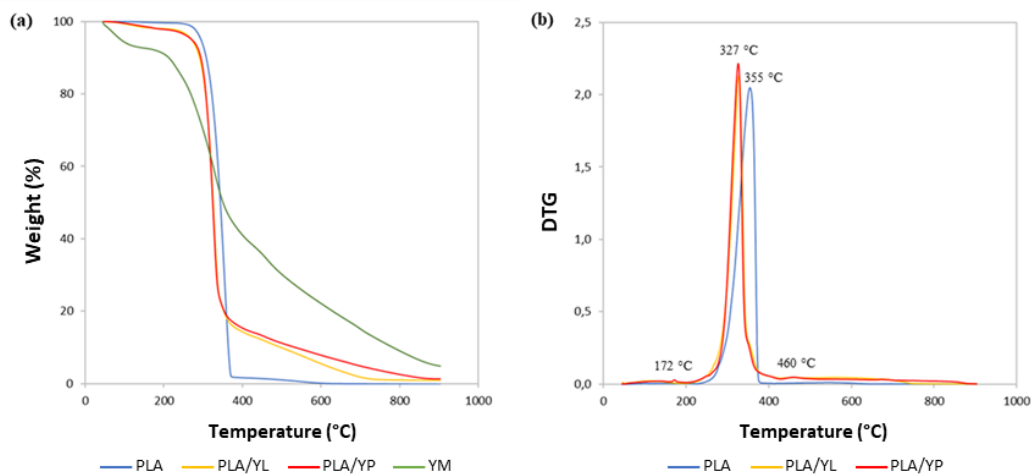

Figure 2 – (a) Superposition of TGA curves for Yerba mate, PLA and composites, and (b) superposition of DTG curves for PLA and composites.

Table 1 – Thermal decomposition characteristics of PLA, PLA/YL and PLA/YP samples.

Sample	$T_{10\%}$ (°C)	%m_1	%m_2	%m_3	%m_4	%m_5	%m_6	%ashes
YM	213	7,0	8,1	13,6	32,6	11,0	22,9	4,8
PLA	308	100,0	ND	ND	ND	ND	ND	ND
PLA/YL	291	2,1	75,0	7,6	14,4	ND	ND	0,9
PLA/YP	294	3,9	73,9	8,1	12,8	ND	ND	1,3

$T_{10\%}$: temperature reached at 10% of mass loss.
%m: mass loss content at each stage of thermal decomposition.
ND: not detectable.

The thermal analysis performed by differential scanning calorimetry (Fig. 3) shows crystallization and melting peaks for both composites and the pure polymer, as well as defined second-order transitions. Due to the diversity of compounds present in the fiber, the thermal curve of YM presents an endothermic band in a wide range of temperatures above 70 ºC. This band refers to evaporation and removal of moisture and extractives from the fiber, which is better visualized in TGA/DTG analysis.

The small exothermic band near the endothermic melting peak, apparent in pure polymer thermogram and highlighted in blue in Fig. 3, is related to the melting of small crystallites and indicates that a large part of the polymer is in an amorphous state [9]. The temperatures at which characteristic events of the material occur, as well as the enthalpy and crystallinity values, are shown in Table 2.

The presence of cellulosic fiber tends to shift the crystallization temperature of the thermoplastic matrix to higher values [10] and the presence of YM particles is responsible for reducing the glass transition temperature of the composites, apart from causing a slight decrease in its melting temperature [6]. This occurs because the polar compounds (polyphenols) present in YM weaken the intermolecular bonds of the polymer chain, improving its mobility [11].

The appearance of a small endothermic peak during the fusion of PLA/YP sample (indicated in red in Fig. 3) probably occurs due to the formation of less stable crystallites during the cold crystallization, imposing the lamellar reorganization of the composite [12]. This phenomenon may

also be associated with the significant reduction of crystallinity suffered by the sample when compared to pure polymer.
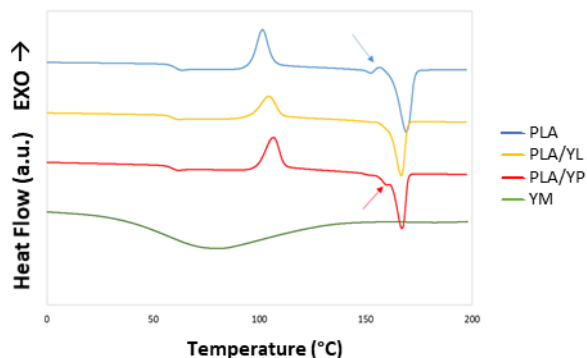

Figure 3 –DSC thermal curves for PLA, PLA/YL, PLA/YP and Yerba Mate.

Table 2 – Thermal properties of PLA, PLA/YL and PLA/YP samples, analyzed by DSC.

Sample	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PLA	61,1	101,4	27,0	169,0	51,8	26,7
PLA/YL	59,0	104,4	18,8	166,7	35,0	24,9
PLA/YP	59,6	106,6	26,3	167,1	33,0	10,3

The adhesion of lignocellulosic fibers to the polymer matrix causes important changes in the mechanical properties of the composite. Fig. 4 represents the significant decrease in impact resistance of composites compared to the pure polymer, with emphasis on the PLA/YL sample (reduction around 40%). The reduction of this mechanical property may be related to insufficient interfacial adhesion between matrix and reinforcement, which can lead to detachment during mechanical tests [13, 14].
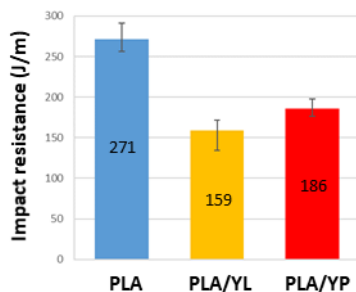

Figure 4 – Impact resistance obtained for PLA, PLA/YL and PLA/YP samples.

Morphologically analyzing the fracture surface using scanning electron microscopy, it is possible to observe the occurrence of holes in the composites structure, contrary to what happens in the pure polymer (Fig. 5-a and Fig. 5-d). Along with the fibers (Fig. 5-e), small voids are visible on the surface of the PLA/YL composite, which are indicated in Fig. 5-b and occur due to the separation of small pieces of fiber during the fracture.

Opposing to what was observed in PLA/YL, the presence of fibers is not discernible in PLA/YP composite, suggesting a better dispersion of the fiber in the matrix (Fig. 5-c). However, the formation of cavities is still notable, as highlighted in Fig. 5-f. The voids may be an evidence of poor interfacial adhesion between fiber and matrix [15], which corroborates the decrease in impact resistance obtained, even though it is expected that the hydrophilic nature of PLA would allow a good interaction between the phases [14].
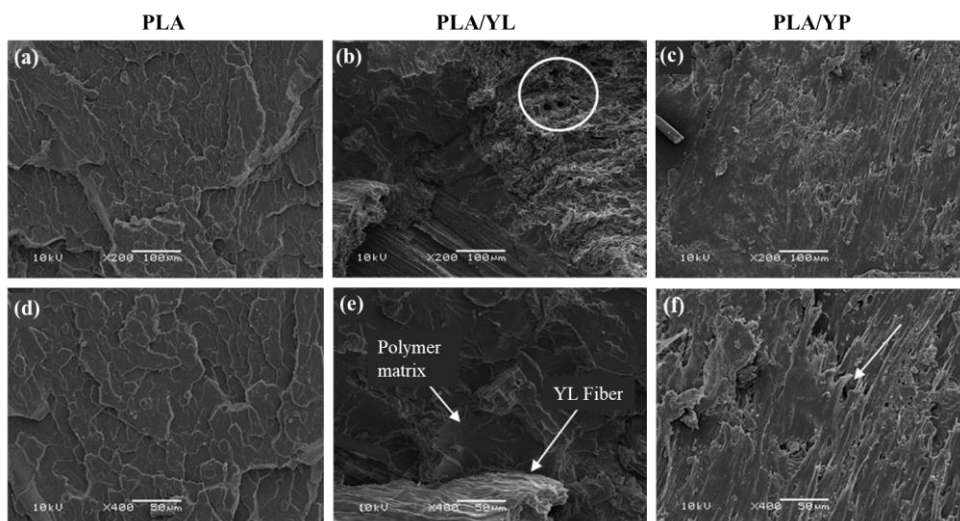
Figure 5 – SEM micrographs of the fracture surface for pure PLA, PLA/YL and PLA/YP in 200x (a, b, c) and 400x (d, e, f).

Conclusions

The thermal analysis showed greater thermal stability of the pure polymer than the composites. The Yerba mate incorporation interacts with the polymer chains, hindering their alignment and consequently the formation of crystals, causing a decrease in the crystallinity fraction of the composites and being related to the reduction of enthalpy associated with the melting peak. The crystallinity of the composite seems to be intrinsically related to the particle size of the dispersed phase, since the sample incorporated with powder particles showed a severe reduction in the crystalline percentage.

A reduction in impact resistance was observed in the composites, probably related to an insufficient interfacial adhesion between matrix and reinforcement. Through SEM, it was found that the morphology of the fracture surface of composites has small voids, which is another indication of weak interaction between the phases.

Acknowledgements

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