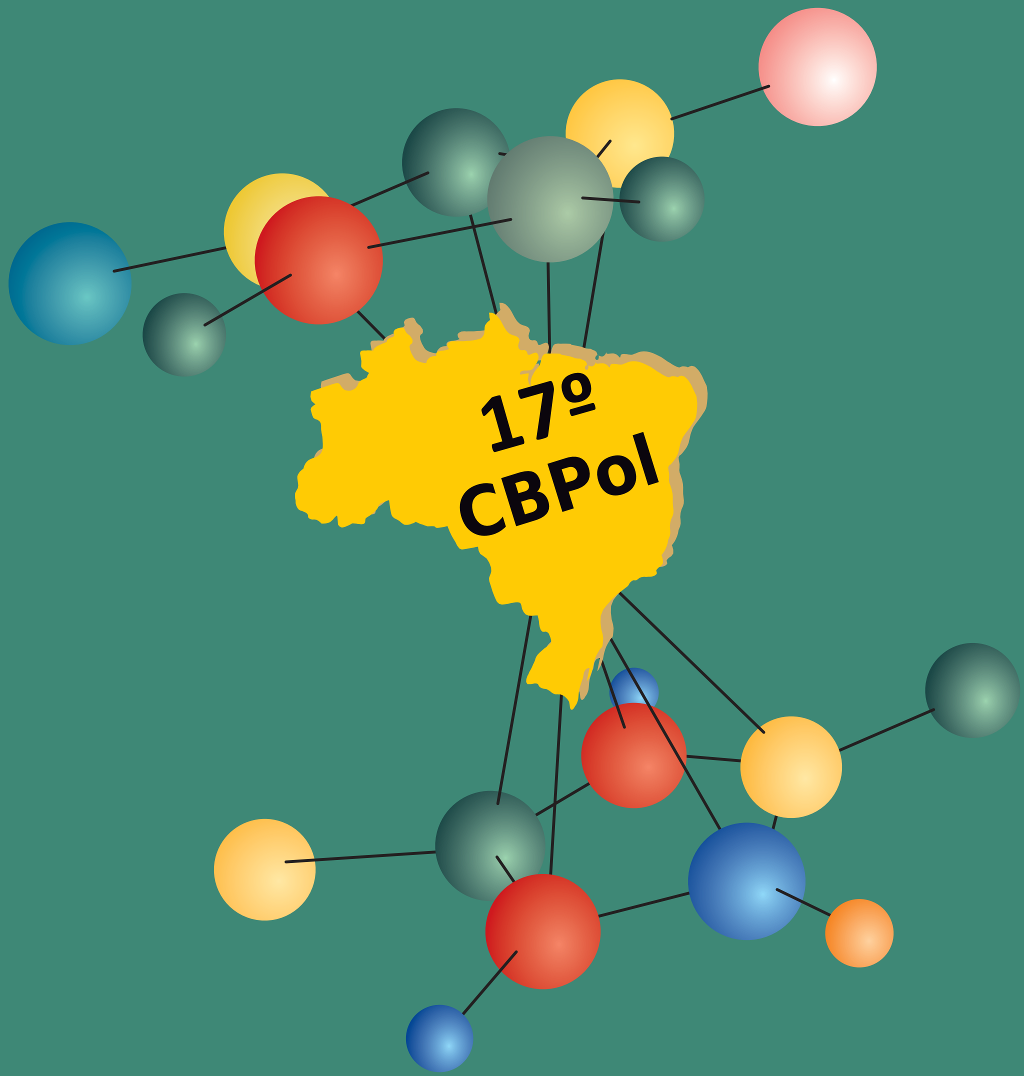

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THERMAL DEGRADATION AND BIODEGRADABILITY OF POTATO STARCH FILMS WITH YERBA MATE EXTRACT AND MALIC ACID

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Abstract - Biodegradable potato starch-based films with 10% and 20% yerba mate extract concentrations were prepared by casting. The thermal degradation and biodegradability of the films obtained were studied, as well as the effect of the addition of malic acid to the composition. By TGA, it was found that the incorporation of yerba mate extract led to a decrease in the percentage of loss mass in the event with the highest degradation kinetics, a behavior amplified with the addition of malic acid. Formulations containing malic acid and yerba mate reached a higher temperature in the most intense mass loss event, suggesting an improvement in the thermal stability of the films, in addition to a higher degradation rate in the natural weathering and composting tests.
Keywords: *Starch films; potato starch; yerba mate; malic acid; thermal degradation; composting; natural weathering*

Introduction

In recent years, natural and biodegradable polymers have gained significant attention for the development of new eco-friendly materials capable of addressing the high consumption of non-renewable resources and the substantial amount of plastic waste generated [1]. Starch represents an interesting alternative due to its high degradation rate, having the potential to contribute to a significant reduction in waste volume and leading to a crucial environmental benefit [2].

The study of polymeric materials requires an efficient evaluation of their resistance to natural aging and biodeterioration by microorganisms since their exposure to the natural environment can modify both their appearance and properties. Additionally, the possibility of composting is important for the study of polymeric waste disposal. Furthermore, to determine their competitiveness and processability, it is essential to evaluate the temperatures supported by the material and its thermal degradation [2-3].

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 [4]. In this context, the addition of yerba mate, a plant of great importance to the southern region of Brazil, was studied as an extract. To enhance the material's thermal stability, the use of crosslinkers carboxylic acids such as malic acid (MA), which is a non-toxic and naturally occurring organic acid found in vegetables and fruits [5], was analyzed.

Experimental

Materials

Potato starch was supplied by Federal Institute of Rio Grande do Sul (IFRS). Glycerol P.A./ACS (NEON) was used as plasticizer and malic acid (DL) P.A. (Êxodo Científica) was used as crosslinking agent. Yerba mate (*Ilex paraguariensis*) extract was simulated using commercial yerba mate purchased at a local market in Porto Alegre, Brazil.

Preparation of the yerba mate extract

The yerba mate extract was prepared by infusing 3 g of sifted yerba mate in 100 g of distilled water at an initial temperature of 80 °C, under agitation [6-7]. After 5 minutes, the liquid was filtered and cooled to room temperature.

Preparation of the potato starch films

The polymeric matrix was developed by mixing 5 g of potato starch (PS) in glycerol (1 g) and distilled water (94 g). For samples containing yerba mate extract (YM), a fraction of distilled water was replaced by the desired concentration of extract (10 g and 20 g). The systems were homogenized under constant agitation at 100 °C until complete starch gelatinization. Subsequently, about 30 g of each filmogenic solution was poured into individual polymeric plates. After casting, the solutions were oven-dried at 30 °C for ~24 h under ventilation to form polymeric films. The same method was followed to prepare samples containing 0.5% malic acid (MA) (wt/vol), with a proportional decrease in the distilled water fraction. The samples produced are described in Table 1.

Table 1 – Composition of potato starch (PS) films with yerba mate extract (YM), with and without malic acid (MA).

Film specimen	Composition
PS	100% potato starch
PS10YM	Potato starch + 10% yerba mate extract
PS20YM	Potato starch + 20% yerba mate extract
MA	100% potato starch + 0.5% malic acid
MA10YM	Potato starch + 10% yerba mate extract + 0.5% malic acid
MA20YM	Potato starch + 20% yerba mate extract + 0.5% malic acid

Thermogravimetric analysis (TGA)

Thermogravimetric tests were performed using a *TA Instruments TGA Q50* equipment. Pieces of each film were heated from room temperature to 900 °C at a rate of 20 °C/min under nitrogen flow of 30 mL/min. From the plots of weight loss values versus temperature, the different degradation phases were obtained.

Natural weathering and composting

Three samples from each formulation (20 mm × 20 mm) were exposed to natural weathering from five and ten days 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, according to D 1435- 99 standard.

The compost degradation was conducted based on G160-12 standard. Samples of each system (20 mm × 20 mm) were buried in containers with soil fertilized with organic compounds (humus) to a depth of approximately 20 mm. At the fifth and tenth days, three samples of each formulation were carefully removed from the soil, oven-dried and weighed on a precision scale. 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.

$$Loss\ of\ mass\ (\%) = ((m_i - m_f)/m_i) \times 100 \quad (1)$$

Results and Discussion

Thermogravimetric analysis (TGA) was carried out in order to analyze the thermal stability of the different starch-based films containing yerba mate extract (Fig. 1). While the thermal decomposition of potato starch takes place in two main stages, notably involving water evaporation (~ 120 °C) and decomposition of amylose and amylopectin (~ 320 °C) [6], the incorporation of yerba mate adds additional steps related to the degradation of pectins and hemicellulose (reportedly between 200 °C and 300 °C [1]), organic components present in the vegetal material. Within this

temperature range, the decomposition of the glycerol-rich phase also occurs. In all cases, this event is hidden by the intense peak observed in the same region [2], which corresponds to the largest drop in the TGA curve and represents the most intense mass loss.
By DTG (Fig. 1-b), a decrease in the peak of the highest degradation kinetics is visible in the samples containing yerba mate, proportional to the amount of extract added to the formulation. This is explained by the fact that this temperature range also corresponds to the degradation of cellulose in yerba mate, which is a less intense event compared to the main starch degradation step [2]. This behavior is replicated in samples containing malic acid (Fig. 1-d), although the addition of this agent is responsible for a significant decrease in the weight loss rate per Celsius degree.

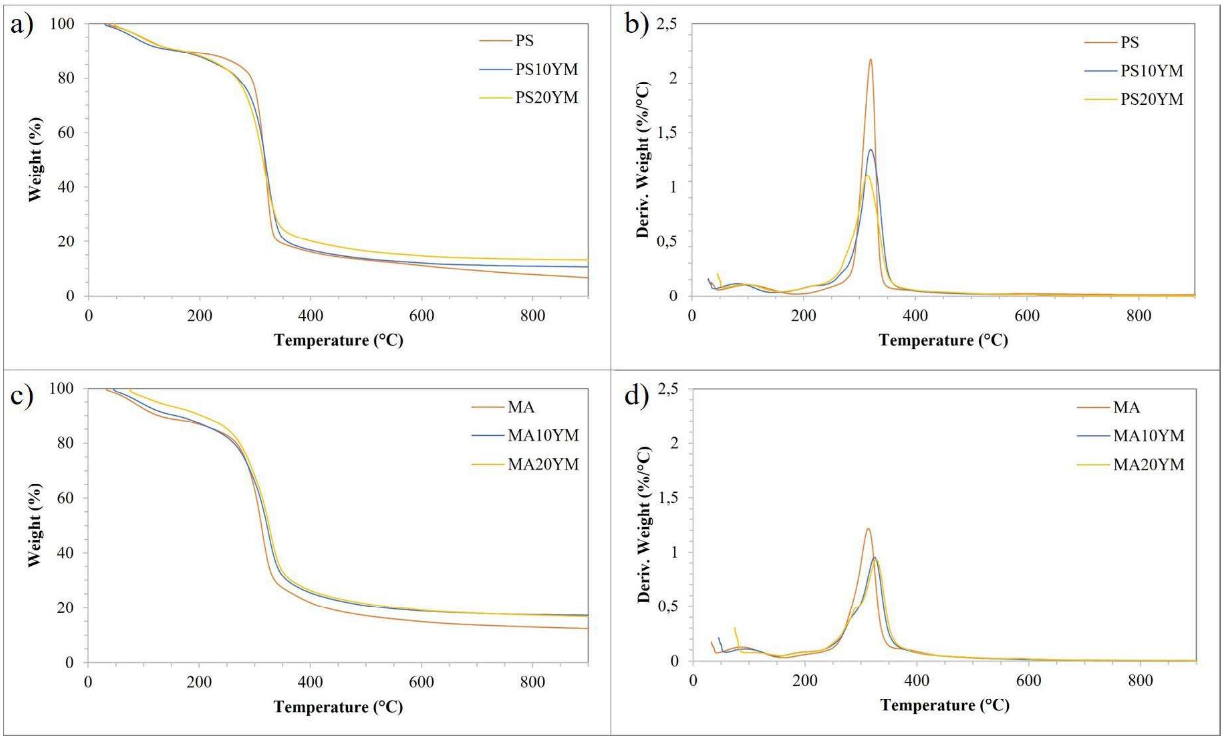

Figure 1 – (a) TGA curves for PS and PS/YM films; (b) DTG curves for PS and PS/YM films; (c) TGA curves for MA and MA/YM films; (b) DTG curves for MA and MA/YM films.

Table 2 presents the decomposition characteristics for the different films produced. Similar to Fig. 1, it can be observed that the percentage of mass loss at the main event decreases with increasing temperature for the samples containing malic acid and yerba mate. For pure PS, this stage occurs at approximately 319.91 °C and degrades 82.69% of the film's mass. In contrast, for the MA20YM sample, this stage eliminates 53.48% of the mass and takes place at approximately 327.23 °C. This implies that the addition of malic acid could improve the thermal degradation temperature, because the crosslinking present in this additive could strengthen the PS backbone chains and create strong linkages, thereby enhancing the thermal degradation temperature of the crosslinked films [5].
The remaining residues at the end of the process for films containing yerba mate are typically composed of aromatic rings, which exhibit stability in their ashes above 600 °C under a nitrogen atmosphere [7]. The high amount of residues in the malic acid films may also suggest the formation of strong crosslinkages between the acids and the potato starch chains [5].

Table 2 – Thermal decomposition characteristics of PS, PS/YM, MA and MA/YM film samples.

Sample	$\%m_1$	$\%m_2$	$\%m_3$	$\%m_4$	%ashes	T peak (°C)
PS	10.64	82.69	ND	ND	6.67	319.91
PS10YM	8.47	6.74	4.88	67.44	12.47	319.09

PS20YM	8.21	5.78	8.04	62.97	15.00	313.21
MA	10.03	4.91	57.34	13.72	14.00	313.40
MA10YM	8.28	5.46	17.05	50.34	18.87	323.97
MA20YM	4.18	5.91	17.13	53.48	19.30	327.23

%m: mass loss content at each stage of thermal decomposition.
T peak: temperature of greatest decomposition kinetics.
ND: not detectable.

In order to study the stability of the systems against degradation, natural weathering and composting tests were conducted for five and ten days. The temperatures in the city of Porto Alegre during the testing period ranged from 10 °C to 27 °C, presenting an average relative humidity between 70% and 95%. Fig. 2 provides a comparison of the percentage of remaining mass for all samples after the tests. All formulations exhibited a higher degree of mass loss during composting compared to natural ageing.

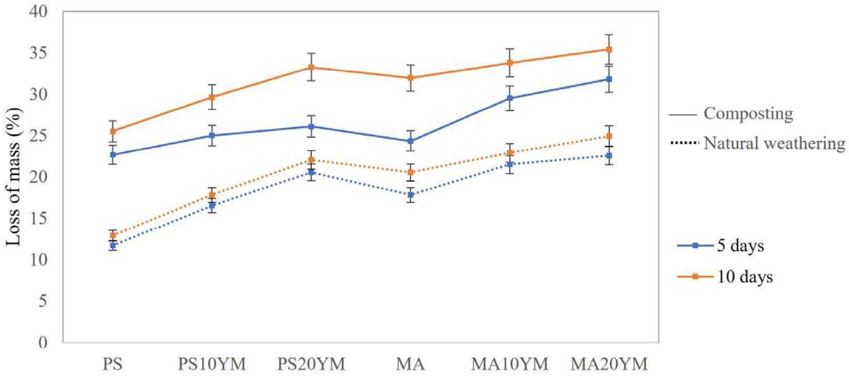

Figure 2 – Loss of mass by formulation as a function of composting time (continuous line) and weathering time (dashed line) for 5 days (blue line) and 10 days (orange line).

Vegetal compounds are easily degraded by microorganisms when buried in the soil [8]. In this sense, the incorporation of yerba mate may be responsible for increasing the rate of degradation of the material in the soil, 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 [1-2]. Furthermore, some of the compounds of yerba mate had low molecular weight and, therefore, are more susceptible to degradation before starch [2].
The presence of lignin in yerba mate is capable of absorbing UV radiation, which accelerates the photodegradation of the samples when exposed to weathering [9]. Furthermore, the high hydrophilic character of vegetal compounds leads to a tendency to absorb atmospheric moisture, resulting in surface wear of the material through dilatation or delamination [10].
It is important to highlight that the addition of malic acid to the formulation is responsible for increasing the degradation rate of the material, resulting in a 35% weight reduction after 10 days of testing. This may indicate that malic acid acts as an anti-retrogradation agent for starch, inhibiting its recrystallization and leading to high moisture absorption, opposite to what is expected with the incorporation of these acids [11].
From Fig. 3, it is possible to compare the visual aspects of pure PS and MA20YM (lower and higher mass loss, respectively) at t_0 and after degradation tests. The absorption of UV radiation by lignin leads to a change in the coloration of the films, as can be observed in MA20YM, which had its color changed from greenish to transparent at the end of the weathering test. Compared to the PS film, the composting test showed the most significant variation in the appearance of the samples, with a thinning of the film with fractures that produced fragmentation and disintegration.

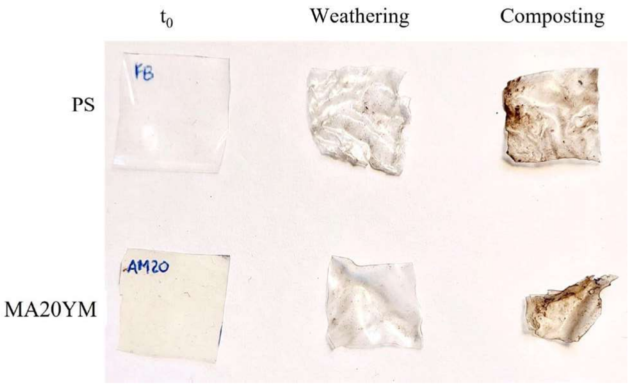

Figure 3 – Visual comparison between the samples PS and MA20YM after 10 days of natural weathering and composting, respectively.

Conclusions

Thermal analysis revealed a lower mass loss in the stage of highest degradation kinetics in the samples containing yerba mate, which is proportional to the amount of yerba mate extract added. This behavior became more apparent with the addition of malic acid to the yerba mate extract, indicating greater thermal stability in the films with this composition. The films with this formulation also exhibited higher mass loss in the biodegradation tests, suggesting that malic acid can act as an inhibitor of starch retrogradation, leading to increased moisture absorption in these samples. The faster degradation in soil of the starch-glycerol-yerba mate extract films makes them very promising to continue with new trends to preserve the environment.

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