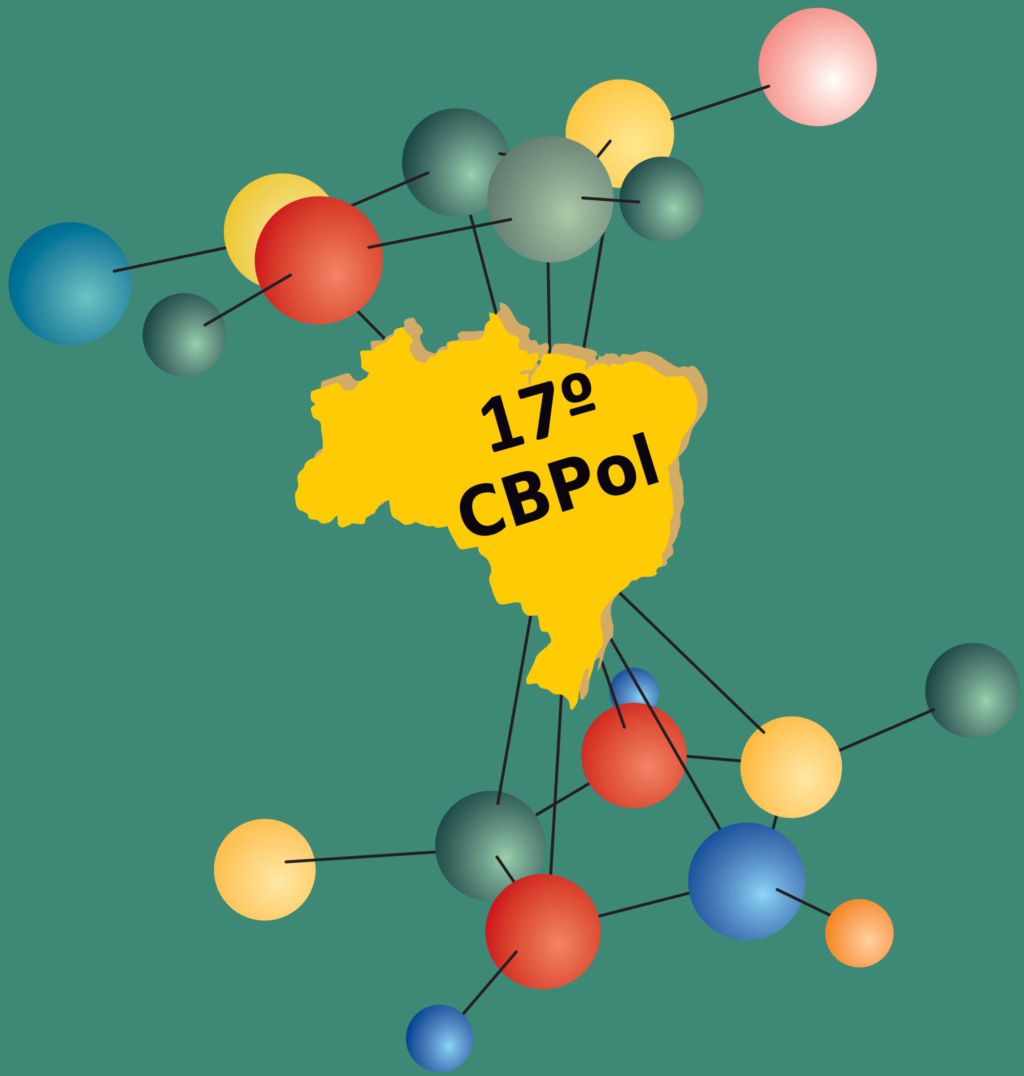

17º Congresso Brasileiro de Polímeros

29 de Outubro a 02 de Novembro de 2023

Joinville - SC

ANAIS

Associação Brasileira de Polímeros

Revisão textual e gramatical: Resposanbilidade dos respectivos autores.

Dados Internacionais de Catalogação na Publicação (CIP)
(Câmara Brasileira do Livro, SP, Brasil)

Congresso Brasileiro de Polímeros (17. : 29 out. - 2 nov. 2023 : Joinville, SC)
Anais do 17° Congresso Brasileiro de Polímeros [livro eletrônico] / organização Associação Brasileira de Polímeros. -- Joinville, SC : Aptor Software, 2023.

PDF

Vários colaboradores.
ISBN 978-85-63273-55-0

1. Polímeros 2. Polímeros e polimerização 3. Química - Congressos I. Título.

24-188263 CDD-540

Índices para catálogo sistemático:

1. Química : Congressos 540

Eliane de Freitas Leite - Bibliotecária - CRB 8/8415

EFFECT OF YERBA MATE EXTRACT AND MALIC ACID ON THE PHYSICAL PROPERTIES OF POTATO STARCH FILMS

Magali Canton Casagranda[1]*, Renan Borges da Silva[1] and Ruth Marlene Campomanes Santana[1]

1 - Department of Materials Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil
magalicanton@gmail.com

Abstract - Yerba mate extract at different concentrations (1%, 10% and 20%) was incorporated into a potato starch-based matrix. In order to enhance the barrier properties of the films, malic acid was added as a comparative. The samples were evaluated for moisture absorption parameters in saturated solutions of sodium chloride (75%) and potassium sulfate (98%), revealing a decrease in the moisture absorption rate and water content in the films containing malic acid. The addition of yerba mate extract also seemed to improve the barrier properties of the starch films, as well as increase their contact angle, indicating a decrease in hydrophilicity.
Keywords: *Starch films; potato starch; yerba mate; malic acid; moisture absorption; wettability*

Introduction

The growing concern for the environment preservation has driven a great interest in replacing synthetic polymers with biodegradable materials. In this sense, starch has become an interesting alternative for the polymeric films production, due to its high availability, low cost, renewability and edible characteristics [1]. However, the high solubility of starch in water, important for its biodegradability, leads to insufficient barrier properties [2]. Polycarboxylic acids, such as malic acid, are used as additives to crosslink the starch matrix, aiming to improve its stability against water permeability [3].
The incorporation of extract of yerba mate (*Ilex paraguariensis*), a plant of great importance to the economy of the southern states of Brazil, was studied as a modifier of the polymeric matrix. The average consumption of processed yerba mate in Rio Grande do Sul state is around 70,000 tons per year and its waste has not found viable alternatives for reuse yet [4-5].
Therefore, this work proposes to study the incorporation of yerba mate extract in potato starch films, as well as to evaluate the malic acid addition in order to improve its physical properties.

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 (1 g, 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 in order 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
PS1YM	Potato starch + 1% yerba mate extract
PS10YM	Potato starch + 10% yerba mate extract
PS20YM	Potato starch + 20% yerba mate extract
MA	100% potato starch + 0.5% malic acid
MA1YM	Potato starch + 1% yerba mate extract + 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

Characterization

The moisture absorption of the films was evaluated by exposing five samples of each formulation to sodium chloride and potassium sulfate saturated solutions in order to simulate environments with 75% and 98% relative humidities, respectively. The solutions were prepared based on the E 104-02 standard and the film specimens were weighted as a function of time. The data obtained was fitted according to a mathematical model suggested by Peleg [8] (Eq. 1).

$$M(t) = M_0 + (t/(k_1 + k_2 t)) \quad (1)$$

Where M(t) is the moisture at the time t (h), M_0 is the initial moisture content, k_1 is the rate constant of Peleg [h/(g water/g solids)] and k_2 is the Peleg capacity constant (g solids/g water).

The surface wettability was determined according to ASTM D 7334-08 standard, considering the contact angle formed between a droplet of water and the films surface. The angles were measured after 3 s and 180 s and an average of six measurements for each sample was considered. The contact angle was determined by *Surftens* software.

Results and Discussion

Due to their hydrophilic nature, starch-based films tend to absorb high amounts of water under elevated relative humidity (RH) conditions [9]. Therefore, the moisture absorption kinetics of the film specimens were studied under 75% RH (sodium chloride solution) and 98% RH (potassium sulfate solution). The measured data was mathematically fitted to the Peleg's equation (Eq. 1) to obtain information about the water interaction with the film components. The Peleg's parameters are shown in Table 2.

As k_1 is inversely proportional to mass transfer, it can be seen that the films containing malic acid tend to absorb moisture more slowly, even in a saturated environment at 98% RH. Whereas the parameter k_2, which is inversely proportional to the amount of absorbed moisture, suggests that the reference specimen, PS, absorbed overall more water and also more rapidly. At a relative humidity of 75%, films with malic acid showed higher values of k_1 and k_2, demonstrating an increased stability against water permeability. Values of r^2 close to 1 indicate that the mathematical model was reliable to predict the moisture content of the films.

Table 2 – Peleg constants (k_1 and k_2) related to the absorption kinetics of films.

Film specimen	NaCl (75%) k_1	NaCl (75%) k_2	NaCl (75%) r^2	K_2SO_4 (98%) k_1	K_2SO_4 (98%) k_2	K_2SO_4 (98%) r^2
PS	0,0129	0,0136	0,9939	0,0214	0,0141	0,9994
PS1YM	0,0193	0,0257	0,9961	0,0261	0,0148	0,9974
PS10YM	0,0163	0,0222	0,9955	0,0180	0,0156	0,9999
PS20YM	0,0233	0,0186	0,9997	0,0239	0,0133	0,9996
MA	0,0288	0,0220	0,9931	0,0273	0,0145	0,9999
MA1YM	0,0330	0,0379	0,9978	0,0369	0,0140	1,0000
MA10YM	0,0407	0,0344	0,9979	0,0345	0,0116	1,0000
MA20YM	0,0255	0,0334	0,9972	0,0282	0,0149	0,9938

Fig. 1 represents the percentage of moisture absorption in starch-based films with increasing levels of yerba mate extract in their formulation, with and without malic acid as an additive. Initially, a high absorption rate is observed; however, this tendency slows down in subsequent measurements.

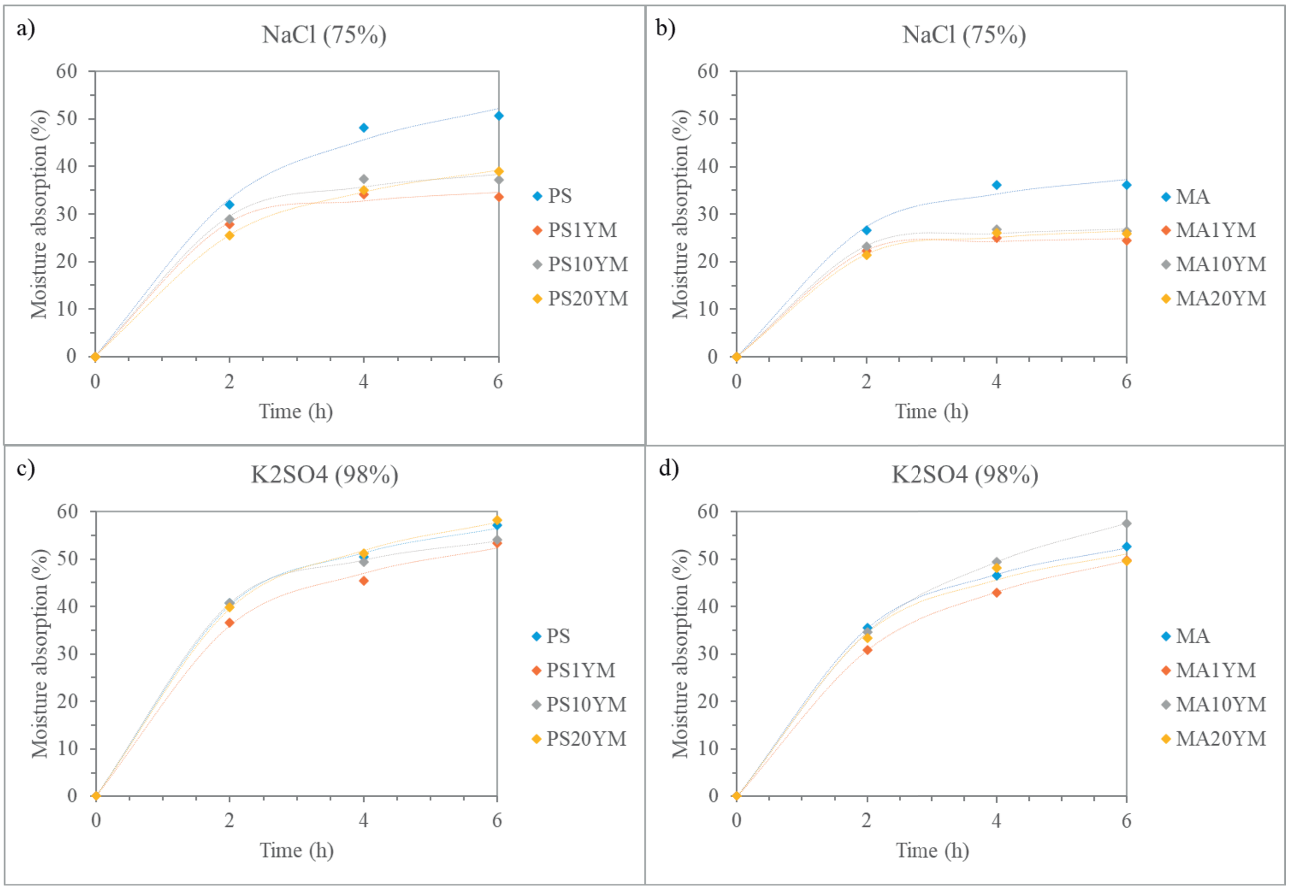

Figure 1 – Moisture kinetics related to exposure time in (a) 75% RH, films without malic acid; (b) 75% RH, films with malic acid; (c) 98% RH, films without malic acid; (d) 98% RH, films with malic acid. Lines represent the Peleg's model.

The comparison between the curves shows a significant increase in moisture absorption in specimens exposed to 98% RH (Fig. 1-c and Fig. 1-d). Over the period of 6 hours, an increase of more than 50% of their initial mass was seen. Under these conditions, no considerable differences were observed in the moisture content of different formulations. In the same way, the constant related to water absorption capacity (k_2) also showed similar values for all compositions, which was lower than those found in the 75% RH environment (Table 2).
However, for 75% RH (Fig. 1-a and Fig. 1-b), the addition of malic acid significantly decreased the moisture absorption capacity of the films, as shown in Fig. 1-b and predicted by Table 2. This is an expected result, as the crosslinks from malic acid are capable of interconnecting starch molecules through covalent bonding, increasing their molecular weight and improving their physical properties [3, 10-11].
It is important to highlight that the incorporation of yerba mate extract also appeared to contribute to lower moisture content values, as can be seen in Fig. 1-a and Fig 1-b. In this case, the increase in extract concentration (1-20%) did not seem to influence this behavior, indicating that a concentration of 1% of the extract was already sufficient to modify the barrier properties of the starch matrix. Yerba mate contains a high content of phenolic compounds, which are miscible with the amylose in potato starch, enabling the formation of hydrogen bonds between starch and water. The covalent interactions between polysaccharides and phenolic compounds can limit the availability of hydrogen groups to form hydrophilic bonds with water, leading to a decrease in the films' affinity for moisture [6].
To evaluate the hydrophilicity of the material, contact angle measurements were performed between a water droplet and the surface of each system. Table 3 shows the variations in the measured contact angle for each formulation. For all evaluated samples, the contact angles reached their maximum values at the beginning of the test (3 s) and decreased with increasing time (180 s). In particular, the specimens containing malic acid exhibited a higher contact angle kinetics (CA) compared to those without the additive.

Table 3 – Contact angle kinetics for potato starch (PS) films with yerba mate extract (YM), with and without malic acid (MA), measured after 3 s and 180 s of contact.

Film specimen	3 s	180 s	ΔCA
PS	65,80° ± 2,46	57,56° ± 4,02	8,24°
PS1YM	62,67° ± 0,89	53,78° ± 2,02	8,89°
PS10YM	74,72° ± 2,10	68,67° ± 3,99	6,05°
PS20YM	76,33° ± 1,45	69,10° ± 1,19	7,23°
MA	45,69° ± 0,75	36,50° ± 1,71	9,19°
MA1YM	44,00° ± 1,49	34,68° ± 3,65	9,32°
MA10YM	54,97° ± 2,35	38,27° ± 2,02	16,70°
MA20YM	67,74° ± 2,69	53,52° ± 2,88	14,22°

A proportional increase in the contact angle was observed with the addition of yerba mate extract. The films formulated with malic acid showed remarkably lower values, indicating a higher hydrophilic character. This can be explained by the relationship between the surface roughness of the material and its hydrophobicity. A rough morphology can increase the fraction of trapped air on the material surface, resulting in an increased contact angle by reducing the contact area between the water droplet and the surface [12]. On the other hand, malic acid provides a smoother texture to the films.
Images of the sample surfaces after 3 seconds of contact with the water droplet can be seen in Fig. 2. It is noticeable that the droplet has a spherical shape on the films without the presence of malic

acid (Fig. 2-a and Fig. 2-b), while the samples with malic acid spread more easily on the polymeric surface (Fig. 2-c and Fig. 2-d).

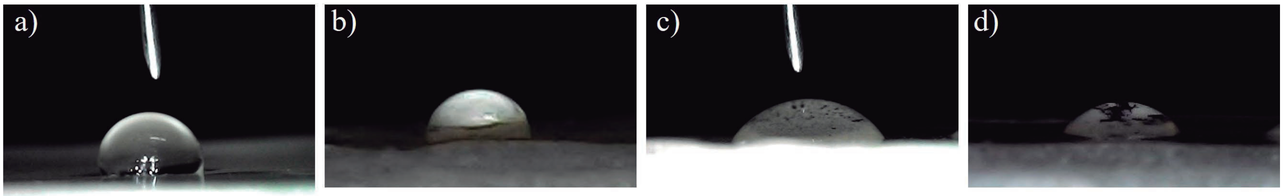

Figure 2 – Drop of water deposited on the surface of: (a) PS; (b) PS20YM; (c) MA; (d) MA20YM.

Conclusions

Starch-based films were successfully produced by casting using potato starch matrix and different levels of yerba mate extract. The addition of malic acid was responsible for reducing the mass transfer kinetics of the samples and decreasing their moisture absorption, suggesting an improvement in their barrier properties. The incorporation of yerba mate extract also resulted in a decrease in water absorption and reduced hydrophilicity of the films. However, the contact angle of the samples with malic acid was significantly lower compared to the specimens without this additive. This could be attributed to the reduction in surface roughness of the material, which facilitates water spreading on its surface.

Acknowledgements

The authors would like to thank to CAPES-PROEX for supporting the research, the Laboratory of Polymeric Materials (LaPol) from Federal University of Rio Grande do Sul (UFRGS) for the infrastructure provided and the Federal Institute of Rio Grande do Sul (IFRS) for donating the potato starch.

References

1. M. A. Knapp et al. Journal of Food Processing and Preservation 2019, 43, 1-12. https://doi.org/10.1111/jfpp.13897
2. L. C. de Azevedo et al. ACS Applied Polymer Materials 2020, 2, 2160-2169. https://doi.org/10.1021/acsapm.0c00124
3. T. G. Dastidar; A. N. Netravali. Carbohydrate Polymers 2012, 90, 1620-1628. https://doi.org/10.1016/j.carbpol.2012.07.041
4. J. P. Lima et al. Journal of Agricultural and Food Chemistry 2016, 64, 2361-2370. https://doi.org/10.1021/acs.jafc.6b00276
5. B. Gullón et al. Industrial Crops and Products 2018, 113, 398-405. https://doi.org/10.1016/j.indcrop.2018.01.064
6. C. M. Jaramillo et al. Starch-Stärke 2015, 67, 780-789. https://doi.org/10.1002/star.201500033
7. D. Piñeros-Hernandez et al. Food Hydrocolloids 2017, 63, 488-495. https://doi.org/10.1016/j.foodhyd.2016.09.034
8. M. Peleg. Journal of Food Science 1988, 53, 1216. https://doi.org/10.1111/j.1365-2621.1988.tb13565.x
9. S. Mali et al. Carbohydrate Polymers 2005, 60, 283-289. https://doi.org/10.1016/j.carbpol.2005.01.003
10. N. Thessrimuang; J. Prachayawarakorn. Journal of Polymers and the Environment 2019, 27, 234–244. https://doi.org/10.1007/s10924-018-1340-2
11. M. Majzoobi et al. Starch-Stärke 2013, 66, 491-495. https://doi.org/10.1002/star.201300188
12. S. I. Kim et al. Macromolecular Research 2014, 22, 1229-1237. https://doi.org/10.1007/s13233-014-2168-9