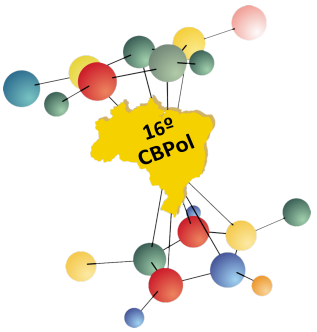

INFLUENCE OF PH ON THE HYGROSCOPICITY OF BLENDS OF GELATIN AND POTATO SKIN STARCH

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Abstract - Biodegradable blends of agricultural origin are exciting alternatives to conventional polymers from fossil sources. In addition, the use of organic waste, such as potato skin, is a way to develop products with higher added value, contributing to the environment. Thus, in this work, starch (A) was extracted from potato skins to produce blends, in which commercial gelatin (G) was also used as raw material. The G/A blends (50:50) were made via casting at the natural pH 5 of the filmogenic solution and neutral pH, which are later submitted to the contact angle and moisture analyses.The results showed that the mixture showed a hydrophobic trend, with greater stability to moisture at acidic pH.
Keywords: *Blend, starch, gelatin, pH, hygroscopicity.*

Introduction

Disposable plastic packages, usually products of petrochemical origin, are considered an environmental problem due to their chemical inertness and low-density characteristics, which generate large volumes, and can take more than hundreds of years to degrade [1]. And, even when degraded, plastics are still present as smaller parts invisible to the naked eye, called microplastics, which contributes to being one of the leading environmental problems today [2]. Given this, the search for more sustainable alternatives has been growing, in which biodegradable polymers are gaining more and more space in research and the market [3]. Among the new materials studied in the literature, biodegradable polymers of agricultural, microbiological, and biotechnological origin have been attracted attention [4].

Polysaccharides, proteins, and lipids are some materials derived from agricultural origin that stand out, mainly due to their availability, low toxicity, biodegradability, filmogenic characteristics, in addition to their low cost [4]. In general, pure films based on starch or protein, such as gelatin, do not show very encouraging results due to the hydrophilic character of these polymers [5]. For this reason, polymer blends emerge as an exciting alternative to improve the properties of pure films since it is possible to make the combined use of polymers, with the advantages of each of the components [6-10]. Thus, the resulting blend basically depends on its composition, interactions, and processing method [8].

In Brazil, potatoes are planted and harvested throughout the year based on demand and the country's appropriate weather conditions [11]. Despite being the fourth food source of humanity [12], this polysaccharide can present, in harvest times, a total produced much higher than consumed, generating an oversupply and consequently transforming it into organic waste. The latter, in turn, has enormous potential, as it is formed by starch, cellulose, hemicellulose, lignin, and impurities [13], and can be used in the production of new products with higher added value [14]. Thus, the objective of this work was to produce blends of gelatin and starch extracted from potato

skins, in the proportion 50:50, at natural and neutral solutions pHs. This work also assesses the effect of this pH variation on the hygroscopic properties of the blend.

Experimental

In this work, commercial gelatin type B and starch extracted from potato skins (*Solanum tuberosum*) were used as polymeric matrix components. Glycerol was used as a plasticizer, water as a solvent, and sodium hydroxide (NaOH) 2 M as pH adjuster.

Starch extraction began with washing the potato skin in running water and sodium hypochlorite (NaClO), at a concentration of 20 mg/L, for 10 min. It is then followed by a mechanical process of grinding, filtering, and decanting, based on the method used by Fernandes [15] and Mahecha [16]. The extracted (hydrated) starch stayed in an environment with a controlled temperature of 60 ºC for 24 h so that the water would evaporate, leaving only the starch.

The blends were obtained by Casting, in triplicate, in which the individual filmogenic solutions were produced. The gelatin solution was obtained by hydrating 10 g of gelatin in 100 mL of distilled water for 1 hour. The starch solution was prepared using 3 g of starch in 100 mL of distilled water. These solutions were heated at 85 °C individually for 10 minutes for gelatin and 3 minutes for starch, followed by the addition of the plasticizer. It was added 20 % of glycerol concerning the dry mass of the raw materials under magnetic stirring until homogenization. Then, the volumetric mixture of the solutions was performed, using 15 mL of gelatin solution and 15 mL of starch solution, forming the blend. PH was adjusted when necessary The 50:50 mixture was homogenized for 15 min at 85 °C, distributed in 25 cm x 18 cm plates, placed in a laboratory oven at 30 °C for 24 h to form the films, and finally to a desiccator for another 24 h.

Film thickness

The average thickness of each blend considers three measurements that were performed at different and random points of the films using a micrometer, Mainard brand, and model M-73010.

Contact angle

A camera provided with focus adjustment and light source was used to project the images, following an adaptation of the ASTM D 7334-08 standard [17]. Samples with 5 cm x 2.5 cm were previously stored in a desiccator 1 h before testing. Then, the films were positioned 3 mm away from the syringe needle tip, which contained deionized water. Ten drops of deionized water were dripped on each sample, photographed 3 seconds after application to assess the stability of the material. The measurements were performed in triplicate, using the Surftens software.

Moisture

A saline solution saturated with sodium chloride (NaCl) with a relative humidity of 75%, following the ASTM E 104-02 [18], was used to determine the moisture of the blends. Samples of 2 cm x 2.5 cm, in triplicate, were placed in the laboratory oven at 60 °C for 1 h and then in the desiccator for 24 h. After the first weighing, the samples were placed in previously weighed containers, whose saline solution was already prepared in accordance with the standard above. These containers were kept in the laboratory oven at 30°C throughout the test. The sample mass was monitored for a total period of 99 h, and the moisture calculation was made based on the mass differences.

Digital microscope

The film surface images were obtained by a digital microscope, brand Cityhua, with 1000 x.

Results and Discussion

Thickness and contact angle

Table 1 shows the results for the average thickness of the plasticized gelatin/starch blends and the contact angle values obtained.

Table 1. Average thickness and contact angle of gelatin/starch blends

Blend G/A 50:50	pH	Average thickness (µm)	Contact angle (º)
G/A - 5	5	60 ± 5	91.12 ± 1.27
G/A - 7	7	52 ± 8	91.38 ± 2.30

It was possible to observe that the blends did not show a significant variation in thickness according to changes in pH. Al-Hassan and Norziah [8] found similar thickness values, between 50 and 70 µm, for starch/gelatin blends.Also reported by Acosta et al. [9], in plasticized films of cassava starch and bovine gelatin.

According to the contact angle results obtained, it was noted that the blends presented hydrophobic characteristics since the values were higher than 90º [19]. Similar results were reported by Nunes [20], in starch blends with tilapia and bovine gelatin. Likewise, Zhang et al. [10] observed that their blends of corn starch and commercial gelatin had angles around 110º for all studied blends. Fig. 1 shows the drops formed in the G/A blends, both rounded, indicating their hydrophobicity and corroborating the numerical data found.

Figure 1. Images of droplets formed on G/A films at pH 5 and 7 (from left to right)

The contact angle indicates the material's wettability and, according to Nunes [20], it can be influenced by the presence of polar and non-polar groups on the surface, as well as by the material's porosity and surface roughness. In addition to other factors such as swelling or deformation when absorbing moisture. In this way, the material is said to be suitable or not for a particular application. Thus, it can be seen that the studied blends did not present a less polished, rough appearance, which could arise due to the presence of fibers and even impurities in the potato skins, as well as not exhibiting insoluble gelatin particles. Furthermore, no significant difference was observed in the contact angle values at pH 5 and 7.

It is noteworthy that the standard deviation values, shown in Table 1, were more accentuated at neutral pH, which may be related to obtaining a lower quality blend at this pH. Fig. 2 depicts the blends at pH 5 and 7. It was noticed that there was a more apparent phase separation at neutral pH, which consequently can compromise the execution of the proposed analyses and the results.

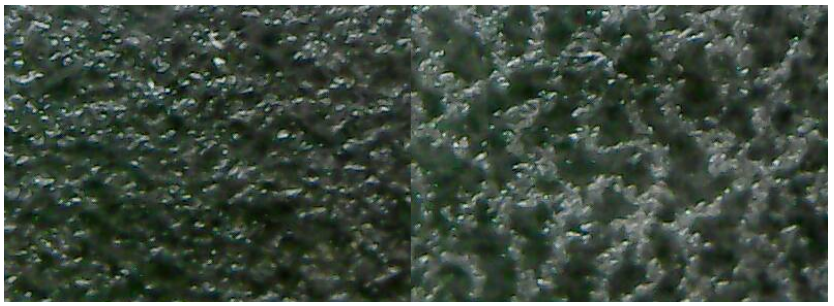

Figure 2. Surface images of G/A films at pH 5 and 7 (from left to right) under a microscope (1000 x)

According to Liu et al. [7], this phase difference may suggest that the blends are immiscible, although compatible, also reported by Acosta et al. [9] and Zhang et al. [10]. This result is possibly associated with the type of interactions, attractive or repulsive, carried out between gelatin and starch, as well as the drying conditions [9]. Another possible explanation is that these zones of discontinuity occurred due to the absence of strong interactions between starch and gelatin, as mentioned by Zhang et al. [10] and Su et al. [21]. According to Su et al. [21], gelatin carboxyl groups ionize at pH above the isoelectric point (pI) of the protein, as pH 7 studied in this work, resulting in a large electrostatic repulsive force that limits the interactions between gelatin and starch. A fact that probably occurred based on the microstructures obtained.

Moisture

Fig. 3 illustrates the mass gain in the blends as a function of time. It is noticeable that the blend at pH 5 (G/A-5) was more stable, showing less sensitivity to moisture. On the other hand, when neutralizing the pH of the blend (G/A-7), it proved to be more unstable and obtained a considerable gain in mass (approximately between 6 h and 21 h of testing). This result may be related to the pH in the pI of the protein, since at this point the charges are in equilibrium, resulting in lower solubility [21]. This explains the lower humidity at pH 5, since the gelatin used in the production of the blends was of bovine origin, with a pI between pH 4.6 and 5.2 [22]. Different from when at pH values above or below pI, as with this the protein will have an excess positive or negative charge, which favors its interaction with water [21], as observed for pH 7.

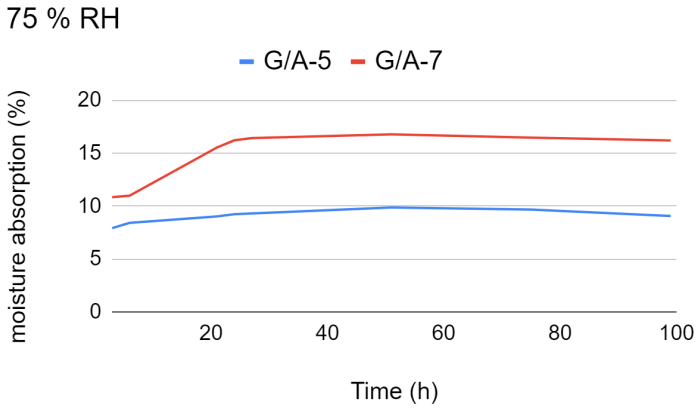

Figure 3. Moisture of gelatin/starch blends as a function of time

Similar results were obtained by Fakhouri et al. [6], who developed blends of corn starch and gelatin, plasticized with glycerol, at acid pH. Furthermore, Fakhouri and colleagues verified that their films had the potential for application as fruit coatings, being completely soluble in acidic medium and, therefore, would be dissolved entirely when a subject ingests the fruit.

Conclusions

This work aimed to investigate the influence of pH on the hygroscopic properties of gelatine/starch blends. Through experiments of contact angle and moisture, hydrophobic characteristics and lower moisture in acidic pH were observed. Thus, at pH 5, the mixture showed promise for future investigations.

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References

1. Q. Wu; L. Zhang. Industrial & Engineering Chemistry Research, v. 40, p. 1879–1883, 2001.
2. M. L. Picchio et al. Food Hydrocolloids, v. 84, p. 424–434, 2018.
3. G. F. Brito et al. Revista Eletrônica de Materiais e Processos, v. 6, n. 2, p. 127-139, 2011.
4. S. S. Farias et al. Geonorte, v. 7, n. 26, p. 61-77, 2016.
5. M. A. S. P. Nur Hazirah; M. I. N. Isa; N. M. Sarbon. Food Packaging Shelf Life, v. 9, p. 55–63, 2016.
6. F. M. Fakhouri. et al. Postharvest Biology and Technology, v. 109, p. 57-64, 2015.
7. X. Liu et al. Chinese Journal of Polymer Science, v. 32, n. 1, p. 108-114, 2014.
8. A. A. Al Hassan; M. H. Norziah. Food Hydrocolloids, v. 26, n. 1, p. 108-117, 2012.
9. S. Acosta et al. Food Hydrocolloids, v. 49, p. 135-143, 2015.
10. N. Zhang et al. Carbohydrate Polymers, v. 92, p. 455– 461, 2013.
11. M. C. C. Silva; P. C. R. Fontes; G. V. Miranda. Horticultura Brasileira, v. 27, n. 1, p. 017-022, 2009.
12. A. C. Ávila et al. Horticultura Brasileira, v. 27, n. 4, 2009.
13. E. Dinand; H. Chanzy; M. R. Vignon. Cellulose, v. 3, p. 183–188, 1996.
14. T. T. Garmus et al. Revista Brasileira de Tecnologia Agroindustrial. v. 3, n. 3, p. 56-65, 2009.
15. A. F. Fernandes. Dissertação de Mestrado, Universidade Federal de Lavras, 2006.
16. M. M. A. Mahecha. Dissertação de Mestrado, Universidade Estadual de Campinas, 2009.
17. American Society for Testing Materials. ASTM D77334-08 Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement, 3 p., Reapproved 2013.
18. American Society for Testing Materials. ASTM E104-02 Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions, 5 p., 2002.
19. P. V. P. Huillca. Dissertação de Mestrado, Universidade de São Paulo, 2015.
20. Y. L. Nunes. Dissertação de Mestrado, Universidade Federal do Rio Grande do Norte, 2014.
21. R. Su et al. Journal of Polymer Science: Part B: Polymer Physics, v. 47, p. 239–247, 2008.
22. E. A. Baldwin; R. Hagenmaier; J. Bai. Edible coatings and films to improve food quality, 2ª edição.CRC Press, USA, p. 1-460, 1994.