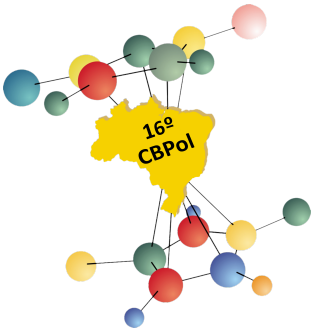

INFLUENCE OF GELATIN CONTENT IN BLENDS WITH STARCH EXTRACTED FROM POTATO SKINS

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Abstract - Biodegradable materials from a natural source, such as polymer blends, are increasingly gaining popularity in research as an alternative to synthetic polymers, which are among the leading environmental problems of our time. Renewable raw materials such as starch and gelatin are attractive, capable of forming films, in addition to being economically viable. Even the potato skins residue has the potential to be used as one of the components of the blend (starch). Thus, blends of starch (A) extracted from potato skins, and different proportions (20, 50, and 80 %) of gelatin (G) were produced in this work. The influence of varying these proportions on the blends G/A were characterized by contact angle, moisture, and scanning electron microscopy analysis. The results indicated that different gelatin ratios interfered in the mixing behavior. Notably, 50:50 blends showed to be more attractive, having hydrophobic characteristics, and being more resistant to moisture, although immiscible.
Keywords: *Blend, starch, potato, gelatin.*

Introduction

Plastic materials originating from fossils are still widely used today, mainly due to their versatility and low cost [1]. However, these materials are considered an environmental problem since they have high molecular weight characteristics, strong intermolecular bonds, and chemical inertness, which may take more than 100 years to degrade [2]. Given this, alternative materials have been sought in which polymer blends gain visibility [3].

Among the new materials studied in the literature, blends of agricultural origin have stood out due to their availability, low toxicity, biodegradability, filmogenic characteristics, and relatively low cost [4]. Thus, gelatin and starch blends have attracted researchers' attention recently [3,5, 6-10]. These mixtures have advantages over the individual components, as they can combine the benefits of each one, providing better mechanical, optical, sensory, barrier, and solubility properties [11]. Nevertheless, the final quality of a blend basically depends on the raw materials used and their proportions and interactions, the formation process, and the desired application [6,9].

Potato shows itself as a relevant starch, the fourth food source of humanity [12], with excellent yield capacity and fundamental nutritional properties [13]. In Brazil, potatoes are planted and harvested throughout the year and, therefore, during harvest times, the total amount of potatoes consumed can be smaller than that produced, which ends up generating agricultural waste. This waste is often mistakenly and even unnecessary discarded since its chemical formation presents itself as a potential raw material for manufacturing products with higher added value [14].

Gelatin is another interesting raw material that has been widely explored in the literature, predominantly comprising the food and pharmaceutical industry, due to its ability to form films [3]. It also attracts attention due to its ability to combine with other biopolymers, such as starch [15]. Therefore, the objective of this work was to evaluate the influence of adding different proportions of gelatin in blends with starch extracted from potato skins when subjected to contact angle, moisture, and scanning electron microscopy (SEM) analyses.

Experimental

To produce the blends, commercial bovine gelatin, brand Dr. Oetker, starch extracted from potato skin (Solanum tuberosum), glycerol plasticizer and water (as solvent) were used. First, the potato peels were washed in running water and solution of sodium hypochlorite (NaClO) at a 20 mg/L concentration for 10 min. Then, based on the methodology proposed by Fernandes [16] and Mahecha [17], a process of mechanical grinding, filtration, and decantation was carried out to extract the starch. The extracted (hydrated) stayed in a controlled temperature environment of 60 ºC for 24 h for water evaporation, leaving only the starch.

The Casting methodology was used to produce blends, in which the filmogenic solutions were prepared individually. The gelatin (G) solution was obtained by hydrating 10 g of gelatin in 100 mL of distilled water for 1 h. The starch (A) solution was prepared using 3 g of starch in 100 mL of distilled water. These solutions were heated at 85 °C for 10 min for gelatin and for 3 min for starch, followed by the addition of 20 % glycerol. It was added concerning the dry mass of the components under magnetic stirring until homogenization. Therefore, the volumetric mixture of these solutions was carried out, that is, the G/A blend, in proportions of 20:80, 50:50 and 80:20. The blends were homogenized for 15 min at 85 ºC. Subsequently, 30 mL aliquots of the blend were distributed in 25 cm x 18 cm plates and placed in a laboratory oven at 30 °C for 24 h to form the films, and then placed in a desiccator for another 24 h. After this period, the films were removed from the plates and submitted to the proposed analyses in triplicate.

Film thickness

Three measurements were performed at different and random points of the films using a micrometer, Mainard brand, and model M-73010.

Contact angle

A camera with focus adjustment and light source was used to project the images, following an adaptation of the ASTM D 7334-08 standard [18], and assisted the contact angle measurement. 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 containing deionized water. On each sample, ten drops were dripped, which were photographed 3 seconds after application to assess the material's stability. The measurements were performed in triplicate, using the Surftens software.

Moisture

A saline solution of sodium chloride (NaCl) with a relative humidity of 75 %, was used to determine the moisture of the blends, following the ASTM E 104-02 [18]. 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 of blends were placed in containers with the saline solution. These containers were kept in the laboratory oven at 30 °C throughout the test. The sample mass was monitored for a total periodo of 99 h, and the moisture calculation was made based on the mass differences.

Scanning Electron Microscopy (SEM)

The evaluation of the morphology of the blends was performed using a scanning electron microscope, model Jeol JSM-6060. The samples were previously metalized in gold.

Results and Discussion

Thickness and contact angle

Table 1 shows 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

Proportion G/A	Average blend thickness (μm)	Contact angle (º)
20:80	57 ± 6	81.95 ± 2.83
50:50	60 ± 5	91.12 ± 1.27
80:20	62 ± 9	84.35 ± 2.51

When verifying the thickness values, it was possible to notice that they were close, suggesting that the amount of protein added to the blend was not enough to cause an increase in thickness. Similar results were found by Davanço, Tanada-Palmu, and Grosso [20] and Fakhouri et al. [5] in blends of corn starch and gelatin. In this context, Acosta et al. [9] analyzed the variation in thickness of their cassava starch and gelatin blends, in 1 and 5 weeks of storage, in which they found that there was no significant variation in thickness, remaining between 60 and 76 μm, values similar to those obtained in this research.

In general, it was observed that the different proportions of gelatin added to the blend influenced the contact angle, making them less hydrophilic, as also mentioned by Zhang et al. [7] and Nunes [21]. This result can be associated with the better barrier properties of the protein. Furthermore, according to Silva et al. [22], gelatin typically improves starch-based materials' performance. However, it can be noted that the effect of the gelatin increment was not proportional to the hydrophobicity, since at the 80:20 ratio the blend became hydrophilic again, as the angle was less than 90º [23]. This behavior is possibly related to the type of interactions carried out between the blend components [9].

Moisture

Fig. 1 illustrates the mass gain in the blends as a function of time. It can be seen that the 50:50 blend remained more stable and with lower mass gain, which indicates greater resistance to moisture compared to the other gelatin/starch ratios. However, the behavior of the blends when subjected to a relative humidity of 75 % did not follow a proportion relationship when adding more gelatin, similar to what was observed for the contact angle values. Thus, making an association between the obtained results, it was noticed that the contact angle values corroborated with the moisture results.

A more significant mass gain was expected at higher proportions of starch, resulting from the higher number of hydroxyl groups available in starch [11], although this occurred in the 20:80 blend. However, the efficiency of blends depends on the proportions of raw materials and their interactions [9]. Therefore, a possible explanation for the most attractive results found for the 50:50 blends is based on the type of connections made between the blend components.

Gelatin and polysaccharides can interact attractively, forming hydrogen bonds. In gelatin/starch blends, these hydrogen bonds can occur between the hydroxyls of the starch and the amino and carboxyl groups of the constituent amino acids of the gelatin. And, therefore, polymer matrix cohesion and water sensitivity can be improved [10]. Furthermore, according to Ye [24], the

excess of one of the polymers leads to exceeding amounts of charges in the system, harming the formation of the blend.

Furthermore, it is important to highlight that both raw materials and glycerol used in the production of blends are hygroscopic: a characteristic that contributes to the sensitivity to moisture [3], and therefore, a certain sensitivity to water was already expected.

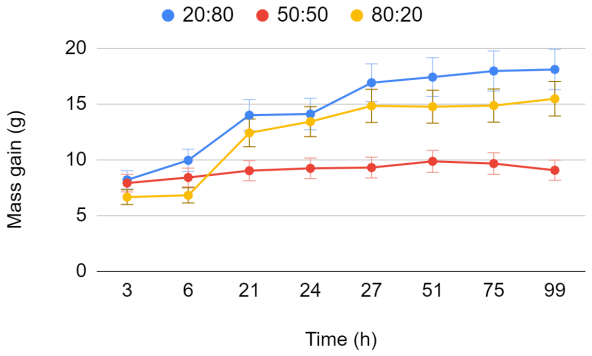

Figure 1. Moisture of gelatin/starch blends as a function of time

Scanning Electron Microscopy (SEM)

Fig. 2 shows SEM images of blends in different gelatin/starch ratios. The presence of small protuberances can be verified as starch is added. It suggests that gelatin and starch form two distinct phases and, therefore, compatible blends, although immiscible [7-9].

Acosta et al. [9] also obtained heterogeneous structures in starch and gelatin blends, in the proportions 25:75 and 50:50. According to Acosta et al. [9], despite the raw materials being macroscopically compatible, due to their similar hydrophilic character, there was a separation into two phases, one rich in starch and the other rich in gelatin. According to Zhang et al. [7] and Liu et al. [8], often, gelatin is presented as a continuous phase and starch as a dispersed phase, which apparently happened in the present work. Furthermore, according to Liu et al. [8], this phase difference may indicate that gelatin and starch shrinkage rates were different during drying or that there was an absence of strong interactions between starch and gelatin.

It is worth remembering that the plates used as a mold are made of polystyrene, and therefore they end up scratching easily, as shown in Fig. 2.

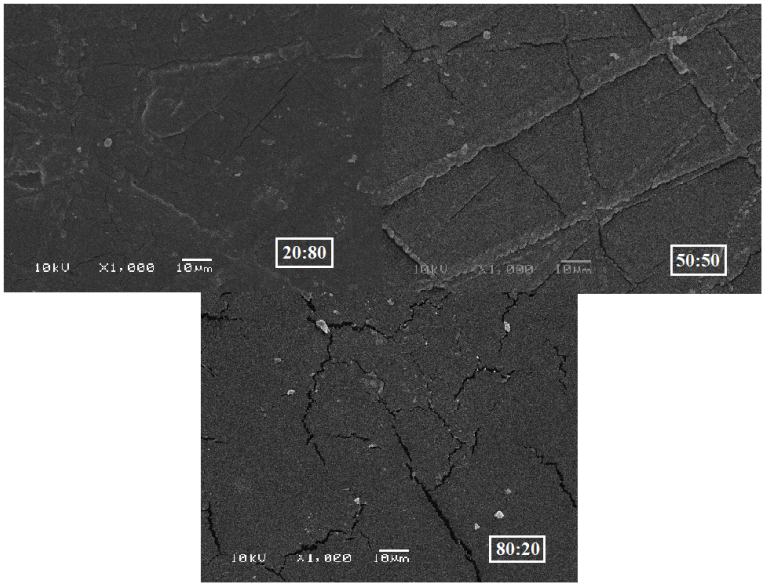

Figure 2. SEM images of different G/A ratios

Conclusions

Based on the results obtained, it was found that increasing the gelatin proportions often led to the improvement of the properties of starch blends. Additionally, the 50:50 G/A blend showed less moisture absorption, indicating that it is less hygroscopic, confirmed by the higher contact angle.

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