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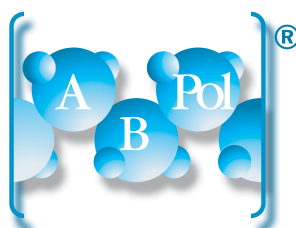
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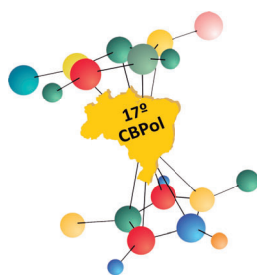
COMPARATIVE STUDY OF METHODS FOR PRODUCING STARCH/PVA BLEND FILMS BY CASTING

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Abstract - Thermoplastic starch is a natural biodegradable polymer with a capability to substitute petroleum based polymers in some applications. However, its high hydrophilicity results in limitations. The production of a blend with corn starch (CS) and polyvinyl alcohol (PVA), a synthetic polymer, could decrease the limitations of CS. Three methods were used to produce blend films (B) of CS/PVA with a 75/25 weight proportion. The first method started by mixing both polymers before the plasticizing of the CS. In the second method the PVA was added after the plasticizing. In the third method, the solubilization of the PVA and the plasticizing of CS were performed separately. Moisture absorption (MA) and contact angle (CA) characterizations had great results. MA was lowered in all of the blends compared to the CS film. The CA of the third blend film compared to the CS film was increased by 17%. All of the results showed that there are benefits to adding PVA to CS, especially with the third method.

Keywords: *biodegradable, starch, polyvinyl alcohol, blend, film.*

Introduction

The global impact of plastic waste has increased the search for alternatives in the industry. According to European Bioplastics, the biodegradable plastic market is expected to grow 12.6% in 2023 [1]. Many substitutions for biobased and biodegradable materials have been successful, but not all applications have suitable options of materials to reduce the pollution. The most common biodegradable polymers still have restrictions or disadvantages relating to properties, cost and large scale production.

Thermoplastic starch is a biodegradable and biobased source for polymeric material that has been largely studied to use as flexible packaging. Starch contains amylose and amylopectin that can be plasticized into a transparent film. It represents 29% of the studies on biodegradable films on Science Direct website (data found researching: "polymeric biodegradable films" and "polymeric biodegradable films starch") [2]. The advantages of using starch are the low cost, multiple sources and easy processing into films. However, its high hydrophilicity results in poor mechanical properties of films produced with this material. It is necessary to use additives, nanofillers or to produce blends using synthetic polymers to improve those properties [3].

Polyvinyl alcohol (PVA) is a synthetic polymer which is also biodegradable and biobased. It is water soluble, which facilitates the production of miscible blends with starch by casting. The production of a blend with starch and PVA, could lower the water interaction properties of both polymers.

This study aims to produce and characterize starch/PVA blend films. The films will be produced by casting using 3 different methods. The goal is to improve properties and select an optimum method to produce such films to be used as flexible packaging.

Experimental

Materials

Corn starch (CS) was received from donation. Polyvinyl alcohol (PVA) was obtained from Dinâmica Química Contemporânea Ltda. The plasticizer, glycerol, was obtained from Vetec Química Fina Ltda.

Production of Films

The films were produced by casting method altering some of the process variables, resulting in 3 blends: B1, B2 and B3. All of the blends were made with CS (75%), PVA (25%), glycerol (33% w/w of CS) and distilled water.

The first method (B1) started by mixing corn CS and PVA with glycerol in distilled water. The solution was heated under stirring for 1 hour for the complete plasticizing of the starch. The second method (B2) consisted in the plasticizing of the starch for 30 minutes, with posterior addition of the PVA. The solution was stirred for another 30 minutes, maintaining the heat, until the total solubilization of the PVA. In the third method (B3), the plasticizing of the starch and the solubilization of the PVA were performed separately, during 30 minutes. Next, the PVA solution was added to the starch solution, then mixed with heat for 10 minutes.

In this study, all of the filmogenic solutions contained a volume of about 75-100 ml distributed in a 330 cm² silicone mold. The amount of polymeric materials (either CS, PVA or both) per film was 4 g. All of the methods used were followed by the evaporation of the solvent in an air circulating oven for 24 hours. After that, the films were peeled from de molds and placed in a silica desiccator until characterization tests. Similar methods were performed to the production of 100% CS and 100% PVA films.

Colorimetry

The optical and colorimetric analysis of the films was made by using a portable spectrophotometer (BYK), following the ASTM D2244-22 norm. The dimensionless parameters obtained were: luminosity (L*), color (a* and b*) and gloss (g). L* varies from white (100) to black (0). The color parameters vary from red (+a*) to green (-a*), and from yellow (+b*) to blue (-b*). And the gloss indicated whether there is more or less reflection of light on the surface of the film. Three measurements were made on each film composition against a white background.

Moisture Absorption

The moisture absorption of the films was measured through the ASTM D5229 method. The film samples were left in closed recipients with sodium chloride saturated saline solution, kept in an oven at 30°C with a relative humidity of 75%, according to the ASTM E104 - 02 norm. Each composition of film was tested with 5 samples.

Thickness

The thickness measurement of the films was done using a micrometer (Mainard, M-73010). Five measurements on 5 samples of each film composition were made.

Contact Angle and Surface Energy

The contact angle of the films was measured by Surftens 3.0 software using photos taken by a digital microscope with a magnification of 1,600 times. The photos were taken 1 second and 1 minute of residency on the films. The angles were measured of 10 drops of water and 10 drops of diiodomethane for every film composition. The surface energy was calculated by the Surftens 3.0 software.

Results and Discussion

The results of the characterization of the films will be used to compare the 3 methods for producing the blends, and to evaluate the effect of the PVA addition to CS. Fig 1 shows a comparison of the visual aspects of the 5 film compositions on different backgrounds. None of the samples seem to have any colors. PVA film is the most transparent film. B2 and B3 films are more translucent than the other films, especially B2. Fig 1 also shows that the blends have good miscibility, due to the fact that they have an homogeneous surface. The low standard deviation values of colorimetry and contact angle also confirm that.
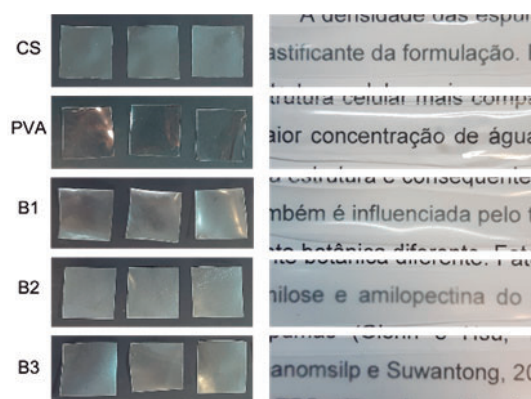

Figure 1 – Samples of the films on black background (left) and on written background (right).

The colorimetry parameters, at Table 1, confirm results previously discussed. The luminosity of the films decreased less than 1% in all of the blends compared to both CS and PVA films. An average of 89% means that the films are very close to the white background used in this test. The color parameters (a* and b*) revealed that the films have an inclination to shades of red and blue. The gloss has decreased on all of the blends, which can be observed as the translucency in Fig 1. The decreases were 2% for B1, 34% for B2 and 12% for B3, compared to the CS film. PVA film had double the gloss of CS film. The lowered gloss on the blend films indicates that a complex of PVA and starch was formed by hydrogen bonding, which reduces the transmittance of light, resulting in more translucent films compared to the transparent PVA film [4].

Table 1 – Colorimetry parameters of the films.

Film	L*	a*	b*	g
CS	89.65 ± 0.04	0.26 ± 0.02	-1.30 ± 0.05	60.87 ± 14.29
PVA	89.40 ± 0.25	0.45 ± 0.03	-1.52 ± 0.11	120.19 ± 7.42
B1	88.89 ± 0.22	0.29 ± 0.02	-1.21 ± 0.10	58.55 ± 4.17
B2	89.00 ± 0.09	0.21 ± 0.00	-1.09 ± 0.09	27.16 ± 1.14
B3	89.26 ± 0.03	0.31 ± 0.01	-1.31 ± 0.06	48.48 ± 4.63

Moisture absorption comparison is shown in Fig 2. All of the blends showed lower absorption, compared to the CS films (50.50%), especially the third blend, which had a 10% reduction. However, PVA film had the lowest absorption of moisture (25.87%), being the most hydrophobic composition. The explanation for the decrease of moisture absorption of the blends is that methyl groups substitute the hydroxyl groups of the amylose and amylopectin structures [5]. It is important to consider that the moisture and the water absorption of the films impact directly on

their biodegradation. The water is important because it allows the microorganism to grow. On the other hand, films with higher moisture content have lower mechanical properties, caused by an impact on the film's physical aspect, which can preclude the use as packaging material.
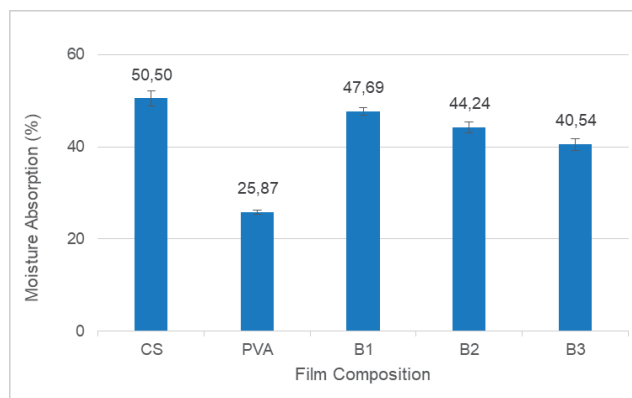

Figure 2 – Percentages of weight gained by moisture absorption of the films with 75% of relative humidity in 24 hours.

After 24 hours, the moisture absorption increased less than 5% for each film. This means that the highest absorption rate occurred within the first 24 hours.

The thickness of the blends were: 183 µm (B1), 164 µm (B2) and 129 µm (B3). The CS film had the lowest thickness (91 µm) and the PVA film had the highest (275 µm). B1 and PVA had the highest standard deviations. The moisture absorption can be related to the thickness of the films. Higher weight results in higher absorption. Amongst the blends, B1 had both the highest absorption and the highest thickness, followed by B2 and B3. The CS and PVA films showed opposite results. CS had the highest absorption with the lowest thickness, and PVA had the lowest absorption with the highest thickness. All of the films contained the same amount of polymeric materials (CS, PVA or both), however the volume of filmogenic solution per cm² can easily be controlled to manipulate the thickness of these films to decrease their moisture absorption.

The contact angle of the 3 blends compared to the CS film had increased, according to results in Fig 3. B1 increased 5%, B2 increased 4% and B3 increased 17% 1 second after the drop. B3 also had less than 2% difference of contact angle from the PVA film. Which means that the hydrophilicity of the third blend greatly increased with only 25% addition of PVA. The blends also had increases between 25 and 35% on the contact angle after 1 min of residency.
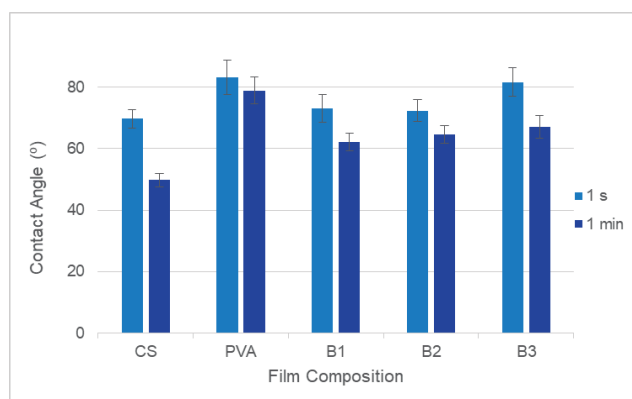

Figure 3 – Contact angles of the films with distilled water with one second and one minute of residency of the drops.

The number of polar groups directly affects the contact angle, because they create hydrogen bonds with water and increase the wettability of the surface [6]. It is noticeable that there are fewer hydroxyl groups on the blends than on the CS film.

To estimate the compatibility of the blends, the surface energy and the interfacial tension were calculated. Table 2 shows the surface energy data obtained by Surftens 3.0. Antonoff's method indicates that the interfacial tension is a subtraction of the surface energy of both polymeric films (CS and PVA) [7]. The results vary from 0.46 mJ/m² (1 s) to 10.82 mJ/m² (1 min), which concludes that the compatibility of the polymers is very high, resulting in highly miscible blends.

Table 2 – Polar (P), dispersive (D) and total (T) surface energy of the films in mJ/m² calculated with one second and one minute or residency of water and diiodomethane drops on the films.

Film	1 s			1 min		
	P	D	T	P	D	T
CS	9.79 ± 0.87	30.64 ± 1.10	40.43 ± 1.31	25.81 ± 1.56	25.62 ± 1.03	51.44 ± 1.60
PVA	3.65 ± 0.62	37.24 ± 1.71	40.89 ± 2,20	4.39 ± 1.01	36.23 ± 2.05	40.62 ± 1.87
B1	8.01 ± 1.82	31.45 ± 1.51	39.47 ± 2.17	16.01 ± 1.39	29.22 ± 1.42	45.22 ± 1.77
B2	7.21 ± 0.64	34.13 ± 0.50	41.34 ± 0.71	12.30 ± 1.10	31.14 ± 0.73	43.44 ± 0.67
B3	3.70 ± 0.97	34.51 ± 1.24	38.21 ± 1.24	11.13 ± 0.94	30.94 ± 1.26	42.08 ± 1.04

Conclusions

The process of producing starch/PVA blends by casting is very simple and shows remarkable results. The general aspect of the films were good, except for the gloss loss. Moisture absorption and water contact angle results showed a lower hydrophilicity of the blend films, compared to the CS film. Those results indicate an advantage of producing starch/PVA blends, especially because it only takes an addition of 25% of PVA to make such an improvement on the hygroscopicity of starch. The characterization results indicate that the blends are apparently miscible. The plasticizing and solubilization processes, when performed separately (B3), improved the properties of the blends.

Acknowledgements

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