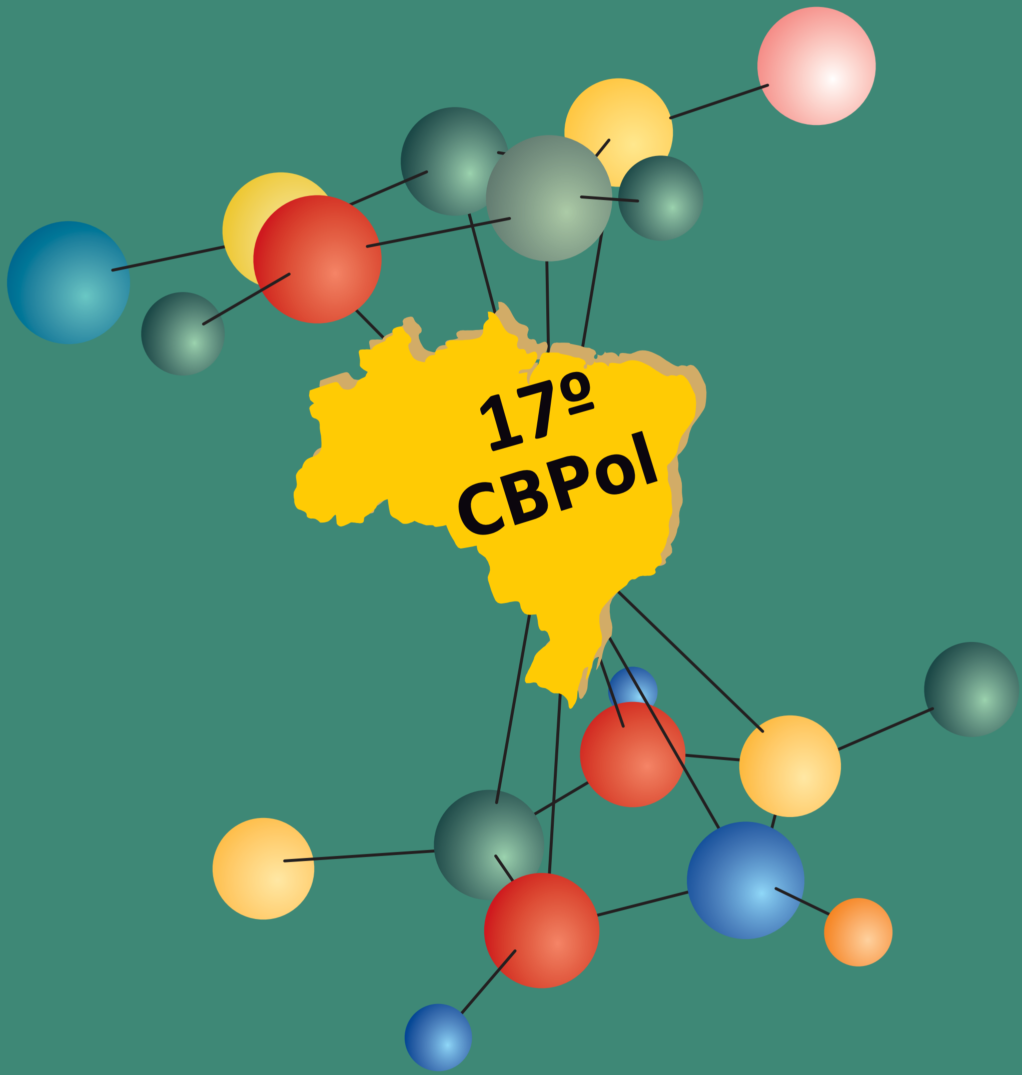

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EFFECT OF THE INCORPORATION OF LIGNIN ON STARCH/PVA BLEND FILMS PRODUCED BY CASTING

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Abstract - Environmental issues caused by polymeric materials residue is an emerging problem. Biodegradable and biobased materials are great alternatives that need improvement on their properties. This study aims to produce and characterize starch/PVA blend films with lignin. The goal is to improve properties of the starch/PVA blend film and select an optimum amount of lignin. Flexible films were produced by casting using 75% of starch, 25% of polyvinyl alcohol and varying quantities of lignin (0, 0.5, 1 and 2%). Optical and water interaction properties were evaluated. The addition of lignin made the films more translucent and with an orange color. Moisture absorption dropped 34% with the incorporation of the additive. The film with 0.5% of lignin had a significant improvement of all the properties tested, showing a potential to be applied as flexible and biodegradable packaging material.

Keywords: *biodegradable, starch, polyvinyl alcohol, lignin, 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. According to data obtained by *ABRELPE,* almost 71 tons of plastic packaging residue was collected and directed to recycling in the year of 2022 in Brazil [2]. Biodegradable polymers are still a better option than recycling. But the most common biodegradable polymers, such as starch, still have restrictions or disadvantages relating to properties, cost and large scale production.

Thermoplastic starch/Polyvinyl alcohol (PVA) blends are made using two biobased biodegradable polymers, a natural one (starch) and a synthetic one (PVA). Starch represents 29% of the studies on biodegradable films on Science Direct website (data found researching: “polymeric biodegradable films” and “polymeric biodegradable films starch”) [3]. 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. The PVA addition to starch shows lower water interaction properties, improved mechanical and barrier properties, and also has excellent compatibility [4]. This blend has potential to be used as flexible packaging, but since both polymers are hydrophilic, the use of additives, such as lignin, can have an even greater impact on the water interaction properties of the film.

Lignin is an aromatic natural and renewable polymer which is extracted from plants. It represents one of the largests residues in the paper industry [5]. When used as an additive to starch films, lignin can increase the elasticity modulus and lower the hydrophilicity. Different properties can also be introduced to the films by adding lignin, such as: antioxidant, antimicrobial, flame retardant and ultraviolet radiation blocking [6].

This study aims to produce and characterize starch/PVA blend films with lignin. The films will be produced by casting using 3 proportions of the additive, to evaluate its effects on the films. The goal is to improve properties of the starch/PVA blend film and select an optimum amount of lignin to produce films and use them as an biodegradable substitute to flexible packaging.

Experimental

Materials

Corn starch (CS) and lignin were 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. The composition of the blends was: CS (75%), PVA (25%), lignin (0, 0.5, 1 and 2% w/w of polymers), glycerol as plasticizer (33% w/w of CS) and distilled water as solvent.

The first step of the production of the films was the removal of the lignin insoluble particles. Distilled water was added to lignin (0.4% w/v), and then filtered using a tulle fabric. Different volumes of the solution were used for each film composition: B (0% lignin), BL05 (0.5% lignin), BL1 (1% lignin), BL2 (2% lignin).

Next, a mixture of starch, water, glycerol and lignin solution was stirred for 30 minutes, with the temperature starting as 40ºC and increasing slowly until 90ºC. After that, the PVA was added to the solution, and stirred for another 30 minutes, maintaining the heat. The filmogenic solution was distributed in a silicone mold, followed by the evaporation of the solvent in an air circulating oven for 24 hours. The films were peeled from de molds and placed in a silica desiccator until characterization tests.

Characterization Tests

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

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 for every film composition. The surface energy was calculated by the Surftens 3.0 software. All of the films were tested using the smoother surface, the one which was in contact with the silicon mold.

Results and Discussion

The results of the characterization of the films will be used to evaluate the effect on the lignin on the blends and to compare the different proportions of lignin. The thickness of the films were (in µm): 164 (B), 141 (BL05), 171 (BL1) and 178 (BL2). The difference of thickness was up to 26%, with an increase of thickness with the increase of lignin, except for the B film.

Fig 1 shows a comparison of the visual aspects of the 4 film compositions on different backgrounds. All of the films have good transparency. The color of the films gets darker with the increase of lignin proportion. Some insoluble particles can be visible, with quantity increasing with the increase of lignin content.

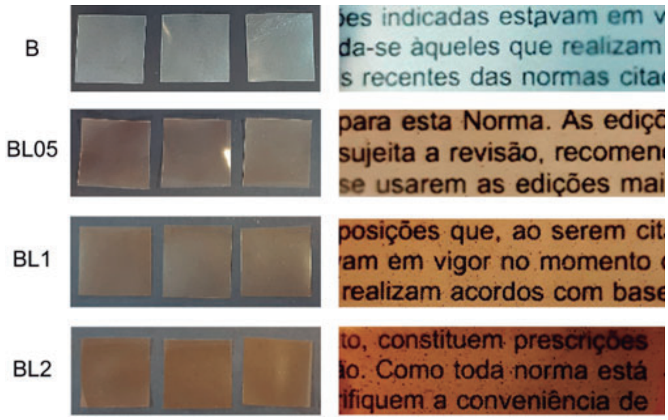

Figure 1 – Samples of the films on black background (left) and on written background (right).

The colorimetry parameters, at Table 1, confirm results previously discussed. The luminosity of the films decreased 10%, 15% and 29% with the addition of 0.5%, 1% and 2% of lignin, respectively. The color parameters (a* and b*) revealed that the lignin films have yellow and red colors, forming a shade of orange. Both color parameters increased with the raise of lignin content. The B film is the film with the lowest gloss. The increase of lignin reduced the gloss of the films. The transparency of the films is related to the size of the particles, if they are about the size of the wavelength of the visible spectrum, they will be more opaque. Also, the ultraviolet radiation blocking, which is important in food packaging applications, can be observed in films with lignin [7]. Further testing should be done to evaluate this property.

Table 1 – Colorimetry parameters of the films.

Film	L*	a*	b*	g
B	89,00 ± 0,09	0,21 ± 0,00	-1,09 ± 0,09	27,16 ± 1,14
BL05	80,10 ± 0,62	2,11 ± 0,22	10,34 ± 0,68	69,91 ± 5,76
BL1	75,70 ± 0,46	3,26 ± 0,14	15,67 ± 0,38	54,64 ± 0,24
BL2	63,25 ± 0,70	8,13 ± 0,41	26,08 ± 0,88	45,18 ± 2,72

Moisture absorption comparison is shown in Fig 2. The absorption decreased an average of 34% with the addition of lignin. BL2 showed the lowest humidity absorption. Those results were similar to many researches using lignin in starch films. The explanation for the decrease of moisture absorption is that lignin, PVA and starch created a strong interaction that reduced the mobility and the diffusivity of the matrix material [8].

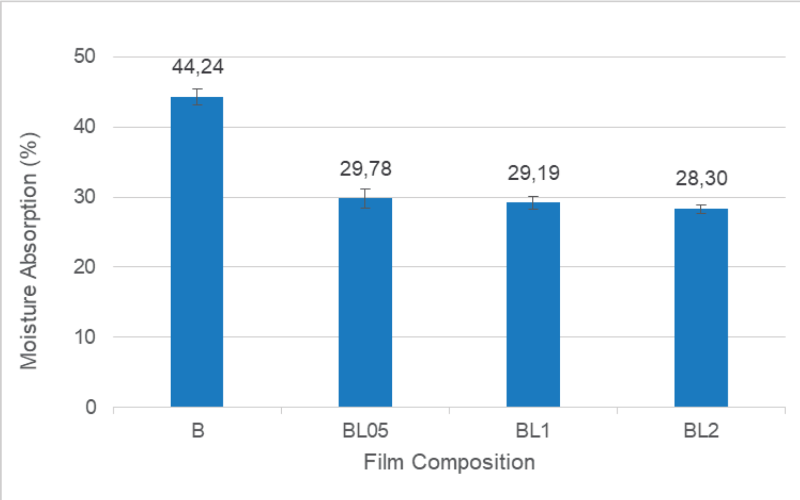

Figure 2 – Percentages of weight gained by moisture absorption of the films with 75% of relative humidity in 24 hours.

After 24 hours, the moisture absorption of the film without lignin increased 4.1% and the films with lignin lowered their mass between 2 and 6%. This means that the highest absorption rate occurred within the first 24 hours for all of the films.

The water contact angle of the films is shown in Fig 3. The only film with an increase of contact angle was the one with the least amount of lignin (BL05). BL1 and BL2 presented with a decrease of contact angle of 13 and 15%, respectively. However, the film without the additive had the highest contact angle after 1 minute of residency of the water drop.

Those results do not prove that the hydrophilicity of the films decreased with lignin, they actually go against the moisture absorption results, but the moisture absorption is not only related to the surface. A reason for this could be because more hydroxyl groups are present on the surface of the film, causing the water contact angle to reduce.

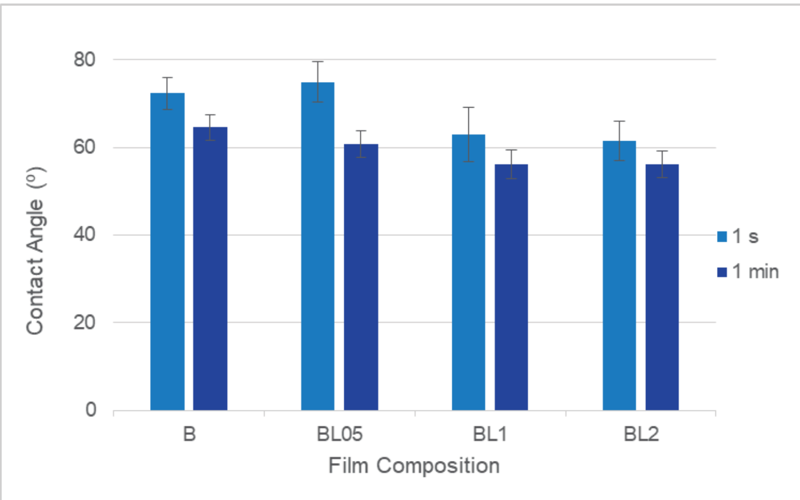

Figure 3 – Contact angles of the films with distilled water with one second and one minute of residency of the drops.

Conclusions

The process of producing starch/PVA blends with lignin is very simple and shows remarkable results. The general aspect of the films were good, except for the presence of some insoluble particles. A different approach on lignin filtering is being considered for the continuation of this research. The films were translucent with an orange color, and have potential to block ultraviolet radiation. Moisture absorption results were excellent even with the smallest amount of lignin. BL05 had the highest contact angle. The difference between the BL05 and the film with the lowest moisture absorption was less than 2%. Also, BL05 was thinner and had the best optical properties. It is noticeable that an addition of 0.5% of lignin resulted in a film with superior properties than 0, 1 or 2%.

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