





Article

Use of Cold Plasma as an Alternative to Improve Corn Starch-Based Films: Effect of the Plasma Application Strategy

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Abstract: Starch-based biodegradable films are a type of packaging material that can naturally decompose in the environment. Current challenges regarding starch-based film applications are their high solubility and low hydrophobicity. Prior studies have shown that plasma application improves the physical, chemical, and mechanical properties of these films. This work evaluates the plasma application strategy regarding the process stage in which plasma should be applied (starch granule, film-forming solution, or film). Three groups of films were produced: a film produced with the plasma-treated starch, a film produced by subjecting the film-forming solution to plasma treatment, and a plasma-treated film produced with the untreated starch. A 2² face-centered experimental design was applied to each group of films to attain the optimal film of each group. The design consisted of applying plasma at 100, 200, and 300 Hz for 0, 10, and 20 min to each group. The results showed significant differences regarding their physical-chemical and morphological properties. Most chemical changes occurred in the starch subjected to plasma prior to film formation, while the films produced with the untreated starch presented physical changes. Plasma-treated films presented reduced solubility and higher hydrophobicity.

Keywords: starch-based films; biodegradable films; packaging; dielectric barrier discharge plasma; natural polymers



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1. Introduction

Biodegradable films are a type of packaging material that can naturally decompose in the environment. They turn into harmless substances that reintegrate into the Earth. These films are a better alternative to traditional packaging materials, such as plastic, which can stay in the environment for a long time. Many industries are adopting biodegradable films to address various environmental, economic, and social issues. These include reducing environmental harm, lowering carbon footprints, mitigating pollution, reducing dependence on fossil fuel-based products, and promoting the principles of the circular economy.

Biodegradable films can be produced from diverse materials, such as plant-based substances, biopolymers, paper, and other natural origins. Within the category of plant-based biopolymers, starch stands out as a natural macromolecule and an edible carbohydrate. Comprising amylose and amylopectin units, starch proves to be valuable in the development of biodegradable films. These starch-based films are increasingly favored for their eco-friendly attributes, serving as a sustainable substitute for conventional plastic films thanks to their biodegradable nature and renewable characteristics [1–3].

Starch can be broken down by enzymes produced by microorganisms, leading to the film's decomposition into more straightforward, environmentally friendly compounds. Starch is derived from crops like corn, potatoes, and cassava, making it a renewable and

sustainable resource [4–8]. This contrasts with petroleum-based plastics, which are derived from fossil fuel sources.

Films derived from starch exhibit several favorable mechanical characteristics and typically appear colorless. These films can be customized to exhibit diverse properties, including flexibility, transparency, and effective barrier properties, rendering them well-suited for various applications. Achieving these customized features may involve modifying the starch or creating composites by combining them with other biodegradable polymers, such as polylactic acid (PLA) or polyhydroxyalkanoates (PHA). These modification processes aim to enhance the overall properties of the tailored films [4,9,10]. Starch-based films can be sensitive to moisture, affecting their mechanical properties and shelf life. Therefore, several studies are being carried out to develop this material further and improve its inherent problems [11–15].

Cold plasma is a non-thermal processing technique that can be used to modify the properties of materials [16]. Cold plasma is a state of matter that exists at or near room temperature. It is created by ionizing a gas, typically a noble gas, such as helium or argon, an inert gas, such as nitrogen, or a mixture of gases like air. Cold plasma technology comprises several types of plasma systems, such as electrical discharge, electromagnetic fields, or radiofrequency excitation [17]. The dielectric barrier discharge (DBD) plasma is widely employed for generating cold plasma. In a typical DBD plasma configuration, two electrodes are positioned with a dielectric material in between. This dielectric material, an insulator, prevents electrical discharge between the electrodes under atmospheric pressure conditions. The electrodes are usually closely situated, forming a gap where the sample to be treated is positioned. A high-voltage alternating current (AC) or pulsed voltage is applied to the electrodes. Upon application of the high-voltage AC or pulsed voltage, the electric field within the gap intensifies, leading to the ionization of the gas and the generation of numerous reactive plasma species [18].

Cold plasma technology can be an effective and sustainable alternative for starch modification through crosslinking/grafting, depolymerization, etching, and conversion of functional groups. The characteristics of the starch matrix undergo alterations based on the specific type of plasma applied and the origin of the matrix [2]. Consequently, this technique is selected to enhance and refine the attributes of starch granules, improving their performance as a packaging material. This includes modifications in solubility, mechanical properties, hydrophilicity, barrier capacity, and thermal stability [19].

The industrial casting process remains challenging, primarily attributed to the elevated viscosity of film-forming solutions based on starch. To address this issue, cold plasma was employed to modify mung bean starch to decrease the viscosity of its film-forming solution [1], thereby facilitating the casting process. Numerous researchers have explored the plasma modification of starch-based films [5,19–23]. These investigations have consistently demonstrated an increase in the amylopectin content of the films, resulting in improved physical and mechanical properties, including higher hydrophobicity, water resistance, and mechanical strength.

Most studies on the plasma modification of starch-based films apply plasma directly to the formed film. However, plasma can be applied to any film production stage, such as the starch, film-forming solution, or the finalized film. As evidenced by Marenco-Orozco et al. [5], the strategies for when to apply plasma result in different changes in the film properties. For example, plasma treatment of the starch granules resulted in a higher elongation at break. In contrast, applying plasma to the film-forming solution increased the resistance to puncture and decreased the solubility of the films. Plasma treatment of the formed film favored higher tensile strength and hydrophobicity.

In this work, we evaluated three plasma application strategies and their effect on amylose content, solubility, water absorbance index, hydrophobicity, surface morphology, and molecular structure. Plasma was applied to the starch granules, film-forming solution, or the formed film. The results of the three strategies for plasma treatment were presented and discussed.

2. Material and Methods

2.1. Materials

In this study, we employed commercial corn starch (Maizena brand, Garanhuns, Brazil). The amylose standard was acquired from Merck (Rahway, NJ, USA) and glycerol from Vetec Química Fina (Rio de Janeiro, Brazil).

2.2. Plasma Application

Plasma treatment was conducted utilizing a DBD plasma system, which consisted of a 30 kV pulsed power source (Inergiae model PLS0130, Florianópolis, Brazil), two aluminum electrodes with a diameter of 8 cm, and acrylic-built dielectric barriers, as detailed in a prior work [23]. The starch and the film-forming solution, which will be explained in Section 2.3, underwent plasma treatment positioned within the 1.5 cm gap between the electrodes. The process was conducted utilizing atmospheric air, and the samples were exposed to three excitation frequencies: 100, 200, and 300 Hz for durations of 0 (control), 10, and 20 min, following a 2² face-centered experimental design. The voltage was set constant at 20 kV.

2.3. Starch-Based Film Preparation

The casting technique was employed to produce the films, following the methodology proposed by Oliveira et al. [8], with adaptations. Corn starch (5 g) was dissolved in 100 mL of distilled water and heated to 95 °C under magnetic stirring for 30 min. Glycerol (25% *w/w*) was added, and the mixture was kept at 60–65 °C for 15 min. The dispersion was homogenized in Ultra-Turrax (IKA model T25, Wilmington, NC, USA) at 10,000 rpm for 15 min. The film-forming solution (10 mL) was poured onto a Petri dish and allowed to dry under ambient conditions (25 °C) until complete evaporation of the solvent (24 h).

Three sets of films subjected to plasma treatment were developed. The first set consisted of plasma-treated films, which were produced and then subjected to plasma treatment. The second set consisted of film-forming solution plasma-treated films, in which the film-forming solution was subjected to plasma (not the film itself). The third set consisted of starch-treated films, in which starch was subjected to plasma, and the films were produced with the plasma-treated starch.

2.4. Characterization of the Film Properties

2.4.1. Solubility and Water Absorption Index (WAI)

Samples, comprising 1% starch (*w/w*) suspensions, were stirred at room temperature (25 °C) for 30 min and then subjected to centrifugation at 10,000 rpm for 15 min. The resultant supernatant and residue were transferred onto Petri dishes and subsequently dried in an oven (Tecnal model TE-394/2-MP, Piracicaba, Brazil).

The samples' cold-water solubility (*S*%) and water absorption index (WAI) were calculated using Equations (1) and (2), following the method described by Fang et al. [24].

$$S(\%) = \frac{W_s}{W_i} 100, \quad (1)$$

$$WAI(\%) = \frac{W_r}{W_i} 100, \quad (2)$$

where *S* is the solubility (%), *W_i* is the initial mass (g), *W_s* is the supernatant mass (g), *W_r* is the residue mass (g), and WAI is the water absorption index.

2.4.2. Hydrophobicity

The contact angle (GBX Scientific Ltd., Dublin, Ireland) was determined according to the ASTM Standard D-5725-99 [25] employing an optical contact meter, where a drop of water was placed on the surface of the films. Film samples (2 × 2 cm) were fixed on a glass support, and an image was captured (Nikon Pixe Link camera, Tokyo, Japan) when the drop touched the surface. The contact angle measurement was based on such an image.

2.4.3. Amylose Content

The determination of amylose content was conducted by employing a modified version of the colorimetric method for measuring the starch–iodine complex, as outlined by Hu et al. [26]. Film segments weighing 0.1 g were immersed in 1 mL of ethanol. Subsequently, 10 mL of 1 mol/L NaOH was added to the suspension. The mixture underwent heating (70 °C) in a water bath for 15 min. After cooling to room temperature, 5 mL of the solubilized starch film solution was extracted, and 46 mL of water, 1 mL of 1 mol/L acetic acid, and 2 mL of iodine in potassium iodide solution (0.2 g I₂ and 2 g KI in 100 mL of water) were added. After allowing the solution to stain for 10 min, its absorbance was measured at 620 nm using a UV-Vis spectrophotometer (Thermo Scientific model Evolution 201, Waltham, MA, USA). A standard curve for amylose concentration was established using amylose samples with varying compositions (Sigma, Livonia, MI, USA).

2.4.4. Chemical Groups and Molecular Structure

The molecular structures of the starch-based films were examined through Fourier-transform infrared spectroscopy (FTIR). This analysis was conducted using an FTIR instrument (Agilent model Cary 630, Santa Clara, CA, USA) equipped with an ATR measurement accessory. Spectra were recorded within the range of 4000 to 400 cm^{−1}. The absorbance values at 995 cm^{−1} and 1022 cm^{−1} were utilized to calculate the short-range ordered structure and the crystalline/amorphous ratio (CAR). The CAR was determined using Equation (3), as suggested by Warren et al. [27].

$$CAR = \frac{Absorbance_{995\text{ cm}^{-1}}}{Absorbance_{1022\text{ cm}^{-1}}} \quad (3)$$

2.4.5. Surface Morphology

Starch-based film samples were mounted on stubs and metalized with a thin layer (20 nm) of gold in a metallizer (Quorum model QT150ES, Laughton, UK). The films were then examined in a scanning electron microscope (Quanta model 450 FEG-FEI, Laughton, UK) with an accelerating voltage of 20 kV.

2.5. Statistical Analysis

Statistical analysis was performed using analysis of variance using the Statistica[®]7 software (Statsoft GmbH, Hamburg, Germany). Tukey's tests and *t*-tests were applied at a 95% confidence level to detect significant differences.

3. Results and Discussion

3.1. Amylose Content

Amylose content is an important parameter that affects starch structure and functional characteristics such as solubility, swelling power, paste viscosity, gelatinization, and retrogradation. Table 1 presents the amylose content of the untreated and plasma-treated films and films produced with plasma-treated starch and film-forming solution. The untreated film produced with untreated corn starch had an amylose content of 23.4 ± 1.0%.

Plasma-treated films tended to have their amylose content reduced, consequently increasing their amylopectin content. The highest reduction was observed at 200 Hz and 20 min of treatment when a reduction of 11% resulted in films with 20.8 ± 0.9% of amylose. Plasma tends to depolymerize linear chains of carbohydrate polymers [28,29], producing shorter carbohydrate chains and carbohydrate radicals. At the same time, the free radicals generated in the plasma react with amylose, creating internal radicals, which polymerize and produce amylopectin. The films produced with the plasma-treated film-forming solution presented a similar trend to the plasma-treated films but with the lowest amylose content observed at 100 Hz. Such results were in accordance with previous studies with plasma-treated banana starch films [5].

Table 1. Amylose content in untreated and plasma-treated starch films and films produced with plasma-treated starch and film-forming solution *.

Plasma Frequency (Hz)	Exposure Time (min)	Plasma-Treated Film	Starch-Treated Film	Film-Forming Solution-Treated Film
0	0	23.4 ± 1.0 ^{ab}	23.4 ± 1.0 ^{ed}	23.4 ± 1.0 ^{bc}
100	10	21.6 ± 0.4 ^b	24.8 ± 0.4 ^d	25.2 ± 0.1 ^b
100	20	23.7 ± 0.9 ^{ab}	22.3 ± 0.1 ^e	20.0 ± 0.2 ^d
200	10	22.1 ± 1.2 ^{bc}	31.0 ± 0.3 ^b	22.3 ± 0.3 ^c
200	20	20.8 ± 0.9 ^c	33.4 ± 0.1 ^a	23.1 ± 0.1 ^c
300	10	22.4 ± 0.4 ^b	28.6 ± 0.3 ^{bc}	24.8 ± 0.3 ^b
300	20	23.7 ± 0.4 ^a	27.2 ± 0.5 ^{bc}	27.0 ± 0.7 ^a

* Values are the mean of three measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$).

The films made from plasma-treated starch showed an opposite trend. These films had an increased amylose content, which reached up to 33.4 ± 0.1. Starch granules have very low humidity (<5%). When the reactive plasma species reacts with the starch granules, it depolymerizes the amylose and amylopectin molecules. Branched polymers such as amylopectin will lose their branches and be transformed into low-carbon number amylose.

Plasma treatment of the starch granules produced a film with a higher amylose content. This usually creates films with a more ordered structure and higher cohesive forces within the film, resulting in stronger starch films with greater tensile strength and lower swelling rates. On the other hand, plasma treatment of the film and the film-forming solution produced a film with a lower amylose content. This usually creates films with better biocompatibility, a higher swelling rate, and higher elongation at break, which is useful in food coating and applications such as wound dressings [30,31].

3.2. Solubility and Water Absorbance Index

Starch has a hydrophilic character; that is, it facilitates water absorption, causing the films to swell, thus impairing their applicability. The water absorption indexes (WAI) for all sets of films are presented in Table 2. The WAI did not change significantly from the control in most tested treatments. The exceptions occurred with the plasma-treated film at 300 Hz for 20 min, significantly reducing the WAI, and the film produced with plasma-treated starch also at 300 Hz for 20 min, significantly increasing the WAI. The difference may be related to the formation of water free radicals, which will occur in the humid film but not in the dried starch granules.

Table 2. Water absorption index for the untreated and plasma-treated starch films and films produced with plasma-treated starch and film-forming solution *.

Plasma Frequency (Hz)	Exposure Time (min)	Plasma-Treated Film	Starch-Treated Film	Film-Forming Solution-Treated Film
0	0	1.97 ± 0.05 ^a	1.97 ± 0.05 ^b	1.97 ± 0.05 ^a
100	10	2.08 ± 0.67 ^{ab}	1.98 ± 0.11 ^b	1.87 ± 0.04 ^a
100	20	1.99 ± 0.56 ^{ab}	1.97 ± 0.04 ^b	1.88 ± 0.22 ^a
200	10	2.01 ± 0.34 ^{ab}	2.07 ± 0.47 ^{ab}	1.93 ± 1.02 ^a
200	20	2.07 ± 0.98 ^{ab}	2.07 ± 0.16 ^{ab}	1.87 ± 0.46 ^a
300	10	1.87 ± 0.09 ^a	2.10 ± 0.10 ^{ab}	1.92 ± 0.34 ^a
300	20	1.68 ± 0.11 ^b	2.18 ± 0.08 ^a	1.91 ± 0.03 ^a

* Values are the mean of three measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$).

Table 3 presents the solubility of the untreated and plasma-treated starch films and films produced with plasma-treated starch and film-forming solutions. Films with low water solubility are desired for most applications. For example, films used to coat fruits

cannot be very water soluble because the humidity of the fruit would dissolve the film, eliminating the protection brought with the film.

Table 3. Solubility of the untreated and plasma-treated starch films, and films produced with plasma-treated starch and film-forming solutions *.

Plasma Frequency (Hz)	Exposure Time (min)	Plasma-Treated Film	Starch-Treated Film	Film-Forming Solution-Treated Film
0	0	90.0 ± 1.6 ^a	90.0 ± 1.6 ^a	90.0 ± 1.6 ^a
100	10	83.8 ± 0.6 ^b	83.8 ± 3.3 ^b	79.1 ± 3.0 ^b
100	20	83.7 ± 0.8 ^b	86.2 ± 3.1 ^{ab}	80.9 ± 3.3 ^b
200	10	82.6 ± 1.4 ^{ab}	75.8 ± 4.1 ^c	79.2 ± 0.4 ^b
200	20	84.0 ± 1.2 ^b	76.5 ± 3.7 ^c	81.8 ± 4.0 ^b
300	10	83.3 ± 1.1 ^{ab}	78.3 ± 4.0 ^c	79.2 ± 2.3 ^b
300	20	82.7 ± 0.8 ^{ab}	79.5 ± 3.3 ^c	79.4 ± 1.7 ^b

* Values are the mean of three measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$).

Plasma treatment reduced the water solubility of the films, which is a positive result of plasma application. The greatest changes in water solubility were attained with the starch-treated films, followed by the film-forming solution-treated films and the plasma-treated films. The lowest water solubility of the starch-treated films is directly correlated to their higher amylose content. Amylose is less soluble in water than amylopectin; thus, films with higher amylose content will also be less soluble. The starch-treated films produced by treating the starch at 200 Hz for 10 min were 16% less soluble in water than the untreated starch-based film, which is a considerable amount for starch-based films.

The film-forming solution plasma-treated films reduced the film solubility by 12%, while the plasma-treated film reduced it by only 8%. Thus, the starch-treated films are a better option for applications requiring higher water resistance films.

The application of cold plasma treatment alters the crystalline structure of starch, as will be detailed in Section 3.4 (Molecular Structure). This process results in changes to the degree of crystallinity, which, in turn, impacts the solubility of starch. This modified starch is better suited for a wide range of food and pharmaceutical products requiring rapid dissolution or increased stability [32].

The solubility of the films is also influenced by the starch granules used to produce them. Figure 1 presents the morphology of the natural and plasma-treated starch granules used to produce the films. The untreated starch granules had a rougher surface, while the plasma-treated starch presented a smoother surface. Such a difference in shape and chemical changes have contributed to the lower solubility of the films produced with the plasma-treated starch.

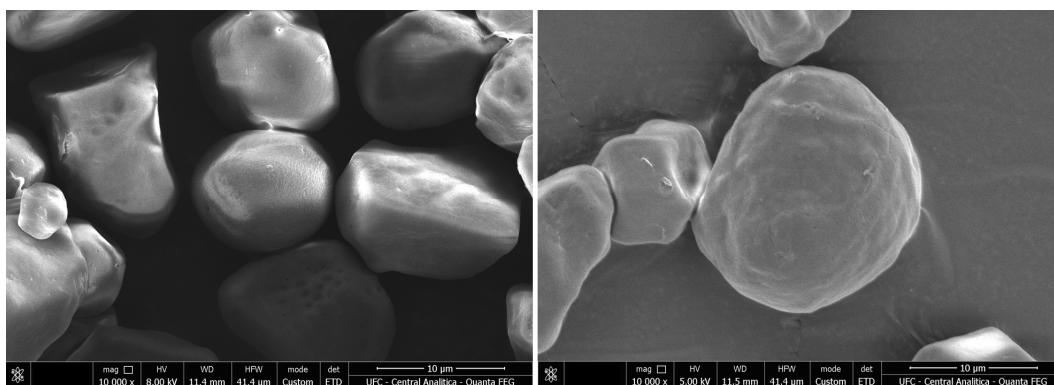


Figure 1. Morphology of the untreated (left) and plasma-treated (right) starch granules. Plasma treatment was carried out at 200 Hz for 20 min.

The solubility of starches reported in the literature varies considerably. Values from 9 to 90% have been reported, raising concerns regarding calculations or the execution of the reported methods. Thus, it is difficult to compare the solubility of different starch films. Among similar methodologies, the film reported herein is more soluble than most starch films, such as *Amaranthus paniculares* (62%), cassava (75%), and potato (70%) films [33–36].

Plasma treatment of the films reduced the solubility of the corn starch film, bringing its solubility level toward the values of starches of lower solubility. Starch-based films with lower solubility have higher water resistance and durability and are more stable when moisture is exposed. The better stability results in better integrity of the film and its mechanical properties over time, which is essential for packaging applications. Since the solubility of the films is still high (>75%), it will present a balance between durability and eco-friendliness, as films with higher solubility tend to break down more easily in natural environments [37,38].

3.3. Hydrophobicity

The contact angle of a film is an important criterion for deciding its suitability in packaging applications. It indicates the tendency of a drop to spread and adhere to the surface of materials, reflecting its wettability and hydrophilicity. The higher the contact angle values, the greater the surface's tendency to repel water [39]. Table 4 presents the contact angles of the untreated and plasma-treated starch films and films produced with plasma-treated starch and film-forming solutions.

Table 4. Contact angles of the untreated and plasma-treated starch films and films produced with plasma-treated starch and film-forming solutions *.

Plasma Frequency (Hz)	Exposure Time (min)	Plasma-Treated Film	Starch-Treated Film	Film-Forming Solution-Treated Film
0	0	54.2 ± 1.1 ^e	54.2 ± 1.1 ^b	54.2 ± 1.1 ^c
100	10	55.9 ± 1.1 ^{de}	54.0 ± 1.7 ^b	56.2 ± 1.4 ^c
100	20	58.5 ± 0.9 ^{cd}	53.2 ± 1.8 ^b	61.0 ± 1.6 ^b
200	10	57.1 ± 0.6 ^d	53.5 ± 1.3 ^{ab}	64.6 ± 1.1 ^a
200	20	64.3 ± 0.6 ^a	55.4 ± 2.2 ^{ab}	62.5 ± 1.2 ^b
300	10	59.2 ± 0.4 ^c	57.0 ± 1.4 ^a	62.5 ± 1.8 ^b
300	20	61.6 ± 0.5 ^b	58.1 ± 1.7 ^a	56.2 ± 1.4 ^c

* Values are the mean of three measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$).

The films produced from plasma-treated starch showed only slight changes (2%) in hydrophobicity when treated at 300 Hz, while no significant changes were observed with the films produced from starch treated at 100 and 200 Hz. The result shows that the change induced in the starch particle did not significantly influence the surface properties of the film.

The plasma-treated film produced with the untreated starch showed a significant increase in hydrophobicity, up to 18%, when treated for 20 min at 200 Hz. Plasma treatment was effective in improving the properties of already-formed surfaces.

The films produced when plasma was applied to the film-forming solution showed the highest hydrophobicity changes (19%). However, these changes were statistically equivalent to those observed when treating the film made with the untreated starch. The results, therefore, indicate that the plasma-induced improvement in hydrophobicity occurs mainly during the formation of the film and after it has been produced.

Higher hydrophobicity is sometimes linked to the higher amylose content in starch-based films since amylose is less soluble in water and does not tend to form a gel after adding water. However, the increase in the amylose content of the films produced with plasma-treated starch (Table 1) did not cause an increase in hydrophobicity. On the other hand, plasma treatment of the film and the film-forming solution increased the hydrophobic

nature of the films' surface even at a low amylose content. Such a result can be considered positive, especially for films produced with starches with a low amylose content.

Ionization by plasma species is the most significant factor in the depolymerization process, which results in starch alteration. The side chains of starch molecules that include amylose and amylopectin depolymerize when exposed to high-energy plasma ions, breaking the molecules apart into smaller pieces. Starch depolymerization is often desirable in food processing and industrial applications and affects several properties, such as hydrophobicity, due to the changes in its molecular structure [32].

The plasma treatment forms hydrogen bonds at the film surface due to starch oxidation and increased helical order, which in turn limits the movement of water molecules. This indicates that the starch and starch-based films obtained after plasma treatment have different amylose content and good hydrophobicity. The microstructure formed on the surface of starch-based films, which will be discussed in more detail in Section 3.5 (Surface morphology), increases the surface roughness, thereby increasing the film's surface hydrophobicity [40].

Plasma treatment efficiently improved the hydrophobicity of starch-based films when applied to the formed film or the film-forming solution. Natural starch is inherently hydrophilic, and the changes induced by plasma may be important in improving its hydrophobicity, extending its stability, and maintaining its physical and mechanical properties for an extended time [40–42].

3.4. Molecular Structure

Based on previous studies, plasma can initiate a sequence of chemical reactions within a substance, such as molecular rearrangements, dehydration, and the hydrogenation of molecules. One approach to examining the resulting structural changes is to analyze the Fourier-transform infrared (FTIR) spectra.

The FTIR spectra of the film produced from the plasma-treated film-forming solution (200 Hz, 20 min, Sft-200-20) did not present significant changes compared to the untreated film (S-C) and the plasma-treated film produced with the untreated starch (S-200-20) (Figure 2). The only more significant change was a slight decrease in the band corresponding to the OH stretching at 3200 cm^{-1} . A similar profile was obtained for the plasma-treated films. The information attained through the FTIR spectra and amylose content indicates that the changes in the film properties were mainly of a physical nature when plasma was applied directly to the film and the film-forming solution.

The film produced with the plasma-treated starch (300 Hz, 20 min, St-300-200) presented a significant reduction in the absorbance of bands related to OH stretching (3200 cm^{-1}) and the bands 1022 , 995 , and 930 cm^{-1} related to CH stretching due to the higher amylose content [8].

The region equivalent to starch morphology (1045 , 1022 , and 995 cm^{-1}) showed significant changes among the treatments. The $995/1022$ ratio is related to starch's short-range orderliness and structural characteristics and its films. The plasma-treated films made with untreated starch showed a stable $995/1022$ ratio, which did not indicate structural changes (Table 5). The film produced with plasma-treated starch presented a $995/1022$ ratio, lower than the control film, with significant changes ($p < 0.05$) related to the control. As such, the film produced with plasma-treated starch presents a less stable helical structure than the film produced with untreated starch. Similar to the film produced with the untreated starch, the film produced by subjecting the film-forming solution to plasma treatment showed little changes related to the control film. The $995/1022$ ratio corroborates the observation that plasma acts mainly in the surface properties of the plasma-treated films and the films produced with the plasma-treated film-forming solution. The reduction in the $995/1022$ ratio observed mainly in films produced with the plasma-treated corn starch was similar to the reduction observed in films produced with plasma-treated banana starch reported by Marenco-Orozco et al. [5].

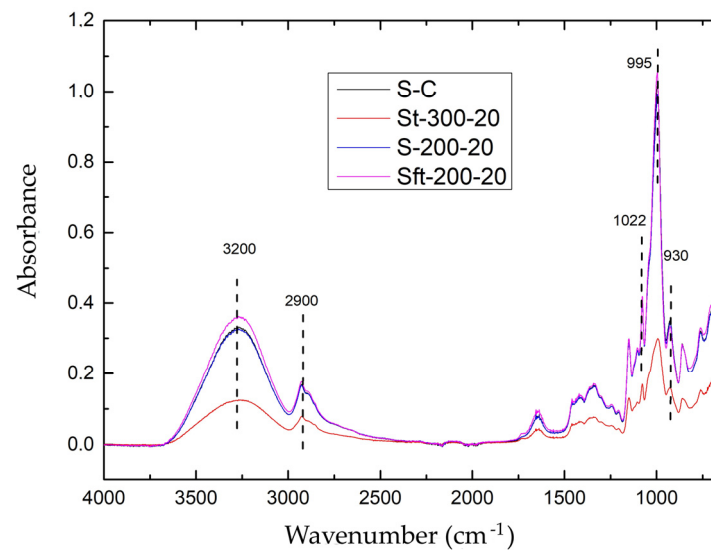


Figure 2. FTIR spectra of the untreated film (S-C), the plasma-treated film produced with the untreated starch (200 Hz, 20 min, S-200-20), the film produced with plasma-treated starch (300 Hz, 20 min, St-300-20), and the film produced with the plasma-treated film-forming solution (200 Hz, 20 min, Sft-200-20).

Table 5. Short-range ordered structure parameters of the starch films *.

Plasma Frequency (Hz)	Exposure Time (min)	Plasma-Treated Film	Starch-Treated Film	Film-Forming Solution-Treated Film
930 cm⁻¹				
0	0	0.14 ± 0.1 ^a	0.35 ± 0.1 ^a	0.35 ± 0.1 ^{ab}
100	10	0.11 ± 0.1 ^{bc}	0.32 ± 0.1 ^b	0.33 ± 0.1 ^b
100	20	0.10 ± 0.1 ^c	0.27 ± 0.1 ^c	0.35 ± 0.1 ^{ab}
200	10	0.12 ± 0.1 ^b	0.32 ± 0.1 ^b	0.36 ± 0.1 ^a
200	20	0.13 ± 0.1 ^a	0.33 ± 0.1 ^{ab}	0.33 ± 0.1 ^b
300	10	0.12 ± 0.1 ^b	0.29 ± 0.1 ^c	0.35 ± 0.1 ^{ab}
300	20	0.11 ± 0.1 ^{bc}	0.16 ± 0.1 ^d	0.34 ± 0.1 ^{ab}
995 cm⁻¹/1022 cm⁻¹				
0	0	1.28 ± 0.1 ^{ab}	1.46 ± 0.1 ^a	1.46 ± 0.1 ^{ab}
100	10	1.26 ± 0.1 ^b	1.36 ± 0.1 ^{bc}	1.39 ± 0.1 ^c
100	20	1.28 ± 0.1 ^{ab}	1.31 ± 0.1 ^{cd}	1.47 ± 0.1 ^a
200	10	1.29 ± 0.1 ^a	1.37 ± 0.1 ^b	1.48 ± 0.1 ^a
200	20	1.27 ± 0.1 ^{ab}	1.44 ± 0.1 ^a	1.43 ± 0.1 ^b
300	10	1.28 ± 0.1 ^{ab}	1.34 ± 0.1 ^c	1.41 ± 0.1 ^{bc}
300	20	1.28 ± 0.1 ^{ab}	1.21 ± 0.1 ^e	1.43 ± 0.1 ^b
1045 cm⁻¹/1022 cm⁻¹				
0	0	0.73 ± 0.1 ^a	0.71 ± 0.1 ^c	0.71 ± 0.1 ^a
100	10	0.58 ± 0.1 ^b	0.71 ± 0.1 ^c	0.69 ± 0.1 ^a
100	20	0.58 ± 0.1 ^b	0.77 ± 0.1 ^a	0.71 ± 0.1 ^a
200	10	0.55 ± 0.1 ^c	0.69 ± 0.1 ^c	0.70 ± 0.1 ^a
200	20	0.56 ± 0.1 ^c	0.72 ± 0.1 ^{bc}	0.70 ± 0.1 ^a
300	10	0.57 ± 0.1 ^{bc}	0.74 ± 0.1 ^b	0.69 ± 0.1 ^a
300	20	0.56 ± 0.1 ^c	0.78 ± 0.1 ^a	0.70 ± 0.1 ^a

* Values are the mean of three measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$).

The 1045/1022 ratio is related to the short-range crystallinity and the state of organization of starch structures. The film produced by subjecting the film-forming solution to plasma treatment did not significantly change, indicating that no significant chemical or

structural change occurred with this process route. The plasma-treated film significantly reduced this ratio, indicating a much lower orderliness and structural stability than the control film. The film produced with the plasma-treated starch, on the other hand, presented a significant increase in orderliness when plasma treatment was carried out for 20 min at 300 Hz.

Starch retrogradation may result in the phase separation of starch and an increase in the rigidity of the film. Therefore, retrogradation has an adverse effect on film quality [43,44]. Within the route studied herein, the films produced with the plasma-treated starch present higher retrogradation and may become more rigid over time.

When applied in the film-forming solution stage, plasma treatment has a two-fold effect in increasing the CAR (crystalline/amorphous ratio) and decreasing film moisture. This stage typically has higher water content compared to other steps in the filmmaking process. Eliminating water in this phase allows for better reorganization of C–O–C type bonds with a low degree of moisture content, as explained by Deeyai et al. [45].

3.5. Surface Morphology

Figure 3 shows micrographs of the starch-based films' surfaces attained by scanning electron microscopy. The film's surface produced with the untreated starch (Figure 3a) is more uniform, with few imperfections. All other films presented surface irregularities, especially the plasma-treated film produced with the untreated starch (Figure 3d), where several surface cracks were observed. Such irregularities were also observed by Shen et al. [46] and Marenco-Orozco et al. [5].

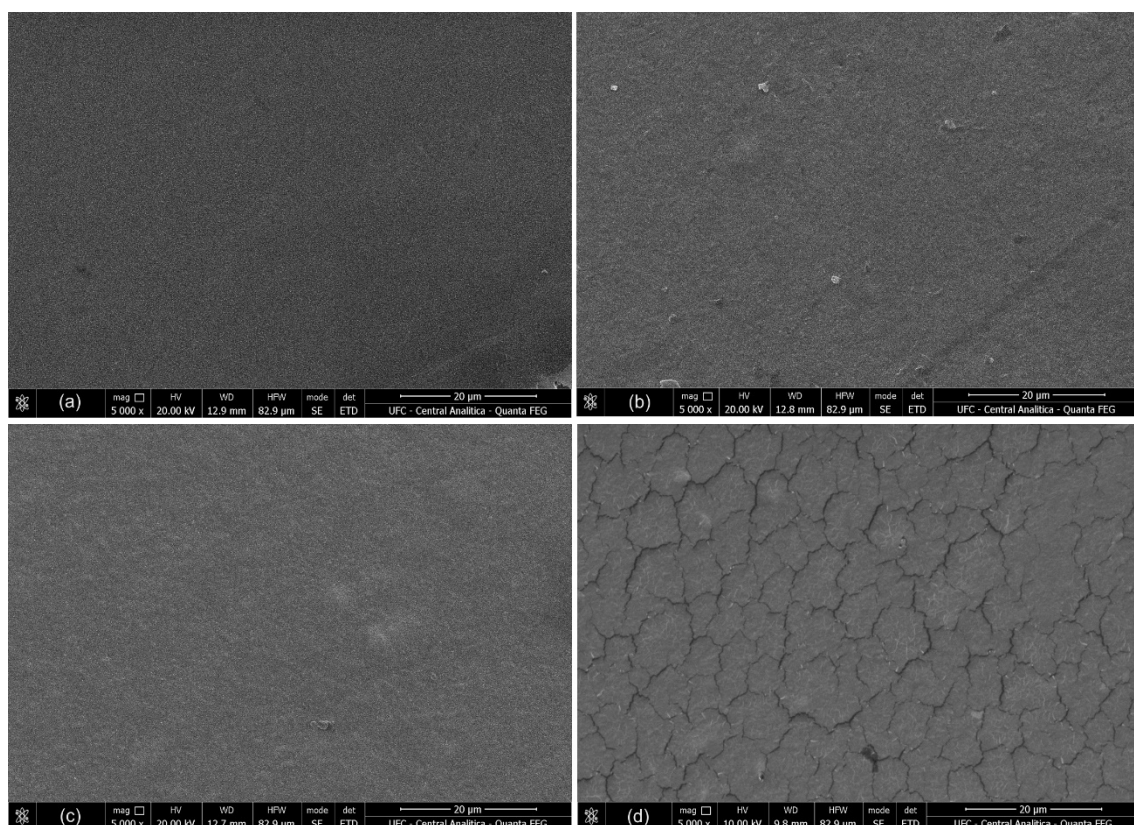


Figure 3. Starch-based film micrographs obtained by SEM at a magnitude of 5000×. (a) Film produced with the untreated starch (control); (b) film produced with the plasma-treated film-forming solution (200 Hz, 20 min); (c) film produced with the plasma-treated starch (300 Hz, 20 min); (d) plasma-treated film produced with the untreated starch (200 Hz, 20 min).

The film produced with the plasma-treated starch (Figure 3c) and the film produced by plasma-treating the film-forming solution (Figure 3b) presented a smothered surface, resembling the untreated film. The differences between the film surfaces show that most imperfections are caused by applying plasma to the already-formed film. This happens because the plasma treatment at the end reduces amorphous structures and available water, which benefits good mechanical strength and hydrophobicity (low solubility in water and greater contact angle). Studies in this field show an increase in the surface roughness of natural polymers, such as starch, soy bran, and casein, directly related to the increase in treatment time and electrical potential. This produces an irregularly shaped texture on the analyzed surfaces [23,47,48].

Natural starch-based films have several limitations, especially due to their high solubility, low hydrophobicity, and limited mechanical properties. Plasma treatment and other processes, such as adding natural substances, can overcome these limitations to a certain extent. These modified starch-based films are eco-friendly alternatives to petrol-based plastics in several applications, making them a more sustainable option for food and other industries. Industrial equipment for casting is commercially available and could be adapted to include the electrodes of a plasma system. The casting of biomaterials, such as starch, is a slow film-producing process that depends on the evaporation of the water contained in the film-forming solution. Water evaporation is carried out in the belt machine section of the process. A plasma system could be mounted at the beginning of the belt machine to treat the film-forming solution or at the end of the belt to treat the formed film. Plasma application is much shorter than the casting of biomaterials, so both could be conducted simultaneously in industrial facilities.

4. Conclusions

The three groups of films showed different alterations in their physical-chemical and morphological properties. Most chemical changes occurred in the starch subjected to plasma before film formation, while the films produced with the untreated starch mainly presented physical changes.

Plasma treatment resulted in films with a higher amylose/amylopectin ratio and reduced solubility compared to the control group, regardless of whether the plasma was applied to the starch granules, the film-forming solution, or the film itself. The plasma-treated films and the films produced from plasma-treated film-forming solutions showed increased hydrophobicity. Films produced with plasma applied at 200 Hz exhibited better physical characteristics, such as lower amylose content (20.8%), lower water adsorption index (1.87), reduced solubility in water (81.8%), and higher hydrophobicity (contact angle at 64.3°) compared to the untreated starch-based films.

Several ways exist to reduce the solubility and increase the hydrophobicity of starch films, such as adding natural substances. Plasma processing, however, has the advantage of being able to change these properties up to a certain limit without resorting to any other substance, reducing the cost of the starch film.

Casting is a slow film-producing process that depends on the evaporation of the water contained in the film-forming solution. Plasma processing is much shorter than casting, and both could be conducted simultaneously in industrial facilities. A plasma system could be mounted at the beginning or end of a continuous casting system.

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