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Corn starch based films treated by dielectric barrier discharge plasma

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ABSTRACT

Cold plasma is an innovative strategy to strengthen the polysaccharide-based films characteristics. This study evaluated the effects of dielectric barrier discharge (DBD) plasma on the hydrophilic character, water vapor permeability (WVP), and tensile properties of corn starch-based films. Starch films were exposed to plasma processing operating at an excitation frequency of 200 Hz for 10, 15, and 20 min. DBD plasma resulted in further enhanced tensile strength and stiffness, and lower hydrophilicity and water solubility; however, it did not present significant effects on the WVP of the resulting films within the ranges studied. Higher hydrophobicity, strength, and stiffness were verified after 20 min. The results presented in this work suggest that the DBD plasma has the potential to make starch-based films a more suitable packaging material.

1. Introduction

The global consumption of petroleum-derived plastics contributes for the exhaustion of fossil resources and results in the accumulation of waste, creating several environmental problems. The production of biodegradable plastics from renewable biopolymers (mainly polysaccharides and proteins) has been increasingly explored, mainly for food packaging applications [1]. Although bio-based polymers do not usually have functional performances comparable to those of petroleum-based polymers [2], they may be used as substitutes of conventional plastics for some applications, e.g. primary food packaging. Moreover, some limitations of bio-based polymers (mainly in terms of mechanical and barrier performances) may be partly overcome by different physical and/or chemical treatments that have been explored to address those limitations, such as ultraviolet light [3], reinforcing agents including nanostructures [4], cross-linking [5], cold plasma [6], and ultrasound [7].

Unlike thermal plasma, cold plasma processes use relatively low temperatures (i.e. near to room temperature). This feature makes it a proper technology for the modification of heat-sensitive materials such as most biopolymers. Dielectric Barrier Discharge (DBD) is one of the plasma generation methods that operate at atmospheric pressure, offering versatility in its mode of operation. It does not involve use of hazardous solvents, and has been reported to result uniform treatment, increased mechanical strength and elongation, and improved hydrophobic properties of films, without compromising the sealing properties of polymers [8,9].

Starch is an abundant and low cost natural biodegradable polysaccharide widely studied for film production. It is composed of two fractions: amylose (mainly linear chain) and amylopectin (branched chain). Higher amylose contents usually result in films with improved tensile and barrier properties, since the linear chains allow amylose to form more hydrogen bonds than amylopectin [10,11].

However, the water absorption resulting from the inherent hydrophilicity of starch conspires against the permanence of their mechanical and barrier properties, which determine the suitability of polymeric films for packaging applications. That is why several studies have been focused on approaches to overcome the great hydrophilicity and water susceptibility of starch-based films. Therefore, employment of modification approaches in which the tensile and barrier properties are improved or at least are not affected by a high humidity environment is very important [12,13].

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There is a tendency to use green technologies to modify starch without generating any residual products, and plasma treatment falls into this category. Investigations have been recently conducted on plasma-induced changes in starch films, showing that the plasma treatment can be efficient in increasing the hydrophobicity of starch films [14,15]. Factors affecting the outcome of plasma treatment include the type and composition of plasma, method of plasma generation, plasma exposure time, power input, and the polymer structure. Properties of starch films as affected by cold plasma were briefed by Zhu [16]. The author compared plasma with other types of starch modification methods and, considering the scarcity of information on plasma modification, concluded that further studies are required. Among research gaps, the understanding of the effect of the type of plasma generation on starch properties and the limit in the extent of the modification of structure and physicochemical properties remains to be explored.

In this sense, the present study aims to evaluate the effects of DBD cold plasma treatment on the hydrophilic character and the mechanical, thermal and barrier properties of starch-based films, hoping to better understand the mechanisms of cold plasma treatment on polysaccharide-based films and its influence on the applicability of the resulting films for food packaging.

2. Materials and methods

2.1. Preparation of starch-based films

Following the methodology proposed by Oliveira et al. [17], 5 g of commercial corn starch (28% amylose content; Maizena®, Fortaleza, Brazil) were dissolved in 100 mL of distilled water and heated to 95 °C under magnetic stirring for 30 min for starch gelatinization. Glycerol was added (25% w/w, based on starch), and the mixture was stirred at 60–65 °C for 15 min. Then, the dispersion was homogenized in Ultra-Turrax T25 (IKA, Staufen, Germany) at 10,000 rpm for 15 min. The air bubbles were removed with a Vacuubrand 1C vacuum pump (Vacuubrand GmbH, Wertheim, Germany). The film forming dispersion was poured onto glass plates coated with a polyester film (Mylar™) and allowed to dry under ambient conditions (25 °C for 24 h) until solvent evaporation was complete.

2.2. Plasma treatment on films

Dielectric barrier discharge plasma treatments were carried out using a benchtop plasma generator system (Inergiae model PLS0130). Plasma was generated in the gap (1.5 cm) between two 8 cm aluminum electrodes, using two 5 mm acrylic plates as dielectric barriers. Plasma was generated by applying a voltage of 20 kV between the electrodes at an excitation frequency of 200 Hz. Plasma was applied for 10, 15, and 20 min. An acrylic Petri dish containing the starch-based film was placed in the gap between the electrodes and subjected to plasma treatment.

2.3. Characterization of films

All starch films were characterized for water solubility, water contact angle and Fourier Transform Infrared analysis. The film with the best performance (lower solubility and higher water contact angle) was also characterized for scanning electronic microscopy, mechanical test, water vapor permeability and differential scanning calorimetry as described below.

2.3.1. Solubility

The water solubility of the films was determined by quantifying the dry matter solubilized after 24 h of immersion in water. The films were cut into 2 cm diameter discs and dried in an oven at 105 °C for 24 h, weighed and immersed in 50 mL of distilled water at 25 ± 2 °C for 24 h under agitation in an orbital shaker (TE-142, TECNAL) at 100 rpm. After this period, the samples were removed and dried in an oven (105 °C for 24 h) to determine the percent unsolubilized matter.

2.3.2. Water contact angle

The contact angle of a film is the angle between the tangent to the film surface and the tangent to a liquid droplet (usually water) placed on it, indicating the water spreadability on the film surface, thus reflecting its wettability and hydrophilicity [18]. Water contact angles (GBX Intrumentation Specifique) were determined according to ASTM D-5725-99 [19] by means of an optical contact meter, where a drop of water was placed on the surface of the films treated or not with plasma. Film samples (2 cm × 2 cm) were fixed to a glass holder and, at the moment when the drop touched the surface, the image was captured (Pixe Link Nikon camera) and the angle was measured. The measurement was conducted at 23 ± 2 °C.

2.3.3. Fourier transform infrared (FTIR)

The spectra of the treated surfaces of the starch films were acquired in Perkin-Elmer Spectrum Two (Perkin-Elmer, Waltham, USA), in the attenuated total reflection mode (ATR), in the wavelength range: 4000–650 cm^{-1}, using 32 scans and 4 cm^{-1} resolution.

The effect of the DBD plasma treatment on the structural stability of the starch films was also investigated. It has been reported that bands in the region 1100–950 cm^{-1} are sensitive to changes in starch structure (especially the ones related to amorphous and crystalline structures - 1022 cm^{-1} and 1047 cm^{-1}, respectively) [20]. In this sense, the 1047:1022 cm^{-1} intensity ratio was used as an indicator of the order degree.

2.3.4. Chemometric analysis of FTIR spectra

A total of 18 samples for the starch film was used for multivariate classification analysis, consisting of 9 control samples (without treatment) and 9 samples after treatment with plasma (lower solubility and higher water contact angle). Infrared spectral region between 4000 and 650 cm^{-1} was used for all the classification modeling.

For numerical matrices construction, each IR spectrum was converted to American Standard Code for Information Interchange (ASCII) file and imported by the Origin™ program (version 9.4). The matrices were exported for supervised chemometric analysis by Partial Least Squares Discriminant Analysis (PLS-DA) using the PLS-Toolbox™ program (version 8.6.2, Eigenvector Research Incorporated, Manson, WA USA). The MSC (Multiplicative scatter correction) algorithm was applied over the spectral variables (wavelengths), and the samples were mean centered for multivariate analysis.

2.3.5. Scanning electronic microscopy (SEM)

The films were dried in a desiccator with silica gel, cut in small pieces, mounted on aluminum stubs and metallized with a thin layer (20 nm) of gold in the Quorum QT150ES metallizer. The scanning electronic microscopy (SEM) micrographs were taken from the film surfaces with a QUANTA FEG-FEI 450, with an acceleration voltage of 20 kV.

2.3.6. Mechanical properties

Tensile properties of 125 mm × 12.5 mm starch film strips (with twelve replicates) were measured according to method ASTM D882-01 [21], using an EMIC DL30000 Universal Mechanical Test Machine with a load cell of 100 N, initial grip separation of 100 mm, and deformation speed of 12.5 $mm \cdot min^{-1}$. The thickness (mm) was measured at 6 random points of each film specimen using a micrometer (Quantumike IP 65, Mitutoyo, Kawasaki, Japan, with an accuracy of 1 μm), before characterization tests.

2.3.7. Water vapor permeability (WVP)

The water vapor permeability (WVP) determination (eight replicates) followed the method ASTM E96-00 [22]. Acrylic permeation cell, with 24 mm in diameter and 10 mm in height were used, containing 1.5

mL of distilled water, and maintained at 25 ± 2 °C in an Arsec DCV040 vertical desiccator. Eight measurements were taken within 24 h, with a minimum interval of 1 h between weighings.

2.3.8. Differential scanning calorimetry (DSC) and thermogravimetry (TGA)

Differential scanning calorimetry (DSC) was performed in an INSTRON equipment (model Q 20) under a dry nitrogen flow rate of 50 mL·min^{-1}. Approximately 1.2 mg of samples were weighed in aluminum pans, which were sealed and subjected to heating and cooling cycles from 30 °C to 350 °C at 10 °C·min^{-1}.

Thermogravimetric analysis was performed in a simultaneous thermal analyzer (STA) (STA 6000, PerkinElmer, Massachusetts, USA). Samples of approximately 15 mg were subjected to a nitrogen atmosphere (20 mL·min^{-1}) at a heating rate of 10 °C·min^{-1} from 20 °C to 700 °C.

2.4. Multivariate statistical analysis of the films dataset

A numerical matrix was built for the data before and after plasma processing, using the following parameters: thickness; water vapor permeability; contact angle; insoluble material; and mechanical properties related to tensile strength, elongation at break and modulus of elasticity (Young's modulus). The resultant matrices were imported by the PLS Toolbox™ software (version 8.6.2, Eigenvector Research Incorporated, Manson, WA USA). Unsupervised chemometric analysis by PCA (Principal Component Analysis) and supervised chemometric analysis by PLS-DA (Partial Least Squares Discriminant Analysis) were developed to investigate the influence of different plasma processing on the aforementioned films parameters. Previously to these multivariate analyses, the film dataset was autoscaled in order to afford the same modeling strength for all variables and samples.

2.5. Statistical analysis

Statistical analysis was performed using analysis of variance (ANOVA) with the Statistic™7 software. Whenever ANOVA showed significant effects ($p < 0.05$), Tukey or *t*-tests were applied to determine differences among treatments ($p < 0.05$).

3. Results and discussion

3.1. Contact angle and solubility

The effect of cold plasma treatment time on the hydrophilic character and solubility of the starch films was investigated and the results are shown in Table 1. It may be noted that after exposing starch films to treatment for 10, 15 and 20 min, a significant gradual increase ($p < 0.05$) in the contact angle (water) was observed for all treatment times as a result of the increased hydrophobicity. The plasma processing may have promoted oxidation of hydroxyl groups into carbonyl groups, leading to formation of new hydrogen bonds that may have decreased the availability of polar groups in the surface, increasing film hydrophobicity, as also observed by Sifuentes-Neves et al. [23].

Table 1
Contact angle and insoluble material for DBD plasma treated starch films for different times.

Starch film	Contact angle, CA (°)	Insoluble matter, IM (wt%)
A-C	55.7 ± 0.8^{d}	3.1 ± 1.0^{c}
A-10	57.1 ± 0.6^{c}	6.2 ± 0.5^{b}
A-15	61.5 ± 0.3^{b}	8.5 ± 0.4^{a}
A-20	64.3 ± 0.6^{a}	9.1 ± 0.1^{a}

Note: Values are the mean of four measurements ± standard deviation; values in the same column not followed by a common letter are significantly different ($p < 0.05$). Starch films were designed as: A-C (control film) and A-x (treated film), "x" being the treatment time in minutes.

The increased hydrophobicity may be also ascribed to changes in morphology, namely increased surface roughness, corroborating SEM results (Fig. 3). According to the literature, the surface roughness is largely affected by the increase in plasma power (voltage) and exposure time [24]. Previous literature [8,25] has reported that plasma could serve as an effective surface modification method for starch. Surfaces with higher contact angles can be obtained by structuring surfaces with proper roughness [26].

The relationship between water contact angle and plasma treatment time is in agreement with the results obtained by Bastos et al. [14] who exposed starch films to cold sulfur hexafluoride (SF_6) plasma at different exposure times. In contrast to our findings, other studies have shown that the contact angle has decreased significantly after cold plasma treatment. For instance, Pankaj et al. [15] examined the plasma treatment on starch films and obtained a 60% decrease in the water contact angle of starch films. It is suggested that plasma treatment at higher voltage levels (60, 70, and 80 kV) increased the surface hydrophilicity by increasing polar groups anchors on the surface of the films. Therefore, it can be inferred that, besides the treatment time and type of the applied gas, power factors are also effective in contact angle results.

The plasma treatment notably decreased the water solubility of control starch film ($p < 0.05$) making it more resistant to water. Actually, the water resistance property of the films has an inverse relationship with the density of polar groups on the surface, reflecting thus the increased hydrophobicity, mainly to films exposed for a longer time (A-20).

Despite the increase in the contact angle, all results were below 90° and thus, the surface is still hydrophilic, according to Chen et al. [27]. The solubility is one of the critical factors to define the maintenance of the integrity of the material when in contact with water or with a moist surface [27].

3.2. FTIR

Fig. 1 shows the FTIR (IR) spectra of the starch films. All samples presented the same overall characteristic starch bands, including the wide O—H stretch band at 3500–3000 cm^{-1}, C—H stretch band at 2910 cm^{-1} related to the amylose content [17], and the anhydroglucose ring stretching vibration band at about 950 cm^{-1} [28]. However, some slight alterations in band position and intensity were detected in the IR spectra of treated starch films compared with the control.

Slight displacement of absorption connections at 1650 cm^{-1} was

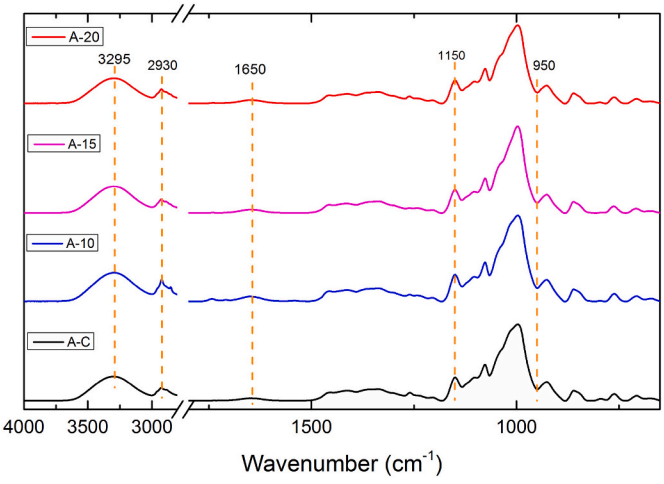

Fig. 1. Infrared spectra of starch films before (A-C) and after plasma processing (A-10, A-15, A-20).

observed (Fig. 1), which may result from an increased density of hydrogen bonds due to surface oxygenation after treatment with DBD plasma [15]. Absorption bands around 1150 cm^{-1}, ascribed to C—O stretching of COH groups, were observed in all samples (treated or not with plasma).

The FTIR spectra did not present evidence for the formation of new functional groups. The films exposed for a longer time (A-20) showed a slight reduction in absorbance intensity in the hydroxyl region (3500–3000 cm^{-1}), shown at 3295 cm^{-1}. This may be associated with a dehydration process that occurs during treatment, indicating a reduced hydrophilicity, which helps to explain the results of contact angle (Table 1). As reported by Campelo et al. [29], the discharge plasma from the dielectric barrier may induce several chemical reactions, including molecular rearrangements, dehydration and hydrogenation of molecules.

The ratio between intensities at 1047:1022 cm^{-1} was extracted and used as an indicator of ordered structure in starch [20]. The degree of change was rather small and substantial changes have been undetected after plasma treatment. As any judgement about the biodegradation of polymers should consider factors like structure, this result suggests that the DBD treatment under the studied conditions did not affect the biodegradability of the corn starch films. However, as the biodegradation of polymers is affected by many other factors (e.g. chemical nature of the polymer, environmental conditions, activity of the microbial population), further investigation should be performed to elucidate this effect.

3.3. Chemometric analysis

Based on the results obtained in Sections 3.1 and 3.2, a multivariate classification analysis by PLS-DA was developed using the FTIR spectra of the films (control and A-20). Due to the relative similarity between the film composition before (A-C) and after plasma processing (A-20), classification models were developed for each type of film, separately.

Processing with DBD plasma affected the starch film, making the sample more heterogeneous, observed with the dispersion of the red dots in the score graphs (Fig. 2a). Fig. 2b shows the relevant loading graph in the polymeric matrix. It may be noted that plasma processing decreased the functional chemical groups in all films, which can be correlated with the non-formation of new chemical groups (negative charges related to the control films).

When a polymer is exposed to cold plasma based on O_2, N_2 or atmospheric air, oxygen- and nitrogen-containing functional groups are introduced, respectively, on the surface of the polymer, due to the interaction of chemically active species generated by plasma with different groups of polymer molecules [30]. Morent, De Geyter, Desmet, Dubruel, & Leys [31] concluded that the plasma affected the surface of a polyester in shallow depth, which may explain the non-uniform action on the different matrices, since the plasma promotes superficial changes in the materials [8].

One of the effects of non-thermal plasma treatment on polymers is the increase in surface energy. This suggests that the plasma particle stream affects only the film surface; therefore, the energetic particles of the plasma cannot diffuse to the depth of the polymers [32]. Recently, there has been considerable interest in studying correlations between the operational conditions of gas discharge and the surface density of the functional groups formed and the permanence of surface changes [33].

3.4. SEM

The effect of plasma treatment on the starch film surface morphology was evaluated by SEM images. The images of the untreated film

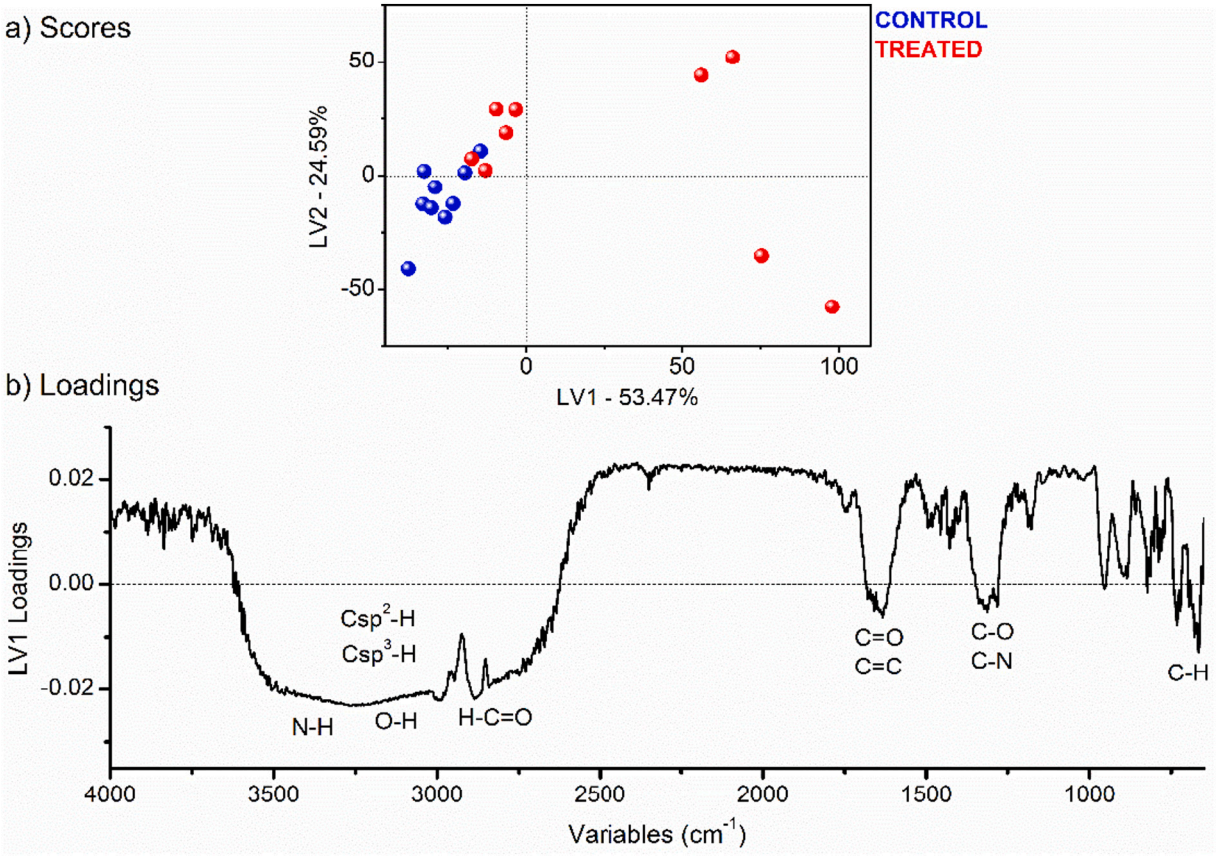

Fig. 2. PLS-DA results from the multivariate classification of starch films before and after plasma processing: a) LV1 × LV2 coordinate system; b) LV1 loadings plotted in lines form.

(control) and the treated starch film are depicted in Fig. 3. Compared to untreated film (A-C), there are noticeable differences for treated film (A-20) morphology, which exhibits a surface with more corrugations.

Similar trends of the plasma treatment results were reported by other researchers for starch film [8,25]. The increase in the surface roughness after plasma treatment has been attributed to the etching effect due to the bombardment of energetic plasma species like electrons, ions, radicals and UV–vis radiations on the surface of polymer films [15,16]. Treatments with cold plasma technology have increased the surface roughness of natural (soybean meal and casein) and synthetic polymers (polypropylene and polyethylene), being directly related to the extension of treatment time and voltage, producing an irregularly shaped texture on the analyzed surfaces [8,25]. In a similar way, this may explain the increase in hydrophobicity [23,25].

3.5. Tensile properties and water vapor permeability

Table 2 describes the results of the water vapor permeability (WVP), tensile strength (TS), elongation at break (EB) and Young's modulus (YM) tests. The films had average thicknesses of 0.54 mm (A-C) and 0.52 mm (A-20) for the tests.

For the starch film (A-20), the cold plasma treatment significantly increased the tensile strength and modulus, corroborating previous findings [34,35]. This behavior may be explained by the possible formation of carbonyl groups, promoting formation of hydrogen bonds, which could have favored the structural integrity of the matrix [23]. Elongation at break (%EB), on the other hand, was decreased in around 30%, which may be related to the new hydrogen bonds and the compact rearrangement of the starch structures during the plasma treatment [36].

The increase in the tensile strength is in agreement with the results obtained from starch films treated by argon plasma [34] and whey protein concentrate/wheat cross-linked starch films modified by DBD plasma treatment [35].

The mechanical properties of films made from plasma-modified corn starch were also evaluated by Sifuentes-Nieves et al. [23]. Amylose content determined the starch modification degree - films made from high amylose content (50% and 70%) showed the highest TS value compared with that made from low amylose content (30%) due to the interactions by hydrogen bonds of the linear amylose chains. Similar behavior was reported for films prepared from oxidized starch, where the highest concentration of chlorine resulted in the lowest tensile strength values [37]. That behavior was attributed to the decreased of hydrogen bonds of starch chains.

Water vapor permeability was not significantly affected by DBD plasma treatment (Table 2), and it did not follow the trend of changes in the other analyses performed. Comparable findings were also stated for plasma treated corn starch by Pankaj et al. (2015) [15]. According to the authors, this may be because of the fact that most of the changes caused by cold plasma are surface changes in hydrophilic groups and polymeric morphological features, while the WVP changes in films are mainly associated to the thermodynamic properties, vapor pressure, and concentration slope on both sides of the film surface. It is worthwhile suggesting that the results of water vapor permeability are in line with results obtained in FTIR, where no evidence of creating cross-linking by plasma treatment was observed.

Table 2
WVP, tensile strength (TS), elongation at break (EB) and Young's modulus (YM) in starch films.

	WVP[a] (g·mm/kPa·h·m^2)	TS[b] (MPa)	EB[b] (%)	YM[b] (MPa)
A-C	1.57 ± 0.03	**11.25 ± 3.59**	**22.50 ± 3.10**	**531 ± 43**
A-20	1.55 ± 0.04	**15.82 ± 7.79**	**16.04 ± 4.17**	**664 ± 61**

Note: values in bold in the same column indicate significant differences at a 95% confidence level.

[a] Values are the mean of eight measurements ± standard deviation.

[b] Values are the mean of twelve measurements ± standard deviation.

3.6. Thermal analysis

3.6.1. DSC

Table 3 summarizes the glass transition (T_g), melting (T_m) and enthalpy (ΔH) temperatures, referring to the samples of the control (A-C) and treated (A-20) films.

An endothermic process was observed between 230 and 290 °C, related to the fusion of the starch film (T_m), onset (T_o) and endset (T_e) temperatures indicating the beginning and end of the fusion process, respectively (Table 3). Pankaj et al. [15] attributed this endothermic variation to the remaining granular structures after heat treatment or recrystallization of amylose. Films from different starch sources without undergoing heat treatments exhibited the same range of endothermic peaks [38].

Table 3
Glass transition temperatures (T_g), onset (T_o), melting (T_m), endset (T_e) and enthalpy (ΔH) for starch films (A-C and A-20).

Samples	T_g (°C)	T_o (°C)	T_m (°C)	T_e (°C)	ΔH (J/g)
A-C	179.1	271.9	290.3	304.4	9.7
A-20	167.2	224.3	232.6	256.1	1.5

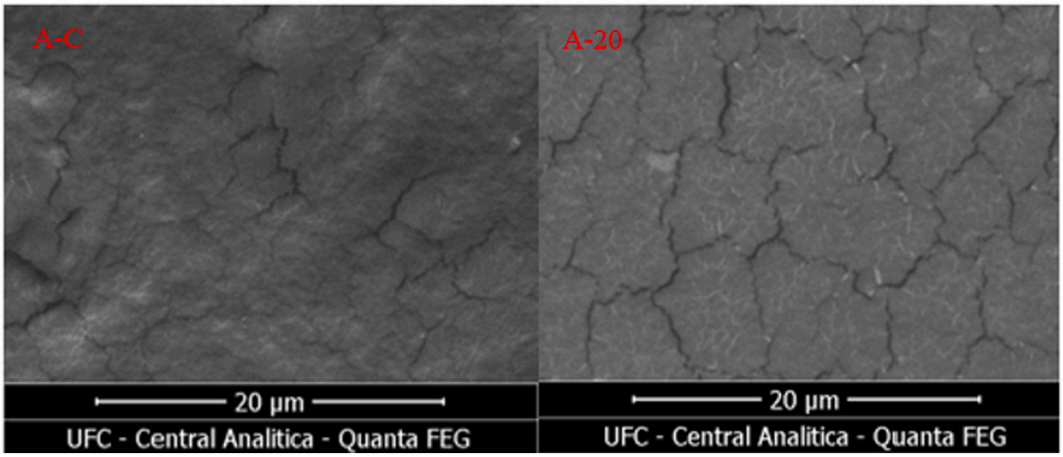

Fig. 3. Scanning electron microscopy images of the untreated films starch (A-C) and plasma treated (A-20) with a 5000 times magnification.

Even with the difficulty of observing in DSC thermograms the glass transition temperature in starch-based polymers [15], it was possible to detect similar values before and after plasma treatment as well as in PET and PET/starch films [39].

None of the starch films showed any spikes on DSC thermograms at the start of the test (below 100 °C), indicating that the starch gelatinization during film production was completed [38].

The knowledge about the melting temperatures (T_o, T_m and T_e), as well as the enthalpy (ΔH) is necessary to determine the processing conditions of the materials as well as its use on food packaging, since heat sealing is a critical point related to the packaging of the product. Understanding the effects of film components and their interaction with the thermal and physical condition of the process is fundamental to the quality of the entire packaging [40]. It is important to note that the film, after plasma treatment, was shown to be thermally stable up to 230 °C. Plasma can degrade or cross-link starch molecules and cause corrosion of the granules. And its impact on thermal properties seems to depend on the types of starch, type of plasma and conditions of the experiments [16].

3.6.2. TGA

Both untreated film (A-C) and treated starch film (A-20) exhibited similar thermal behaviors. Three main events of weight loss were noted. The first one was observed in the range of 95–120 °C, which is related to the loss of free and absorbed water, remaining even after exposure to plasma. The second and third events are associated with the degradation of the starch film. The thermal degradation of corn starch started at 200 °C and the maximum degradation temperature for the films was 357.5 °C (A-20), and 353.4 °C (A-C), with a higher weight loss for A-20, around 10% in relation to the control film. This behavior suggests a modification of the intra and inter-molecular interactions between the starch molecules [23].

The third phase of weight loss was observed in the range of 370 and 520 °C, corroborating previous findings [20]. The slight decrease observed in the maximum temperature of degradation can be attributed to corrosion and cleavage of the random chain of the starch polymer after treatment with plasma DBD [15].

3.7. Variability of the starch films based on plasma processing

Unsupervised chemometric analysis by PCA was applied to each starch film data set in order to explore the variability of the samples according to different plasma processing. Sequentially, the supervised classification analyses by PLS-DA highlighted the parameters related to the starch films discrimination according to different plasma processing. Fig. 4a illustrates the PLS-DA results of the variation of thickness, water vapor permeability (WVP) and the mechanical properties related to the tensile strength (TS), elongation at break (EB) and modulus of elasticity (Young's modulus – YM) for non-processed and processed films. Fig. 4b presents the variations of contact angle (CA) and insoluble matter (IM) based on processing duration (10, 15 and 20 min) at 200 Hz. Fig. 4 presents the most important variables for films discrimination related to the plasma processing based on VIP analysis (Variables Important for Projection).

Fig. 4a presents the strong separation of the starch films before and after plasma processing (200 Hz during 20 min) related to the LV1 axis (>61%). Increases of the tensile strength (TS) and the modulus of elasticity (YM) were clearly detected after plasma processing. In addition, the greater relevance of the tensile strength (TS), elongation at

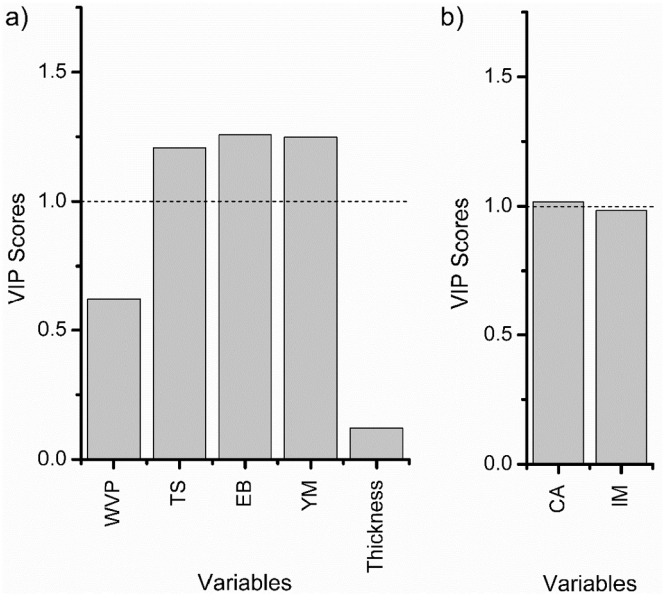

Fig. 5. Results from the evaluation of the Variables Important for Projection (VIP) for starch films discrimination based on the plasma processing: a) at 200 Hz during 20 min on thickness, water vapor permeability (WVP), tensile strength (TS), elongation at break (EB) and the modulus of elasticity (Young's modulus – YM); b) at 200 Hz during 10, 15 and 20 min on contact angle (CA) and insoluble material (IM).

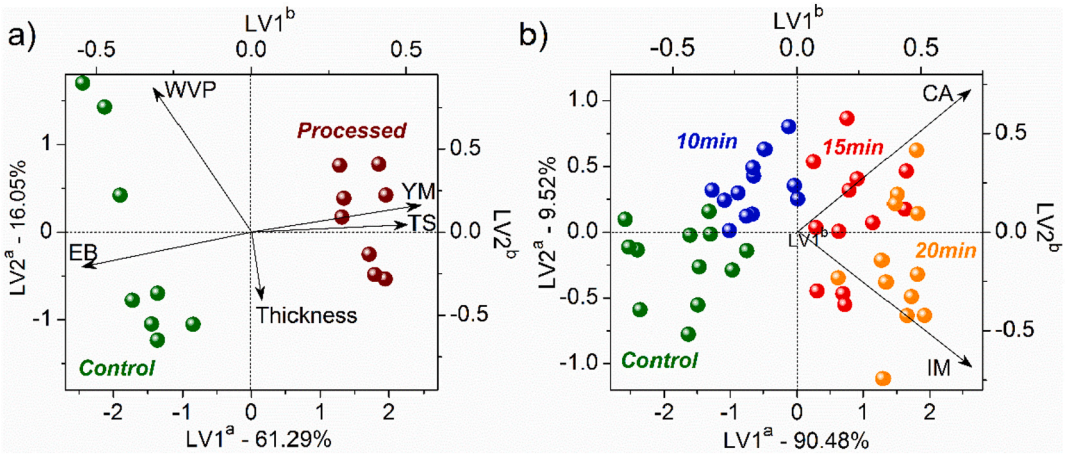

Fig. 4. PLS-DA coordinates systems for evaluation of the influence of plasma processing on starch film: a) at 200 Hz during 20 min on thickness, water vapor permeability (WVP), tensile strength (TS), elongation at break (EB) and the modulus of elasticity (Young's modulus – YM); b) at 200 Hz during 10, 15 and 20 min on contact angle (CA) and insoluble matter (IM). [a]Axes refer to scores axes; [b]axes refer to loadings axes with variables represented by vectors from the origin.

break (EB) and the modulus of elasticity (YM) for the films discrimination were achieved by the VIP analysis (Fig. 5a).

The multivariate evaluation of the processing duration at 200 Hz in the contact angle and insoluble matter showed an increase in both variables with an increase in the processing duration. Furthermore, the plasma processing during 20 min presented greater influence to increase the contact angle, as well as to increase the insoluble matter. Both variables showed approximately the same influence for samples discrimination according to the VIP analysis (Fig. 5b).

4. Conclusions

Starch films are clearly influenced by the plasma treatment and important properties are positively influenced by exposure time. Significant changes are detected by the DBD (20 kV) processing during 20 min, such as the reduction in hydrophilicity and water solubility as well as increase in strength and stiffness. These effects are attributed to the possible oxidation of hydroxyl to carbonyl groups, resulting in the formation of hydrogen bonds, as well as surface topographic changes, which are directly responsible for the reduction of the hygroscopic nature of the starch films. No significant change in the water vapor permeability was observed. In this sense, the effects of plasma on the performance of the films presented in this study suggest that this technology has the potential to make starch-based films a more suitable packaging material.

CRediT authorship contribution statement

Mayara Lima Goiana: Data curation, Investigation, Writing - original draft. Edy Sousa de Brito: Conceptualization, Methodology, Formal analysis, Validation, Writing, Elenilson Godoy Alves Filho: Data curation, Chemometric analysis. Emílio de Castro Miguel: Methodology, Microscopy analysis. Fabiano André Narciso Fernandes: Conceptualization, Resources, Formal analysis, Methodology, Investigation, Writing - review & editing. Henriette Monteiro Cordeiro de Azeredo: Formal analysis, Methodology, Writing - review & editing, Morsyleide de Freitas Rosa: Conceptualization, Funding acquisition, Formal analysis, Writing - original draft, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they do not have any conflict of interest.

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References

[1] P. Romani, B. Olsen, M.P. Collares, J.R.M. Oliveira, C. Prentice, V.G. Martins, Cold plasma and carnauba wax as strategies to produce improved bi-layer films for sustainable food packaging, Food Hydrocoll. 108 (2020), 106087, https://doi.org/10.1016/j.foodhyd.2020.106087.

[2] H. Kargarzadeh, M. Mariano, J. Huang, N. Lin, I. Ahmad, A. Dufresne, S. Thomas, Recent developments on nanocellulose reinforced polymer nanocomposites: a review, Polymer 132 (2017) 368–393, https://doi.org/10.1016/j.polymer.2017.09.043.

[3] C.G. Otoni, R.J. Avena-Bustillos, B.S. Chiou, C. Bilbao-Sainz, P.J. Bechtel, T. H. McHugh, Ultraviolet-B radiation induced cross-linking improves physical properties of cold-and warm-water fish gelatin gels and films, J. Food Sci. 77 (2012) 215–223, https://doi.org/10.1111/j.1750-3841.2012.02839.x.

[4] A.P.M. Silva, A.V. Oliveira, S.M. Pontes, A.L. Pereira, M.F. Rosa, H.M. Azeredo, Mango kernel starch films as affected by starch nanocrystals and cellulose nanocrystals, Carbohydr. Polym. 211 (2019) 209–216, https://doi.org/10.1016/j.carbpol.2019.02.013.

[5] M. Shahbazi, S.J. Ahmadi, A. Seif, G. Rajabzadeh, Carboxymethyl cellulose film modification through surface photo-crosslinking and chemical crosslinking for food packaging applications, Food Hydrocoll. 61 (2016) 378–389, https://doi.org/10.1016/j.foodhyd.2016.04.021.

[6] M. Fazeli, J.P. Florez, R.A. Simão, Improvement in adhesion of cellulose fibers to the thermoplastic starch matrix by plasma treatment modification, Compos. Part B 163 (2019) 207–216, https://doi.org/10.1016/j.compositesb.2018.11.048.

[7] Y. Liu, S. Wang, W. Lan, W. Qin, Development of ultrasound treated polyvinyl alcohol/tea polyphenol composite films and their physicochemical properties, Ultrason. Sonochem. 51 (2019) 386–394, https://doi.org/10.1016/j.ultsonch.2018.07.043.

[8] X. Wu, Q. Liu, Y. Luo, M.S. Murad, L. Zhu, G. Mu, Improved packing performance and structure-stability of casein edible films by dielectric barrier discharges (DBD) cold plasma, Food Packag. Shelf Life 24 (2020), 100471, https://doi.org/10.1016/j.fpsl.2020.100471.

[9] S. Beikzadeh, M. Ghorbani, N. Shahbazi, F. Izadi, Z. Pilevar, A.M. Mortazavian, The effects of novel thermal and nonthermal technologies on the properties of edible food packaging, Food Eng. Rev. 12 (2020) 333–345, https://doi.org/10.1007/s12393-020-09227-y.

[10] R. Colussi, V.Z. Pinto, S.L.M. El Halal, B. Biduski, L. Prietto, D.D. Castilhos, E. da Rosa Zavareze, A.R.G. Dias, Acetylated rice starches films with different levels of amylose: mechanical, water vapor barrier, thermal, and biodegradability properties, Food Chem. 221 (2017) 1614–1620, https://doi.org/10.1016/j.foodchem.2016.10.129.

[11] L. Fu, J. Zhu, S. Zhang, X. Li, B. Zhang, H. Pu, L. Li, Q. Wang, Hierarchical structure and thermal behavior of hydrophobic starch-based films with different amylose contents, Carbohydr. Polym. 181 (2018) 528–535, https://doi.org/10.1016/j.carbpol.2017.12.010.

[12] A.A. Al-Hassan, M.H. Norziah, Effect of transglutaminase induced crosslinking on the properties of starch/gelatin films, Food Packag. Shelf Life 13 (2017) 15–19, https://doi.org/10.1016/j.fpsl.2017.04.006.

[13] C. Menzel, Improvement of starch films for food packaging through a three-principle approach: antioxidants, cross-linking and reinforcement, Carbohydr. Polym. 250 (2020), 116828, https://doi.org/10.1016/j.carbpol.2020.116828.

[14] D.C. Bastos, A.E. Santos, M.L. da Silva, R.A. Simão, Hydrophobic corn starch thermoplastic films produced by plasma treatment, Ultramicroscopy 109 (8) (2009) 1089–1093, https://doi.org/10.1016/j.ultramic.2009.03.031.

[15] S.K. Pankaj, C. Bueno-Ferrer, N.N. Misra, L. O'Neill, B.K. Tiwari, P. Bourke, P. J. Cullen, Dielectric barrier discharge atmospheric air plasma treatment of high amylose corn starch films, LWT Food Sci. Technol. 63 (2) (2015) 1076–1082, https://doi.org/10.1016/j.lwt.2015.04.027.

[16] F. Zhu, Plasma modification of starch, Food Chem. 232 (2017) 476–486, https://doi.org/10.1016/j.foodchem.2017.04.024.

[17] A.V. Oliveira, A.P.M. da Silva, M.O. Barros, M. de Sá M. Souza Filho, M.F. Rosa, H. M. Azeredo, Nanocomposite films from mango kernel or corn starch with starch nanocrystals, Starch-Stärke 70 (2018), 1800028, https://doi.org/10.1002/star.201800028.

[18] N.M. Farhan, H. Aziz, H.V. Tafreshi, Simple method for measuring intrinsic contact angle of a fiber with liquids, Exp. Fluids 60 (5) (2019) 1–8, https://doi.org/10.1007/s00348-019-2733-2.

[19] ASTM D 5725-99, Standard Test Method for Surface Wettablility and Absorbency of Sheeted Materials Using an Automated Contact Angle Tester, ASTM International, West Conshohocken, PA, USA, 2003.

[20] I. Sifuentes-Nieves, G. Mendez-Montealvo, P.C. Flores-Silva, M. Nieto-Pérez, G. Neira-Velazquez, O. Rodriguez-Fernandez, G. Velazquez, Dielectric barrier discharge and radio-frequency plasma effect on structural properties of starches with different amylose content, Innovative Food Sci. Emerg. Technol. 68 (2021), 102630, https://doi.org/10.1016/j.ifset.2021.102630.

[21] ASTM D882-01, Standard Test Method for Tensile Properties of Thin Plastic Sheeting, ASTM International, West Conshohocken, PA, USA, 2001.

[22] ASTM E96-00, Standard Test Method for Water Vapor Transmission of Materials, ASTM International, West Conshohocken, PA, USA, 2000.

[23] P.C. Flores-Silva Sifuentes-Nieves, C. Gallardo-Vega, E. Hernández-Hernández, G. Neira-Velázquez, G. Mendez-Montealvo, G. G. Velazquez, Films made from plasma-modified corn starch: chemical, mechanical and barrier properties, Carbohydr. Polym. 237 (2020), 116103, https://doi.org/10.1016/j.carbpol.2020.116103.

[24] R. Bahrami, R. Zibaei, Z. Hashami, S. Hasanvand, F. Garavand, M. Rouhi, S. M. Jafari, R. Mohammadi, Modification and improvement of biodegradable packaging films by cold plasma; a critical review, Crit. Rev. Food Sci. Nutr. (2020) 1–15, https://doi.org/10.1080/10408398.2020.1848790.

[25] L.W. Wong, C.Y. Hou, C.C. Hsieh, C.K. Chang, Y.S. Wu, C.W. Hsieh, Preparation of antimicrobial active packaging film by capacitively coupled plasma treatment, LWT Food Sci. Technol. 117 (108612) (2020).

[26] Y.A. Oh, S.H. Roh, S.C. Min, Cold plasma treatments for improvement of the applicability of defatted soybean meal-based edible film in food packaging, Food Hydrocoll. 58 (2016) 150–159, https://doi.org/10.1016/j.foodhyd.2016.02.022.

[27] G. Chen, Y. Chen, N. Jin, J. Li, S. Dong, S. Li, Z. Zhang, Y. Chen, Zein films with porous polylactic acid coatings via cold plasma pre-treatment, Ind. Crop. Prod. 150 (2020), 112382, https://doi.org/10.1016/j.indcrop.2020.112382.

[28] F. Han, C. Gao, M. Liu, F. Huang, B. Zhang, Synthesis, optimization and characterization of acetylated corn starch with the high degree of substitution, Int. J. Biol. Macromol. 59 (2013) 372–376, https://doi.org/10.1016/j.ijbiomac.2013.04.080.

[29] P.H. Campelo, E.G. Alves Filho, L.M. Silva, E.S. de Brito, S. Rodrigues, F. A. Fernandes, Modulation of aroma and flavor using dielectric barrier discharge

plasma technology in a juice rich in terpenes and sesquiterpenes, LWT Food Sci. Technol. 130 (2020), 109644, https://doi.org/10.1016/j.lwt.2020.109644.
[30] R. Morent, N. De Geyter, L. Gengembre, C. Leys, E. Payen, S. Van Vlierberghe, E. Schacht, Surface treatment of a polypropylene film with a nitrogen DBD at medium pressure, Eur. Phys. J. Appl. Phys. 43 (3) (2008) 289–294, https://doi.org/10.1051/epjap:2008076.
[31] R. Morent, N. De Geyter, T. Desmet, P. Dubruel, C. Leys, Plasma surface modification of biodegradable polymers: a review, Plasma Process. Polym. 8 (3) (2011) 171–190, https://doi.org/10.1002/ppap.201000153.
[32] M.H. Moosavi, M.R. Khani, B. Shokri, S.M. Hosseini, S. Shojaee-Aliabadi, L. Mirmoghtadaie, Modifications of protein-based films using cold plasma, Int. J. Biol. Macromol. 142 (2020) 769–777, https://doi.org/10.1016/j.ijbiomac.2019.10.017.
[33] R. Morent, N. De Geyter, M. Trentesaux, L. Gengembre, P. Dubruel, C. Leys, E. Payen, Influence of discharge atmosphere on the ageing behaviour of plasma-treated polylactic acid, Plasma Chem. Plasma Process. 30 (4) (2010) 525–536, https://doi.org/10.1007/s11090-010-9233-8.
[34] Z. Sheikhi, L. Mirmoghtadaie, M.R. Khani, M. Farhoodi, S. Beikzadeh, K. Abdolmaleki, F. Kazemian-Bazkiaee, B. Shokri, S. Shojaee-Aliabadi, Physicochemical characterization of argon plasma-treated starch film, J. Agric. Sci. Technol. 22 (4) (2020) 999–1008. http://jast.modares.ac.ir/article-23-28357-en.html.
[35] J. Song, B. Jiang, Y. Wu, S. Chen, S. Li, H. Sun, X. Li, Effects on surface and physicochemical properties of dielectric barrier discharge plasma-treated whey protein concentrate/wheat cross-linked starch composite film, J. Food Sci. 84 (2) (2019) 268–275, https://doi.org/10.1111/1750-3841.14387.
[36] G.A. Arolkar, M.J. Salgo, V. Kelkar-Mane, R.R. Deshmukh, The study of air-plasma treatment on corn starch/poly (ε-caprolactone) films, Polym. Degrad. Stab. 120 (2015) 262–272, https://doi.org/10.1016/j.polymdegradstab. 2015.07.016.
[37] L.M. Fonseca, J.R. Gonçalves, S.L.M. El Halal, V.Z. Pinto, A.R.G. Dias, A.C. Jacques, E. da Rosa Zavareze, Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films, LWT Food Sci. Technol. 60 (2) (2015) 714–720, https://doi.org/10.1016/j.lwt.2014.10.052.
[38] P. Pająk, I. Przetaczek-Rożnowska, L. Juszczak, Development and physicochemical, thermal and mechanical properties of edible films based on pumpkin, lentil and quinoa starches, Int. J. Biol. Macromol. 138 (2019) 441–449, https://doi.org/10.1016/j.ijbiomac.2019.07.074.
[39] A.E. Wiącek, M. Jurak, A. Gozdecka, M. Worzakowska, Interfacial properties of PET and PET/starch polymers developed by air plasma processing, Colloids Surf. A Physicochem. Eng. Asp. 532 (2017) 323–331, https://doi.org/10.1016/j.colsurfa.2017.04.074.
[40] W.S. Lim, S.Y. Ock, G.D. Park, I.W. Lee, M.H. Lee, H.J. Park, Heat-sealing property of cassava starch film plasticized with glycerol and sorbitol, Food Packag. Shelf Life 26 (2020), 100556, https://doi.org/10.1016/j.fpsl.2020.100556.