Physicochemical Modification and Rearrangement of Structure in Potato Starch-based Film-forming Solutions Treated with Plasma-activated Water

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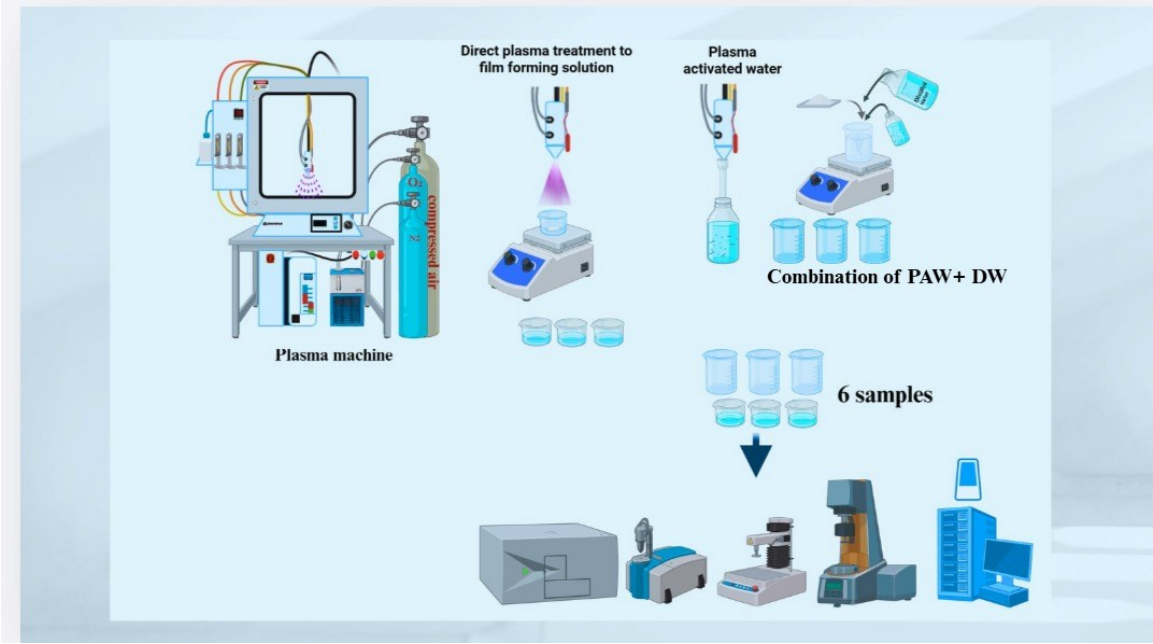
GRAPHICAL ABSTRACT



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Cold plasma is an eco-friendly approach for tailoring starch-based film-forming solutions (FFS) through reactive oxygen and nitrogen species (RONS). This study compared (i) plasma-activated water (PAW) blended with distilled water at 10:90, 20:80, and 30:70 (PAW:DW) and (ii) direct plasma treatment of potato starch FFS for 5, 10, and 15 min, evaluating rheological, textural, optical, and structural responses. PAW exhibited strong activation (pH 2.56; ORP 434.7 mV) with elevated conductivity and dissolved solids, indicating ionic enrichment. Apparent viscosity increased in all treated samples relative to the control, with the highest viscosity observed for PAW-blended FFS. Dynamic oscillatory measurements indicated that direct plasma exposure reduced viscoelastic moduli in a time-dependent manner, consistent with disruption of the starch network at higher treatment intensities, whereas PAW blends partially preserved elasticity. Color analysis showed increased lightness and whiteness index in PAW-treated samples, indicating improved optical uniformity. FTIR spectra showed changes in O–H stretching intensity and emergence/ intensification of oxidation-related bands, which is consistent with chemical modification of the starch matrix. Overall, direct plasma and PAW blending induced distinct molecular rearrangements in hydrated starch systems, offering tunable pathways for tailoring starch-based film-forming systems for potential biodegradable packaging applications, as a precursor to future film-level investigations.

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Keywords: Biodegradable packaging materials; Cold plasma; FTIR spectroscopy; Functional group modification; Rheological properties

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INTRODUCTION

Food packaging not only protects food from physical, chemical, and biological damage but it also extends its shelf life and conveys essential product information (Goiana *et al.* 2022). The most commonly used packaging materials are petroleum-based plastics, including poly-ethylene (PE) and polypropylene (PP), which offer numerous advantages, such as good mechanical and high barrier properties, and cost-effectiveness. However, the extensive use of non-biodegradable plastics has led to significant environmental pollution, ecosystem disruption, and health risks. Therefore, green, sustainable, and biodegradable bioplastics have emerged as preferred alternatives. Compared to petroleum-based plastics, which may require up to 500 years (or sometimes more) to break down, these materials

decompose naturally in a short time (several months to years) (Li *et al.* 2024). Consequently, researchers, governments, and industries are coming together to reduce the amount of plastic materials and come up with new sustainable packaging alternatives (Panou and Karabagias 2023). Recent advancements in biodegradable and/or edible films and coatings have highlighted the natural biodegradable materials derived either from animal sources (*e.g.*, gelatin, casein, and shellac) or plant and marine origins (*e.g.*, starch, cellulose, chitosan, sodium alginate, and hemicellulose) (Cheng *et al.* 2021; Onyeaka *et al.* 2022).

Among the most favorable biopolymers to conventional materials, starch, being a renewable, biodegradable, and edible resource, is widely used and is not based on fossil fuels. Onyeaka *et al.* (2022) stated that starch has the potential to be utilized as plastic film substitutes, laminates, and natural fiber compositions. For instance, it can be used as a substitute form of plastic foam. Films produced using starch have good physical characteristics, such as being tasteless, colorless, odorless, and impermeable to oxygen. The characteristics of starch films vary depending on the source of starch, especially in the proportion of amylose and amylopectin. Wheat, corn, and potatoes are some of the examples of rich sources of starch (Cheng *et al.* 2021). Potato starch has larger granule sizes and contains phosphate monoesters, which enhance its film-forming ability, water-binding capacity, and responsiveness to physicochemical modifications such as plasma treatment. Potato starch contains an optimal ratio of amylose and amylopectin, with amylopectin usually representing 70 to 80% of the total starch content. Amylopectin has a highly branched molecular structure, containing approximately 4 to 6% α-(1→6) linkages. Amylopectin consists of numerous short chains with an average degree of polymerization (DP) of 2,000 to 3,000 glucose residues. Amylose, the minor component, is a primarily linear polymer composed of glucose units connected by α-(1→4) linkages, typically containing 200 to 500 residues (Bertoft and Blennow 2016).

The main limitations in developing biodegradable packaging materials are their relatively low thermal, mechanical, and barrier properties as compared to conventional plastics. To overcome these limitations, various physicochemical modification techniques, including cross-linking, nanoparticle incorporation, and plasma treatment, have been employed (Shahidi and Hossain 2022; Mohammadi *et al.* 2026). Notably, cold plasma treatment has demonstrated a strong ability to alter physical, chemical, and structural characteristics of biopolymers and biopolymer-based films. For example, starch has been modified using cold plasma technology to enhance its functional properties and improve its applicability in packaging food (Zhang *et al.* 2023). Plasma, often referred to as the fourth state of matter, is an ionized gas composed of highly reactive species, such as free radicals, molecules, atoms, electrons, and ions, which may exist in either excited or ground states. Depending on the operating temperatures and pressures, plasma can be classified into thermal and non-thermal (cold) types (Hossain *et al.* 2025). Thermal plasma is defined by thermodynamic equilibrium among its species, typically generated under high pressure ($> 10^5$ Pa) and power (> 50 MW). In contrast, non-thermal or cold plasma operates under non-equilibrium conditions, where energetic electrons coexist with neutral gas molecules at near-ambient temperatures (Mehta and Yadav 2022).

Cold plasma is a highly diverse treatment because its particles can break chemical bonds and initiate reactions on surfaces, allowing it to be applied in various material modification processes (Pankaj and Keener 2017). However, the effectiveness of plasma treatment depends on various parameters, including operating pressure, discharge power, and gas composition. Gases that are commonly employed to carry out this process are air,

oxygen, argon, and nitrogen, which are capable of altering the surface properties of different materials, as they determine the type and concentration of reactive species generated during the process (Katsigiannis *et al.* 2022). Although cold plasma and plasma-activated water (PAW) have been increasingly studied for polymer modification, most research to date has focused on dry films or solid-state materials, leaving a significant knowledge gap regarding how plasma and PAW interact with biopolymer molecules in the liquid-phase film-forming solutions (FFS). The physicochemical reactions and molecular rearrangements that occur in this hydrated environment are likely to differ considerably from those on solid surfaces yet remain poorly understood.

To address this gap, the present study explored the effects of both direct plasma treatment and PAW incorporation (in ratios of 10:90, 20:80, and 30:70; PAW to distilled water) on potato starch-based film-forming solutions. Treatments were conducted using a combination of oxygen and nitrogen gases at varying exposure times (5, 10, and 15 min). The impact of cold plasma treatment on the textural, physical, rheological, and structural (FTIR) properties of the film-forming solutions was comprehensively evaluated to elucidate the molecular rearrangement and structural rearrangements induced by plasma exposure. It should be noted that this study focused on physicochemical and structural modifications in film-forming solutions as precursor systems. The interpretations were based on indirect evidence, and definitive confirmation of covalent crosslinking requires advanced molecular-level analyses, which are beyond the scope of the present work.

EXPERIMENTAL

Procurement of Material

Commercially available potato starch was procured from the chemical store British Columbia (Vancouver, Canada). Molecular biology grade glycerol (≥ 99.0% purity) was obtained from Sigma Aldrich (Merck, Darmstadt, Germany). Ultrapure distilled water was prepared using a Barnstead E-Pure Ultrapure Water Purification System (Thermo Fisher Scientific, MA, USA). Remaining reagents and chemicals used in this study were obtained from Sigma-Aldrich (St. Louis, MO, USA).

Preparation of Film-forming Solutions

Two methods were used for the preparation of FFS: direct plasma treatment and a combination of PAW and distilled water.

Combination of PAW and Distilled Water

Preparation of PAW

A total of 200 mL of distilled water was exposed to cold plasma. The distance between the plasma nozzle tip and the beaker wall was maintained at 1 cm. The PAW was generated using an OPENAIR^{TM} plasma system equipped with an FG5001 plasma generator combined with a CD50 plasma jet (Plasmatreat GmbH Inc., IL, USA) for 15 min. The generator input voltage was 320 V and was gradually raised to 1 kV. A built-in transformer raised the voltage to 20 kV for ignition, with an arc drop voltage of 2 kV and a discharge frequency of 15 to 25 kHz. A mixture of oxygen (O_2) and nitrogen (N_2) gases was used for ionization. The ionization gas flow rate was maintained at 3 L/min, and compressed air was supplied as the carrier gas at a rate of 9 L/min, following the manufacturer's recommendation (Mohammadi *et al.* 2025).

Preparation of FFS

The PAW and distilled water were mixed with three different ratios: Potato starch with cold plasma (PS-CP) 10:90 (10% PAW and 90% distilled water), 20:80 (20% PAW and 80% distilled water), and 30:70 (30% PAW and 70% distilled water) and solution prepared with only distilled water was considered as a control. Potato starch (2 g) was dissolved in 95.5 mL of a combination of PAW-distilled water mixture according to the designated ratios. The solution was heated to 90 °C on a hot plate for 1 h with magnetic stirring for gelation of starch and then immediately cooled to 40 °C. After cooling, glycerol (3% v/v) was added and mixed thoroughly to prepare the final FFS. Finally, the solution was left to stand overnight to remove air bubbles and then used for further analyses.

Direct plasma treatment

Potato starch (2 g) was gelatinized in 95.5 mL of distilled water at 90 °C. After cooling to 40 °C, 3% glycerol was added and mixed thoroughly to obtain the final FFS. The FFS were then subjected to direct CP treatment (without CP treatment was considered as control) in a 121-type treatment chamber equipped with a magnetic stirrer. A 100 mL portion of the solution was treated under constant stirring for PS-CP 5, 10, and 15 min.

Physicochemical Properties of PAW

pH, oxidation-reduction potential (ORP), salinity, electrical conductivity (EC), and total dissolved solids (TDS)

The pH value, ORP, salinity (salt content), EC, and TDS of PAW were measured using a portable multimeter. The multimeter was calibrated with standard calibration solution before measurement (Wongsagonsup *et al.* 2014).

Characterization of FFS

Color

A colorimeter was used to determine the color parameters of FFS samples. The sample was poured into a beaker, and the color values were recorded in terms of L^* (lightness), a^* (green/red), and b^* (yellow/blue) coordinates. Chroma, hue angle, and whiteness index (WI), were subsequently calculated using the colorimeter data (Li *et al.* 2022). The Chroma (C^*) value, hue angle (h°), and WI were determined according to the following Eqs. 1 to 3:

$$h^\circ = \tan -1 \left(\frac{b^*}{a^*}\right) \quad (1)$$

$$C^* = \sqrt{(a*)^2 + (b*)^2} \quad (2)$$

$$\text{WI} = 100\text{-} \sqrt{(100 - L*)^2 + (a*)^2 + (b*)^2} \quad (3)$$

Rheological properties

The rheological properties, including viscosity and viscoelasticity, of potato starch (PS) and PAW/distilled water (DW)-blended FFS were characterized using a rheometer (Anton Paar GmbH, Graz, Austria) equipped with a cone-plate geometry (diameter = 40 mm, cone angle = 2°, and a gap = 1000 μm) at 25 °C. Measurements were conducted over a shear rates range of 0.1 to 100 s^{-1}. The flow behavior of the samples was described using the power-law model, expressed as Eq. 4,

$$\tau = K\dot{\gamma}^{n} \quad (4)$$

where τ is the shear stress (Pa), K is the consistency index (Pa·s^n), γ is the shear rate (s^{-1}), and n is the flow behavior index.

Dynamic oscillatory tests were conducted within the linear viscoelastic region to verify that the material's structural reliability remained intact and rheological properties were independent of strain. A frequency sweep test was accomplished at a fixed strain of 1%, within a frequency range of 0.1 to 100 rad/s. Storage modulus (G') and the loss modulus (G'') were determined as functions of the applied frequency (Mohammadi *et al.* 2025).

Textural profiling

A Texture Analyzer (TA-XT, Stable Micro Systems, UK) with a TA-25 mm cylindrical probe was used to determine the texture of the FFS. The experiment was conducted with a 100 g applied force at 25 °C. During analysis, the samples were compressed by 20 mm from their original depth. The compression probe speed was 0.5 mm/s, while the pre-test and relaxation probe speeds were 2 mm/s. The texture profile parameters measured included hardness, consistency, cohesiveness, adhesiveness, gumminess, springiness, chewiness, penetration force, and elasticity (Cui *et al.* 2022).

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra of various solutions were examined using a PerkinElmer Spectrum 100 FT-IR Spectrometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) with an attenuated total reflectance (ATR) sampling accessory. The spectra were scanned with a total of 32 scans with absorbance array from 550 to 4000 cm^{-1}, at 4 cm^{-1} resolution (Oleyaei *et al.* 2016).

Cold Plasma Absorbance

The absorbance of cold plasma in film solutions was evaluated using a UV–Vis spectrophotometer (TECAN Infinite® M200 Pro, Tecan Systems Inc., San Jose, CA, USA). Absorbance values were recorded at 600 nm. The plate was read at 24 and 25 °C, using 25 flashes per well to enhance measurement precision (Singh *et al.* 2020).

Statistical Analysis

Statistical analysis was performed between different treatment times and combinations. The data were represented as mean ± standard deviation of triplicate measurements. Data were analyzed using one-way analysis of variance (ANOVA), and using Statistix software 8.1 (Analytical Software, Tallahassee, FL, USA).

RESULTS

Physicochemical Properties of PAW: pH, ORP, Salinity, E, and TDS

The PAW exhibited a pH of 2.56 (Table 1), indicating a high degree of acidity. The ORP was 434.7 mV, reflecting strong oxidative power. The salinity (623 ppm) and EC (1234 µS/cm) values were significantly increased compared to distilled water, suggesting substantial ionic enrichment within the PAW matrix. The plasma ionization of atmospheric gases (N_2 and O_2) and water molecules increased the concentration of reactive ionic species such asNO^{2-}, NO^{3-}, and H^+.

Table 1. Physicochemical Properties PAW and DW

Parameter	pH	*E* (µs/cm)	TDS (ppm)	Salt (ppm)	ORP (mv)
PAW	2.56 ± 0.005^{b}	1234.3 ± 0.03^{a}	890.3 ± 0.005^{a}	623.4 ± 0.01^{a}	434.7 ± 0.003^{a}
DW	6.54 ± 0.05^{a}	18.3 ± 0.005^{b}	11.7 ± 0.005^{b}	8.7 ± 0.005^{b}	246 ± 0.001^{b}

Data represent mean values for each sample ± standard deviation. Different lowercase letters for each column indicate significant differences ($p < 0.05$) among treatments; DW, distilled water

Characterization of FFS

Color

Color is a vital physicochemical indicator that reflects structural and chemical changes in starch molecules following plasma modification. The color parameters measured included *L**, *a**, and *b** (Table 2).

Table 2. Color Values of FFS

Treatments	*L**	*a**	*b**	*h*°	Chroma	WI
Control	4.35 ± 0.06^{e}	0.23 ± 0.72^{bc}	0.65 ± 0.04^{ab}	19.3 ± 1.90^{e}	0.69 ± 0.19^{c}	4.34 ± 0.72^{bc}
PS-CP 5M	4.33 ± 0.005^{e}	0.77 ± 0.01^{ab}	0.54 ± 0.01^{ab}	55.19 ± 0.89^{d}	0.94 ± 0.22^{bc}	4.33 ± 0.80^{bc}
PS-CP 10M	4.61 ± 0.01^{d}	0.14 ± 0.41^{c}	1.24 ± 0.03^{ab}	6.42 ± 0.29^{f}	1.25 ± 0.40^{b}	4.60 ± 0.19^{c}
PS-CP 15M	4.77 ± 0.01^{c}	0.43 ± 0.02^{abc}	3.49 ± 4.76^{a}	7.13 ± 0.90^{f}	3.52 ± 0.24^{a}	4.71 ± 0.30^{bc}
PS-CP 10:90	5.48 ± 0.09^{b}	0.54 ± 0.03^{abc}	0.14 ± 0.03^{b}	75.47 ± 2.35^{b}	0.55 ± 0.35^{c}	5.48 ± 0.82^{ab}
PS-CP 20:80	5.59 ± 0.06^{a}	0.83 ± 0.03^{a}	0.05 ± 0.17^{b}	86.58 ± 0.72^{a}	0.83 ± 0.51^{c}	5.59 ± 0.72^{a}
PS-CP 30:70	5.67 ± 0.02^{a}	0.42 ± 0.01^{abc}	0.23 ± 0.02^{b}	60.79 ± 0.33^{c}	0.48 ± 0.68^{bc}	5.67 ± 0.65^{a}

Notes: Data represent mean values for each sample ± standard deviation. Different lowercase letters within each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water, and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%) and DW (90%); PS-CP 20:80 PAW (20%) and DW (80%); PS-CP 30:70 PAW (30%) and DW (70%).

The control sample exhibited baseline color (*L** = 4.35, *a** = 0.23, *b** = 0.65, hue = 19.3°, chroma = 0.70, and WI = 4.35), representing the dull appearance of unmodified native starch granules. After direct plasma treatment, there was a progressive increase in the *L** values, especially at 10 min (4.61) and 15 min (4.78), indicating a gradual lightening of the samples. At 5 min (*a** = 0.77, *b** = 0.54), the slight increase in redness and yellowness suggested partial oxidation of hydroxyl and carbonyl groups. After 10 min (*a** = 0.14, *b** = 1.24), the higher *b** value reflected enhanced yellowness, while after 15 min (*a** = 0.43, *b** = 3.49, and chroma = 3.52), the starch developed a distinct yellowish-brown coloration. The hue angle also changed markedly from 19.3° (control) to 55.19° (5 min),

6.42° (10 min), and to 7.13° (15 min), indicating a shift toward warmer hues with increasing plasma exposure. In the PAW-treated samples, lightness values also went higher to 5.49 (10:90), 5.60 (20:80), and 5.67 (30:70), confirming a brightening effect. The hue angle rose progressively from 75.47° (10:90) to 86.58 (20:80), indicating a change towards the lighter yellow to white. This observation was further supported by the increase in WI (from 4.35 to 5.67), reflecting improved brightness and optical uniformity of the treated starch solutions.

Rheological Properties

The storage modulus of the control starch solution was the highest (94.4 Pa at 100 rad/s), which indicated that the starch solution had a comparatively strong elastic network structure. Direct exposure to plasma, however, decreased *G′* values in a time-dependent manner, with PS-CP15M exhibiting the largest decrease (26.5 Pa at 100 rad/s). In PS-CP30:70, recorded *G′* values of 77.3 Pa at 100 rad/s, whereas PS-CP20:80 attained a *G′* value of 75.0 Pa, which was higher than the untreated solution. In contrast, PS-CP10:90 was moderately resistant (Fig. 1).

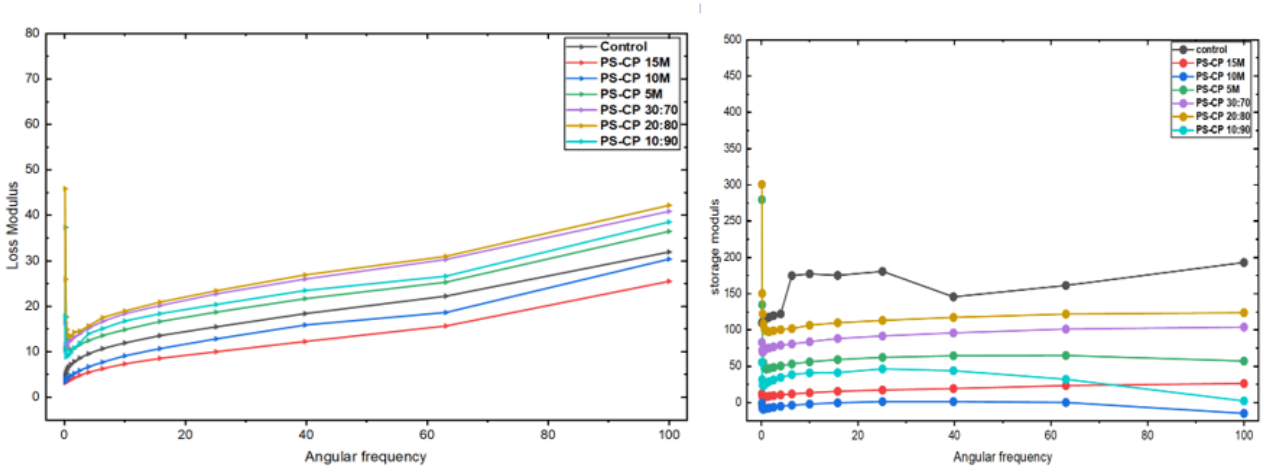

Fig. 1. Rheological properties, storage modulus *G′* and loss modulus (*G″*), as a function of angular frequency for control and plasma treated FFS. Data represent mean values for each sample ± standard deviation. Different lowercase letters for each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%) and DW (90%); PS-CP 20:80 PAW (20%) and DW (80%); PS-CP 30:70 PAW (30%) and DW (70%)

Viscosity

The viscosity data showed different flow behavior in treatments. Potato starch in distilled water (control sample) exhibited the lowest values of viscosity at all shear rates; however, it sharply decreased at low shear (< 10 s^{-1}) and leveled off. Conversely, direct plasma-treated samples (PS-CP 5M, 10M, and 15M) had increasingly greater viscosities with more plasma exposure, with PS-CP 15M having a significantly higher baseline viscosity than PS-CP 5M. The viscosity of plasma-activated water mixtures (PS-CP 10:90, 20:80, and 30:70) were significantly higher than both controls and direct plasma-activated treatment, although the highest viscosity level was observed in PS-CP 20:80 (Fig. 2).

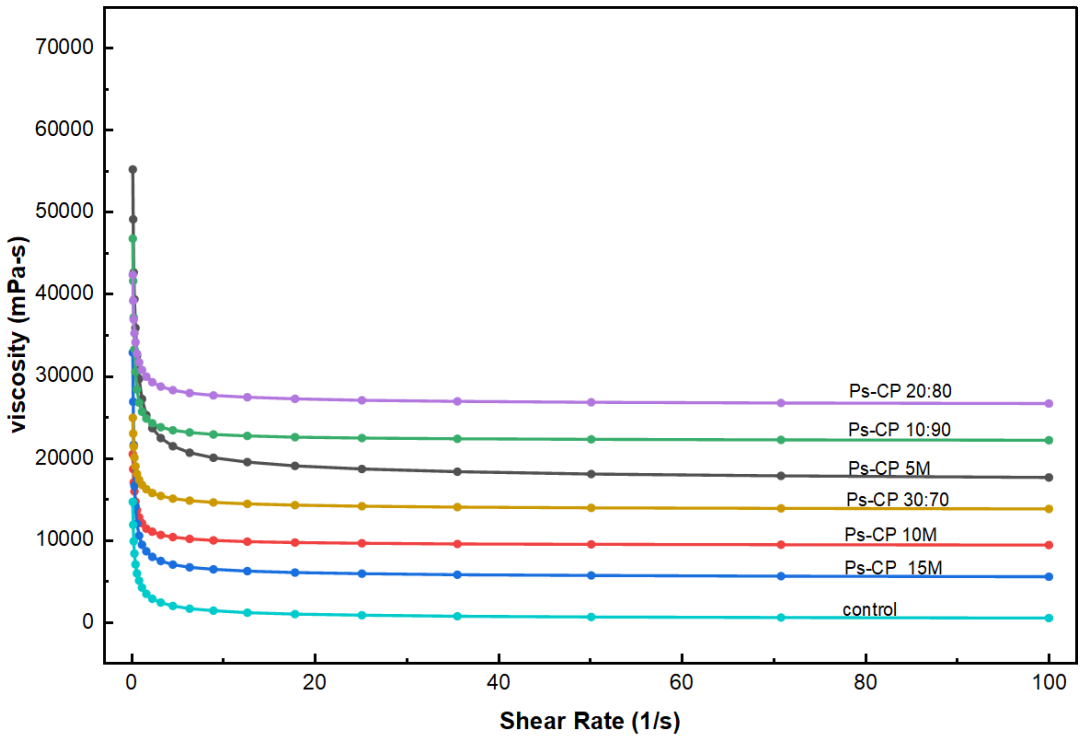

Fig. 2. Apparent viscosity of film-forming solutions as a function of shear rate for control and plasma treated FFS. Data represent mean values for each sample ± standard deviation. Different lowercase letters for each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water, and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%), and DW (90%); PS-CP 20:80 PAW (20%), and DW (80%); PS-CP 30:70 PAW (30%), and DW (70%)

Textural Analysis

The firmness and work of penetration findings showed significant treatment differences (Table 3).

Table 3. Textural Analysis Film Forming Solutions

Treatment	Firmness	Work of Penetration
Control	29.75 ± 30.65^{e}	85.9 ± 8.98^{de}
PS-CP 5M	31.73 ± 31.73^{e}	90.7 ± 7.95^{cd}
PS-CP 10M	41.3 ± 0.33^{d}	106.9 ± 8.91^{c}
PS-CP 15M	24.28 ± 0.33^{f}	73.38 ± 1.53^{e}
PS-CP 10:90	64.87 ± 1.69^{a}	189.31 ± 16.53^{a}
PS-CP 20:80M	45.89 ± 1.67^{c}	125.99 ± 3.85^{b}
PS-CP 30:70M	50.14 ± 1.45^{b}	142.8 ± 2.73^{b}

Data represent mean values for each sample ± standard deviation. Different lowercase letters within each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water, and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%), and DW (90%); PS-CP 20:80, PAW (20%), and DW (80%); PS-CP 30:70, PAW (30%), and DW (70%).

There were variations in direct plasma treatments based on exposure time. PS-CP 5M showed a middle level of firmness (31.7 N) and penetration work (90.7 mJ), which means that the structure is strengthened to some level relative to the control starch gel. PS-CP 10M also increases firmness to 41.3 N and penetration work to 107 mJ, even so, after prolonged exposure PS-CP 15M, firmness (24.3 N) and penetration work (73.4 mJ) decreased. The combination of PAW treatments showed a unique concentration-dependent effect. The PS-CP 20:80 showed a better firmness (45.9 N) and penetration work (126 mJ) than direct plasma treatments. Additional improvement of these textural properties was made by increasing the proportion of PAW, PS-CP 30:70 (50.14 N; 142.8 mJ) and PS-CP 10:90 (64.87 N; 189.31 mJ), which yielded the highest values of firmness and penetration work.

FTIR Spectroscopy

In the control potato starch FTIR spectrum, a broad absorbance band at 3304 cm^{-1} was observed, corresponding to O-H stretching vibrations associated with hydroxyl groups (Fig. 5). A medium-intensity absorbance at 1632 cm^{-1} was attributed primarily to H-O-H bending of absorbed water, with a possible minor contribution from carbonyl-related vibrations. In plasma-treated samples, a faint but clear band was observed at 2134 cm^{-1}, which may be associated with oxidation-related changes and/or alterations in bound water; however, it does not provide definitive evidence of carbonyl formation or covalent bond generation.

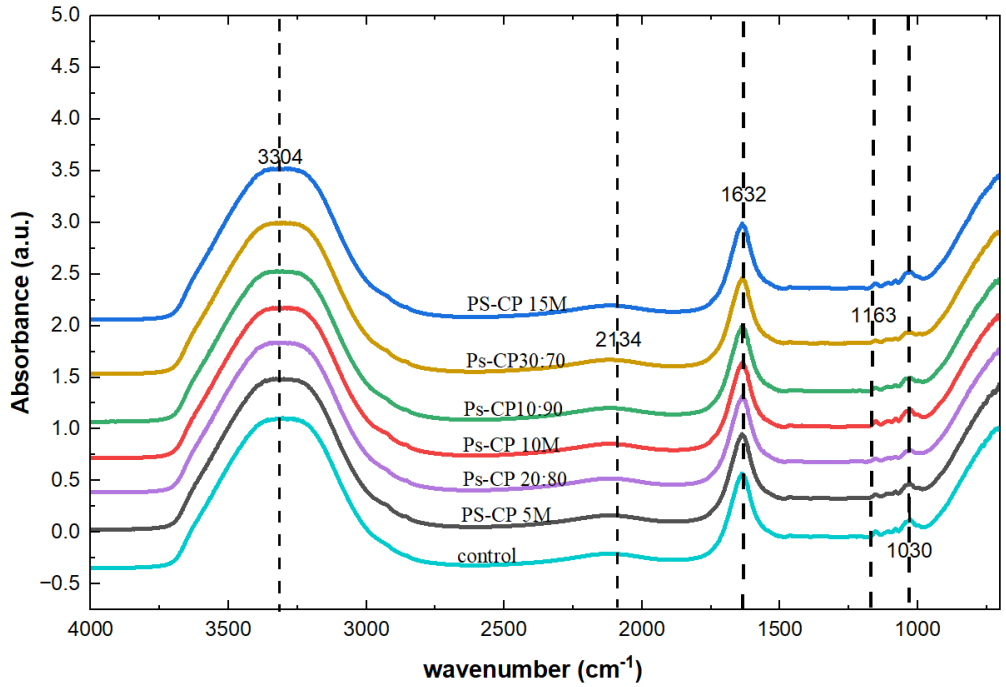

Fig. 3. FT-IR spectra of control and plasma-treated solutions. Characteristic peaks show functional group modifications following plasma exposure time for control and plasma-treated FFS. Data represent mean values for each sample ± standard deviation. Different lowercase letters for each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water, and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%), and DW (90%); PS-CP 20:80 PAW (20%), and DW (80%); PS-CP 30:70 PAW (30%), and DW (70%).

The fingerprint area exhibited characteristic bands at 1163 and 1030 cm^{-1}, corresponding to C–O–C and C–O stretching vibrations of glycosidic bonds, confirming the polysaccharide composition of the starch. A progressive decrease in the intensity of the OH band at 3304 cm^{-1} was observed with increasing plasma treatment time, suggesting disruption of hydrogen bonding and structural rearrangement within the starch matrix. The PS-CP 15M sample showed the most pronounced reduction, along with increased intensity in the 1632 cm^{-1} band, suggesting enhanced water binding and possible oxidation-related modifications. However, these spectral changes cannot be directly attributed to specific functional group formation without complementary analyses. The PAW treatments (PS-CP 20:80, PS-CP 30:70, PS-CP 10:90) exhibited more moderate spectral changes compared to direct plasma treatment. Slight increases in the 1632 cm^{-1} band suggest enhanced hydration effects, while reduced intensity in the glycosidic region (1163 and 1030 cm^{-1}) may indicate alterations in intermolecular organization rather than significant chemical modification.

Electronic Absorption of Cold Plasma

It was found that the control sample with no treatment had the greatest mean absorbance (0.505) indicating that the native starch solution contained more light-absorbing chromophores. Conversely, the absorbance of all the plasma-treated samples was significantly lower reaching a value of 0.086 (PS-CP 20:80) to 0.176 (PS-CP 10:90). During the direct plasma treatments, there was a time-dependent increase in absorbance with treatment. The mean absorbance of PS-CP 5M was 0.114, whereas PS-CP 10M and 15M were higher at 0.125 and 0.137, respectively.

Table 4. Electronic Absorption of Cold Plasma in Film Forming Solutions

Treatments	Absorbance
Control	0.51 ± 0.07[a]
PS-CP 5M	0.11 ± 0.006[cd]
PS-CP 10M	0.12 ± 0.12b[cd]
PS-CP 15M	0.13 ± 0.004b[cd]
PS-CP 10:90	0.17 ± 0.01[b]
PS-CP 20:80M	0.08 ± 0.009[d]
PS-CP 30:70M	0.17 ± 0.003[bc]

Data represent mean values for each sample ± standard deviation. Different lowercase letters within each column indicate significant differences ($p < 0.05$) among treatments. Control, distilled water, and potato starch: PS-CP 5M, direct plasma treatment for 5 min; PS-CP 10M, direct plasma treatment for 10 min; PS-CP, direct plasma treatment for 15 min; PS-CP 10:90, PAW (10%), and DW (90%); PS-CP 20:80, PAW (20%), and DW (80%); PS-CP 30:70, PAW (30%), and DW (70%).

DISCUSSION

Physicochemical Properties of PAW

The parameters of physical properties, such as pH, ORP, saltiness (salt content), CON, and TDS, are the key parameters that are expected to affect the reactivity and oxidative strength of PAW. Such conditions place constraints on the concentrations of the reactive oxygen and nitrogen species (RONS) formed during the exposure of the plasma and therefore determine the influence of PAW on the process of starch modification (Clod Plasma *et al.* 2024). The interaction of these variables with treatment time is the reason for

energy transfer that modifies the chemistry of water, ultimately modifying the FFS and molecular behavior of starch (Gupta *et al.* 2025). This study was carried out to evaluate the potential of physicochemical changes in distilled water after different treatments with plasma. The plasma-activated water had a pH of 2.56 (Table 1), which indicated a high degree of acidity. This was likely due to the formation of reactive species commonly reported in plasma-activated water, such as nitrate, nitrite, nitric and nitrous acids, and hydrogen peroxide; however, these species were not directly quantified in the present study. This reduction in pH towards near-neutral values (approximately 6.8 in untreated water) is symbolic of high concentrations of acidic radicals (Amarnath *et al.* 2023). The acidic environment also increases the availability of protons, which facilitates the hydrolysis of glycosidic linkages in starch. The oxidation-reduction potential of 434.7 mV indicates a high oxidative power, which is likely associated with the high amounts of RONS, such as OH, O_3, and NO_3. This high oxidation level can easily split C-O-C and C-H bonds into amylose and amylopectin (structural rearrangements) (Gupta *et al.* 2023). These changes will increase the hydrophilicity and transparency of starch-based films. Salinity (623 ppm) and conductivity (1234 µS/cm) were significantly increased, meaning that the ionic enrichment was observed in the PAW matrix. Plasma ionization of atmospheric gases (N_2, O_2) and water molecules leads to an increase in ionic content, which forms ions such as NO_2, NO_3, and H^+. These ions also contribute to charge transfer and mobility to increase the reactivity with organic molecules (Janik *et al.* 2023). High conductivity means that there are more charged particles and dissolved radicals, which increases the ability of PAW to interact with starch granules by electrostatic and hydrogen bonding interactions (Shi *et al.* 2025).

In the same way, the TDS of 890.33 ppm indicates the presence of ionic by-products and dissolved radicals due to more prolonged contact of plasma with water, which increases the load of solute and chemical activity of water (Gebremical *et al.* 2024). The physicochemical modification of PAW observed is closely connected with the starch modification mechanisms. The combination of low PH and high ORP facilitates partial oxidation of the amylose and amylopectin, resulting in depolymerization or physicochemical modification, respectively, based on the intensity of treatment (Yan *et al.* 2022). These alterations in hydrogen bonds also affect the structure of the bonding of starch molecules inside the films. The density of crosslinks also positively impacts film flexibility and tensile strength, which is positively correlated with an increase in conductivity and ORP of PAW. The PAW also leads to improved swelling of starch granules due to osmotic effects in the enriched ionic environment to enable a deep penetration of the reactant species and more uniform modification of the polymer matrix (Gebremical *et al.* 2024). Overall, the water generated after 15 min treatment was characterized by a high degree of activation in all aspects (low pH, high ORP, high conductivity, and high ionic enrichment). These alterations indicate the presence of a very reactive aqueous environment that can cause desired oxidation and reorganization in starch molecules. The results indicate that PAW is a chemical modifier and functional medium, which enhances the physicochemical properties of starch and starch-based film-forming solution by regulating oxidative and ionic reactions. However, physicochemical parameters measured in this study provide indirect evidence of PAW activation and oxidative potential but do not allow identification or quantification of specific RONS. Future studies involving direct chemical analysis of PAW (*e.g.*, nitrate, nitrite, and hydrogen peroxide quantification) would provide deeper insight into the mechanisms of starch modification.

Color

Color is a vital physicochemical indicator that indicates some changes in starch molecules after being modified by plasma. Variations in these color parameters are directly related to the oxidation and rearrangements of the amylose-amylopectin interactions with the formation of reactive species in the plasma treatment (Yan *et al.* 2022b). The control sample had the values of the baseline color (Table 2), which signified a slightly dull image of the native starch particle that was not modified. After direct plasma treatment, there was a progressive rise in the *L** values, especially at 10 min (4.61) and 15 min (4.78), which indicates a slight reduction of the samples. This can be attributed to surface oxidation and the elimination of impurities (Yan *et al.* 2024). In the meantime, the *a** and *b** parameters exhibited non-linear changes, which reflect complicated interactions between chromophoric groups and structures. At 5 min, the redness and a slight yellowish color change indicate some oxidation of hydroxyl and carbonyl groups. Nevertheless, at 10 min, the considerable *b** value was associated with stronger yellowness, which was a result of greater energy input and by high values of RONS. The starch had a clear yellowish-brown color at 15 min and a high chroma (3.52), which is due to intense coloration between carbonyl and conjugated double-bond structures and plasma oxidation of glycosidic bonds (Zuo *et al.* 2024). The hue angle also changed radically from 19.3 (control), 55.19 (5 min), 6.42 (10 min) to 7.13 (15 min), which indicates radical changes in the color shade because of oxidation and intermolecular rearrangement of starch molecules and due to depolymerization of amylose and amylopectin. Prolonged plasma exposure (15 min) increased light scattering of roughened granule surfaces and increased chromophoric group formation, which was in favor of the high chroma values.

In the PAW treatments, the lightness values also went higher to 5.49 (10:90), 5.60 (20:80), and 5.67 (30:70). This shows that there was an increase in whitening with the dilution effect of PAW and a decrease in oxidation. The hue angle gradually changed to 75.5 in 10:90 to 86.6 in 20:80, indicating a change towards the lighter yellow to white. This observation is supported by the increase in whiteness index (4.3 to 5.7), showing an improvement in brightness, which is caused by the stabilization of the oxidized groups by hydration and relocation of the amylopectin helices. Hydroxyl groups were presumably altered by the presence of reactive radicals, such as H_2O_2, NO_3, and OH radicals in PAW, to form a more hydrophilic compound, which decreases the roughness of the film surface (Gupta *et al.* 2025). Other researchers, such as Amarnath *et al.* (2023) have demonstrated similar results, indicating that starches treated by plasma were found to be whitening because of oxidation-induced rearrangements of the microstructure. The highest chroma (3.5) in PS-CP 15 M depicted the strongest coloration in contrast to PAW-diluted treatments (particularly PS-CP 30:70), which portrayed the weakest chroma (0.5) and (5.7) whiteness. These results indicate that direct exposure to plasma mainly led to oxidative browning, whereas PAW mixtures led to bleaching and whitening because of dilution and regulated exposure to radicals. With the development of oxidation and depolymerization, the amylose chains are crosslinked or fragmented, so that they alter the film-forming properties and optical clarity (Gupta *et al.* 2023). The rise in lightness and whiteness index of PAW-treated samples improved film uniformity and transparency, which is the preferred feature of biodegradable packaging. In contrast, high chroma and low hue values at long exposure to plasma indicate a higher coloration associated with molecular oxidation and heterogeneity of the structure (Shi *et al.* 2025).

Therefore, it can be asserted that the behavior of color in plasma-modified potato starch indicated two opposite effects: (i) direct plasma treatments increased color *via* the

formation of an oxidative chromophore, and (ii) the increase of whiteness in the plasma-activated water combinations with a reduction in color saturation. These modifications are closely associated with amylose-amylopectin interaction, oxidation of the surfaces of the granules, and demonstrate how the exposure of plasma can adjust the structure as well as aesthetic characteristics of starch-based films.

Rheological Properties

Rheological characterization can give essential details of structural integrity, viscoelastic behavior, as well as the network-forming capacity of starch-based film-forming solutions (Castanha *et al.* 2020). The responses to direct cold plasma treatment and PAW incorporation of potato starch solutions with respect to storage modulus (G'), loss modulus (G''), shear stress, and strain at a variety of angular frequencies were evaluated in this study. The storage modulus of the control starch solution was the highest, which indicated that the starch solution had a comparatively strong elastic network structure. Direct exposure to plasma, however, decreased G' values in a time-dependent manner, with PS-CP15M exhibiting the maximum decrease (Fig. 1). The reduction in G' values with increasing plasma exposure suggests weakening of the starch network, which may be attributed to chain scission or disruption of intermolecular interactions rather than crosslink formation. Such weakening indicates that long-term exposure of starch to plasma breaks the intermolecular interactions of hydrogen bonds. The same decrease in viscoelasticity after plasma treatment has been observed in starch suspensions, which could be explained by oxidation, depolymerization due to RONS (Yan *et al.* 2022a). In PS-CP30:70, recorded G' values of 77.3 Pa at 100 rad/s, whereas PS-CP20:80 attained a G' value of 75.0 Pa, which was higher than the untreated solution. This implies that water was activated by plasma, and it contained a high concentration of nitrates, nitrites, and peroxides that promoted partial crosslinking or the addition of functional groups (*e.g.*, carbonyl, carboxyl) to strengthen the starch structure (Gebremical *et al.* 2024a). In contrast, PS-CP10:90 was moderately resistant, which indicates that the best PAW concentration was crucial to maintaining a balance between structural change and hydration. The shear stress and strain responses indicated that all the specimens were mostly of an elastic nature ($G' > G''$) throughout the whole frequency range, which supports the weak gel nature of starch-based systems. The Control sample demonstrated a sharp fall in the storage modulus at lower frequencies, as compared to the PAW-treated specimens, which showed high elasticity over the entire frequency range. This frequency-dependent stiffening indicates a greater entanglement and stability of the starch matrix. Similar reinforcement properties of PAW have been reported in protein- and polysaccharide-based biopolymers, where RONS modifications increase cross-linkage of the polymer and thus enhance rheological stability (Akhila *et al.* 2024). In contrast to the previous findings, the direct plasma treatments seem to have caused progressive reduction of the viscoelastic network with time. The modulus values of the specimens exposed to 5 and 10 min of plasma exposure (PS-CP 5M and PS-CP10M, respectively) were intermediate, and the exposure to 15 min showed significant degradation; this suggests that prolonged plasma treatment can cause undue depolymerization and fragmentation of the amylose and amylopectin chains. This behavior is also in line with previous studies that have shown that carbonyl and carboxyl functionalities enriched by cold plasma through oxidative cleavage induce a corresponding molecular weight and viscosity decrease (Sifuentes-Nieves *et al.* 2024). Overall, the current data outline divergent effects of different plasma treatments: direct plasma application inhibits the mechanical strength of starch gels by depolymerizing them.

However, oxidative depolymerase cross-linkage and PAW increase the rigidity of the matrices by oxidatively cross-linking polymer chains. These findings support the dual purpose of RONS in polymeric systems, in which superset-physiological oxidation causes material to become degraded. However, moderate, controlled oxidation promotes material strengthening. Overall, the current data outline divergent effects of different plasma treatments: direct plasma application inhibits the mechanical strength of starch gels by depolymerizing them through oxidative depolymerase cross-linkage, and PAW increases the rigidity of the matrices by oxidatively cross-linking polymer chains. These findings, therefore, support the dual purpose of RONS in polymeric systems, in which superset-physiological oxidation causes material to become degraded, but moderate, controlled oxidation promotes material strengthening.

Viscosity

The viscosity data showed different flow behavior in treatments. Potato starch in distilled water (control sample) exhibited the lowest values of viscosity at all shear rates; however, it sharply decreased at low shear ($< 10\ s^{-1}$) and leveled off, which is typical of a shear-thinning system of the starch granules, and the amylose molecules become unscrambled (Goiana and Fernandes 2023). Conversely, direct plasma-treated samples (PS-CP 5M, 10M, and 15M) had increasingly greater viscosities with increasing plasma exposure, with PS-CP 15M exhibiting a significantly higher baseline viscosity than PS-CP 5M. This behavior suggests plasma-induced structural modifications, such as partial depolymerization and changes in intermolecular interactions among amylose and amylopectin chains, leading to altered network organization (Flores-Silva *et al.* 2023). The increased viscosity observed in PAW-treated samples is attributed to enhanced hydration and intermolecular associations, rather than the formation of permanent covalent networks. The viscosity outcome showed individual flow patterns between treatment conditions. The lowest viscosity values were observed at all shear rates with a steep drop in viscosity at low shear (less than $10\ s^{-1)}$ and then leveled off, as expected of a shear-thinning system. This is because the potato starch in distilled water is oriented, and amylose molecules are disentangled (Chou *et al*. 2023). Conversely, samples directly treated with plasma (PS-CP 5M, 10M, and 15M) showed an increasing viscosity as plasma was exposed, where the PS-CP 15M had a significantly higher viscosity at the baseline compared to PS-CP 5M. This suggests that the great structural changes, which were induced by plasma exposure, partially depolymerized or cross-linked amylose and amylopectin (Zhu *et al*. 2024). The viscosity of PAW mixtures (PS-CP 10:90, 20:80, and 30:70) was significantly higher than both controls and direct plasma treatment (Fig. 2). The highest viscosity level was observed in PS-CP 20:80, and this indicates stronger intermolecular associations. These findings indicate that the activation of water by the plasma generates reactive oxygen and nitrogen species that change the hydrogen bonding and glycosidic bonds and thus strengthen intermolecular interactions and restrict the free mobility of starch chains (Sifuentes-Nieves *et al.* 2020a). The interpretation of these results indicates an important role of amylose and amylopectin behavior in determining viscosity results. It is possible that plasma treatment stimulated the amylolysis process and increased amorphous domains that subsequently facilitated the swelling of the granules, thus adding to the increase in viscosity (Sifuentes-Nieves *et al.* 2020b).

In comparison of the treatments, the control samples exhibited the weakest intermolecular interaction and low viscosities. PS-CP 5M-15M had the most gradual alteration over time, and PS-CP 20:80 and PS-CP 30:70 were found to have the most

strengthened structure. The observed patterns of viscosity are supported by the altering glycosidic and hydrogen bonding networks, and this can affect flow behavior and film properties. To conclude, viscosity measurement showed that the structural and functional characteristics of potato starch were altered considerably by plasma treatment and plasma-activated water, resulting in wide flow behavior. Direct plasma treatments were moderately effective in increasing viscosity over time, whereas plasma-activated water treatments brought stronger plateaus in viscosity and molecular associations. These results reveal the equilibrium between the amylose-amylopectin interactions, hydrogen bonding, and the rheological response. Finally, the identified alterations in viscosity are directly linked to enhanced film-forming capabilities, which demonstrates that the use of plasma-modified starch systems can be useful in sustainable packaging.

Textural Analysis

Textural analysis was performed to determine the effect of direct cold plasma exposure and PAW on the mechanical properties of potato starch-based solutions. The texture is an important parameter that determines the functional and sensorial properties of the starch-based solutions because it indicates changes in the starch structure, such as starch-water interactions, gelatinization degree, and polymer entanglement (Thirumdas *et al.* 2017a). The firmness and work of penetration findings showed significant treatment differences. There were variations in direct plasma treatments based on exposure time. PS-CP 5M showed a middle level of firmness and penetration work (Table 3), which means that the structure was strengthened to some level relative to the control starch gel. PS-CP 10 M also increased firmness to 41.3 N and penetration work to 107 mJ, indicating that the intermediate exposure of plasma could be helpful in the molecular rearrangement of the starch matrix, perhaps by introducing carbonyl and carboxyl functional groups and thereby providing the ability to form intermolecular interactions. Even so, after prolonged exposure (PS-CP 15M), firmness and penetration work decreased; this is evidence of overreaching depolymerization and chain scission of starch polymers, which consequently result in a weaker gel structure. These tendencies are in line with the reports that moderate treatments of plasma can enhance structural rigidity, whereas overexposing starch to plasma causes the breakdown of starch granules, resulting in the weakening of gels (CABI 2025). The combination of PAW treatments showed a unique concentration-dependent effect. The PS-CP 20:80 showed a higher firmness (45.9 N) and penetration work (126 mJ) than direct plasma treatments, which means that PAW could facilitate moderate oxidation and hydration of starch granules and increase their ability to swell and gelatinize. Additional improvement of these textural properties was made by increasing the proportion of PAW, PS-CP 30:70, and PS-CP 10:90, which yielded the highest values of firmness and penetration work. These results indicate that increased PAW concentrations produced an increased number of RONS, which add crosslinks of oxidation and increase gel rigidity. Other research has also found similar improvements to the starch gel strength and viscoelasticity following incorporation of PAW in their studies, in which oxidation produced by PAW altered the morphology of the starch granules and facilitated intermolecular interactions (Gupta *et al.* 2023). In addition to firmness and penetration, other textural analyses, like cohesiveness, springiness, chewiness, gumminess, and adhesiveness, are affected by plasma treatment as well. More gumminess and chewiness are anticipated to be found in stronger gels (such as PS-CP 10:90) because of more intertwined polymer and ultimately more elastic and resistant structures. In contrast, weaker gels (PS-CP 15M) will exhibit less cohesiveness, indicating structural disruption

and deformation. The main factors that contribute to these differences in textural behavior are plasma-induced structural changes at the micro level, such as partial depolymerization, oxidation of amylose/amylopectin chains, and changes in hydrogen bonding (Carvalho *et al.* 2021). Compared to the published literature, the current findings are consistent with the overall finding that cold plasma treatments and PAW incorporation can alter the physicochemical and mechanical characteristics of starch-based systems. Ma and Jiang (2024) found that non-thermal changes, such as plasma, could be used to improve starch functionality by altering its gelatinization and retrogradation behavior. On the same note, research on biopolymer gels has indicated that PAW treatment enhances firmness and cohesiveness because of the crosslink density. The drop in the strength of the textures with increased time of exposure to the plasma is, however, not constant as compared to some reports, probably because of variations in the intensity of the plasma, the composition of the source gas, or the botanical origin of starch (Chou *et al.* 2023a). Overall, the analysis of the texture showed that direct plasma and PAW treatments had a major impact on the firmness and penetration of potato starch gels. Although moderate exposure to plasma enhanced the textural properties. The gel structure was affected by a longer exposure because of the degradation of the polymer within high concentrations. The PAW treatment always resulted in increased firmness and work of penetration, implying that oxidative functionalization and intermolecular interactions effects are more pronounced under high concentrations of PAW. These findings add weight to the possibility of cold plasma technologies as a sufficient means of modification of the textual and mechanical characteristics of starch-based solutions.

The hardness, as well as gumminess, were much higher with the use of PAW in combination treatments (particularly 10:90), which means that the structures were denser and more resistant to deformation. Intra-sample cohesiveness was comparatively high and indicated a high degree of internal bonding, especially in PS-CP 15M, in which the structural reorganization probably increased internal binding, although at reduced firmness. The highest values of springiness and chewiness were in PA-CP 10:90, which indicated elastic recovery and mechanical resilience, which is preferable in film applications.

FTIR Spectroscopy

The change in the structure of potato starch was examined using FTIR after direct treatment of cold plasma and in combination with the PAW. FTIR was chosen because it can provide a molecular fingerprint of functional groups, which shows chemical alterations caused by exposure to plasma (Okyere *et al.* 2022). In the control potato starch FTIR spectrum, a vast and sharp absorption region was observed at 3304 cm^{-1}, indicating the intra and intermolecular hydrogen bonding in the amylose and amylopectin matrices. The broadness and high intensity of this band highlight the hydrophilic nature of the starch. The intensity of the OH band at 3304 cm^{-1} in the PS-CP 5M sample was slightly reduced in comparison with the control, which indicates that the hydrogen bonds were initially disturbed. PS-CP 10M displayed an additional decrease in this band in addition to a slight change towards lower wavenumbers, which is in line with more oxidation and rearrangement of the structure. The sustainable changes were observed in PS-CP 15M, as the intensity of the OH band was reduced significantly and the band at 2134 cm^{-1} was more pronounced, showing that new groups with oxygen atoms were formed. Additionally, the intensity of the 1632 cm^{-1} band grew, suggesting an increase in the water-binding capacity or the simplicity of the creation of carbonyl functions due to plasma oxidation.

The plasma-activated water treatments (PS-CP 20:80, PS-CP 30:70, and PS-CP 10:90) showed moderate differences from the direct plasma. The OH band was still broad but with a lesser reduction in intensity, indicating that hydrogen bonding was not totally lost. The aqueous content of the plasma in the 1632 cm^{-1} band marginally rose with the increase in water content, indicating hydration and slight oxidation. Glycosidic region (1163 and 1030 cm^{-1}) was also less pronounced in these samples than direct treatment by plasma, thereby showing that indirect treatment by plasma using water caused less severe chemical alterations. The variations between treatments may be explained by the extent of the reaction of the reactive species with starch molecules. Direct exposure to plasma offers high-energy electrons, reactive oxygen, and nitrogen species, which directly cleave glycosidic bonds and oxidize hydroxyl groups, giving rise to new carbonyl and carboxyl functionalities (Liu *et al.* 2024). Stable reactive species (nitrate, hydrogen peroxide) in plasma-activated water, however, are moderate and do not cause significant cleavage. In general, the findings of the FTIR show that cold plasma treatment changes the starch structure by suppressing hydroxyl-related hydrogen bonding, introducing carbonyl groups, and marginally changing glycosidic bonds. The degree of modification was time-dependent in the case of treatment in direct plasma and concentration dependent in the case of plasma-activated water. These results are comparable with previous research involving rice and corn starches that also found a reduction of OH bands, new carbonyl absorption, and a change in crystallinity after exposure to plasma (Thirumdas *et al.* 2017c). Thus, FTIR analysis showed that cold plasma led to systematic chemical changes in potato starch, and PAW resulted in less severe structural changes. These changes give molecular-level support of the interaction of plasma and starch, which was the larger goal of improving the functionality of starch using non-thermal plasma technologies. While the observed changes in FTIR spectra, rheological behavior, and physicochemical properties suggest plasma-induced modification of the starch system such as oxidation-related modifications and alterations in hydrogen bonding, these findings do not constitute direct evidence of covalent crosslinking. The modifications are therefore interpreted as oxidative and structural rearrangements within the polymer network. Confirmation of covalent bond formation would require advanced techniques such as NMR spectroscopy, molecular weight distribution analysis, or thermal characterization (*e.g.*, DSC). Additional analytical approaches, such as conductometric titration or quantitative functional group analysis, could provide further insight into oxidation-related changes and help distinguish them from possible crosslinking effects that are investigated in our future study.

Electronic Absorption of Cold Plasma

The UV-visible absorption was measured to assess the absorption of cold plasma treatment and PAW on the optical characteristics of potato starch-based film-forming solutions. It is important to monitor UV absorption, as it indicates changes in the starch structure and composition, such as depolymerization and oxidation. These changes are vital in the development of bio-based film and functional properties of FFS (Thirumdas *et al.* 2017b) (Table 4). It was found that the control sample with no treatment had the highest mean absorbance, indicating that the native starch solution contained more light-absorbing chromophores. Conversely, the absorbance of all the PAW samples was significantly lower reaching a value of 0.086 (PS-CP 20:80) to 0.176 (PS-CP 10:90). The gradual loss of visual density in comparison with control indicates that the exposure of plasma or the addition of PAW modified the structure of starch, *via* oxidative cleavage of the glycosidic bond, and partial polymerization of amylose and amylopectin groups, resulting in a reduced number

of UV-absorbing chemical species (Chou *et al.* 2023b). The reduction in absorbance in plasma-treated samples suggests modification or degradation of chromophoric groups, consistent with oxidative processes. During the direct plasma treatments, there was a time-dependent increase in absorbance with treatment. The mean absorbance of PS-CP 5M was 0.114, whereas that of PS-CP 10M and 15M was higher at 0.125 and 0.137, respectively. This steady increase suggests that prolonged exposure of plasmas to the molecules increases molecular modification. The same has been reported in plasma-treated starches, where longer treatment times were linked to the increased occurrence of carbonyl derivatives, along with structural rearrangements, which enhance UV absorption (Gebremical *et al.* 2024b). Conversely, there was a different pattern in treatment using PAW. The lowest mean absorbance (0.086) occurred in the PS-CP 20:80, PS-CP 30:70 and PS-CP 10:90 samples had significantly high values (0.173 and 0.176, respectively). This indicates that the dilution ratio of 20:80 of PAW is significant in the determination of UV absorption. The decreased absorbance at moderate incorporation of PAW (20:80) can be possibly attributed to the partial hydrolysis and increased solubilization of starch granules, resulting in the formation of fewer chromophores. In contrast, increased concentrations of PAW can cause excessive RONS to induce oxidation and the formation of conjugated bonds, thus increasing absorbance. Comparison with previously published studies indicates both similarity and difference. Cold plasma treatment alters starch crystallinity and triggers the chemical restructuring, which influences the light absorption. Moreover, Misra *et al.* (2019) also found that PAW causes oxidative alteration of biopolymer matrices, which changes UV-vis spectra. Such a difference could be explained by the fact that the ratio between the action of dilution and the concentration of the RONS can significantly depend on the source of plasma, the input of power, and the treatment medium. In general, the findings validate that both direct plasma treatment and PAW had a sustainable effect on the UV absorption characteristics of potato starch solutions. Direct exposure is likely to increase absorbance progressively over more prolonged exposure, whilst the effects of PAW are susceptible to dilution ratio, indicating that absorption is both suppressed and accelerated. These results suggest that cold plasma technology may be strategically designed to direct the optical and possibly barrier properties of starch-based films, which could be helpful in food packaging and biopolymer functions.

Therefore, UV–vis spectroscopy showed that cold plasma treatments decreased absorbance compared to the control, and that longer direct exposures accelerated an absorbance effect, whereas incorporating PAW proved to be a dilution-dependent effect. These observations explain both the depolymerization and oxidative functionalization of the starch-based film solution matrices under the influence of plasma. Together, these observations indicate that cold plasma is a promising green processing technology to customize the physicochemical and functional properties in starch-based FFS.

Certainly, the specified study did not focus on the use of other functional additives along with plasma-treated pure potato starch base film-forming solutions. Future research should focus on adapting the treatment condition to achieve the optimal balance between increased functionality and structural stability and also aim to develop additional hydrocolloid-based films by incorporating cold plasma modification or active compounds to improve their functionality as innovative biodegradable food packaging materials.

CONCLUSIONS

1. This study showed that cold nitrogen and oxygen plasma treatment effectively modified the physicochemical properties of potato starch-based film-forming solutions, with distinct effects depending on whether the treatment was applied directly to the film-forming solution or by means of plasma treatment of distilled water, followed by mixing.
2. Both treatments on the solution led to physical, functional, and structural modifications. Rheological analysis revealed a significant viscosity reduction in direct plasma-treated solutions over longer time periods, which inhibited the mechanical strength of starch gels by depolymerizing them through oxidative depolymerase cross-linkage. By contrast, plasma-activated water (PAW) increased the rigidity of the matrices by promoting oxidative modifications and enhanced intermolecular interactions within the starch network chains.
3. Fourier transform infrared (FTIR) analysis showed that cold plasma led to systematic chemical changes in potato starch, and plasma-activated water resulted in less severe structural changes. The interaction of plasma and starch is molecularly supported by these changes, which were the primary aim in enhancing the functionality of starch by the non-thermal plasma technologies. It was noted that the gel strength of the film-forming solution decreased during a long period of exposure to plasma treatment, most likely due to destabilization of intermolecular interaction.
4. The occurrence of this loss of strength of the structural network adversely affected the process of forming solid and stable films of the solution. In contrast, rheological behavior, physical integrity, and functional performance of the obtained formulation which significantly enhanced upon the incorporation of PAW into distilled water. Such enhancements indicate that the PAW-distilled water mixture can be considered an advantageous medium to create the biopolymer film, which can be attributed to its controlled oxidative factors and the balanced proportion of ions.
5. Changes in rheological properties, texture, and optical characteristics of film-forming solutions provide useful insight into the organization and interactions of polymer chains in the precursor system. However, further studies are required to evaluate the mechanical, thermal, barrier, and solubility properties of the resulting films, as well as detailed molecular characterization, before confirming their suitability for sustainable packaging applications.

Author Contributions

Uzma Islam: writing—original draft preparation, methodology, software, formal analysis, conceptualization; Muhammad Yasir: writing, review and editing, data curation; Xanyar Mohammadi: review and editing, visualization; Abul Hossain: writing, reviewing, and editing; Majid Hussain supervision, project administration; Anubhav Pratap-Singh: Writing – original draft, validation, supervision, software, resources, project administration, investigation, funding acquisition, formal analysis, data curation.

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