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**Effects of Plasma Activated Water (PAW) on Rheological, Thermal, Hydration and Pasting Properties of Normal Maize, Waxy Maize and Potato starches**

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## **Abstract**

Plasma-activated water (PAW), characterized by acidic pH and content of highly reactive species (nitrite, nitrate, hydrogen peroxide, ozone), was applied as a strategy to modify the structure and functionality of potato, normal maize, and waxy maize starches. PAW was generated with a corona discharge at 15kV, 5 kHz for 1 min. Starches were mixed with PAW just after generation for 20 min and then dried. Native and PAW-treated starches were evaluated for rheological, pasting, gelatinization, and hydration properties, and subjected to Fourier-transform infrared (FTIR) spectroscopy. Results showed significant ( $p < 0.05$ ) changes in almost all the considered parameters, dependent on the starch characteristics. While an increase in most pasting and rheological parameters and gel hardness was observed for normal maize and potato starches, the opposite result was found for waxy maize. FTIR results indicated significant changes in functional groups related to the ability to bind water for all starches. The results obtained in this study highlighted PAW as a promising novel and green alternative method to modify the properties of starch; however further research needs to be tailored to the specific properties of the raw material.

**Keywords:** Cold Plasma; starch functionality; hydration properties; viscosity; FTIR.

## 1. Introduction

Starch is utilized as a gelling, thickening, stabilizing, texturing agent, colloidal stabilizer, bulking agent, water retention agent, freeze-thaw stabilizer, sweetener, emulsifying agent, for fermented products and as flavor encapsulating agent in the baking, brewing, and confectionery industries (Abbas, Khalil, & Hussin, 2010; Mason, 2009; J. Singh, Kaur, & McCarthy, 2007). However, in its native form, it is often characterized by high unreactivity, poor hydration properties, low shear resistance, gel shrinkage, insolubility, prone to retrogradation, and instability (Grgić et al., 2019; Kaur & Singh, 2019; Akua Y Okyere, Rajendran, & Annor, 2022).

To solve the abovementioned inherent defects, various physical (Hong & Liu, 2018; Kim, Kim, & Baik, 2012; Polesi & Sarmento, 2011; Zhu, 2015), enzymatic (Prompiputtanapon, Sorndech, & Tongta, 2020), and chemical (Fan & Picchioni, 2020; Prompiputtanapon et al., 2020; Ren et al., 2016) methods have been used to modify the functional, thermal, molecular, morphological, and technological properties of native starches. However, there are many disadvantages during the modification, such as issues of environmental pollution, food safety concerns, chemical residues, waste disposal, long treatment time, and costs (Chaiwat et al., 2016). To overcome these limitations and achieve innovation in the utilization of starch, other green and innovative starch modification methods should be investigated.

Plasma-activated water (PAW) is generated by exposing water to a plasma discharge that contains reactive species such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), nitrite ( $\text{NO}_2^-$ ), and nitrate ( $\text{NO}_3^-$ ), creating an acidic environment, which causes changes in the redox potential and conductivity (R Laurita, Barbieri, Gherardi, Colombo, & Lukes, 2015; Romolo Laurita, Gozzi, et al., 2021) with the advantages of uniform treatment, green and environmental eco-friendly characteristics (Y. Yan et al., 2022). PAW has been widely investigated for

its use in food and agriculture, aimed at microbial inactivation (Joshi, Salvi, Schaffner, & Karwe, 2018; Romolo Laurita, Gozzi, et al., 2021; Soni, Choi, & Brightwell, 2021; Xiang et al., 2020; D. Zhang et al., 2022), seed germination (Bafail et al., 2018; Ji et al., 2015), and food preservation (Liu et al., 2020; Xiang et al., 2019). While gaseous plasma has been studied by different authors as a strategy for starch modification (Akua Yeboah Okyere, Bertoft, & Annor, 2019), PAW has been only rarely applied for food components functionalization. Its effect on starch modification and the rheological, pasting, hydration, and thermal behaviours of treated starches have not been elucidated. Therefore, the objective of this research was to investigate the effect of PAW treatment on the rheological, thermal, hydration properties and functional groups of three selected starches, namely potato, normal maize and waxy maize starches.

## **2. Materials and methods**

### **2.1. Materials**

Three starches potato (P), normal maize (NM), and waxy maize (WM) were obtained from Padovana Macinazione, Padova, Italy.

### **2.2. Preparation of PAW**

In this study, PAW was produced using distilled water as described in detail by (Romolo Laurita, Contaldo, et al., 2021). The high-voltage electrode consisted of a stainless-steel pin-electrode connected to a microsecond pulsed generator (Alma Pulse, Alma Plasma s.r.l., Italy) at a fixed frequency of 5 kHz. Distilled water (500 mL) was grounded and placed in an Erlenmeyer flask on a stirrer (set at the speed of 700 rpm). The distance between the tip of the plasma source and the water was set at 5 mm, and the plasma discharge was generated for 1 min. A high voltage probe (Tektronix P6015A) and a current probe (Pearson 6585) connected to a digital oscilloscope (Tektronix DPO4034, 350 MHz, 2.5 GSa s<sup>-1</sup>) were used to measure voltage (V) and the current (i) during

plasma treatment. The average discharge power (P) was calculated by applying the following formula:

$$P = 1/T \int_0^T i(t) V(t) dt, \quad (1)$$

where T is the applied voltage period.

The Amplex® Red Hydrogen Peroxide Assay Kit (Thermo Fisher Scientific, Waltham, MA, USA) and the Nitrate/Nitrite colorimetric assay (ROCHE, Baesel, Switzerland) were used for the measurement of H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub><sup>-</sup> concentrations in PAW respectively using a microplate reader (Rayto, P.R. China). Moreover, the pH was evaluated by the means of inoLab® pH 7110 and Oakton Instrument: Con 6+ Meter. All measurements were performed at least 3 times immediately after treatment.

### 2.3. Treatment of starches

The starches were mixed with PAW straight after its generation, in a 1:2 (w/v) ratio, and stirred continuously for 20 minutes. This treatment time was chosen based on preliminary experiments conducted to determine the highest PAW efficiency in terms of optimal modification of our experimental conditions (data not reported). A sample mixed with distilled water was considered native starch. Native and PAW-treated starches were oven dried at 40 °C overnight, grounded, sieved, and stored for further analysis.

### 2.4. Pasting properties

The pasting properties of starches were measured using a modular compact rheometer (MCR102, Austria) based on the method described by Zhu and Cui (2020). The starches were prepared by adding 25 ml to 3 g of sample in the starch cell measuring cup (CC26ST aluminum) equipped with an electrically heated cylinder system with a fluid cooling system, and mixed by stirrer (ST24). Then the mixture was fast mixed for 10 s at 960 rpm, 50 s, held at 160 rpm and 50°C, and then heated from 50 °C to 95°C for 7.5 min at a 6 °C/min rate, held for 5 min at 95°C and finally, the sample was cooled to 50 °C for 7.5

min and held at 50 °C for 2 min. The rotation speed was held at 960 rpm for 10s and the rest of the process was continued at 160 rpm. Parameters such as pasting temperature (PT), peak viscosity (PV), breakthrough viscosity (BV), holding strength viscosity (HSV), setback viscosity (SBV), and final viscosity (FV) were recorded.

## 2.5. Rheological characterization

### 2.5.1. Static shear test

The static shear tests were carried out using a modular compact rheometer (MCR102, Anton Paar, Austria) on a starch dispersion (12%) using a plate-plate geometry (50 mm diameter), with a gap of 1 mm. The temperature was controlled by a Peltier system (H-PTD200) to prevent water evaporation. The shear rate was varied from 1 to 100 s<sup>-1</sup> at 25 °C and finally, the power law dependence of the apparent viscosity on the shear rate was investigated using the following equation

$$\tau = K \dot{\gamma}^n \quad (2)$$

Where  $\tau$  is the shear stress (Pa),  $\dot{\gamma}$  is the shear rate (s<sup>-1</sup>),  $K$ , the consistency index (Pa.s<sup>*n*</sup>), and  $n$ , the index flow behavior (dimensionless).

### 2.5.2. Frequency sweep

The frequency sweep was undertaken at a strain within the linear viscoelastic region for frequency values ranging from 1 to 100 rad/s at 25 °C. The dependence of  $G'$  and  $G''$  on frequency ( $\omega$ ) was modelled according to the power law depicted in Eqs. 3 and 4:

$$G' = A' \omega^{B'} \quad (3)$$

$$G'' = A'' \omega^{B''} \quad (4)$$

where  $G'$  is the elastic modulus (Pa);  $G''$  is the loss modulus (Pa);  $\omega$  is the frequency (rad s<sup>-1</sup>),  $A'$  and  $A''$  are constants (Pa.s<sup>*B*</sup>);  $B'$  and  $B''$  represent exponential factors. A preliminary strain sweep test was carried out to determine the linear viscoelastic region.

## 2.6. Starch gelatinization

To study the gelatinization behaviours of starch before and after PAW treatment a Differential Scanning Calorimeter (DSC) (mod. Q20, TA Instruments, Germany) was used according to the method described by X. Yan et al. (2019) with slight modifications. In detail, starch samples were weighed in an aluminum pan (Tzero Pan) and distilled water was added with the help of a micro syringe to obtain a starch: water suspension of 1:3. The pan was hermetically sealed with Tzero Hermetic Lid and allowed to equilibrate for 24h. The sample pans were heated from 25 to 110 °C at the rate of 10 °C/min, then, onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), conclusion temperature ( $T_c$ ), and enthalpy of gelatinization ( $\Delta H_{gel}$ ) were determined using TA instrument Universal Analysis 200 software.

## 2.7. Gel hydration properties

The swelling power (SP) and water solubility index (WSI) were analyzed according to Y. Yan, Feng, Shi, Cui, and Liu (2020) method. Briefly, 0.5 g ( $W_i$ ) of the starch sample was mixed in 25mL distilled water and subjected to 90 °C for 30 min in the water bath. After cooling, the sample was centrifuged for 20 min at 3000 rpm. The supernatant was oven-dried overnight at 110 °C. Gel residues ( $W_r$ ) and dried supernatants ( $W_s$ ) were weighed to calculate the SP and WSI parameters as follows:

$$SP \text{ (g/g)} = W_r / (W_i - W_s) \quad (5)$$

$$WSI \text{ (g/g)} = W_s / W_i \quad (6)$$

## 2.8. Gel strength

Starch gel strength was determined using a Texture Analyzer (TA-HDi, Stable Micro Systems, Surrey, UK) according to Martins, Gutkoski, and Martins (2018) with slight modifications. The starches at a 12% (m/v) suspension were gelatinized in a boiling bath for 30 min. Then, the gelatinized starches were placed in a 30 × 30 mm cylindrical mould

and cooled at 4 °C for 24 h. Cooled gels were removed from the cylindrical mould and kept at room temperature (25 °C) for 1 h; then the gels were analyzed using a cylindrical probe (P/50), 20% of compression, pre-test velocity of 2 m·s<sup>-1</sup>, velocity of test 2 m·s<sup>-1</sup> and post-test speed of 3 m·s<sup>-1</sup>. Maximum gel strength (N) was measured using 4 replicates from each sample.

## 2.9. Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectra were acquired using a Tensor 27 TM FTIR spectrometer system (Bruker Optics, Ettlingen, Germany), equipped with an interferometer Rocksolid and a DigiTect detector system, and attenuated total reflectance accessory (ATR, PIKE Technologies, Madison, WI, USA). A small amount of sample was placed on the ATR surface, and by using a pressure clamp a thin layer was obtained. The spectrum of each sample was achieved through the average of 64 scans with a speed of 10 kHz in a range from 4000 to 600 cm<sup>-1</sup>, with 4 cm<sup>-1</sup> of spectral resolution. For each sample, 5 replicates were performed using the air as background, measured in the same instrumental conditions (25 °C).

## 2.10. Statistical Analysis

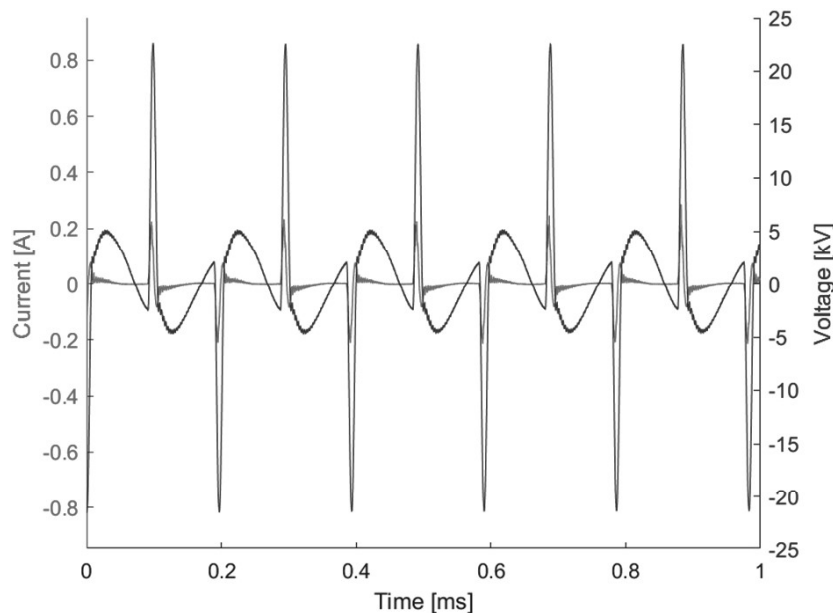
Significant differences between the means of the parameters of native and treated samples (within the same starch) were evaluated through the Student-*t* test, (*p-level* > 0.05). The homogeneity of variance was evaluated by the Levene test (IBM-SPSS 20, USA). Concerning the FT-IR spectra, the regions between 2410 and 2260 cm<sup>-1</sup>, were deleted as it contains no useful chemical information, but only instrumental noise information. Subsequently, absorbance spectra were smoothed (Savitzky-Golay method; polynomial order: 2; smoothing points: 15) to reduce noise, and subsequently pre-processed by multiplicative scatter correction (MSC), and then mean centered (MC). PCA analysis was used as an explorative technique to group samples as a function of starch type

or treatment. The spectral elaboration was carried out by using PLS Toolbox for Matlab2018a ®.

### 3. Results

#### 3.1. Characterization of plasma-activated water

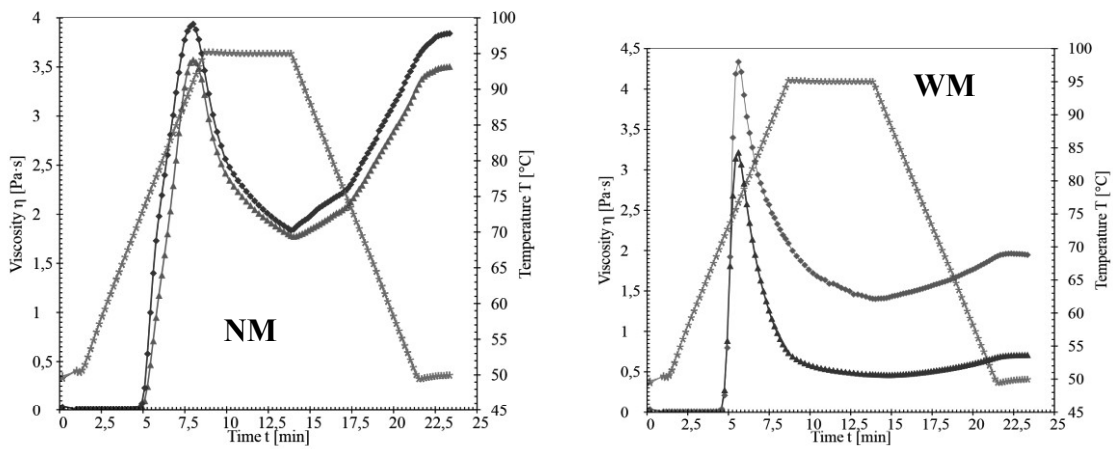
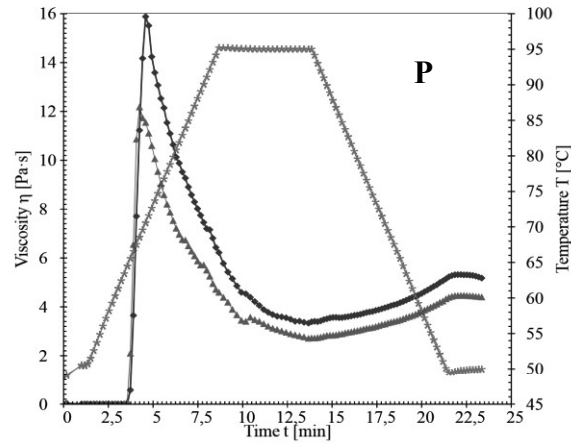
The average discharge power was  $167.12 \pm 12.42$  W, and a typical current and voltage waveform is reported in Fig. 1 and Table 1; the concentrations of the main long-lived species are reported, highlighting the production of hydrogen peroxide, nitrites, and a reduction of pH.



**Fig. 1.** Voltage and current as a function of time

#### 3.2. Pasting properties

The pasting curves of potato (P), normal (NM), and waxy maize (WM) are presented in Fig. 2, and their pasting parameters of peak temperature (PT, °C), peak viscosity (PV, Pa•s), breakdown viscosity (BV, Pa•s), holding strength viscosity (HSV, Pa•s), setback viscosity (SBV, Pa•s) and final viscosity (FV, Pa•s)) are reported in Table 2.



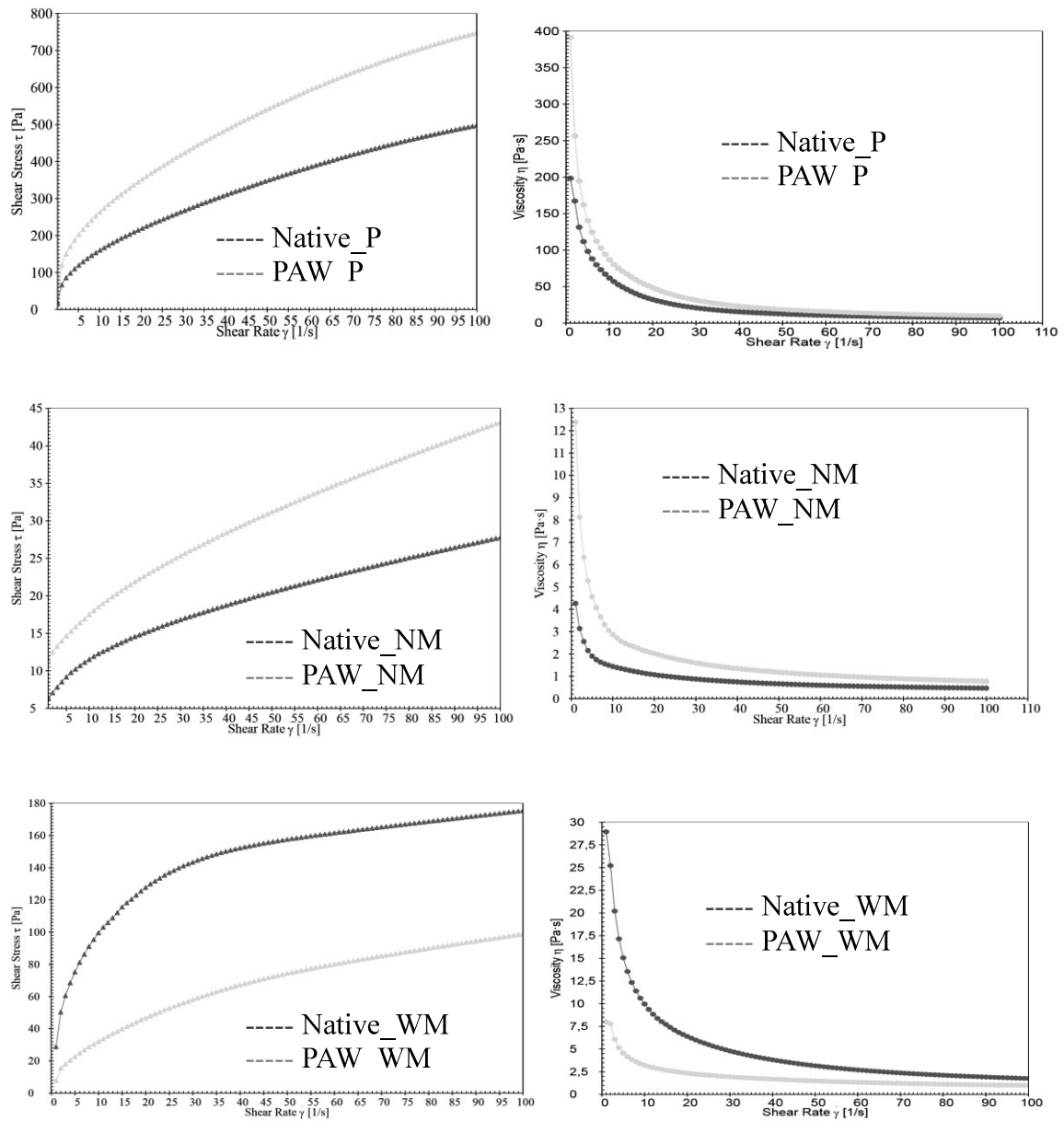
**Fig. 2.** Pasting curves of P (potato), NM (normal maize), and WM (waxy maize). Green, blue, and red lines refer to the untreated sample, PAW treated sample, and temperature, respectively.

For the P sample, statistical analysis revealed that PAW-treated samples are characterized by significantly higher values for all parameters compared to the native one, except for the SBV parameter. Similarly, except for PT, other values were increased for the NM sample, although differences were found significant only for BV. On the other hand, PAW treatment significantly ( $P < 0.05$ ) reduced the value of PV, HSV, SBV, and FV in WM compared to the native one.

### 3.3. Rheological properties

#### 3.3.1. Static shear test

The flow properties of native and PAW-treated P, NM, and WM starch pastes are shown in Fig.3 and Table 3.



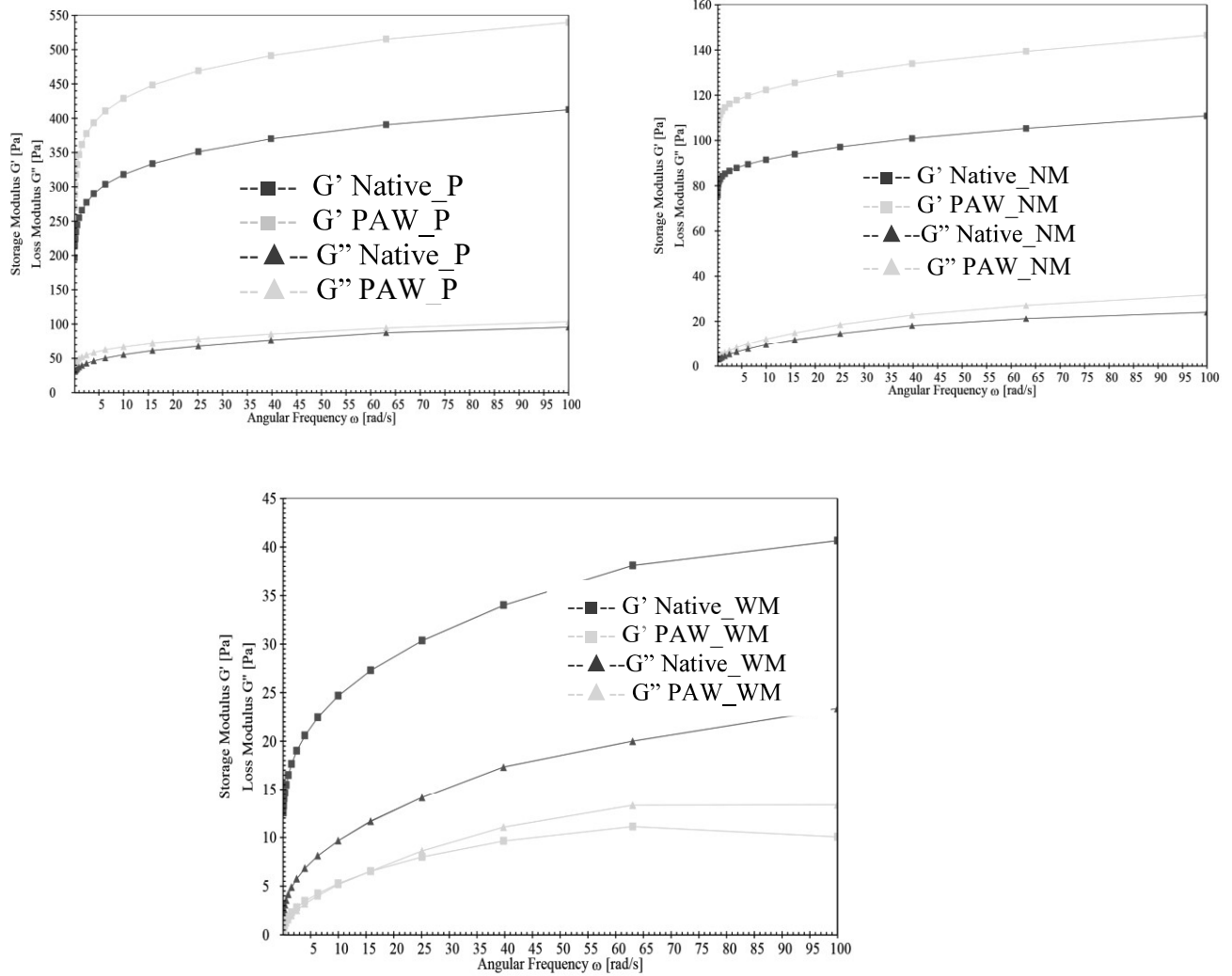
**Fig.3.** Effect of PAW on the steady shear behavior of starches. P (potato), NM (normal maize), and WM (waxy maize).

In general, even if the consistency coefficient ( $k$ ) and the flow index ( $n$ ) were different for the three analyzed starches, the flow behaviors of all three samples were typical of

pseudo-plastic fluids (shear thinning region) because  $n < 1$ . As depicted in Table 3, the correlation coefficients ( $R^2$ ) was 0.95–0.99 for all samples, indicating a satisfying fit. PAW treatment resulted in a substantial and significant ( $P < 0.05$ ) increase in the viscosity value ( $K$ ) and a decrease of the flow behavior index ( $n$ ) between native and PAW-treated samples for P and NM samples. On the contrary, the viscosity of WM starch was significantly decreased by the PAW.

### 3.3.2. Frequency sweep

The results of the frequency sweep test performed on the samples are shown in Fig.4. All untreated starches showed a dominant elastic or solid-like behavior since all had  $G'$  higher than  $G''$  and  $G''/G' < 1$ . When P and NM were subjected to PAW,  $G'$  and  $G''$  were increased compared to the native ones, probably due to increased cross-linking and augmentation between the starch chains by reduction of hydroxyl from the glucose side. A similar result was observed by (K. Zhang et al., 2022). On the contrary, WM treated with PAW showed reduced  $G'$ , while  $G''$  increased compared to the native one, consequently, the  $G''/G'$  ratio turned towards values higher than one when the frequency ( $\omega$ , rad/s) increased, and liquid-like response paste was observed.



**Fig.4.** Curves of storage modulus ( $G'$ , Pa) and loss modulus ( $G''$ , Pa), obtained in the oscillatory regime as a function of the frequency ( $\omega$ , rad/s).

Power law parameters calculated from the results of the frequency sweep test (equations 3 and 4) of starch samples are indicated in Table 4. For dynamic viscoelastic characteristics, the B value is related to the hardness and nature of the gel (Chaiwat et al., 2016; Khondkar, Tester, Hudson, Karkalas, & Morrow, 2007; Yoneya, Ishibashi, Hironaka, & Yamamoto, 2003). According to Khondkar et al. (2007), the higher the (B) value, the weaker and depolymerized gel, but the lower the B the stronger the gel. As a result, PAW-treated P and NM samples had higher viscosity (lower B) values and higher (A) values compared to the native one, which might be due to the cross-linked starch

(reinforcement of starch molecules) (Kumar & Khatkar, 2017). However, the gel of waxy maize was not as strong as the gel of potato and normal maize.

### 3.4. Starch Gelatinization

The gelatinization profiles of starches were analyzed before and after PAW treatment and the results are represented as onset ( $T_o$ ), peak ( $T_p$ ) end ( $T_e$ ) temperatures, and enthalpy of gelatinization ( $\Delta H$ ), depicted in Table 5. According to Van Hung and Morita (2005) and Gunaratne and Hoover (2002), variations in gelatinization temperatures can occur due to the molecular structure of amylopectin, lipid content, size, presence of phosphorus, amylose and amylopectin amount, origin and environmental conditions.

$\Delta H$  indicates the crystallinity in terms of quantity and quality, and it is associated with the loss of molecular order within the granule (Zhu & Cui, 2020), while gelatinization temperature measures the crystal quality.

In both P and NM samples, PAW treatment led to an increase in some values related to the gelatinization temperatures and the enthalpy. In P starch, an increase was observed for  $T_o$ ,  $T_e$ , and  $\Delta H$  from  $61.14 \pm 0.04$  to  $77.44 \pm 0.42$ , and  $13.18 \pm 0.05$  to  $63.82 \pm 0.14$ ,  $67.59 \pm 0.18$ ,  $79.32 \pm 0.29$  and  $14.92 \pm 0.19$ , respectively. Specifically, the  $T_e$  and  $\Delta H$  of normal maize starch were increased from  $85.36 \pm 0.83^\circ\text{C}$  and  $11.46 \pm 0.36\text{J/g}$  to  $86.6 \pm 0.45^\circ\text{C}$  and  $12.58 \pm 0.29\text{J/g}$  respectively. On the other side, gelatinization parameters including  $T_o$ ,  $T_p$ ,  $T_e$ , and the  $\Delta H$  of PAW-treated WM were decreased significantly ( $P < 0.05$ ) compared to the native one.

### 3.5. Gel hydration properties and hardness

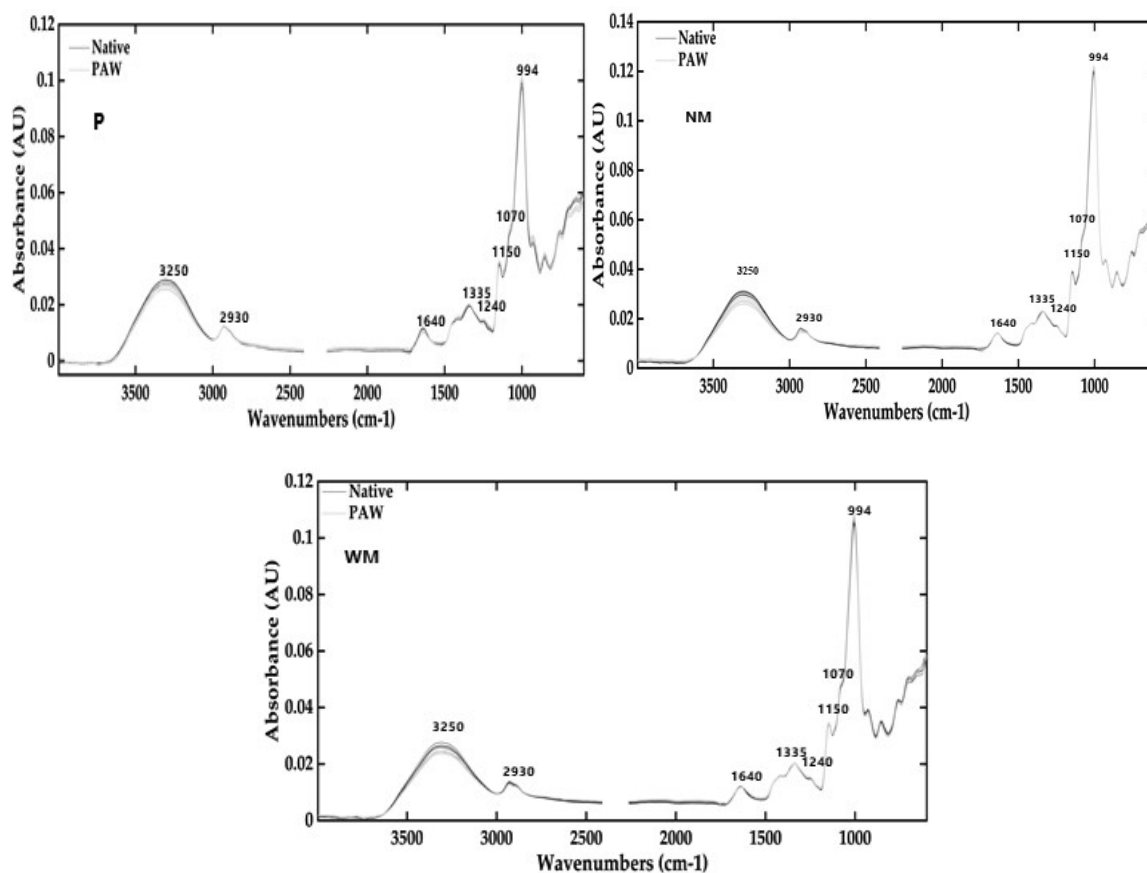
The effect of PAW treatment on the gel hydration properties namely Swelling Power (SP) and Water Solubility Index (WSI) at  $90^\circ\text{C}$  and on the gel hardness is reported in Table 6. PAW treatment is found to significantly ( $p < 0.05$ ) change the SP value of

starches, from  $11.98 \pm 1.80$ ,  $15.07 \pm 0.91$  and  $12.98 \pm 0.23$  for native WM, NM, and P, to  $22.49 \pm 6.86$ ,  $16.52 \pm 0.23$  and  $18.07 \pm 0.61$  in PAW treated samples, respectively.

The water solubility index (WSI) of starches treated with PAW was higher than the native ones, but in a significant way only for NM and WM. Concerning gel hardness, similarly to other parameters, a different behavior was observed in relation to the types of starch. Increased hardness was detected for P and NM starches after PAW treatment, while PAW applied on WM starch caused a decrease.

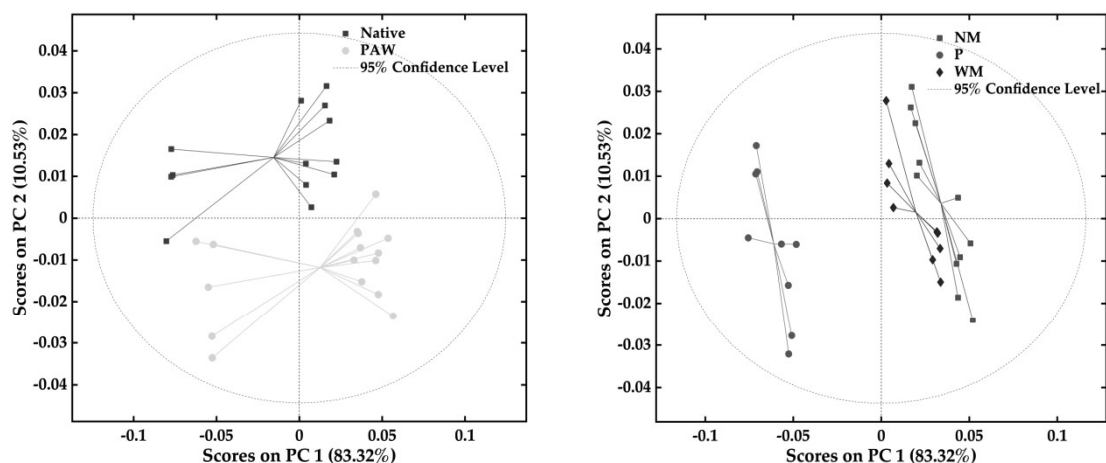
### 3.6.FTIR

Pre-processed spectra by smoothing and MSC of all replicas are shown in Fig.5. For all three types of starch, the main spectral features are identified at similar wavenumbers. Particularly, the range of  $3000\text{--}3500\text{ cm}^{-1}$  is related to O–H of hydroxyl groups in adsorbed water (stretching vibration), the characteristic two peaks at about  $2930\text{ cm}^{-1}$  were attributed to C–H deformation vibration of glucose element, the peak at  $1640\text{ cm}^{-1}$  has been considered to relate to the bending vibration of the O–H in water and associated to the non-crystalline region of starch (amorphous region). Furthermore, the peaks at about  $1150$ ,  $1070$ , and  $994\text{ cm}^{-1}$  corresponded to asymmetric stretching (C–O–C), stretching (C–O), and bending (C–O–H) vibration, respectively (Sifuentes-Nieves et al., 2021; Srangsomjit, Bovornratanaraks, Chotineeranat, & Anuntagool, 2022; K. Zhang et al., 2022).

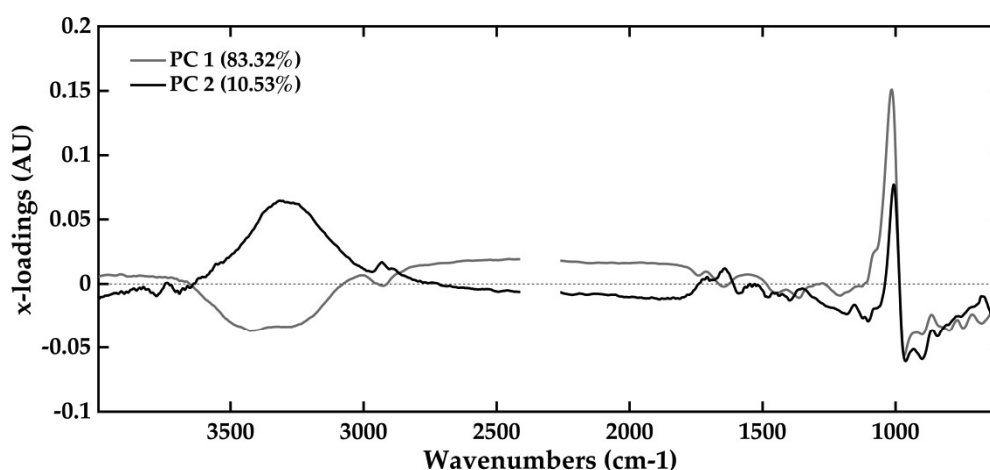


**Fig.5.** FTIR spectra of P (potato), NM (normal maize ), and WM (waxy maize) starch samples subjected to PAW. P (potato), NM (normal maize), and WM (waxy maize).

PCA was used as an explorative technique to group samples as a function of the starch type and plasma treatment. The obtained score plots are shown in Fig.6. The potato starch samples (P) were separately grouped from the other two along the PC1 (83.32%). Furthermore, a clear separation between native and treated samples (five replicas for each sample) was mainly observed along PC2 (10.53%) regardless of starch type. Evaluating the X-loading plot (Fig.7), it was possible to assert that the discrimination along PC2 is mainly due to the region from 3000 to 3500  $\text{cm}^{-1}$  and the peak around 994  $\text{cm}^{-1}$ .



**Fig.6.** Score plots obtained by the PCA developed considering all the FT-IR spectra



**Fig.7.** X-loadings of the first two components obtained by the PCA developed considering all the FT-IR spectra

#### 4. Discussions

As observed in Table 2, P starch showed characteristics substantially different compared to the two maize ones, specifically, a lower PT, and higher PV, HSV, and BV while similar SBV, concerning pasting behaviour, high consistency coefficient (K) measured by rheometric measurements compared to the maize ones, as already observed by (Mishra & Rai, 2006),  $G''/G' < 1$  paralleled by lower, onset, peak, and end temperature of gelatinization. These results are consistent with literature reports (Zhu & Cui, 2020).

Indeed, potato starches start developing viscosity at a lower temperature compared to cereal ones due to the presence of negatively charged phosphate groups and higher granule size (Waterschoot, Gomand, Fierens, & Delcour, 2015; Zaidul et al., 2007), while the lower rheological and pasting properties observed in NM compared to P starch during frequency sweep and pasting might be partly attributed to the restricted granular swelling (lipids amylose complexes reinforce the interactions of starch molecules), leaching out of amylose and smaller granular size (Zhu & Cui, 2020).

On the other hand, as confirmed in the present study (Table 2), starches from WM have been observed to show lower breakdown (BV), lower setback (SBV), and pasting temperature (PT) compared to their regular counterparts (Schirmer, Höchstätter, Jekle, Arendt, & Becker, 2013). Also, the same authors state that waxy starches have low thermal stability and the swollen starch granules are susceptible to thermal and mechanical breakdown, corresponding to large breakdown viscosities. Moreover, the very low amylose content in WM (<1%) corresponds to limited amylose leaching and less re-association of starch molecules after cooling. On account of their lower ability to form a gel network, the hardness of the gel is also very low, as shown in Table 6 and already reported by (Waterschoot et al., 2015).

Besides the differences observed among the three native starches which confirm previous literature reports, the finding of the present study shows that PAW treatment affected differently the investigated characteristics. In particular, for most of the investigated parameters, PAW affected similarly P and NM starches, and contrarily, the WM sample. PAW imparted higher pasting viscosity to the P and NM starches, higher  $G'$  and  $G''$ , enhancing the consistency coefficient ( $k$ ) and reducing flow behavior indices ( $n$ ), increasing gelatinization parameters, and reducing  $\Delta H$ . These differences might be explained by the reduction of hydroxyl groups in the starch structure due to the reactive

species in PAW, such as  $O_3$ , an entanglement of the starch structure which improved the ability of starch to combine with water (Banura, Thirumdas, Kaur, Deshmukh, & Annapure, 2018; Li et al., 2013; Wang & Wang, 2003).

The increase observed in gelatinization parameters for P and NM suggests that important changes occurred in the amylose helical configuration restricting the gelatinization due to the stability of its crystals (Alimi & Workneh, 2018), and an increased intermolecular bond between the starch chains (K. Zhang et al., 2022). The increase in gelatinization parameters and enthalpy was also observed by (Alimi & Workneh, 2018), and was attributed to an improved intermolecular interaction between amylose and amylopectin, reducing the mobility of starch chains in the amorphous lamellae that was followed by a higher thermal energy requirement.

On the other hand, the behaviour of physical properties of WM upon PAW treatment was the opposite for many parameters: a decrease in pasting viscosity (Table 2), consistency coefficients (k),  $G'$  (Table 3 and Table 4), gelatinization temperature and  $\Delta H$  (Table 5) and gel hardness (Table 6) were observed, while  $G''$  increased compared to the native sample, consequently, the values of  $G''/G' > 1$  when the frequency ( $\omega$ , rad/s) increased. The main difference between WM and other starches is the content of amylose, which is almost absent in WM. Therefore, considering that PAW composition and exposure time was the same, the observed differences are attributable to this aspect. These results might be linked to the dissociation (rupture of glycosidic bonds) of double helices of amylopectin and reduced granule crystallinity of PAW-treated starch (Banura et al., 2018; Lv et al., 2018; Zhou, Yan, Shi, & Liu, 2018). A similar decrease was observed in waxy maize and also in other cereals upon plasma treatment (Thirumdas, Deshmukh, & Annapure, 2016; Y. Yan et al., 2020). The depolymerization effect could be due to the cleaving of the glycosidic bonds starch by PAW oxidative species, such as hydrogen

peroxide and ozone, and triggered by the acidic environment, which further changed the short-range order of the starch molecule (Deeyai, Suphantharika, Wongsagonsup, & Dangtip, 2013; Misra, Pankaj, Segat, & Ishikawa, 2016; Zhou et al., 2018).

Water intake during treatment is measured by gel hydration and depends on the loss of amylopectin crystalline structure and amylose leaching out from starch granules (Chaple et al., 2020). Initial values related to the hydration properties of the starches were different due to the lipids complexed with amylose in NM (may inhibit granular swelling), structural integrity, phosphorus groups present in P, and a negligible amount of amylose in WM (Castanha, da Matta Junior, & Augusto, 2017; Zhu & Cui, 2020). However, the swelling power and solubility of all starches treated with PAW increased compared to the untreated samples, as indicated in Table 6.

SP is related to hydration, interactions between starch molecules, intermolecular bonds, and crystalline structure (S. Singh, Singh, Isono, & Noda, 2010; Zhang et al., 2020). The increase of this parameter might be due to hydrolysis phenomena due to the acidity present in the PAW, damage to the starch granule surface, and leaching out of starch fragments caused by PAW reactive particles, that, in turn, increased starch hydrophilicity and solubility (Aaliya et al., 2022; Sun et al., 2022; X. Yan et al., 2019). Considering the extent of the variation, it is noticeable that values were remarkably increased (doubled) in WM after treatment compared to the untreated sample, while for P and NM, the increase was more limited, and therefore, WM seemed to be more affected. This result should be confirmed by evaluating the etching effect (through SEM).

The absorption bands obtained by FTIR measurements of the treated and untreated starches were mostly overlapping. However, a clear reduction in peak height of the O–H stretching region ( $3250\text{ cm}^{-1}$ ) was observed compared to the native in all PAW-treated starches as indicated in Fig.5, suggesting that the active species of plasma changed the

starch ability to bind water. Similar results were achieved also by (Ge et al., 2022; Akua Y Okyere, Boakye, Bertoft, & Annor, 2022). Also, the absorbance at 1640 cm<sup>-1</sup> (tightly bound water in the starch,) was weakened by the PAW reactive species, especially for the potato starch, suggesting that treatment could promote the removal of some water molecules from the starch. Similar results were reported by (Hernandez-Perez et al., 2021; Sun et al., 2022) for a different kind of starch treated by cold plasma.

## **5. Conclusions**

This research investigated the effect of PAW treatment on the rheological, thermal, pasting, and swelling behaviour of three starches characterized by different botanical origins and different compositional and structural properties. Observed modifications can be attributed to the synergistic effect of NO<sub>3</sub>, NO<sub>2</sub>, O<sub>3</sub>, acidic environment, and other reactive species of PAW, showing that cereal and tuber/roots starches can be successfully modified by PAW, resulting in a promising strategy for starch modification as “green” alternative for existing methods in the food industry. Results obtained in this study, however, show that the degree of modification is strongly dependent on the starch type (botanical, amylose, and amylopectin content). Therefore, process optimization based on the specific substrate appears necessary for obtaining tailored functionality. Further research is needed to better understand the variations related to the starches-water interactions, and the effect on starch crystallinity and microstructure, also in terms of assessment of treated starch functionality in a real formulated food product, and its interaction with other food constituents.

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## List of tables

**Table 1.** Concentrations of NO<sub>2</sub><sup>-</sup>, H<sub>2</sub>O<sub>2</sub> and pH in PAW and native samples

Sample	NO <sub>2</sub> <sup>-</sup> [mg/l]	H <sub>2</sub> O <sub>2</sub> [mg/l]	pH
DW	0	0	6.12 ± 0.05
PAW	13.98 ± 3.47	1.18 ± 0.06	3.48 ± 0.08

**Table 2.** Pasting parameters of native and PAW treated potato (P), normal maize (NM), and waxy maize (WM)

Starches		PT(°C)	PV(Pa.s)	HSV(Pa.s)	BV(Pa.s)	SBV(Pa.s)	FV(Pa.s)
P	Native	64.19±0.68 <sup>b</sup>	12.34±0.19 <sup>b</sup>	2.73±0.01 <sup>b</sup>	9.61±0.20 <sup>b</sup>	1.73±0.14	4.46±0.14 <sup>b</sup>
	PAW	65.05±0.60 <sup>a</sup>	15.78±0.9 <sup>a</sup>	3.26±0.10 <sup>a</sup>	12.52±0.03 <sup>a</sup>	1.9±0.07	5.16±0.03 <sup>a</sup>
NM	Native	75.54±0.95 <sup>a</sup>	3.67±0.19	1.78±0.04	1.88±0.15 <sup>b</sup>	1.78±0.13	3.57±0.17
	PAW	71.72±0.22 <sup>b</sup>	3.85±0.17	1.83±0.02	2.02±0.15 <sup>a</sup>	1.92±0.14	3.75±0.16
WM	Native	70.72±0.20	4.25±0.12 <sup>a</sup>	1.37±0.03 <sup>a</sup>	2.87±0.10	0.55±0.02 <sup>a</sup>	1.93±0.04 <sup>a</sup>
	PAW	70.63±0.25	3.22±0.18 <sup>b</sup>	0.46±0.07 <sup>b</sup>	2.75±0.13	0.24±0.03 <sup>b</sup>	0.71±0.10 <sup>b</sup>

Values are means ± SD of three replicates. Means with different letters in the same column and for the same sample indicate significant differences (P<0.05). PT: peak temperature, PV: peak viscosity, BV: breakdown viscosity, HSV: holding strength viscosity, SBV: setback viscosity, FV: final viscosity.

**Table 3.** Values of consistency coefficients (K) and flow behavior indices (n) of native and PAW-treated potato (P), normal maize (NM), and waxy maize (WM)

Sample		K (Pa.s <sup>n</sup> )	n	R <sup>2</sup>
P	Native	47.91±0.12 <sup>b</sup>	0.50±0.03 <sup>a</sup>	0.99
	PAW	88.74±1.14 <sup>a</sup>	0.44±0.02 <sup>b</sup>	0.99
NM	Native	11.7±0.64 <sup>b</sup>	0.46±0.01 <sup>a</sup>	0.99
	PAW	58.56±2.42 <sup>a</sup>	0.24±0.01 <sup>b</sup>	0.95
WM	Native	6.85±0.59 <sup>a</sup>	0.38±0.01	0.99
	PAW	4.63±0.18 <sup>b</sup>	0.39±0.01	0.99

Values are means ± SD of three replications. Means with different letters in the same column and for the same sample differ significantly (P<0.05).

**Table 4.** Effect of PAW treatment on the viscoelastic properties of native and PAW-treated potato (P), normal maize (NM) and waxy maize (WM)

Sample		Storage Modulus ( $G' = A'\omega^{B'}$ )			Loss Modulus ( $G'' = A''\omega^{B''}$ )		
		A' (Pa.s <sup>B'</sup> )	B'	R <sup>2</sup>	A'' (Pa.s <sup>B''</sup> )	B''	R <sup>2</sup>
P	Native	281.62±2.29 <sup>b</sup>	0.10±0.01	0.99	40.57±0.91 <sup>b</sup>	0.18±0.01	0.97
	PAW	344.65±8.85 <sup>a</sup>	0.09±0.01	0.99	50.82±0.40 <sup>a</sup>	0.14±0.10	0.96
NM	Native	84.03±0.70 <sup>b</sup>	0.049±0.01	0.94	4.06±1.09	0.39±0.02	0.98
	PAW	112.64±3.63 <sup>a</sup>	0.047±0.01	0.95	5.41±1.20	0.38±0.03	0.98
WM	Native	16.70±1.12 <sup>a</sup>	0.19±0.01 <sup>b</sup>	0.98	4.22±0.85 <sup>a</sup>	0.37±0.01 <sup>b</sup>	0.99
	PAW	2.21±0.01 <sup>b</sup>	0.36±0.01 <sup>a</sup>	0.96	1.87±0.38 <sup>b</sup>	0.45±0.03 <sup>a</sup>	0.97

Values are means ± SD. Means with different letters in the same column for the same sample differ significantly (P<0.05). G': elastic modulus, G'': loss modulus;  $\omega$ : frequency, A' and A'' are constants, and B' and B'' represent exponential factors.

**Table 5.** Effect of PAW on gelatinization temperatures and change of enthalpy of native and PAW treated potato (P), normal maize (NM) and waxy maize (WM)

Samples		To (°C)	Tp (°C)	Te (°C)	ΔH (J/g)
P	Native	61.14±0.04 <sup>b</sup>	67.45±0.20	77.44±0.42 <sup>b</sup>	13.18±0.05 <sup>b</sup>
	PAW	63.82±0.14 <sup>a</sup>	67.59±0.18	79.32±0.29 <sup>a</sup>	14.92±0.19 <sup>a</sup>
NM	Native	68.66±0.14	73.56±0.20	85.36±0.83 <sup>b</sup>	11.46±0.36 <sup>b</sup>
	PAW	68.15±0.07	73.97±0.11	86.6±0.45 <sup>a</sup>	12.58±0.29 <sup>a</sup>
WM	Native	67.61±0.17 <sup>a</sup>	73.05±0.08 <sup>a</sup>	83.91±0.16 <sup>a</sup>	14.43±0.35 <sup>a</sup>
	PAW	65.86±0.02 <sup>b</sup>	70.87±0.12 <sup>b</sup>	80.77±0.91 <sup>b</sup>	9.36±0.24 <sup>b</sup>

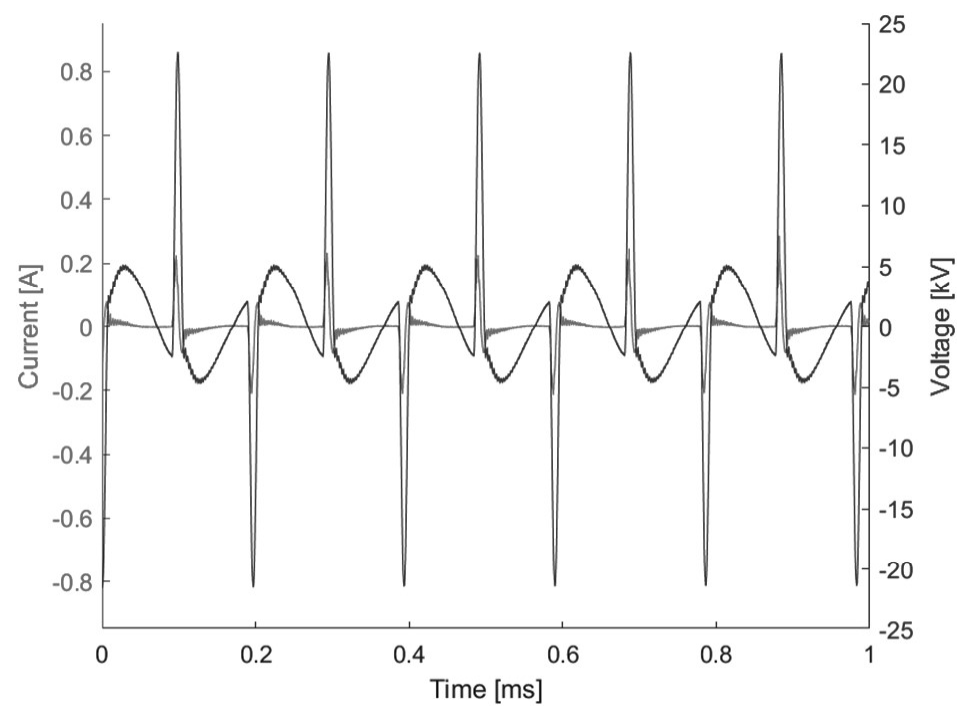
Values are means ± SD of three replicates. Means with different letters in the same column and for the same sample differ significantly (P<0.05). To (onset temperature), Tp (peak temperature), Te (end temperature), and ΔH (the enthalpy of gelatinization).

**Table 6.** Influences of PAW treatment on gel hydration and gel strength of native and PAW treated potato (P), normal maize (NM) and waxy maize (WM)

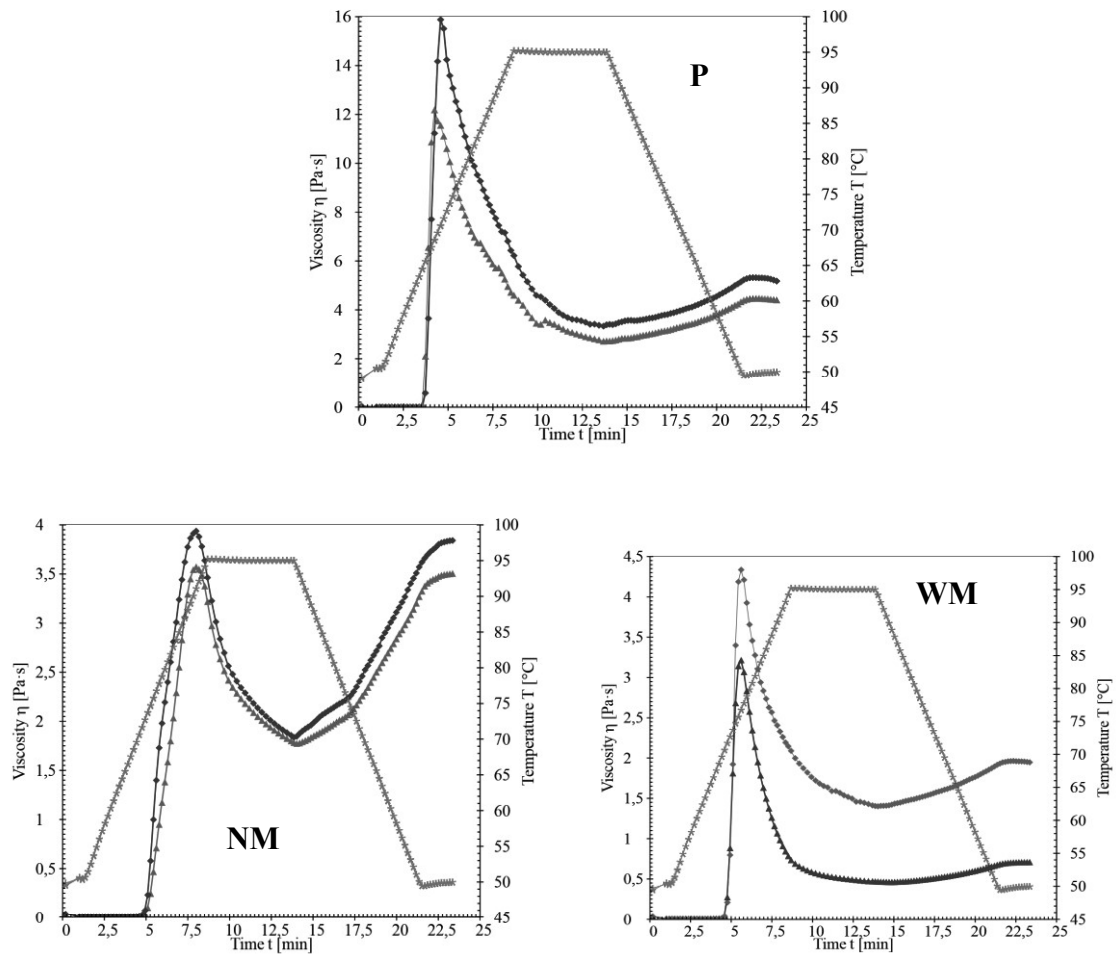
Starches		SP (g/g)	WSI (g/g)	Hardness (N)
P	Native	12.98±0.23 <sup>b</sup>	6.23±0.53	4.26±0.51 <sup>b</sup>
	PAW	18.07±0.61 <sup>a</sup>	6.45±0.37	6.90±0.44 <sup>a</sup>
NM	Native	15.07±0.91 <sup>b</sup>	10.85±1.29 <sup>b</sup>	4.67±0.10 <sup>b</sup>
	PAW	16.52±0.23 <sup>a</sup>	12.78±1.74 <sup>a</sup>	5.25±0.23 <sup>a</sup>
WM	Native	11.98±1.80 <sup>b</sup>	22.52±3.86 <sup>b</sup>	0.57±0.05 <sup>a</sup>
	PAW	22.49±6.86 <sup>a</sup>	44.88±2.85 <sup>a</sup>	0.44±0.02 <sup>b</sup>

Values are means ± SD. Means with different letters in the same column and for the same sample differ significantly (P<0.05). SP (Swelling power) and WSI (Water Solubility Index).

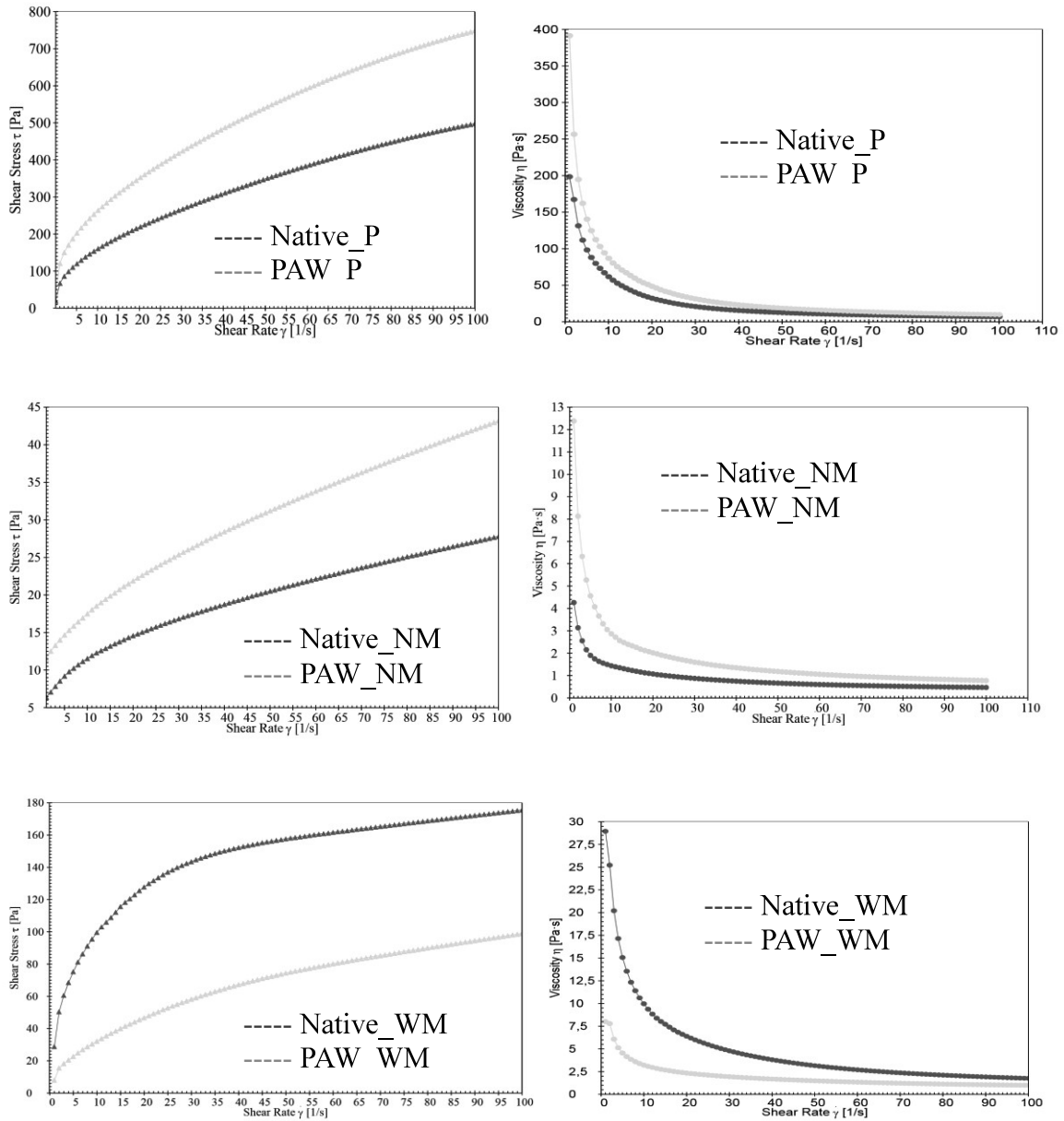
**Figure 1.** Voltage and current as a function of time



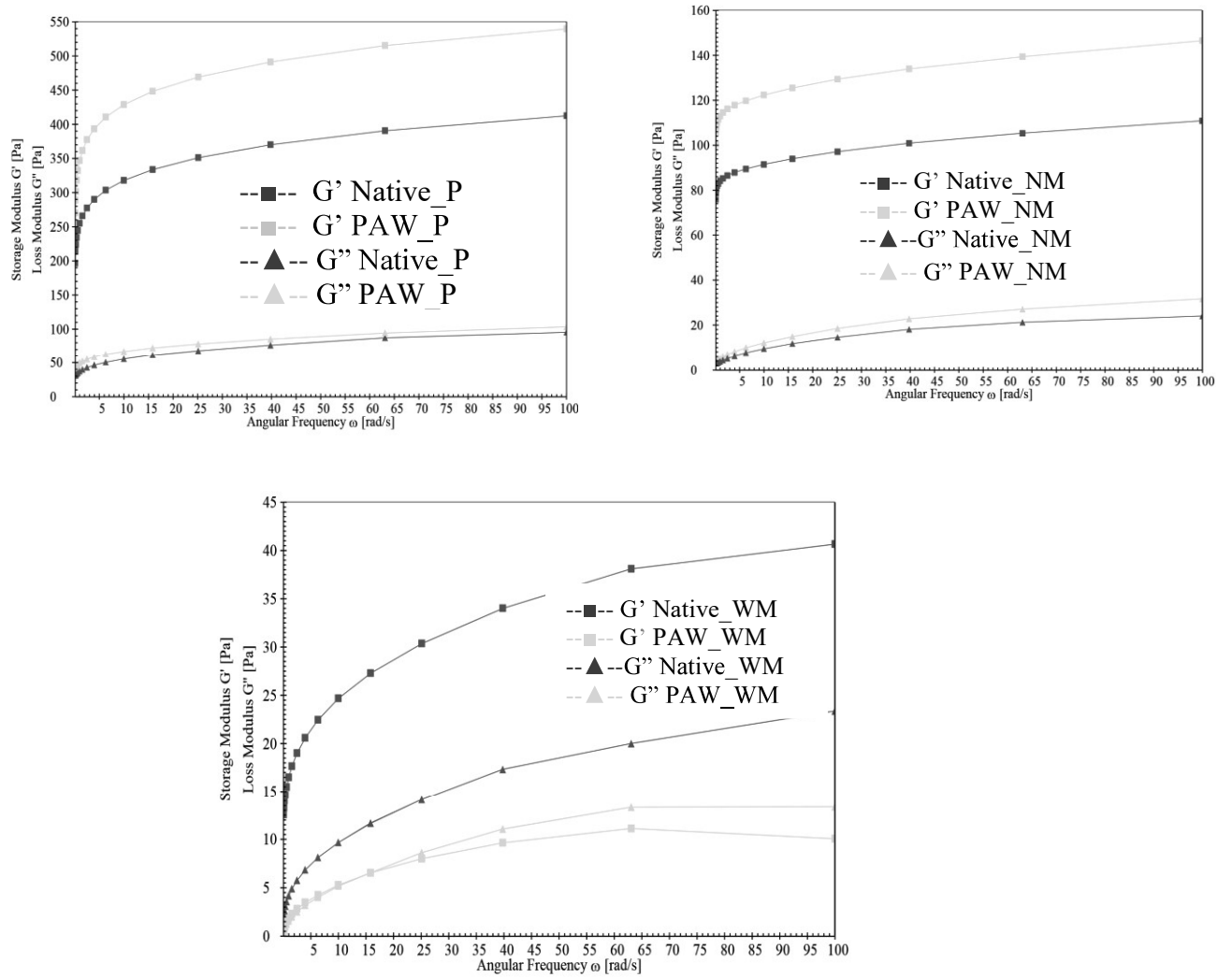
**Figure 2.** Pasting curves of P (potato), NM (normal maize), and WM (waxy maize). Green, blue, and red lines refer to the untreated sample, PAW treated sample, and temperature, respectively.



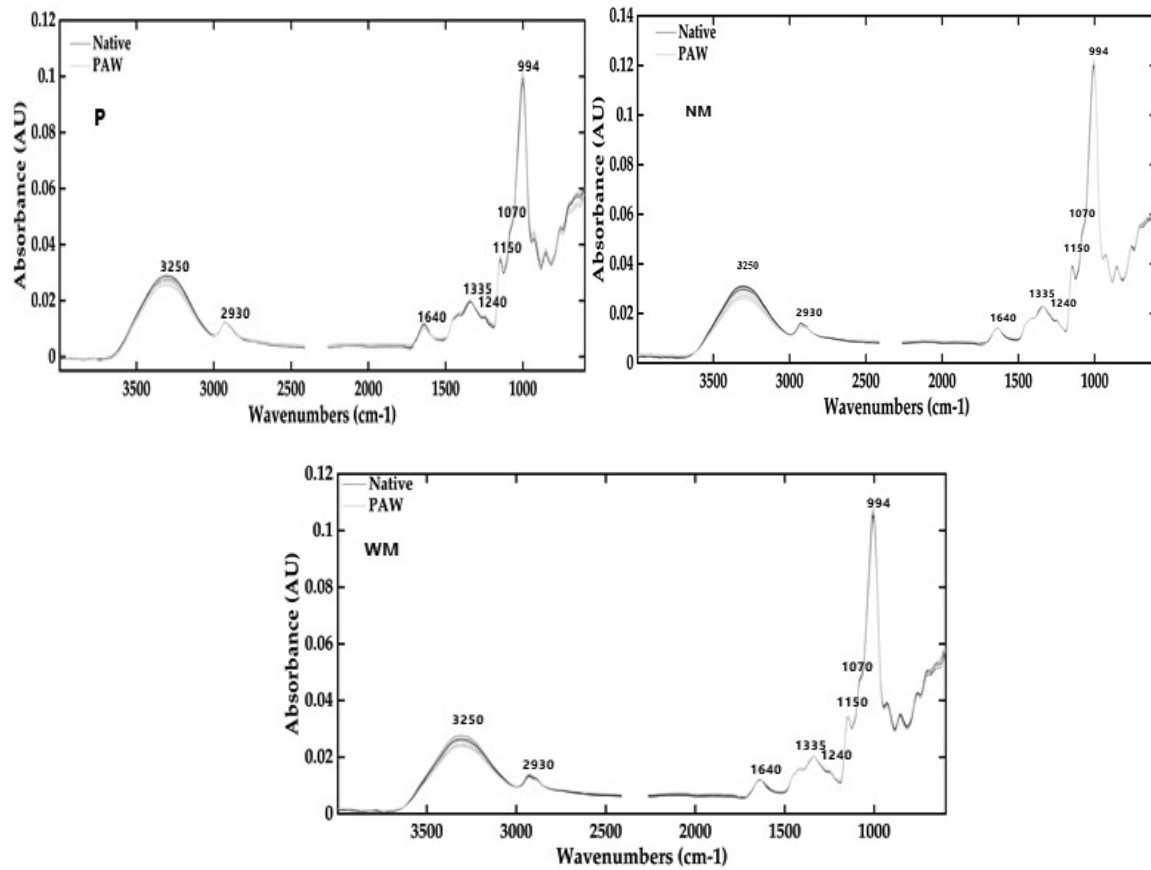
**Figure 3.** Effect of PAW on the steady shear behaviour of starches. P (potato), NM (normal maize), and WM (waxy maize).



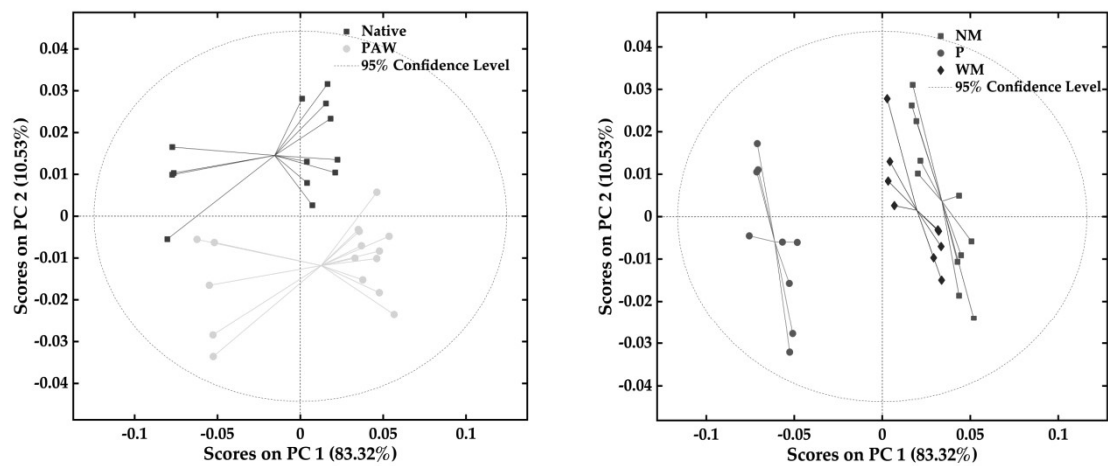
**Figure 4.** Curves of storage modulus ( $G'$ , Pa) and loss modulus ( $G''$ , Pa), obtained in the oscillatory regime as a function of the frequency ( $\omega$ , rad/s).



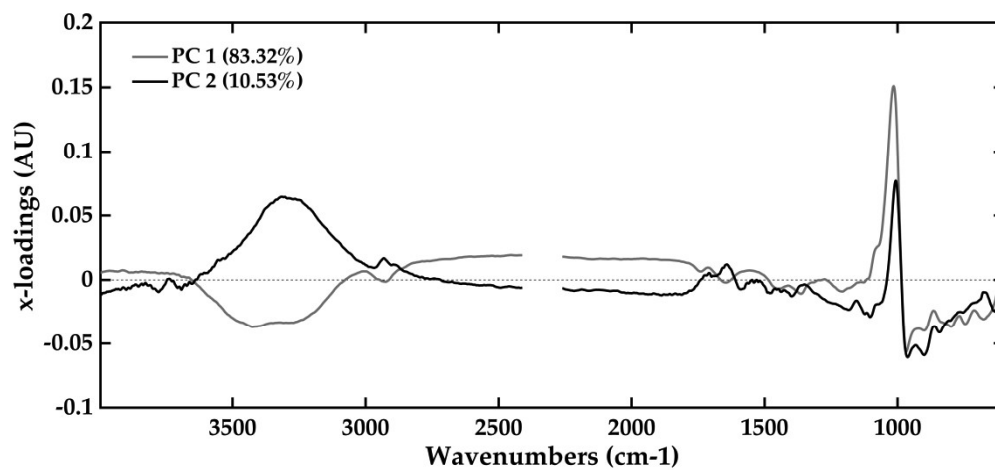
**Figure 5.** FTIR spectra of P (potato), NM (normal maize ), and WM (waxy maize) starch samples subjected to PAW.



**Figure 6.** Score plots obtained by the PCA developed considering all the FT-IR spectra



**Figure 7.** X-loadings of the first two components obtained by the PCA developed considering all the FT-IR spectra



### **Declaration of Competing Interest**

The authors declare that they have no known competing interests