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Plasma-activated water (PAW) and annealing for the modification of potato starch: Effects on sorption isotherms, thermodynamic and gelatinization kinetics of potato starch

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ABSTRACT

Chemical modifications of starch can be laborious and often require significant amounts of chemicals and solvents. Therefore, it has become use of modifications like plasma-activated water (PAW), which is considered an environmentally friendly technology. The aim of this study was to evaluate the effect of PAW, alone or combined with annealing (ANN) on the techno-functional properties, sorption isotherms and thermodynamic characteristics of potato starch. PAW was generated by subjecting distilled water to a corona discharge with a voltage of 15 kV and a fixed frequency of 5 kHz for 1 min. ANN was obtained by incubating starch with distilled water (DW-ANN) or PAW (PAW-ANN) for 4 h at 55 °C. The moisture sorption and the thermodynamic properties of the potato starch were determined using a dynamic vapor sorption analysis method at temperatures of 25, 35 and 45 °C. The sorption kinetic was then modelled using the GAB model. Results showed that the equilibrium moisture content of PAW-ANN and DW-ANN samples was significantly lower than that of native and PAW. Variations in binding sites and agglomeration led to changes in specific surface area (SA), mono layer (Mo) and sorption enthalpy (qst), changes in entropy (△S), and Gibbs free energy (△G). Moreover, for these samples, a significant reduction ($p < 0.05$) in swelling power, solubility, light transmittance (T %) and syneresis (%) was observed when potato starch was treated with PAW-ANN and DW-AANN. The combined PAW-ANN proved to be a promising technique for modifying starch and altering the kinetics of water sorption-desorption, hydration and rheological properties at different temperatures without the use of enzymes, acids or crosslinking agents, demonstrating its potential to improve starch stability.

1. Introduction

Starch is one of the most abundant food components that provides energy to the human body and is widely used in the food industry as a low-cost ingredient, thickener, gelling agent, colloidal stabilizer, and bulking agent (Suri & Singh, 2023; Wu et al., 2022). However, in the development of food products with desired properties, native starch has several disadvantages, due to some inherent limitations such as low stability and high tendency to retrograde (Wu et al., 2022). Hence, much research work has been conducted to modify starches to tailor their properties and improve the applicability of starch for the food industry (Maniglia, Castanha, Rojas, & Augusto, 2021; Obadi & Xu, 2021; Raghunathan, Pandiselvam, Kothakota, & Khaneghah, 2021; Wang, Li, & Zheng, 2021).

Among the modification strategies, physical methods such as atmospheric cold plasma, plasma-activated water (PAW), and annealing with distilled water (ANN) have gained wide acceptance and have a high potential for starch modification and improved applicability of starch considering their safety, environmental friendliness and cost-effectiveness, without generating chemical waste (Aaliya et al., 2022; Chauhan, Kalaivendan, Eazhumalai, & Annapure, 2023; Chou, Tseng, Hsieh, & Ting, 2023; Flores-Silva et al., 2023; Fonseca, El Halal, Dias, & da Rosa Zavareze, 2021; Gebremical et al., 2023; Akua Y Okyere, Boakye, Bertoft, & Annor, 2022; Taslikh et al., 2022; Yan, Feng, Shi, Cui, &

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Liu, 2020). Research on the above modification methods mainly focused on thermal/gelatinization (Chou et al., 2023; Hu, Wang, Li, Xu, & Zheng, 2020; Kaur & Annapure, 2023; Akua Yeboah Okyere, Bertoft, & Annor, 2019), pasting (Aaliya et al., 2022; Song et al., 2014), rheological properties (Aaliya et al., 2022; Gebremical et al., 2023; Gebremical et al., 2024; Kalaivendan, Mishra, Eazhumalai, & Annapure, 2022; Siwatch, Yadav, & Yadav, 2022; Yan et al., 2022), swelling index and solubility (Chou et al., 2023; Kaur & Annapure, 2023; Shi et al., 2021; Yan et al., 2020), FTIR (Carvalho et al., 2021; Ji et al., 2019; Yan et al., 2020; Yan et al., 2022), digestibility (Carvalho et al., 2021; Shi et al., 2021; Yan et al., 2020), freeze-thawing (Kalaivendan et al., 2022; Simsek, Ovando-Martínez, Whitney, & Bello-Pérez, 2012), paste clarity (Chou et al., 2023; Golshahi, Taslikh, Nayebzadeh, & Arjeh, 2023; Kaur & Annapure, 2023), changes in granule morphology (Shi et al., 2021; Sudheesh et al., 2019; Yan et al., 2020; B. Zhang, Chen, Li, Li, & Zhang, 2015), water absorption and binding capacity (Akua Y Okyere et al., 2022; Zhou, Yan, Shi, & Liu, 2018) of the different starches. The results indicate significant changes in the hydrophilic fraction (due to depolymerization), hydrophobic fraction (due to crosslinking), and granule surface including etching and crystallinity of the different starches depending on the treatment conditions. Therefore, it is possible to hypothesize that the behavior of the starch will differ in terms of sorption isotherm and thermodynamic properties of the starch.

The sorption isotherms describe the relationship between the relative equilibrium moisture content and the equilibrium moisture content of the material at constant temperature (Kaymak-Ertekin & Gedik, 2004). It helps to understand the microstructure of food, the physical phenomena occurring on the food surfaces and sorption kinetic parameters (McMinn & Magee, 2003). From sorption isotherms it is also possible to postulate the thermodynamic properties of water and to know the affinity of water molecules for the surface of a solid (Dotto, Vieira, Esquerdo, & Pinto, 2013). In particular, it is possible to calculate the binding energy of water molecules at a given degree of hydration associated with water binding and repulsion forces with starch (Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006) and the degree of order or disorder in the solid water (Apostolopoulos & Gilbert, 1990).

Foods have a complex structure, and the main water-binding polymers in foods (e.g. starch) have water-binding sites with varying degrees of activity (Martín-Santos, Vioque, & Gómez, 2012).

The behavior of foods such as starch is largely determined by the interactions between water and their other components (Witczak et al., 2016), as well as by the interactions between the hydrophilic active functional groups of starch and the polar water molecules, which makes it possible to predict the degree of change in the product during treatment. However, the influence of PAW in combination with annealing or alone on the sorption isotherm and thermodynamic properties of starch has not yet been reported.

PAW is a “green” physical method generated by treating water with discharging atmospheric plasma, consisting of an acidic environment with high redox potential, electrical conductivity and the presence of enormous reactive oxygen and nitrogen species (Laurita et al., 2021), while ANN is an environmentally friendly approach to starch modification that involves the incubation of starch at a temperature above the glass transition, but below the onset of gelatinization with excess water (>40%, *w*/w) for a specified incubation time (Fonseca et al., 2021). The development and application of environmentally friendly and efficient modification techniques (in combination or separately) is an important research area in the starch processing industry. In a previous study (Gebremical et al., 2024), we showed that PAW and ANN had a synergistic effect during incubation and promoted significant changes in the rheological, thermal and pasting properties of starch.

However, to our knowledge, there is no research report on the effects of PAW alone and in combination with annealing on sorption, thermodynamics and rheological kinetics. These determinations could improve our understanding of the interactions between the starch matrix and water, the energy requirements of the hydration process, the microstructural state and the physical surface phenomena as affected by these treatments.

Therefore, the present study aims to gain a further insight into the effects of PAW and annealing treatments on the techno-functional properties, sorption isotherms and thermodynamic characteristics of potato starch.

2. Materials and methods

2.1. Raw material

The native potato starch with 18% moisture and 23% amylose used for the experiment was supplied by Ar. Pa S.r.l. (Ozzano dell’Emilia, Italy).

2.2. Plasma activated water (PAW) generation

PAW was generated using a prototype developed by AlmaPlasma S.r.l. (Bologna, Italy), by exposing distilled water to a corona discharge with a voltage of 15 kV and a fixed frequency of 5 kHz for 1 min, as described by (Laurita et al., 2021). Distilled water (500 mL) was grounded and placed in an Erlenmeyer flask on a stirrer (set to a speed of 700 rpm). The distance between the tip of the plasma source and the water was set to 5 mm, and the plasma discharge was generated for 1 min. The average discharge power (P), Hydrogen Peroxide (H_2O_2), pH, and NO_2^- concentrations of PAW generated was measured and reported in our previous published paper (Gebremical et al., 2023).

2.3. Treatment of potato starch

Potato starch was treated by mixing starch with PAW in a ratio of 1:2, and incubated for 4 h (PAW sample). Annealing was performed using distilled water (DW-ANN sample) with the same ratio 1:2 incubated for 4 h at 55 °C using a shaking water bath (mod. ST30, Turkey). The combined treatment was carried out using PAW with annealing (PAW-ANN sample). The incubation time (4 h) was selected according to our recently published work (Gebremical et al., 2024). The paste was then centrifuged at 2000 *g* (10 min), and the supernatant was carefully discarded. The paste was washed with distilled water and centrifuged three times at 2000 *g* (10 min). The remaining paste was then dried at 40 °C in a drying oven, ground, packaged and stored at 4 °C for further analysis.

2.4. Analysis of sorption isotherm

A Q5000 SA dynamic vapor sorption analyzer (TA Instruments, USA) equipped with an autosampler and a microbalance capable of weighing with a sensitivity of <0.1 μg was used. The desired relative humidity (RH) in the equilibration chamber is achieved by automatically mixing dry and humid air gas streams, allowing the humidified gas to flow continuously. All humidity isotherms were performed at an operating temperature of 25, 35 and 45 °C and a stepwise increase in RH was programmed. A sample (~4 mg) of native, PAW, DW-ANN and PAW-ANN potato starch was loaded and a RH of 0% was maintained until the relative change in sample mass remained below 0.01% for 5 min, then the measurement started. A stepwise adsorption from 0 to 95% RH was used. At each RH step, equilibration was stopped when the RH change in sample mass remained below 0.01% for 5 min and the next RH step was automatically applied. Measurements were performed in duplicate.

The data points were collected and plotted as isothermal equilibrium moisture content (EMC) versus water activity (a_w) using the software TGA Q5000SA V3.17 Build 265 (TA Instruments, USA). The relationship between the EMC and the a_w value of starch samples was predicted by the Guggenheim-Anderson-de Boer (GAB) model using Eq. (1):

$$EMC = \frac{M_o C_g a_w}{(1 - ka_w)(1 - ka_w + Cka_a)} \quad (1)$$

Where: *Mo* is the moisture content in a layer (g water/g solids), C_g is the energy constants, *K* is the constant that corrects the properties of the multilayer molecules with respect to the liquid phase, EMC is the equilibrium moisture content (g water/100 g solids or %db) and a_w is the water activity. The fitting GAB equation was evaluated with the mean value of the relative percentage deviation (%P) using the following equation:

$$\%P = \frac{100}{N} \sum_{i=1}^{N} \frac{|M_{ei} - M_{ci}|}{M_{ei}} \quad (2)$$

Where: M_{ei}, M_{ci}, and *N* are experimental and predicted moisture content values, respectively, and N is the number of experimental data. A model is considered acceptable if the % *P* value is below 10% (Kaymak-Ertekin & Gedik, 2004).

2.4.1. hermodynamic parameter analysis from the sorption isotherm

2.4.1.1. Net isosteric heat of sorption. The net isosteric heat of sorption or differential enthalpy of sorption (q_{st}) is defined as the difference between the total heat of sorption (Q_{st}) and the heat of vaporization of the pure liquid ($\triangle H_{vap}$) and indicates the strength of the interaction between the water molecules and the absorbing material (Moussaoui, Kouhila, Lamsyehe, Idlimam, & Lamharrar, 2020) and is given by

$$q_{st=} Q_{st-} \triangle Hvap \quad (3)$$

Where; Q_{st} is the amount of energy required to remove water from the material, ΔH_{vap} is the amount of energy required for normal water vaporization.

The net isosteric heat of adsorption for a given EMC was calculated using the Clausius-Clapeyron equation (Eq. (4))

$$\left[\frac{\partial \ln (a_w)}{\partial \frac{1}{T}}\right] = -\frac{q_{st}}{R} \quad (4)$$

q_{st} was calculated from the slope resulting from plotting $In(a_w)$ against 1/T for a given EMC. The slope is equal to q_{st}/R; therefore, $q_{st} = -R \times$ slope. The procedure was repeated for several EMCs to determine the relationship between the q_{st} value and MC at three temperatures (25, 35, and 45 °C). Where R is the universal gas constant (8.314 J/mol/K), a_w, is the water activity and T is the absolute temperature (K).

2.4.1.2. Sorption differential entropy. The sorption entropy change ($\triangle S$) helps to know the crystallization, swelling, dissolution processes and the number of available sorption sites at a certain energy level (Moussaoui et al., 2020) and was calculated using Eq. (5)

$$-ln(a_w) = Q_{st}/(RT) - \left(\Delta S/R\right) \quad (5)$$

The EMC data from the GAB model were used to determine the $\triangle S$ at each MC. The $\triangle S$ for a given moisture level was calculated using the intercept ($\triangle S/R$) ($\triangle S = R \times$ intercept) of the plot of *In* (a_w) versus 1/T. The procedure was repeated for several EMCs to measure the relationship between the $\triangle S$ value and MC at three temperatures (25, 35, and 45 °C).

2.4.1.3. Determination of Gibbs free energy. The a_w data generated by the GAB model for the sorption isotherms were used to determine the change in free energy ($\triangle G$) due to the change in EMC in potato starch, which indicates the adsorbent's affinity for water. The $\triangle G$ changes were then calculated at different EMCs for each temperature (25, 35, and 45 °C) using Eq. (6).

$$\Delta G = -RTln(a_w) \quad (6)$$

2.5. Determination of specific surface area of sorption

The specific surface area of sorption was computed using Eq. (7):

$$SA = (Mo \times NA \times Am)/Mwat \quad (7)$$

Where: SA is the sorption area of the solid (m^2/g solid), *Mo* is the moisture content in a monolayer (g/100 g), NA is the Avogadro number (6.02 × 10^23 molecules/mol), Am is the area of a water molecule (1.06 × 10^-19 m^2/mol) and M*wat* is the molecular weight of the water (18 g/mol).

2.6. Pasting clarity, hydration, and syneresis analysis

2.6.1. Paste clarity

According to the method of Castanha, da Matta Junior, and Augusto (2017), the clarity of the paste was evaluated based on the transmittance (%T) of the sample. Samples were prepared by mixing 0.2 g of starch in 20 mL of deionized water in screw-capped test tubes. The test tubes were then placed in a thermal bath with boiling water for 30 min and stirred 5 times every 5 min. They were then cooled to room temperature and measured in glass cuvettes at 650 nm wavelengths in a UV spectrophotometer mod. UV-1601 (Shimadzu, Japan).

2.6.2. Gel hydration properties

The swelling power (SP) and water solubility index (WSI) were measured according to the method of Martins, Gutkoski, and Martins (2018) with minor modifications. In brief, 0.5 g (Wi) of the starch samples were mixed in 25 mL of distilled water and heated to 90 °C in a water bath for 30 min. After cooling, the samples were centrifuged at 3000 rpm for 20 min. The supernatant was dried overnight at 105 °C in an oven. The gel residues (Wr) and the dried supernatant (Ws) were weighed to calculate the parameters SP and WSI as follows:

$$SP\ (g/g) = Wr/(Wi - Ws) \quad (8)$$

$$WSI\ (g/g) = Ws/Wi \quad (9)$$

2.6.3. Freeze-thaw stability (% syneresis)

Syneresis was measured according to the method of Kaur and Annapure (2023). In brief, starch suspensions of 3% (*w/v*) were prepared, kept in a boiling water bath and stirred for about 10 s at 2 min intervals for 30 min. The gels were brought to room temperature after being frozen at −20 °C for 48 h and thawed in a water bath at 30 °C for 2 h. They were then centrifuged for 20 min (3000 rpm) and the amount of water released was measured to give the syneresis (%) using the formula:

$$\text{Syneresis } (\%) = \frac{\text{Amount of supernatant}}{\text{Weight of sample taken}} \times \text{concentration of starch suspension} \times 100 \quad (10)$$

2.7. Structuring velocity and kinetic modeling of rheological data

The rheological data at non-isothermal kinetics based on a combination of Arrhenius equation and time–temperature relationship were measured according to the method of (Ahmed & Auras, 2011; Ahmed, Ramaswamy, Ayad, & Alli, 2008). A dispersion of 12% potato starch in distilled water was prepared and then heated at 90 °C. The potato starch gel was subjected to a dynamic temperature scanning test in which the initial temperature was set at 40 °C. A system with parallel plates (PP/50 mm) was used, with a distance of 1 mm between the plates. The strain and frequency were set to 0.5% and 1 Hz respectively. A temperature sweep was performed in which the temperature was varied between 40 and 90 °C at a rate of 2 °C/min. G′ (elastic) and G" (viscous) were

recorded with the increase in temperature. Among the different kinetic models, the non-isothermal method (combination of reaction rate, time–temperature profile and Arrhenius relationship) is considered the best method because most gelatinization experiments with starch were performed in situ at a constant heating rate (slower heating rate) and the variation of G′ (elastic modulus) measures the structure development rate (dG′/dt) (Ahmed, 2012; Basak & Annapure, 2022).

$$ln\left(\frac{1}{G'^{n}}\frac{dG'}{dt}\right) = lnk_{o-}\left(\frac{E_a}{R}\right)\frac{1}{T} \quad (11)$$

A plot was drawn between $ln\left(\frac{1}{G'^{n}}\frac{dG'}{dt}\right)$ versus 1/T to obtain the parameters E_a from the slope. Where G′ is the elastic modulus (kPa); k_0 is the pre-exponential factor (kPa.min^{-1}), E_a is the activation energy (kJ/mol), R is the universal gas constant (8.314 J/mol K^{-1}), T is the temperature (K), t is the time associated with the temperature sweep (min). Multiple linear regression was used with the starch kinetics data set to determine the order of reaction (n) after changing the above Eq. (11) to the following linear forms Eq. (12):

$$ln\left(\frac{dG'}{dt}\right) = lnk_o + nlnG' - \left(\frac{E_a}{R}\right)\frac{1}{T} \quad (12)$$

2.8. Statistical analysis

The statistical package SPSS (IBM, SPSS v20, USA) was used for the analysis of statistical significance and the regression analysis. Analysis of variance (ANOVA) and Duncan's test ($p < 0.05$) were used to compare the mean values. All measurements of sorption isotherms were performed in duplicate, others in triplicate, and observations were expressed as mean ± standard deviation.

3. Results and discussion

3.1. Moisture sorption isotherms of potato starch

The experimental results for the equilibrium moisture content (EMC) of Native, PAW, DW-ANN, and PAW-ANN potato starch as a function of water activity (a_w) at three different temperatures (25, 35 and 45 °C) are shown in Fig. 1. As expected, the EMC increased with increasing water activity (a_w) at a constant temperature.

The adsorption isotherms of potato starch showed the typical sigmoidal shape of type II. This is consistent with the results obtained for potatoes (Kaymak-Ertekin & Gedik, 2004; McMinn & Magee, 2003; Witczak et al., 2016) and it is common for many other starchy and powdered products (Abebe & Ronda, 2015; Hawa, Ubaidillah, Damayanti, & Hendrawan, 2020). The sorption behavior of both Native and PAW-treated starch at lower water activity showed considerable amount of absorbed moisture, which was due to high hydrophilicity and presence of polar groups (more active sites). In contrast, DW-ANN and PAW-ANN samples started to absorb water at higher a_w, which could be due to the fact that PAW with annealing treatment increases hydrophobicity and crystalline regions, that typically contrast moisture penetration and have less favorable sorption sites (Mutungi et al., 2011). The effect of temperature on EMC was not pronounced at water activities of <0.1a_w, but an increase in temperature leads to visible changes in equilibrium moisture content.

The higher values of the EMC for native and PAW (Table 1) is due to the high content of amorphous starch and the greater availability of hydroxyl groups in the starch chain, which leads to a greater number of sorption sites (Fonyuy et al., 2023). However, annealing process (DW-ANN and PAW-ANN samples) can increase the degree of crystallinity, structural density, cross-linking, hydrophobicity and integrity of the starch structure (Alamri, Mohamed, Hussain, Ibraheem, & Abdo Qasem, 2018; Cova, Sandoval, Balsamo, & Müller, 2010; Gebremical et al., 2023; Vamadevan & Bertoft, 2015), resulting in lower moisture uptake and a lower probability of being penetrated by water. In addition, the sorption property is related to the hydration properties (swelling capacity and solubility) of starch.

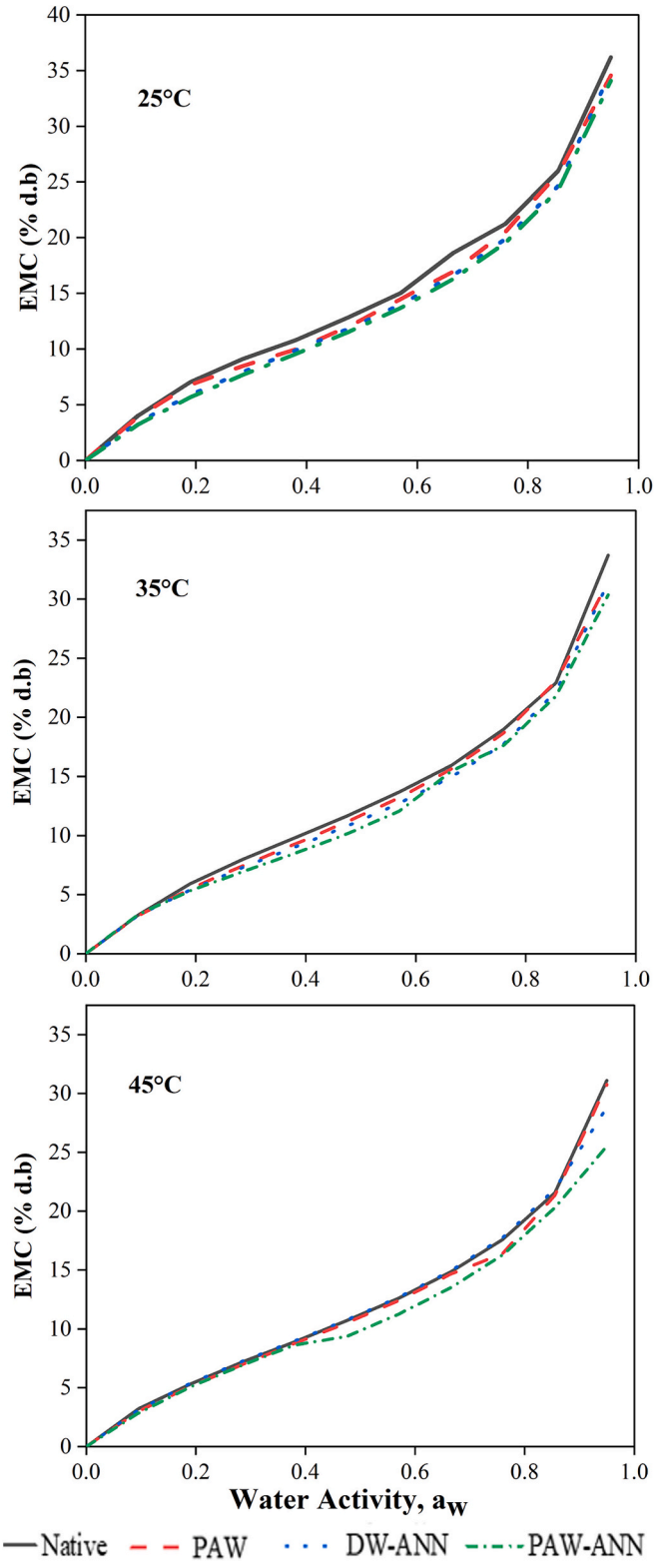

Fig. 1. Experimental values of equilibrium moisture content (g of water/g of sample dry matter) (EMC) as a function of a_w for potato starch at different temperatures.

Table 1
Estimated values of GAB model coefficients (M_o, C_g, K), surface area (SA) and statistical data of coefficient of determination (R^2) and root mean square (% P).

Samples	T (°C)	M_0 (g water/ g dm)	C_g	K	R^2	% P	SA (m^2/g)
Native	25	0.1	9.54	0.81	0.9998	0.24	356.01 ± 16.38^{g}
	35	0.095	8.87	0.8	0.9999	0.93	336.68 ± 6.46^{f}
	45	0.084	8.54	0.8	0.999	0.39	298.77 ± 8.41^{d}
PAW	25	0.095	8.89	0.79	0.999	0.88	338.19 ± 4.14^{f}
	35	0.085	8.38	0.76	0.998	0.26	302.34 ± 8.18^{d}
	45	0.079	7.69	0.76	0.998	1.08	281.82 ± 12.34^{bcd}
DW-ANN	25	0.09	7.32	0.77	0.997	1.4	320.98 ± 0.96^{e}
	35	0.084	7.48	0.78	0.998	0.13	297.17 ± 3.94^{bc}
	45	0.076	6.88	0.79	0.999	1.35	271.17 ± 0.12^{b}
PAW-ANN	25	0.082	7.45	0.75	0.997	1.25	290.23 ± 5.29^{dc}
	35	0.079	6.62	0.73	0.997	0.11	279.83 ± 3.69^{d}
	45	0.072	6.36	0.73	0.998	1.11	255.57 ± 5.46^{a}

Different letters indicate significant differences ($p < 0.05$).

3.2. Evaluation of GAB model fitting and parameters

The results of the non-linear regression analysis to fit the GAB equation (Eq. (1)) to the experimental data are shown in Table 1 at the three temperatures (25, 35 and 45 °C). The GAB equation fitted the moisture sorption isotherms for native and modified starch quite well, as shown by the R^2 and root mean square (% P) values in Table 1. The GAB sorption model showed a higher R^2 and a lower % P. All $R^2 > 0.997$ and % *P* values were < 10, which was recommended for models that best fit the sorption data for all samples at three temperatures (25, 35, and 45 °C); the results confirmed that the GAB model provided satisfactory prediction of adsorption behavior for a wide range of water activity for all experimental data.

Calculated coefficients of GAB model (*Mo*, C_g, and *K*) and SA obtained using the *Mo* values from the GAB equation (1) are shown in Table 1. The moisture content of *Mo* (g water/g solids) is the amount of water required to cover specific sites used to determine the stability, structural properties and availability of active sorption sites (Azhar et al., 2021; Yogendrarajah, Samapundo, Devlieghere, De Saeger, & De Meulenaer, 2015). The estimated value of *Mo* for native potato starch decreased with increasing temperature from 0.1 g water/g dm at 25 °C, 0.095 g water/g dm at 35 °C and 0.084 g water/g dm at 45 °C, falling within the range given for starchy products, which is between 0.0045 and 0.127 g water/g dm at different temperatures (Cova et al., 2010).

The GAB constant C_g stands for the strength of the binding of water molecules to the primary binding sites (net enthalpies of monolayer sorption) on the product surface (Mutungi et al., 2011; Sormoli & Langrish, 2015) or the difference between the monolayer (first sorption layer) and the chemical potential of the various multilayers (Almeida, Magalhães, Souza, & Gonçalves, 2018), while *K*, is a correction factor for multilayer molecules, which is related to the interactions or the heat of sorption between the molecules of the multilayer layers (Almeida et al., 2018; Viganó, Gabas, & Telis-Romero, 2014). Changes in SA affect how quickly and thoroughly water molecules hydrate on the surface (Rosa, Moraes, & Pinto, 2010; Tavares, Sousa, Magalhães da Silva, Lima, & Oliveira, 2023).

For all samples, the temperature increase contributed to a decrease in the number of sorption sites actively binding water (Borges-Machado et al., 2024; Zuo, Rhim, & Lee, 2015). It is possible to hypothesize that at higher temperatures, water molecules attain the necessary energy to detach from their sorption sites, leading to an increase in the distances between molecules and a subsequent reduction in attractive forces between sorption sites and water molecules. This, in turn, results in lower *Mo*, C_g, and SA values (Tavares & Noreña, 2021; Yogendrarajah et al., 2015).

The GAB parameters and SA values were at all temperature higher in native potato sample in comparison to PAW, DW-ANN and PAW-ANN samples. This suggests that native starch possess an hydrophilic surface characterized by a substantial number of active polar sites (Tavares et al., 2023), resulting in high water binding to the surface and the formation of strong bonds between water molecules and the hydrophilic sites in the monolayer of potato starch (Almeida et al., 2018; Silva et al., 2021; Tavares, Barros, Vaghetti, & Noreña, 2019; Tavares & Noreña, 2021). Conversely, the reduction of *Mo*, C_g, and SA observed after the different applied treatment, may indicate a weakening of water-starch interactions. The observed reduction was stronger for the PAW-ANN sample, this could be attributed to cross-linking or an augmentation in the starch's hydrophobicity, potentially influenced by the combined effects of the annealing treatment and PAW (characterized by acidic nature and the presence of nitrogen and oxygen reactive species) (Aaliya et al., 2022; Chen, Kuo, & Lai, 2009). This phenomenon might also be associated with low porosity, as suggested by Moussaoui et al. (2020), leading to a reduction in sorption area (SA), with a more pronounced decrease observed for PAW-ANN and DW-ANN (Prasantha & Amunogoda, 2013). The obtained value of *K* was <1 for all samples, indicating that the water molecules on the surface of the monolayer were more tightly bound than those in the multilayer (Arthur et al., 2018). The value of *K* is slightly higher in native starch, indicating that it can absorb more water at high values of water activity (Cova et al., 2010).

3.3. Thermodynamic properties of potato starch

3.3.1. Net isosteric heat of sorption

The magnitude of the isosteric heat of sorption (q_{st}) at a given moisture content is related to the internal energy of a product and it is an indicator of the intermolecular attractive forces between the sorption sites and the water vapor and thus of the physical state and the stability of the food material under a given condition (McMinn & Magee, 2003; Yogendrarajah et al., 2015). The variation of q_{st} of native and modified potato starches as a function of moisture content is shown in Fig. 2A.

The q_{st} value was determined by plotting $\ln a_w$ against 1/T using the data derived from the sorption isotherms. It is high at low moisture content and decreases exponentially with increasing moisture content. Similar results have been reported by (Fonyuy et al., 2023; Moussaoui et al., 2020; Sormoli & Langrish, 2015; Thys, Noreña, Marczak, Aires, & Cladera-Olivera, 2010).

The high values of q_{st} at low moisture content indicate high interactive energies between the available–OH (polar sites) and the moisture of the starch approaching a monolayer of water molecules (Bonner & Kenney, 2013). At low water content, the q_{st} of native and PAW samples was higher than that of DW-ANN and PAW-ANN ones, due to the presence of active binding sites (with the largest q_{st}) on the surface of the starch, which are covered with water molecules forming a monolayer. When these active sites are covered with a monolayer of water, they become less available with lower binding activation energies (at low latent heat) resulting in a lower q_{st} (Kaymak-Ertekin & Gedik, 2004).

The change in the sorption properties of the starches after annealing and the combined PAW-ANN treatment are probably due to physicochemical and structural changes that resulted in a weak water binding at low product moisture, which can be mainly explained by a lower activity of hydroxyl groups (–OH), resulting in low interaction energy between the starch and water molecules (Bahar et al., 2017; Esteban et al., 2009;

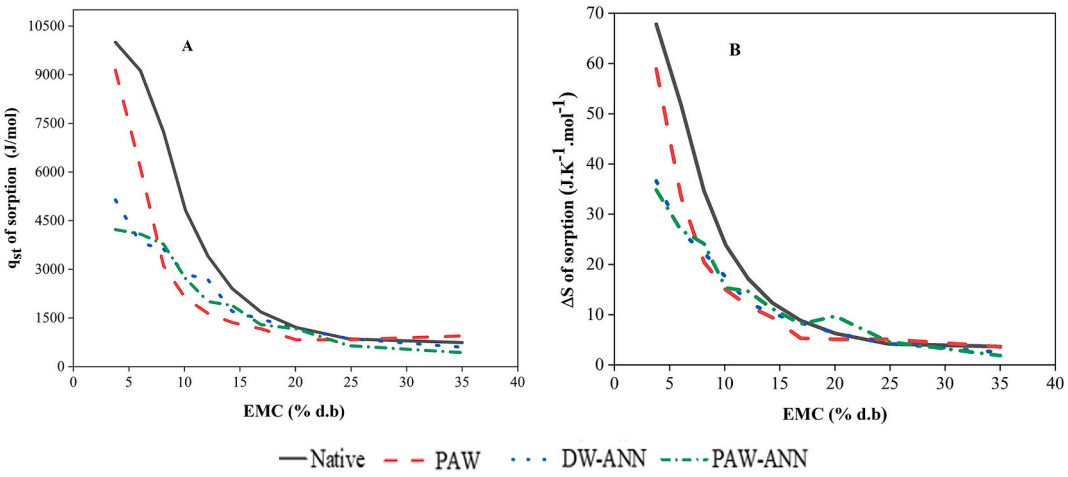

Fig. 2. Variations of net isosteric heat of sorption (qst) (A) and sorption entropy (△S) (B) of native, PAW, PAW-ANN, and DW-ANN starch samples.

Fonyuy et al., 2023; Moussaoui et al., 2020; Sawhney, Sarkar, Patil, & Sharma, 2014).

3.3.2. *Entropy heat of sorption*

The value of differential entropy (△S) for the sorption of native and modified potato starch at a given moisture content was calculated by linear regression using Eq. (5), and it is plotted as a function of moisture content in Fig. 2B. Similarly to q_{st}, sorption entropy also follows the same trend, which is strongly dependent on moisture content (Fig. 2B) (Thys et al., 2010). When moisture decreases, many active polar sites are available on the surface, and the difficulty in breaking hydrogen bonds justifies this high energy requirement. Similar patterns have been reported by Fonyuy et al. (2023).

In general, at the lowest water content, a higher △S was obtained with native starch followed by the PAW one and then the DW-ANN and PAW-ANN samples. The △S measures the extent of disorder, a spatial arrangement between the water and food matrix, or the randomness of water on the surface (Moussaoui et al., 2020; Silva et al., 2021). Therefore, results indicate that the water molecules in the native and PAW samples are less ordered than in DW-ANN and PAW-ANN ones, due to the degree of modification and cross-linking of the starch promoted by the treatments. This result indeed suggests that the molecular motion or disordered state of water molecules at low ΔS is due to the fact that –OH is less available in the DW-ANN and PAW-ANN samples than in native and PAW ones. In general, as the moisture content increased, the active sites on the surface could be occupied by the water molecules and therefore had a lower sorption capacity, leading to a decrease in entropy.

3.3.3. *Gibbs free sorption energy*

Gibbs free energy (ΔG) is an affinity of water for sorbents (Villa-Vélez, Váquiro, Bon, & Telis-Romero, 2012; Zhang, Li, Jia, & Liu, 2022). Fig. 3 shows the variation of ΔG for native, PAW, DW-ANN, and PAW-ANN at 25, 35 and 45 °C as a function of moisture content. The rate of change of △G of the adsorbent at higher moisture content was very slow, as △G is related to the energy required to provide sorption sites; therefore, it becomes smaller with increasing temperature and higher moisture content.

At low moisture content, higher ΔG values were calculated for the native starch, as these have a high freedom from water adsorption due to their hydrophilic properties in a food (Taitano, Singh, Lee, & Kong, 2012). In contrast, the ΔG value of PAW-ANN treated starch was lower. This indicates the existence of few water-binding sites in the plasma-treated starch in combination with annealing, as ΔG is related to the energy required to provide sorption sites for swelling, hydrophilic/hydrophobic properties and removal of water from the starch (Silva et al., 2021). In addition, the decrease in ΔG with an increase in moisture and temperature indicates that at high humidity and temperature, there are few active sites to bind with water during adsorption. Furthermore, this can be attributed to the weakening of the affinity between the water and the absorbing material (Zhang, Li, Jia and Liu, 2022). Similar results have been previously reported (Fonyuy et al., 2023; Yogendrarajah et al., 2015).

3.4. *Paste clarity, hydration, and syneresis analysis*

The solubility (%), the swelling power (g/g), the syneresis (%) and the paste clarity (% transmittance) measured in the native, PAW, DW-ANN and PAW-ANN starch samples are shown in Fig. 4. For all considered parameters, no differences ($p > 0.05$) were observed between the control and the PAW treated sample, while lower values were obtained for DW-ANN and even lower for the PAW-ANN sample.

The reduction of solubility might be due to the rearrangement of the rigid crystalline structure in starch that hinders its solubility by restricting amylose leaching out (Aaliya et al., 2022). Previous studies (Fonseca et al., 2021) have shown that annealing (DW-ANN) leads to a decrease in solubility, as the bonds are strengthened and the interactions between amylose and amylopectin molecules increase, forming a more stable structure.

The reduction in swelling power for the DW-ANN and PAW-ANN treatment could be due to the reduced moisture uptake and retention capacity of amylopectin (Aaliya et al., 2022) due to cross-linking (the hydrogen bonds between starch chains), which reduces the hydration tendency (Van Hung, Vien, & Phi, 2016). This change can be associated with the reduction of the monolayer and surface area obtained from the sorption isotherms (Table 1).

Syneresis (%) shows the amount of water oozed from the starch gel and measures the degree of retrogradation (Kalaivendan et al., 2022; Kaur & Annapure, 2023). As for the other indices, the decrease observed can be related to cross-linking of starch as it has the tendency to degrade of the starch granules, which leads to greater gelling and makes it more difficult for light to penetrate (Chou et al., 2023; Kaur & Annapure, 2023).

Paste clarity may (indirectly) indicate possible cross-linking of the starch (Chaiwat et al., 2016) or depolymerization (Chou et al., 2023). Cross-linked starch has a more integrated structure, which makes it more difficult for light to pass through and thus reduces the clarity of the paste (Chou et al., 2023).

The DW-ANN and PAW-ANN starch samples exhibited significantly lower paste clarity (%T) compared to native and PAW-treated starch samples, likely due to the high cross-linked and crystalline structure, and less content of polar groups. The cross-linking reaction that probably

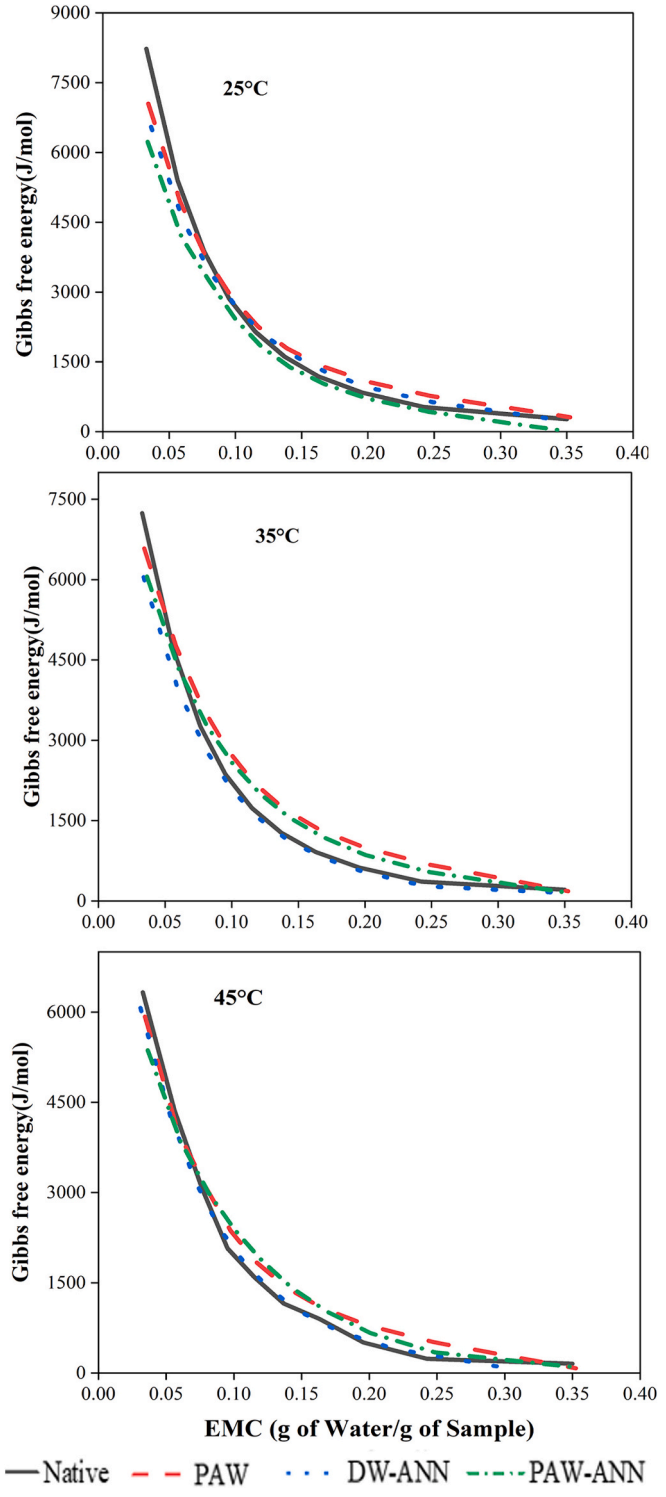

Fig. 3. Gibbs free energy (J/mol) change during adsorption of native and modified potato starch at different temperatures (25 °C, 35 °C, and 45 °C).

occurred during the DW-ANN and PAW-ANN treatment prevents starch chains from dissociating and enhances interactions between starch functional groups, resulting in clusters of helical amylopectin side chains. Similar results have been reported by (Chou et al., 2023).

3.5. Structuring velocity and kinetic modeling of rheological data

Fig. 5A shows the structuring rate (dG'/dt) determined by the first derivative of G' (modulus of elasticity) with respect to time. dG'/dt increased rapidly and reached G'max (kPa) at the given temperature (TG'max, °C) and then decreased continuously in the considered temperature range. The peak value of G'max for native, PAW, DW-ANN and PAW-ANN was 4.03 ± 0.02, 4.54 ± 0.32, 7.18 ± 0.04 and 8.18 ± 0.24, respectively (Table 2). A notable rise in G'max, observed when potato starch undergoes simple annealing (DW-ANN) and annealing combined with plasma treatment (PAW-ANN) during the heating process, results from the creation of a three-dimensional gel network. This network is formed by leached amylose and further strengthened by robust interactions among the expanded starch particles. The heightened G'max is linked to the gels formed in DW-ANN and PAW-ANN starches, signifying the presence of cross-linked network structures and enhanced elasticity (Aaliya et al., 2022). As shown in Table 2, potato starch treated with DW-ANN and PAW-ANN was able to delay the gelatinization process by delaying the gelatinization temperature (TG'max).

The kinetic modeling (gelatinization) of potato starch was quantified rheologically under oscillatory deformation in the temperature range for kinetic analysis from 40 °C to the maximum temperature (TG'max, °C) required to reach the maximum modulus of elasticity (G'max), as shown in Fig. 5B and Table 2. As a result, the reaction order of native, PAW, DW-ANN and PAW-ANN obtained according to the equation (12) using multiple regressions was found to be 1.007, 1.003, 0.927 and 0.951, respectively, with a high R^2 and lower standard errors (SE) (Table 2). Since the determined value for the reaction order (n) was almost equal to one ($n \approx 1$), the first-order reaction kinetics for native and modified starch gelatinization were considered. There is ample evidence for the applicability of first-order reaction kinetics for starch gelatinization (Ahmed & Auras, 2011; Ahmed et al., 2008; X. Zhang, Tong, Zhu, & Ren, 2013).

The activation energy (*Ea*) is very important in revealing the mechanism of the reaction (Malecki, Prochowska-Klisch, & Wojciechowski, 1998), and the *Ea* of potato starch gelatinization was calculated from the slope of the Arrhenius plot according to Eq. (11). An average value for the *Ea* of 88.71, 88.49, 74.12 and 68.70 kJ/mol was obtained for Native, PAW, DW-ANN and PAW-ANN, respectively. The higher *Ea* values for gelatinization in the Native and PAW samples can be attributed to the competition in water availability and higher availability of the hydroxyl group (Ahmed, 2012; Alvarez, Cuesta, Herranz, & Canet, 2017).

A higher *Ea* value indicates how sensitive a process is to temperature (Turhan & Gunasekaran, 2002). As shown in Table 2, both DW-ANN and PAW-ANN starch granules are more resistant to destruction by further heating, indicated by a higher TG'max (delays gelatinization due to low temperature sensitivity), whereas native and PAW starch granules are sensitive to temperature (lower TG'max) and reduce elasticity after heating (Alvarez et al., 2017). The lower *Ea*, higher dG'/dt and TG'max mean that gelation is more favorable and less energy is required to reach the critical gel rigidity (Ahmed et al., 2008).

4. Conclusions

The sorption and gelatinization behavior, thermodynamic and techno-functional properties of native and modified potato starch were analysed. Results confirmed the synergistic effects of the PAW and ANN treatments in modifying the behavior of potato starch in terms of water interaction and the resulting functional properties.

In particular, the obtained data suggested an increase of starch hydrophobicity and a reduction of water binding sites leading generally to a lower affinity with the water. This effect, combined with the cross-linking effect that decreased molecular motion and entropy, resulted in a lower hydration property, syneresis and clarity of the starch. Finally, starch granules resulted less sensitive to temperature, promoting a delay in the gelatinization and a higher gelation effect and gel elasticity linked to cross-linking.

These results provided an insight into the mechanism of modification of starches induced by PAW and annealing. Future work should be

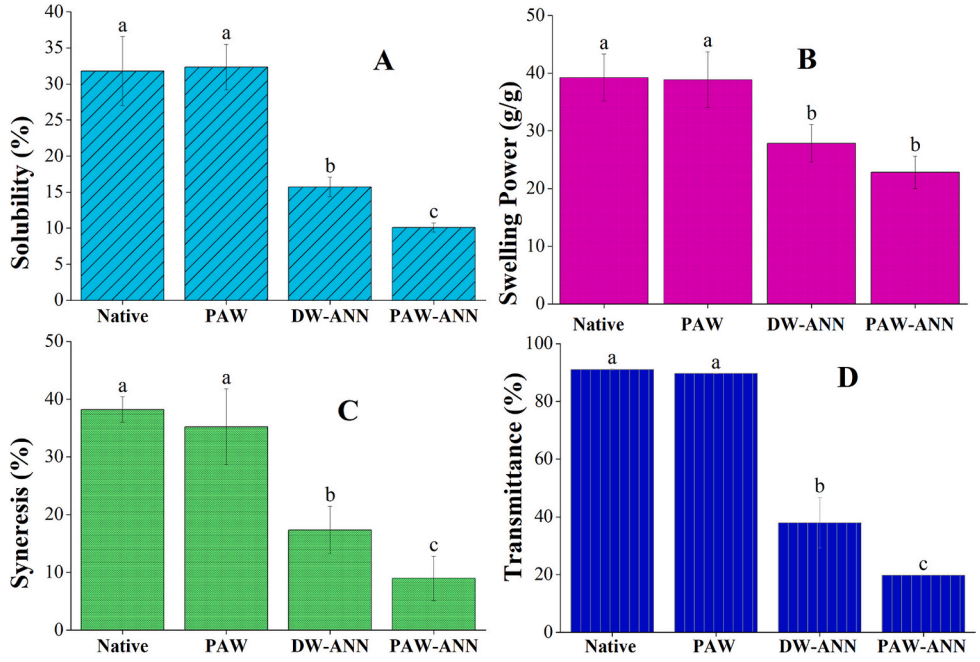

Fig. 4. Solubility (A), swelling power (B), syneresis (C) and paste clarity (D) of native and modified potato starch. Different letters indicate significant differences ($p < 0.05$).

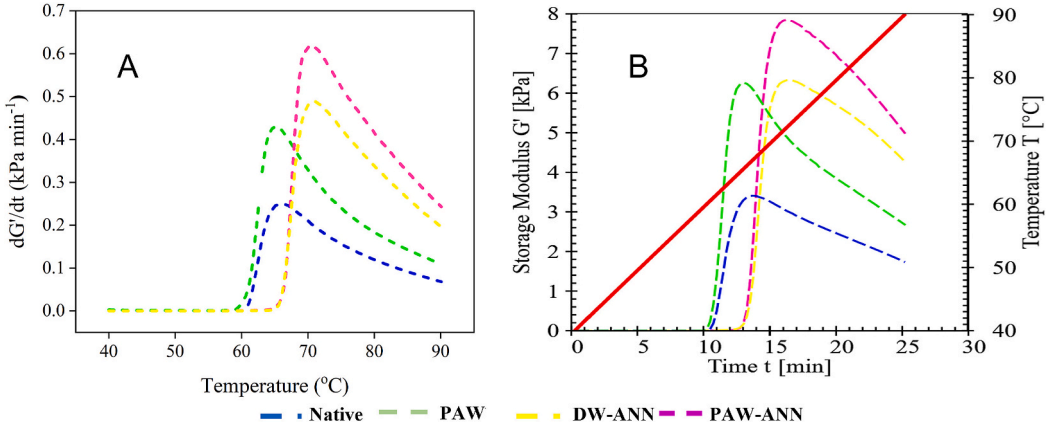

Fig. 5. Rate (dG'/dt) (A) and variation of storage modulus (kPa, G') (B) in the temperature range of (40–90 °C).

Table 2
Multiple linear regression parameters for non-isothermal theological kinetic of potato starch.

Sample	Reaction order (n)	E_a (kJ/mol)	R^2	SE	TG'max (°C)	G'$_{max}$ (kPa)
Native	1.007	88.71^a	0.9981	0.3384	65.86 ± 0.34^b	4.03 ± 0.02^c
PAW	1.003	88.49^a	0.9986	0.3385	65.10 ± 0.01^b	4.54 ± 0.32^c
DW-ANN	0.927	74.12^b	0.999	0.1846	72.87 ± 0.35^a	7.18 ± 0.04^b
PAW-ANN	0.951	68.70^c	0.9973	0.309	74.12 ± 0.35^a	8.18 ± 0.24^a

Different letters indicate significant differences ($p < 0.05$).
Where; *Ea*, activation energy (kJ/mol); SE, standard error; TG'max (°C), temperatures at which G' reaches its maximum during temperature sweep; G'max, maximum G' during temperature sweep.

carried out to clarify porosity (pore size), morphology, and crystallinity of the granules affected by the proposed treatments.

CRediT authorship contribution statement

Gebremedhin Gebremariam Gebremical: Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. **Silvia Tappi:** Writing – review & editing, Supervision, Conceptualization. **Romolo Laurita:** Writing – review & editing, Supervision, Conceptualization. **Filippo Capelli:** Supervision, Formal analysis, Conceptualization. **Federico Drudi:** Methodology, Formal analysis. **Santina Romani:** Writing – review & editing, Supervision, Conceptualization. **Pietro Rocculi:** Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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