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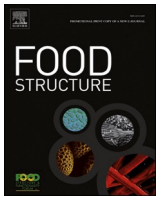

Insights on the molecular interactions of tapioca starch with xylitol, Arabic gum, and pectin and their effects on its pasting properties and retrogradation kinetics

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ABSTRACT

Pasting properties and retrogradation kinetics of tapioca starch (TS) systems with different added concentrations of xylitol (X), Arabic gum (AG), and pectin (P) were evaluated by nuclear magnetic resonance (^{1}H-NMR) and differential scanning calorimetry (DSC) after storage at 4 °C for 21 days. The incorporation of the additives reduced the peak, final and setback viscosity of the pastes, indicating limiting gelatinization of TS for the establishment of non-covalent interactions with water and/or starch, restricting further hydration and swelling. Based on ^{1}H-NMR results, free water molecules were involved in the reassociation of amylose and amylopectin chains; thus, their molecular mobility decreased with the progress of starch retrogradation, as evidenced by the diminishment of the spin-spin relaxation times. DSC results confirmed that the addition of X delayed TS retrogradation, possibly due to the generation of hydrogen bonds interactions, while opposite results were obtained when AG was added, which promoted TS molecules reorganization. P showed a concentration-related effect, since it delayed TS retrogradation at 1 % level and accelerated it at 2 % concentration. Results from this study provide insights on the molecular interactions of TS with xylitol, Arabic gum, and pectin and their modulating effects on starch retrogradation, which are valuable for the development of gluten-free products with varied industrial applications.

1. Introduction

Starch, a semicrystalline biomacromolecule composed of amylose and amylopectin, constitutes the main component of multiple grain crops, such as cereals and pseudocereals, for which it is one of the most important energy sources world-wide (Horstmann et al., 2017; Tappiban et al., 2020). Given its gelling, thickening, and structuring properties, among others, it is largely used in the food, cosmetic, pharmacological and textile industries for varied applications (Cornejo-Ramírez et al., 2018). Particularly in the food industry, native or modified starches are used to increase the viscosity or as structuring agents of the food matrixes, especially when they are heated in the presence of enough water for the occurrence of the gelatinization process (Kiprop et al., 2021; Milde et al., 2012; Sigüenza-Andrés et al., 2021; Zhang et al., 2017). With the progress of the thermal treatment in excess water, starch granules absorb water and they break down. Consequently, amylose molecules leach out the granules and lose crystallinity, causing the formation of a paste that increases the viscosity of the systems (Donmez et al., 2021). Starch gelatinization occurs in aqueous media at different temperatures according to the botanical source and variety of the starch, but normally ranges between 60 °C and 80 °C. After gelatinization, when the temperature lowers and with the progress of time, starch molecules tend to reorganize at different rates according to the starch type and the environmental conditions, and recrystallization occurs (Cornejo-Ramírez et al., 2018; Donmez et al., 2021; Wang et al., 2015). This time-dependent process is called starch retrogradation.

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Retrogradation is the main responsible for the quality definition and shelf-life of starchy foods. It is associated, for example, to the staling of bread and bakery products, limiting their shelf-life for the rise in firmness and other negligible effects on sensory and organoleptic properties (Milde et al., 2012; Sigüenza-Andrés et al., 2021). On the other hand, starch retrogradation may increase the nutritional value of food as starch crystallites are considered fiber components since they cannot be digested and are fermented by gut microbiota (Donmez et al., 2021). Moreover, in some products such as breakfast cereals, a certain level of starch retrogradation facilitates their handling and improves their final texture (Wang et al., 2015).

The gluten network provides viscoelasticity and act as a barrier for starch molecules reassociation. Thus, in gluten-free formulations, starch retrogradation is the main determinant of shelf life and sensory acceptance (Horstmann et al., 2017). As molecular mobility, water availability, and inter- and intra- non-covalent interactions are involved in the kinetics of the retrogradation process, any modification interfering the reordering of crystalline configurations may result in changes of the retrogradation kinetics. Therefore, this time-dependent process can be modulated for different industrial applications (Donmez et al., 2021). One of the main approaches for altering starch retrogradation kinetics is the addition of other compounds that can either modify the non-covalent interactions between starch and/or water, or impart steric hindrance, or even alter the viscosity of the system and modify the molecular mobility of the present compounds, among other mechanisms. This approach has been studied by many researchers (Baranowska et al., 2012; Beck et al., 2011; Ma et al., 2019; Rolandelli et al., 2024; Sheng et al., 2018; Wu et al., 2023; Yang et al., 2021; Zhang et al., 2018; Zheng et al., 2019).

Particularly, tapioca starch (*Manihot esculenta*, TS) can be isolated from cassava roots, which is one of the most cultivated crops world-wide and has low growing requirements, making it an economical source of energy (Milde et al., 2012; Tappiban et al., 2020). TS has lower pasting temperatures when compared with other starches, but forms clear pastes and viscous gels with bland flavor, for which it is highly used in the food industry (Chen et al., 2015; Sheng et al., 2018; Singh et al., 2017). The control of involved mechanisms of TS retrogradation is a key factor for the development TS-based gluten-free foods (Kiprop et al., 2021; Milde et al., 2012; Sigüenza-Andrés et al., 2021; Zhang et al., 2017), and these are still not fully elucidated, especially when TS is mixed with other ingredients (Chen et al., 2015; Kiprop et al., 2021; Sheng et al., 2018).

Therefore, in this study, the effects of adding natural polyhydroxy compounds with varied chemical structure and physicochemical properties such as xylitol, Arabic gum, and pectin on the retrogradation kinetics of tapioca starch were evaluated. Rheological, thermal and molecular techniques were employed with the aim of getting in-depth understanding of the molecular implications of tapioca starch retrogradation and for the improvement of the organoleptic properties and physicochemical stability of tapioca starch-based systems during storage. The selected natural additives were chosen due to their different structure, hydrophilicity, molecular size, and functional groups, which will ultimately affect the molecular interactions with water molecules and tapioca starch chains during processing and storage. In this regard, pectin and Arabic gum are hydrocolloids with large molecular size that can bind water molecules and could limit starch hydration and further reorganization. Both hydrocolloids are of anionic nature, but Arabic gum (with carboxyl groups from galacturonic acid) presents ramifications and displays mainly thickening effects while pectin (with carboxyl groups from guluronic acid) is a more linear hydrocolloid with gelation capabilities. Moreover, the net molecular charge of these polyanions could also affect their inter- and intramolecular interactions (Chen et al., 2015; Gawkowska et al., 2018; Kiprop et al., 2021; Ma et al., 2019). On the other hand, xylitol is a small molecule with multiple hydroxyl groups and low molecular weight, thus could potentially interfere in starch spatial organization by its minor steric hindrance that promotes the establishment of hydrogen bonds and other non-covalent interactions and competes for water molecules (Yang et al., 2021; Zhang et al., 2017). The molecular features of the selected and widely used compounds and their different associations with starch make them interesting additives to evaluate their role on the pasting properties and retrogradation kinetics of tapioca starch.

2. Materials and methods

2.1. Raw materials

Native tapioca starch (*Manihot esculenta*, TS, 15 % water content (dry basis, d.b.)) with 17 % amylose content was purchased from a local market (Buenos Aires, Argentina). Xylitol (X) (X3375, $\geq$ 99 % purity) and pectin from citrus peel (P) (P9135, $\geq$ 74 % galacturonic acid, $\geq$ 6.7 % methoxy groups) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Arabic gum (AG) from *Acacia* tree (molecular weight of 250,000 g/mol) was purchased from Biopack S.A. (Buenos Aires, Argentina).

Samples containing only TS were used as a control and TS-based systems with different amounts of natural compounds were prepared: 1 % and 2 % of xylitol (X1 % and X2 %, respectively), 0.5 % and 1 % of Arabic gum (AG0,5 % and AG1 %, respectively) and 1 % and 2 % of pectin (P1 % and P2 %, respectively). All samples had the same final concentration. In this study, not only the presence of the additives, but also the effects of their concentrations on the functional properties of tapioca starch were evaluated. The amounts of compounds added were done by replacement of starch content in each system. The concentrations added in each case were in the same range as reported by other studies for similar systems (Kiprop et al., 2021; Ma et al., 2019; Santamaria et al., 2023; Yang et al., 2021).

2.2. Pasting properties

A rheometer (Anton-Paar, Modular Compact Rheometer (MCR) 302, Graz, Austria) was used to evaluate the pasting properties of TS-based systems with 8 % of solids (w/w) following the method described by Hayes et al. (2020). Briefly, paddle rotating speed was set at 960 rpm for the first 10 s and then fixed at 160 rpm for the rest of the study. Samples were held at 50°C for 1 min, followed by heating up to 95 °C at 6 °C/min and then held at 95 °C for 5 min. Finally, samples were cooled at 6 °C/min up to 50 °C and kept at that temperature for 2 min. All samples were evaluated in triplicates and the pasting temperature (PT), peak viscosity (PV), hot paste viscosity (HPV), breakdown viscosity (BD), final viscosity (FV), and setback viscosity (SB) were calculated from the resulting curves and expressed as mean $\pm$ standard deviation. PT is the temperature at which viscosity starts to rise, PV is the highest viscosity value during heating up to 95 °C, HPV is the lowest viscosity value when the sample is kept at 95 °C, BD is the difference between PV and HPV, FV is the final viscosity value during cooling up to 50 °C, and finally SB is the difference between HPV and FV (Santamaria et al., 2023).

2.3. Analysis of starch retrogradation

2.3.1. Molecular mobility by ^{1}H-NMR

Proton mobility of TS-based gels during storage was evaluated as a measure of the progress of starch retrogradation. Mobility of proton was analyzed by measuring the spin-spin transverse relaxation time (T_2) through ^{1}H-nuclear magnetic resonance (^{1}H-NMR). A pulsed nuclear magnetic resonance instrument (Bruker, model Minispec mq 20, Karlsruhe, Germany) with a magnetic field of 0.47 T and 20 MHz of frequency was used. Measurements were done at room temperature (25 °C), but the magnet temperature was kept at 40 °C to allow accurate tempering of the unit.

TS-based systems with a concentration of 8 % (w/w) were heated in a water bath at 95 °C for 10 min to assure complete starch gelatinization. Then, all samples were cooled to room temperature (25 °C) and the same

amounts of TS-based gels were placed in 10 mm diameter sealed glass tubes to reach the instrument detector's height (≈ 25 mm). Freshly prepared samples were analyzed and then stored at 4 °C during 1, 3, 7, 14, and 21 days to allow starch retrogradation for further analysis. Samples were maintained at room temperature for 30 min before each measurement.

Given the high water content of the gels, the Carr-Purcell-Meiboom-Gill (CPMG) sequence (Ruan & Chen, 1998) was used to analyze the mobility of protons with long relaxation times (≥ 100 ms). A 90° pulse length of 2.82 μs, 180° pulse length of 5.34 μs, recycle delay of 4 s, detection angle (broad) of 66°, detection angle (narrow) of 65°, gain of 87 dB, 908 magnetic field steps, 8 scans, and pulse separation of 1 ms were set as CPMG sequence parameters and 2000 data points were obtained for each measurement. Results were fitted to a bi-exponential curve, as follows (Eq. (1)):

$$I = A_{21}e^{\left(\frac{-t}{T_{21}}\right)} + A_{22}e^{\left(\frac{-t}{T_{22}}\right)} \quad \text{(Eq. 1)}$$

where I is the ^{1}H-NMR signal intensity at time t, T_{21} and T_{22} are the relaxation times of protons with short and long mobility, respectively, and A_1 and A_2 are associated to the number of protons responsible for the T_{21} and T_{22} signals, respectively. Relaxation times were also processed through UpenWin software (Alma Mater Studiorum, University of Bologna, Bologna, Italy) to obtain proton population distribution of every sample during storage through an inverse Laplace transformation (Rolandelli et al., 2024). All measurements were performed in triplicates, the results were expressed as average ± standard deviation, and proton populations distribution were plotted using GraphPad Software version 6 (San Diego, CA) in a logarithmic scale.

2.3.2. Differential scanning calorimetry (DSC)

A differential scanning calorimeter (Mettler Toledo, model 822, Zürich, Switzerland) was used to evaluate the gelatinization and retrogradation parameters of the different TS-based systems, following the method described in a previous study (Rolandelli et al., 2024) and in similar conditions as reported by other authors (Beck et al., 2011; Liu et al., 2019; Tappiban et al., 2020; Wu et al., 2023; Zhang et al., 2017). Briefly, 10 mg of TS or TS-blends were added with 30 μL distilled water (solids:water ratio of 1:3 to assure complete starch gelatinization and further retrogradation during storage) in aluminum pans and hermetically sealed. All pans were stored at 4 °C for 24 h to allow homogeneous water distribution. Then, the samples were evaluated under nitrogen atmosphere in the range of 25–100 °C at 10 °C/min of heating rate, using an empty pan as reference. Gelatinized samples were stored at 4°C during 1, 7, 14, and 21 days to promote starch retrogradation and re-run under the same above-mentioned conditions. All systems were analyzed in triplicates using the STARe software version 6.1 (Mettler Toledo, Zürich, Switzerland).

The recovered enthalpy (ΔH, J•g^{-1} of starch) after storage was proportional to the re-crystallized or retrograded starch. Thus, retrogradation degree (%) of each TS-based gel during storage was calculated as the percentage of the ratio of the enthalpy recovered of each system at storage time t and gelatinization enthalpy of the control TS system. Moreover, the Avrami equation (Eq. (2)) was used to evaluate the retrogradation kinetics of each TS-based system, as follows:

$$X(t) = \frac{\Delta H_t - \Delta H_0}{\Delta H_\infty - \Delta H_0} = 1 - \exp(-kt^n) \quad (2)$$

where $X(t)$ is the crystallized fraction, ΔH_t is the retrogradation enthalpy (J•g^{-1} of starch) at storage time t, ΔH_0 is the retrogradation enthalpy (J•g^{-1} of starch) at time zero (which is equal to zero), ΔH_∞ is the retrogradation enthalpy (J•g^{-1} of starch) at the end of the storage (21 days), k is the retrogradation rate constant, and n is the Avrami exponent, which gives an indication of the nucleation characteristics of starch molecules during crystallization (Beck et al., 2011; Wu et al., 2023). The Avrami parameters n and k were obtained by non-lineal regression analysis employing the GraphPad Prism library (GraphPad Software version 6, San Diego, CA). Moreover, to properly evaluate and compare the effects of X, AG, and P on the retrogradation kinetics of TS during storage at 4 °C, the retrogradation enthalpy of the control (TS) after 21 days of storage was used as the term ΔH_∞ in the Avrami equation for all the TS-based systems. Similarly, n value changes for the different samples and consequently k has different units (days^{-n}) in each case, disabling direct comparison among formulations (Longinotti et al., 2002). Therefore, the crystallization half time-values ($t_{1/2}$, days) (Eq. (3)) were calculated for each sample considering the Avrami parameters n and k (Longinotti et al., 2002) to make comparisons among systems valid, as follows:

$$t_{1/2} \quad (days) = -\left(\frac{\ln 0.5}{k}\right)^{1/n} \quad (3)$$

2.4. Statistical analysis

All measurements were performed in triplicates and results were expressed as mean ± standard deviation (SD). Significant differences among systems were evaluated using analysis of variance (ANOVA) and Tukey post hoc test (p-value ≤ 0.05). For determining significant differences among formulations regarding the n and k parameters of the Avrami equation and the crystallization half time values a one-way ANOVA and Tukey post hoc test (p-value ≤ 0.05) were used.

3. Results and discussion

3.1. Pasting properties

The pasting curves of the different TS-based systems can be seen in Fig. 1, which shows differences among them according to the type and amounts of the added natural compounds. From these curves the pasting temperature (PT), peak viscosity (PV), hot paste viscosity (HPV), breakdown viscosity (BD), final viscosity (FV), and setback viscosity (SB) of each sample were calculated as explained in Section 2.2, and results are shown in Table 1.

PT ranged between 63.6 °C and 65.7 °C, without significant differences among samples (p-value > 0.05) (Table 1). This result indicated that the addition of xylitol (X), Arabic gum (AG), or pectin (P) at any concentration did not affect the temperature at which viscosity of the suspension starts to rise due to TS absorbing water molecules during heating. However, significant differences among formulations (p-value ≤ 0.05) were found regarding PV. As shown in Fig. 1 and Table 1, the control system (TS) and P2 % presented the highest PV values, followed by P1 %, X1 %, X2 % and AG1 % and AG0,5 % showing the lowest. Apart from P2 %, the addition of the rest of the compounds reduced the maximum viscosity of the TS-based suspensions, which indicated a lower gelatinization rate of TS due to the presence of the additives. A concentration-related effect was observed for X, as X2 % suspensions resulted with lower PV values than X1 %. Yang et al. (2021) also reported diminished PV of wheat starch suspensions with added X and other polyols and attributed it to the establishment of hydrogen bonding interactions between polyols and starch that generated an inhibition effect on the swelling and gelatinization of starch granule. Given that xylitol is a small molecule with multiple hydroxy groups, the formation of hydrogen bonding with starch and water molecules is highly favored and could have limit the hydration of TS, thus limiting its further gelatinization during heating (Wang et al., 2015; Zhang et al., 2017). Increasing X concentrations led to lower PV values for the presence of more hydroxy groups that could interact with starch and water molecules. Regarding AG, no significant differences were observed between AG0,5 % and AG1 %. It is expected that hydrocolloids addition to starch suspensions causes viscosity increase; but as reported by Singh et al. (2017), the incorporation of low molecular weight gums, as the case of

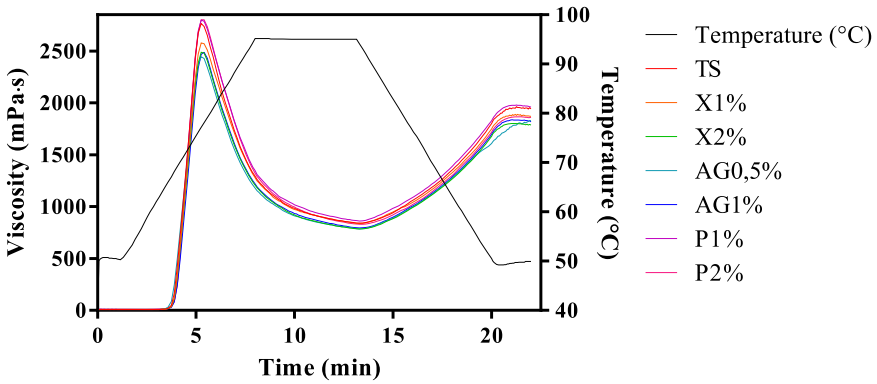

Fig. 1. Pasting profile of the different tapioca starch-based systems with 8 % (w/w) of solids. TS: tapioca starch; X1 %: TS + 1 % xylitol; X2 %: TS + 2 % xylitol; AG0,5 %: TS + 0,5 % Arabic gum; AG1 %: TS + 1 % Arabic gum; P1 %: TS + 1 % pectin; P2 %: TS + 2 % pectin.

Table 1
Pasting properties of the different tapioca starch-based systems*.

Sample	Pasting temperature, PT (°C)	Peak viscosity, PV (mPa·s)	Hot paste viscosity, HPV (mPa·s)	Breakdown viscosity, BD (mPa·s)	Final viscosity, FV (mPa·s)	Setback viscosity, SB (mPa·s)
TS	65.7 ± 0.5^{a}	2751 ± 21^{a}	852 ± 13^{a}	1899 ± 34^{b}	1936 ± 9^{a}	1085 ± 22^{a}
X1 %	65.2 ± 0^{a}	2588 ± 13^{c}	$835 \pm 3^{a,b}$	1754 ± 17^{d}	1870 ± 0^{b}	$1035 \pm 3^{b,c}$
X2 %	64.7 ± 0.4^{a}	2484 ± 5^{d}	784 ± 2^{c}	1701 ± 2^{e}	1789 ± 5^{d}	1006 ± 7^{c}
AG0,5 %	64.6 ± 0.5^{a}	2430 ± 20^{e}	$794 \pm 11^{b,c}$	1636 ± 31^{f}	$1848 \pm 27^{b,c}$	$1054 \pm 16^{a,b}$
AG1 %	65.1 ± 0^{a}	$2461 \pm 37^{d,e}$	788 ± 11^{c}	$1674 \pm 27^{e,f}$	$1805 \pm 18^{c,d}$	$1018 \pm 7^{b,c}$
P1 %	63.6 ± 0.3^{a}	2664 ± 50^{b}	$834 \pm 38^{a,b}$	1831 ± 12^{c}	1859 ± 1^{b}	$1025 \pm 37^{b,c}$
P2 %	64.1 ± 0^{a}	2795 ± 10^{a}	$824 \pm 8^{a,b,c}$	1971 ± 2^{a}	$1850 \pm 14^{b,c}$	$1026 \pm 6^{b,c}$

TS: tapioca starch; X1 %: TS + 1 % xylitol; X2 %: TS + 2 % xylitol; AG0,5 %: TS + 0,5 % Arabic gum; AG1 %: TS + 1 % Arabic gum; P1 %: TS + 1 % pectin; P2 %: TS + 2 % pectin.
*Results are expressed as average ± standard deviation ($n = 3$). Values followed by different letters in each column indicate significant differences among samples (p-value ≤ 0.05).

current AG with 250,000 g/mol (Section 2.1), promotes lower viscosity systems than the control samples without additives, in agreement with present results (Table 1). Similarly, the addition of AG to TS has been reported to reduce the PV of the suspensions due to the coating effect of AG that promotes starch molecules associations and restricts swelling and consequent increment of viscosity (Chen et al., 2015; Zheng et al., 2019). Another explanation could be the retardation of starch granule destruction and leaching of amylose in the presence of anionic AG molecules (Kiprop et al., 2021; Singh et al., 2017). The addition of P1 % significantly reduced PV, while no significant differences with the control were obtained when P was added in 2 %. Similar results were reported by Ma et al. (2019) in corn starch systems, and the authors attributed it to a covering effect of P molecules around starch granules when added at low concentrations, inhibiting starch swelling and reducing PV. On the other hand, these authors reported that higher concentrations of P interspersed within the continuous phase of starch, rising the viscosity of the suspension and increasing the effective concentration of starch granules or leached amylose molecules, which could also explain current results.

Although close results were found among samples, TS, X1 %, P1 % and P2 % presented the highest HPV values, while AG0,5 %, AG1 % and X2 % presented the lowest (Table 1). Similarly, since all samples showed close HPV values, a similar tendency and samples comparison as that of PV for the TS-based formulations can be done for SB results. In this regard, increasing concentrations of X generated lower BD values (Table 1), indicating protective effects of X against TS destruction during heating. These results could be explained by the establishment of non-covalent interactions between X and leached amylose and with the surface of starch granules that protect them against disintegration, leading to reduced BD results (Yang et al., 2021). Similarly, the presence of AG stabilized the integrity of TS and retarded its swelling and shear-thinning, as lower BD values than those of the control system were obtained for suspensions containing this gum, without significant differences regarding the concentration of AG (p-value > 0.05) (Table 1). The protective effects of AG, that were previously described could explain these results. P1 % addition generated a protective effect while higher BD results than the control were obtained for P2 %. In a previous study from our group, a similar concentration-dependent effect was described for P in sweet potato starch suspensions (Rolandelli et al., 2024). It can thus be stated that low concentrations of P (1 %) cover the surface of starch granules and compete with them for water molecules, limiting their swelling and reducing the resulting viscosity (Zhang et al., 2018), but at higher P concentrations, intermolecular distances are shortened and non-covalent interactions such as hydrogen bonding or hydrophobic associations among pectin chains are favored, enhancing starch-water interactions and further structural modifications during heating and shear (Gawkowska et al., 2018).

During cooling down up to 50 °C the reassociation, cross-linking and entanglement of disrupted and leached amylose and amylopectin molecules into a more ordered structure takes place with consequent increment of the viscosity and turbidity of the suspension due to gel formation, reaching a final value that is called FV (Santamaria et al., 2023; Cornejo-Ramírez et al., 2017). Leached amylose chains have a predominant role at this point for their rapid double-helical reassociation compared to amylopectin molecules. The latter reorganize more slowly and, therefore, are responsible for the long-term retrogradation of starch (Donmez et al., 2021; Wang et al., 2015). TS (control) presented the highest FV values, followed by X1 %, P1 %, P2 %, AG0,5 % without significant differences among them, then AG1 %, that did not differ with AG0,5 % or P2 %, and finally X2 %, with the lowest results. Due to lower swelling degree of TS in the presence of the added compounds at any concentration, it is expected that the FV of the blends

resulted in lower values than the control, with differences among them according to the degree of interaction with starch or to the display of their protective effects against disintegration or amylose leaching. Hydrogen bonding interactions between the hydrophilic compounds and water may have limited starch hydration, further swelling and gelatinization. Moreover, non-covalent interactions between starch and the additives may have interfered with the reorganization of amylose and amylopectin molecules during cooling, limiting the rise of FV (Rolandelli et al., 2024).

SB is associated with the reorganization of starch molecules during cooling, particularly amylose molecules and, therefore, can be used as an indicator of the short-term retrogradation (Kiprop et al., 2021). Considering SB results of TS-based systems shown in Table 1, the formulations can be listed in the following order according to their susceptibility towards short-term retrogradation: TS ≥ AG0,5 % ≈ X1 % ≈ P2 % ≈ P1 % ≈ AG1 % ≥ X2 %. Apart from AG0,5 %, all samples presented lower SB values than the control, confirming a delaying effect towards short-term retrogradation. It was previously described that the addition of X, AG, and P limited amylose leaching and that amylose-additive non-covalent interactions were established, affecting amylose reorganization during cooling down, which could explain these results (Ma et al., 2019). Particularly, X2 % presented the lowest SB values, indicating the highest resistance against recrystallization. The establishment of multiple hydrogen bonds between X and starch may have affected the reorganization of starch molecules, diminishing FV and SB values (Yang et al., 2021; Zhang et al., 2017). Moreover, competition for water molecules may have restricted starch hydration and further recrystallization, which could also explain current results (Rolandelli et al., 2024; Zhang et al., 2018). X was particularly effective in lowering the viscosity of TS-based suspensions and the effects were enhanced at higher X concentrations. Since X is a compound with low molecular weight, its presence could have hindered the interactions between TS and water molecules, limiting TS gelatinization (Zhang et al., 2017). Moreover, given its smaller molecular size compared to P and AG, X could have also interfered in the reorganization of amylose and amylopectin chains during cooling, leading to low SB values.

3.2. Storage assay: retrogradation analysis

3.2.1. Molecular mobility of water and proton population distribution

As a measure of the progress of TS retrogradation, changes in the molecular mobility of water proton populations during storage at 4 °C in TS-based systems were analyzed by evaluating the spin-spin transverse relaxation times (T_2) and their respective associated relative amplitude (A, %). Results were fitted to a bi-exponential equation (Eq. (1)), from which the parameters T_{21} (short spin-spin relaxation time), T_{22} (long spin-spin relaxation time), and the corresponding amplitudes A_{21} and A_{22}, respectively, were obtained for each system during 0, 1, 3, 7, 14, and 21 days of storage and compared among formulations (Fig. 2).

T_{21} ranged between 21.8 and 203.3 ms (Fig. 2 A) and corresponded to relaxation times of water protons with weak interactions with solids ("multilayer water"), and A_{21} is an indicator of the relative amount of proton molecules that were present in this population; T_{22} varied between 335.4 and 907.1 ms (Fig. 2 B) and corresponded to the relaxation times of water protons with higher mobility, also known as "free water", and A_{22} indicates the relative amount of proton molecules that constituted this water population from the total (Rolandelli et al., 2024).

For most of the samples T_{21} and T_{22} values progressively decreased during storage, with a significant diminishment after 1 and 3 days of storage, reaching the lowest results after 21 days (Fig. 2 A and B, respectively). The relative amplitudes A_{21} varied between 0.85 % and 5.1 %, while A_{22} ranged between 94.9 % and 99.1 % (Fig. 2 C and D, respectively), which indicated a predominance of the free water population over the weakly interacting with solids one throughout the assay. Particularly, the relative amplitude of multilayer water proton population (A_{21}) also decreased with the progress of storage, while A_{22} increased throughout the period of study, with significant modifications in both cases within the first 3 days of storage for all systems (Fig. 2 C and D, respectively). These modifications are indicative of the reaccommodation of starch molecules and water during the progress of

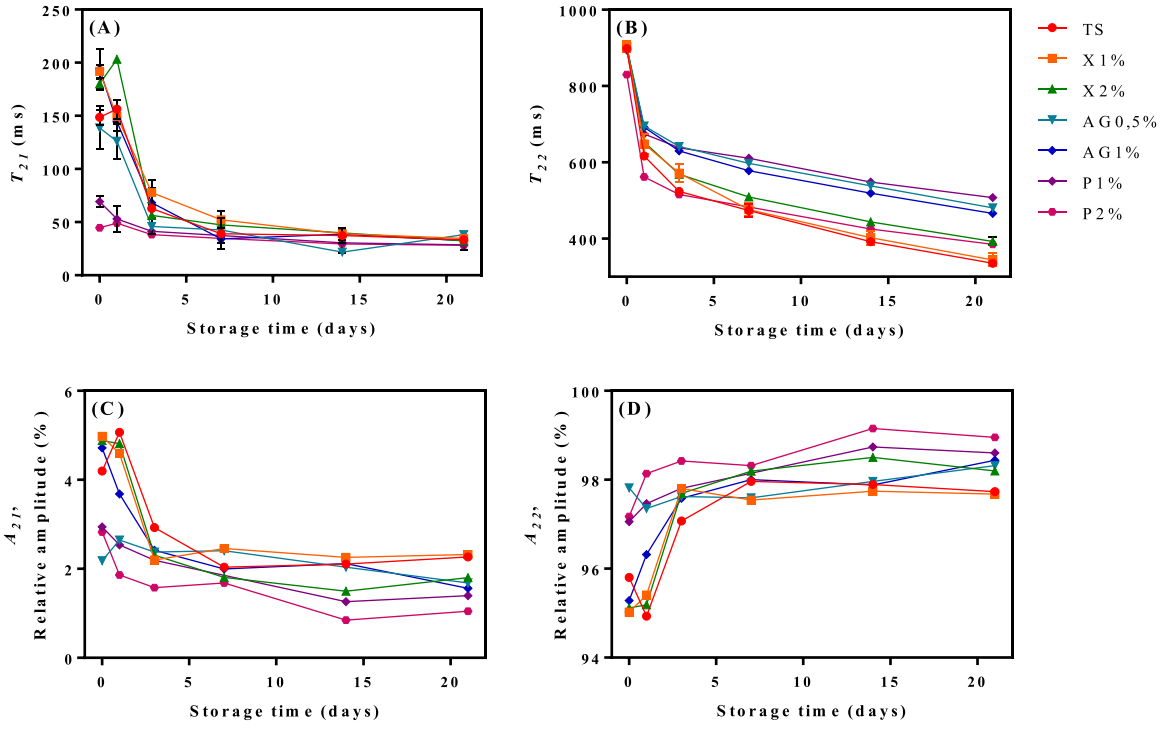

Fig. 2. Changes in relaxation times (T_2, ms) and relative amplitudes (%) of the proton populations of the different tapioca starch-based systems during storage at 4°C for 21 days. TS: tapioca starch; X1 %: TS + 1 % xylitol; X2 %: TS + 2 % xylitol; AG0,5 %: TS + 0,5 % Arabic gum; AG1 %: TS + 1 % Arabic gum; P1 %: TS + 1 % pectin; P2 %: TS + 2 % pectin. (A) T_{21}, (B) T_{22}, (C) A_{21}, and (D) A_{22} as a function of storage time (days).

TS retrogradation: the longer the storage time, the more TS molecules tend to reassociate, increasing their inter- and intra-molecular interactions. Consequently, lower T_{21} reflected the reduced strength of the starch network and of its molecular mobility (Wang et al., 2015), with simultaneous displacement of multilayer water molecules towards the free water molecules population (smaller $\%A_{21}$ and higher $\%A_{22}$) (Yang et al., 2021; Zheng et al., 2020). Regarding the T_{22} decrease, the lower molecular mobility of the water protons has been linked to the progressive conversion of starch chains from the amorphous to the crystalline state during which some free water molecules rearrange in the crystalline region (Liu et al., 2019; Zheng et al., 2019; Zheng et al., 2020). It is important to note that the more mobile water proton population increased (higher A_{22}), but its molecular mobility decreased (lower T_{22}) due to TS molecules reassociation with the progress of time (Yang et al., 2021). T_{22} values decrease during storage at 4°C has also been described in other TS-based systems (Baranowska et al., 2012).

When evaluating the effects of the additives, in general terms, P-containing systems presented the lowest T_{21} and T_{22} values and A_{21} percentages after gelatinization (0 days of storage), with P2 % showing lower values than P1 % (Fig. 2 A, B and C, respectively). Similarly, higher A_{22} results than the control were obtained (Fig. 2 D). This trend continued throughout the entire evaluated period. These results indicate that P addition diminished the amount of water molecules weakly interacting with solids (lower A_{21}) and promoted the accumulation of free water (higher A_{22}) in TS-based systems, but strengthened their interactions causing a reduction in their mobility (lower T_{21} and T_{22} values). In this regard, higher P concentrations enhanced these effects, which could be due to the establishment of higher number of non-covalent interactions between P and TS or water, limiting their molecular mobility (Gawkowska et al., 2018; Ma et al., 2019; Rolandelli et al., 2024).

On the contrary, X addition, particularly X2 %, enhanced the mobility of multilayer and free water molecules at 0 and 1 day of storage when compared to the control, since higher T_{21} and T_{22} values than those of TS were obtained, but their amplitude values were not significantly affected. This indicates that multilayer and free water molecules became more mobile in the presence of X, but the number of molecules did not differ for both populations when compared to the control.

In AG containing systems, similar T_{21} values to the control were obtained after 0 and 1 day of storage, but lower A_{21} values resulted from its addition, particularly at 0.5 %, indicating that multilayer water mobility was not significantly affected, but less amounts of water molecules were present in this population. Similarly, higher T_{22} and A_{22} values than the control resulted from the addition of AG at 0 and 1 day of storage, particularly at 0.5 %, indicating that TS retrogradation was favored due to the enhancement of molecular mobility and the increased number of free water molecules when compared to the control. This is in agreement with the SB values discussed in Section 3.1. Zheng et al. (2019) also reported increased syneresis and retrogradation degree of lotus seed starch in the presence of AG for the promotion of amylopectin reorganization when AG was added. The authors explained that this could be due to an increment of the amylose and amylopectin effective concentration in the continuous phase by the addition of AG that promotes retrogradation during storage. It seems that AG molecules are more likely to interact to each other rather than to starch or water molecules given their branched structure. In this regard, Masuelli (2013) described that AG are nonlinear molecules that are displayed in a random coil shape in aqueous solutions, but tend to aggregate or compact with increasing temperatures, supporting current explanations.

As previously stated, with the progress of storage, T_{21}, A_{21}, and T_{22} values gradually decreased while A_{22} gradually increased for all samples. This could be explained by the re-association of TS molecules during storage, enhancing their inter and intramolecular interactions and limiting the mobility of water molecules (lower T_{21}). During this reassociation, weakly bound water migrates towards the free water molecules population (lower A_{21} and higher A_{22}) while at the same time free water molecules are involved in the reorganization of amylopectin molecules, limiting their mobility (lower T_{22}). The above-mentioned effects of the additives on water migration and TS reassociation explain the differences in the TS retrogradation kinetics.

For a better visualization of the diminishment of T_{22} values and the increase of A_{22} with the progress of storage, this proton population was plotted in a logarithmic scale for each system as a function of time (Fig. 3) after an inverse Laplace transformation (Section 2.3.1). After gelatinization (0 days of storage) the gel was recently formed, and a free water molecules population with a wide distribution of relaxation times and a relatively smaller amplitude was detected. In contrast, after 1 day of storage, the gel was completely formed and solidified, generating a defined water population, but with lower relaxation times due to the strengthened TS gel. Similarly, with the progress of storage time and TS retrogradation, relaxation times tend to diminish but relative amplitudes tend to increase in all cases, as previously discussed in relation to Fig. 2. After 21 days of storage, the free water molecules population presented the lowest relaxation times, but the highest relative amplitude percentages. A similar tendency was reported for locus seed starch-based systems (Zheng et al., 2020).

3.2.2. *Differential scanning calorimetry (DSC)*

The gelatinization and retrogradation temperatures (onset, peak, and endset) of the different TS-based systems during storage at 4°C have been determined (Supplementary File 1). The gelatinization onset (0 days of storage) ranged between 60.3 °C and 59 °C, without significant differences among samples. The gelatinization enthalpies (ΔH) varied between 11.9 and 8.7 $J \bullet g^{-1}$ of starch (Table 2). All blends showed significantly lower gelatinization enthalpies than the control sample, which could be related to a restriction of TS gelatinization in the presence of the additives, as discussed in Section 3.1, due to coating effects, competition for water molecules and/or the establishment of hydrogen bonds and other non-covalent interactions between TS and the additives, limiting its further swelling and gelatinization. Retrogradation onset temperatures (1–21 days of storage at 4 °C) were lower than the gelatinization ones (Supplementary File 1) as less amount of energy is necessary to swell starch molecules with less ordered structures than native starch molecules (Wang et al., 2015). For most samples, retrogradation onset at 1 day of storage was higher than for longer days of storage (7, 14 and 21 days). This could be due to a rapid reorganization of starch molecules within the first 24 h of storage.

Table 2 also shows the retrogradation degree (%) of the different TS-based systems during storage that were calculated from the enthalpy values (ΔH, $J \bullet g^{-1}$) at each time. With the progress of storage time, enthalpy values increased in all cases due to the larger reassociation of amylose and amylopectin molecules and the formation of higher amounts of organized crystallites, but at a varying rate according to the composition of the system. After 1 day of storage, AG-containing formulations, P1 % and TS systems showed the highest retrogradation degree of all formulations (8–9.5 %), while P2 % and X-based systems, the lowest (of around 5 %). A significant increase occurred after 7 days of storage for all systems, with AG1 % presenting the highest retrogradation degree, followed by P2 %, AG0,5 %, and TS, without significant differences among them, and then X1 %, P1 %, and X2 %, showed the lowest values. These results suggest that AG at both concentrations and P at 2 % accelerate the retrogradation kinetics of TS, while X at both concentrations and P at 1 % inhibit it. As described before, AG promotes the reorganization of TS molecules, favoring the retrogradation. Chen et al. (2015) have also reported accelerated syneresis of TS in the presence of AG. On the contrary, X establishes hydrogen bonds with starch and water molecules, limiting their mobility and weakening TS reassociation and further recrystallization (Yang et al., 2021). Zhang et al. (2017) also reported reduced retrogradation enthalpy in TS-based systems added with low molecular sugars.

The retrogradation degree kept rising with the progress of storage at 4°C, but at a lower rate than the first 7 days of storage. After 14 days,

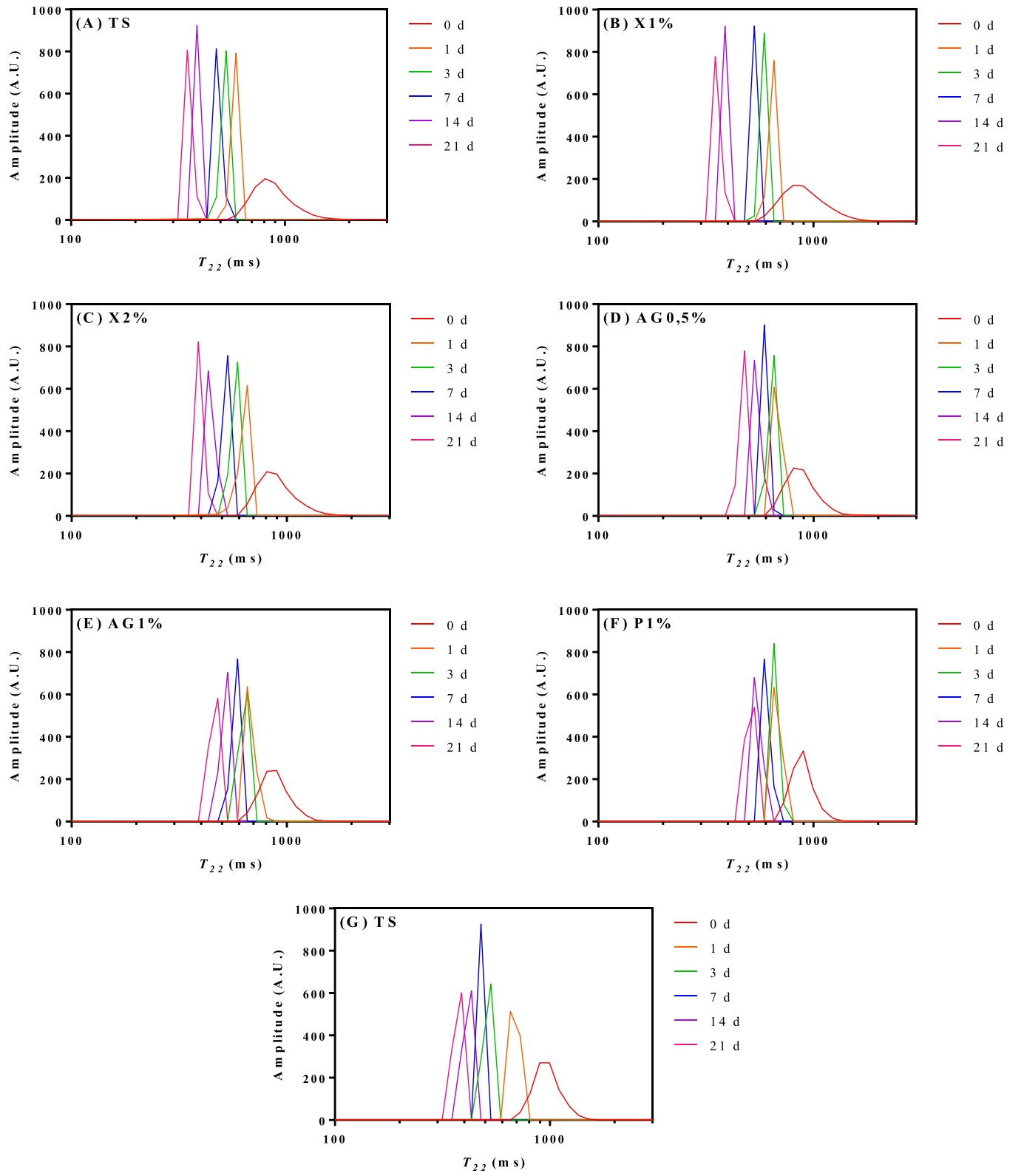

Fig. 3. Proton population distribution of the different tapioca starch-based systems during storage at 4°C for 21 days. (A) TS: tapioca starch; (B) X1 %: TS + 1 % xylitol; (C) X2 %: TS + 2 % xylitol; (D) AG0,5 %: TS + 0,5 % Arabic gum; (E) AG1 %: TS + 1 % Arabic gum; (F) P1 %: TS + 1 % pectin; (G) P2 %: TS + 2 % pectin. d: days of storage at 4°C.

AG-containing systems presented the highest values among formulations (37–39 %), followed by TS (35 %) and then, the rest of the samples (28.9–32 %), without significant differences among them (Table 2). A similar tendency was observed after 21 days of storage, in which the addition of AG at any concentration resulted in increased retrogradation degree when compared to the control, while lower values resulted from the addition of X. As for P, when 1 % was added, lower retrogradation degree was observed, but higher when present in 2 %. The promotion of

Table 2
Gelatinization enthalpy (ΔH, J•g^{-1} of starch) and retrogradation degree (%) of the different tapioca starch-based systems during storage at 4 °C.*.

Systems	Gelatinization enthalpy (ΔH, J•g^{-1} of starch)	Storage time (days)			
		1	7	14	21
TS	11.9 ± 0.2^{a}	$8 \pm 1^{abc,D}$	$28.4 \pm 0.3^{bc,C}$	$35 \pm 1^{b,B}$	$38.2 \pm 0.2^{bc,A}$
X1 %	10.3 ± 0.3^{bc}	$5.5 \pm 0.2^{bcd,C}$	$26.2 \pm 0.4^{cd,B}$	$32 \pm 1^{c,A}$	$34 \pm 1^{d,A}$
X2 %	10.9 ± 0.1^{b}	$5 \pm 1^{cd,D}$	$25 \pm 1^{d,C}$	$28.9 \pm 0.2^{c,B}$	$35.4 \pm 0.4^{cd,A}$
AG0,5 %	10.2 ± 0.3^{bcd}	$8 \pm 1^{ab,D}$	$29 \pm 2^{bc,C}$	$37 \pm 1^{ab,B}$	$40 \pm 1^{ab,A}$
AG1 %	9.4 ± 0.4^{de}	$9.5 \pm 0.2^{a,D}$	$33.9 \pm 0.5^{a,C}$	$39 \pm 2^{a,B}$	$42 \pm 2^{a,A}$
P1 %	9.5 ± 0.4^{cd}	$4.8 \pm 0.4^{d,D}$	$25.3 \pm 0.2^{d,C}$	$30 \pm 1^{c,B}$	$33.3 \pm 0.4^{d,A}$
P2 %	8.7 ± 0.3^{e}	$8 \pm 1^{abcd,C}$	$29 \pm 2^{b,B}$	$32 \pm 1^{c,B}$	$38.3 \pm 0.4^{bc,A}$

TS: tapioca starch; X1 %: TS + 1 % xylitol; X2 %: TS + 2 % xylitol; AG0,5 %: TS + 0,5 % Arabic gum; AG1 %: TS + 1 % Arabic gum; P1 %: TS + 1 % pectin; P2 %: TS + 2 % pectin.
*Results are expressed as average ± standard deviation ($n = 3$). Values followed by different letters in each column indicate significant differences: for the retrogradation degree minuscule letters indicate differences among systems for each storage time, while capital letters represent differences among storage time for each system (p-value ≤ 0.05). Significant differences among gelatinization enthalpy values are indicated by different minuscule letters for each system (p-value ≤ 0.05).

starch retrogradation kinetics by the addition of AG has also been reported by Zheng et al. (2019) and Zheng et al. (2020) in lotus seed starch-based system, while the inhibiting effects of different polyols or low molecular sugars on wheat and tapioca starch retrogradation were reported by Yang et al. (2021) and Zhang et al. (2017), respectively. A similar concentration-related effect in P containing systems was described in a previous study (Rolandelli et al., 2024) and it was attributed to different inter and intramolecular interactions between pectin and starch that change with pectin concentration. While present at 1 %, P molecules cover starch granules and limit their hydration, gelatinization and further retrogradation during storage for their high water uptake given their hydrophilicity (Zhang et al., 2018). Nevertheless, at higher concentrations, pectin-pectin non-covalent interactions are favored for the reduction of the intermolecular distances, favoring water-starch associations and enhancing TS retrogradation (Gawkowska et al., 2018; Han et al., 2017).

The Avrami equation (Eq. (2), Section 2.3.2) was used to obtain TS retrogradation kinetics parameters n and k. From these parameters, the crystallization half time-values ($t_{1/2}$) were calculated (Eq. (3), Section 2.3.2) for a deeper evaluation of the modulation effects of the studied additives. Results of Avrami parameters and $t_{1/2}$ can be seen in Table 3. All coefficients of determination (R^2) were ≥ 0.97, indicating good data fitting to the equation. n values ranged between 0.83 and 1.07, with significant differences among formulations, but this result indicated that recrystallization of starch molecules occurred in an unidimensional way for all samples and with a rod-like shape (Beck et al., 2011; Wu et al., 2023; Zhang et al., 2017). Significant differences among formulations were also obtained for k values, but since its units change according to the n value, $t_{1/2}$ results are more valid for a proper comparison among samples (Longinotti et al., 2002). In this regard, X2 %, P1 % and X1 % required higher amount of time to reach the 50 % of starch retrogradation than TS, confirming its inhibiting or delaying effects, while shorter times were found for AG0,5 %, AG1 % and P2 %, indicating promoting or enhancing effects. Particularly, it is important to highlight that close results to the control were found for P2 %, although with significant differences.

Table 3
Avrami fitting parameters (n and k) and crystallization half-time values ($t_{1/2}$) of the different tapioca starch-based systems.*.

Systems	Avrami parameters			
	n	k (days^{-n})	R^2	$t_{1/2}$ (days)
TS	0.9091 ± 0.0001^{c}	0.2323 ± 0.0001^{c}	0.9979	3.328 ± 0.001^{e}
X1 %	0.8564 ± 0.0002^{d}	0.1932 ± 0.0001^{e}	0.9874	4.444 ± 0.001^{c}
X2 %	0.851 ± 0.002^{de}	0.1764 ± 0.0001^{g}	0.9822	4.993 ± 0.002^{a}
AG0,5 %	0.975 ± 0.003^{b}	0.229 ± 0.002^{d}	0.9886	3.114 ± 0.001^{f}
AG1 %	1.074 ± 0.004^{a}	0.2821 ± 0.0002^{a}	0.9723	2.309 ± 0.003^{g}
P1 %	0.8265 ± 0.0002^{f}	0.1852 ± 0.0001^{f}	0.9802	4.937 ± 0.002^{b}
P2 %	0.8481 ± 0.0001^{e}	0.2484 ± 0.0003^{b}	0.9727	3.353 ± 0.002^{d}

TS: tapioca starch; X1 %: TS + 1 % xylitol; X2 %: TS + 2 % xylitol; AG0,5 %: TS + 0,5 % Arabic gum; AG1 %: TS + 1 % Arabic gum; P1 %: TS + 1 % pectin; P2 %: TS + 2 % pectin. R^2: coefficient of determination.
* Results are expressed as average ± standard deviation ($n = 3$). Values followed by different letters in each column indicate significant differences among systems (p-value ≤ 0.05).

3.3. General discussion

Structural differences among the added compounds led to distinct TS behavior during storage and affected the retrogradation kinetics. On one hand, xylitol (X) is a small molecule with 5 hydroxyl groups. This allows the establishment of multiple hydrogen bonds and other non-covalent interactions with water, limiting starch hydration and further gelatinization during heating (Yang et al., 2021), which explains the less capacity towards pasting properties of TS-based systems in the presence of X (Section 3.1). Moreover, higher X concentrations enhanced these modifications for the higher presence of hydroxyl groups. During storage, these interactions also diminished the level of reorganization of starch chains, explaining the inhibition of TS retrogradation, as demonstrated during ^{1}H-NMR analysis for the lower molecular mobility of proton populations (Section 3.2.1). In addition, its lower molecular size could have interfered amylose and amylopectin chains reaccommodating (Zhang et al., 2017), which could also explain the lower retrogradation degree and higher $t_{1/2}$ values (Section 3.2.2). On the other hand, Arabic gum (AG) is a large and branched molecule with coating properties. Therefore, its addition diminished the peak, hot paste, breakdown and final viscosities of the suspensions (Table 1) for these coating effect that limited TS hydration and further gelatinization. Nevertheless, the presence of AG favored TS retrogradation. This could be due to conformational changes of AG molecules after heating, which adopt a more compact structure (Masuelli, 2013), with consequent increment of starch effective concentration in the continuous phase that favors its recrystallization (Zheng et al., 2019), as confirmed by ^{1}H-NMR and DSC results. Finally, pectin (P) addition at 1 % was effective in delaying TS retrogradation, but promoted it when present at 2 %. The presence of P at lower amounts cover starch granules and compete with them for water uptake, with consequences in the pasting and retrogradation properties. Nevertheless, higher concentrations favor pectin-pectin interactions and cross-linking junctions between the hydrophobic regions for a reduction in the intermolecular distances that ultimately favors TS interactions with water and further reaccommodating during storage (Gawkowska et al., 2018; Han et al., 2017; Zhang et al., 2018). Similar P concentration-related results were reported in a previous study (Rolandelli et al., 2024).

4. Conclusions

Tapioca starch (TS) pasting properties and retrogradation kinetics during storage at 4°C were modulated by the addition of xylitol, Arabic gum, and pectin, which showed different effects based on their molecular characteristics and the level of associations with starch and water. Xylitol was particularly effective in inhibiting TS retrogradation given its hydrophilicity and the establishment of hydrogen bonds with TS and/

or water, limiting its hydration and further swelling, as evidenced by the lower viscosity of the resulting pastes and the retrogradation enthalpy and kinetics parameters when compared to the control. These effects were enhanced at higher xylitol concentrations. Moreover, its small molecular size could have interfered in the recrystallization of TS during storage, inhibiting its retrogradation and these effects were enhanced at higher xylitol concentrations. On the contrary, the addition of Arabic gum enhanced TS retrogradation, as higher retrogradation degree, lower crystallization half time values and more free water molecules with higher mobility were obtained. This is attributed to a coating effect of Arabic gum that facilitates intermolecular interactions, increasing starch chains concentrations in the continuous phase and further reassociation. For pectin, a concentration-dependent effect was observed, as 1 % addition limited TS retrogradation, but promoted it when 2 % was added, which is due to changes in the inter- and intra- non-covalent interactions with starch according to pectin concentration. Moreover, it was found that with the progress of starch retrogradation, molecular mobility of the more mobile water molecules decreased as they were involved in the reorganization of starch molecules. Current results broaden the potential industrial utilization of natural additives for their modulating effects on starch retrogradation for the development of gluten-free products with multiple applications.

CRediT authorship contribution statement

Rodriguez Silvio: Writing – original draft, Funding acquisition, Formal analysis, Data curation. **Rolandelli Guido:** Writing – original draft, Investigation, Formal analysis, Data curation. **Buera Pilar:** Writing – original draft, Visualization, Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

All authors declare that there is no conflict of interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.foostr.2025.100450.

Data availability

Data will be made available on request.

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