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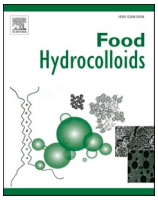

Impact of starch-hydrocolloid interaction on pasting properties and enzymatic hydrolysis

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ABSTRACT

Hydrocolloids are extensively used for food processing because their techno functional properties (emulsifier, stabilizer, and structural agent). But there is increasing interest in their role connected with nutritional improvements, particularly related to starch hydrolysis rates, which might involve the viscosity resulting from starch-hydrocolloid interaction. The objective of this research was to investigate the impact of gels viscosity on the enzymatic hydrolysis of a range of starch gels made with different starches and hydrocolloids. Heterogeneous systems (starch-hydrocolloid) were prepared with several starches (corn, wheat, rice, potato, cassava, pea) and hydrocolloids (locust bean gum, guar gum, xanthan gum, hydroxypropylmethylcellulose K4M, psyllium) at different concentrations (0%–0.5% - 2.5%). The starch-hydrocolloid pasting behavior and their susceptibility to amylase hydrolysis was recorded with the Rapid Viscoanalyzer following a rapid method (Santamaria, Montes, Garzon, Moreira, & Rosell, 2022a). The viscosity decay due to alpha-amylase activity was modeled to obtain starch gels hydrolysis rate (k). A negative correlation was found among kinetic constant (k) and viscosity at 37 °C ($r = -0.55$), setback ($r = -0.50$), and area under the pasting curve ($r = -0.42$). For instance, xanthan gum and psyllium addition showed strong negative correlation between kinetic constant and viscosity at 37 °C ($r = -0.75$) and setback ($r = -0.79$), respectively, particularly when blended with potato starch. These correlations indicate that pasting properties of the starch-hydrocolloid systems might be predictors of the enzymatic digestion rate of the gels, allowing the design of foods with controlled postprandial glucose response.

1. Introduction

Hydrocolloids are crucial players in food processing due to their thickening, gelling, foaming and, water-holding capacity, but also their functionality is extended to food nutrition, specifically digestion and gastrointestinal transport of nutrients (Abdel-Aal, 2009; McClements, 2021). Particularly important is the role of hydrocolloids in starch-based systems because they limit the water molecules availability and in turn the gelatinization performance of the starch. However, that effect is greatly dependent on the starch-hydrocolloid binomial (Rosell, Yokoyama, & Shoemaker, 2011).

Regarding the role of hydrocolloids on the digestion of starch-based systems, numerous studies have been carried out. Gularte and Rosell (2011) analyzed the association between hydration and pasting properties with the *in vitro* digestibility of corn and potato starches in the presence of different hydrocolloids (high methoxylated pectin, guar gum, carboxymethylcellulose-CMC, xanthan gum, and hydroxypropylmethylcellulose -HPMC). The enzymatic hydrolysis rate was lower in guar gum - potato starch mixture, which was correlated with a viscosity increase that decrease the diffusion and activity of the amylase enzyme. Fabek, Messerschmidt, Brulport, and Goff (2014) studied the impact of several hydrocolloids (guar gum, locust bean gum, fenugreek gum, flaxseed gum, xanthan gum, and soy-soluble polysaccharide) on the digestibility of waxy corn starch gels. The addition of hydrocolloids decreased glucose diffusion, and there was an inverse correlation between the digesta viscosity they induce, and the glucose amount released from starch hydrolysis. Likewise, Sasaki, Sotome, and Okadome (2015) analyzed the enzymatic hydrolysis of gelatinized potato starch, containing xanthan gum, guar gum, pectin, or konjac-glucomannan at different concentrations (5, 10, or 15%). Xanthan gum showed the most pronounced suppressive effect on the digestibility of gelatinized potato starch, which was attributed to xanthan gum interaction with potato amylopectin, producing a firm barrier that impedes starch hydrolysis. Conversely, the interaction

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hydrocolloid-amylose was mentioned by Jung et al. (2017), who studied high amylose rice gels made with different concentrations (0.3, 0.5, or 0.7%) of xanthan gum, Arabic gum, guar gum, or locust bean gum. Arabic and xanthan gum showed the greatest effect lowering glucose release, due to the high digesta viscosity. Nevertheless, Zhou et al. (2020) reported higher reduction of corn starch digestion when blending it with 2.5% guar gum, stressing the importance of the hydrocolloid concentration.

Therefore, different hypothesis have been proposed to explain the hydrocolloids effect on starch digestibility, namely hydrocolloid interaction with starch granules through amylose or amylopectin (Sasaki et al., 2015), the formation of a hydrated layer encapsulating starch granules, or the viscosity increase of the digesta (Wee & Henry, 2020). It has been described that digesta viscosity has a significant impact on food digestion, since it reduces gastric emptying, decreases mass transfer and may slow down enzymatic action (Manzoor, Singh, Bandral, Gani, & Shams, 2020; Santamaria, Garzon, Moreira, & Rosell, 2021), but there is scarce information about potential relationship between those systems viscosity and the digestion rate.

Considering that starch-hydrocolloid interaction is dependent on both, the starch source, and the type of hydrocolloid, as well as the concentrations used, the aim of this study was to analyze the impact of gels viscosity on the enzymatic hydrolysis, of a range of starch gels made with different starches and hydrocolloids. To allow a large screening using different conditions, a simple, rapid, and reliable method reported by Santamaria et al. (2022a) was applied, recording the rheological behavior of starches and their performance during α-amylase hydrolysis. Several starches (corn, wheat, rice, potato, pea, and cassava) and hydrocolloids (locust bean gum, xanthan gum, guar gum, hydroxypropylmethylcellulose K4M and psyllium) at different concentrations (0%–0.5% - 2.5%) were used to investigate their impact in the rate of starch hydrolysis.

2. Materials and methods

2.1. Materials

The starches from corn (CO), wheat (W), potato (PO) (EPSA, Valencia, Spain), green pea (PE) (Esteve Santiago, Valladolid, Spain), rice (R) and cassava (CA) (local market) were employed and further characterized in the present study. Their moisture contents were 13.74%, 12.12%, 17.86%, 10.96%, 12.85% and 10.52% respectively. Regarding the hydrocolloids, locus bean gum (LBG) was generously provided by G.A Torres (Valencia, Spain), xanthan gum (XG) and guar gum (GG) were from Grupo Desarrollo (Valencia, Spain), psyllium (Isabgol, sterilized psyllium husk powder) (P) was provided by Sarda Biopolymers (Mumbai, India) and hydroxypropylmethylcellulose K4M (HPMC) was obtained from Sigma Aldrich (St Louis, Misuri, USA).

The enzyme used was VI-B α-amylase from porcine pancreas (EC 3.2.1.1) from Sigma Aldrich (Sigma Chemical, St. Louis, USA) dissolved into 0.3 M sodium maleate buffer (pH 6.9). Solutions were made using deionized water. Reagents were of analytical grade.

2.2. Physicochemical composition of starches and hydrocolloids

The protein content was determined according to ISO 16634–2:2016. The amylose content of starches was quantified using a commercial amylose/amylopectin assay kit (K-AMYL 06/18, Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland) based on amylopectin complexes with the lectin concanavalin A. Molecular weight of starches were determined by Size-Exclusion Chromatography (SECurity 1260, Polymer Standard Service, Mainz, Germany) coupled with Multi Angle Light Scattering (MALS). The mobile phase was DMSO with 0.1 M LiCl. Samples were dissolved at 80 °C, then centrifugated for 10 min at 5000 rpm and filtered through a 0.2 μm filter before being injected into the Gel Permeation Chromatography (GPC). An analytical column (PSS-Suprema, 10 μm, 10,000 Å, ID 8.0 mm × 300 mm) was used at 70 °C with 0.5 mL/min of flow rate.

The particle size of starches and hydrocolloids was determined by Mastersizer equipment (Scirocco 2000; Malvern Instruments Ltd., Worcestershire, UK), by laser diffraction technique and the results obtained were estimated based on volume. The volume-weighted mean diameter D (4,3) was calculated by Eq. (1). The measurement was carried out in three replicates.

$$D(4,3) = \Sigma \text{ di} \bullet \text{Vi} / \Sigma \text{ Vi} \quad \text{Eq. (1)}$$

Hydrocolloid viscosity was measured in 2% suspensions of hydrocolloid: water. The mixtures were shaken in Vibromatic (J.P Selecta S.A, Abreda, Barcelona, Spain) for 20 min. Then, samples were stored in a shaker incubator SKI 4 (ARGO Lab, Carpi, Italy) at 25 °C under constant stirring at 200 rpm for 24 h. Viscosity suspensions were measured with a HAAKE viscotester 3 (Thermo Scientific, Massachusetts, US) using rotor no.1 with the measuring range (300 mPa s to 15000 mPa s).

2.3. Pasting behavior and digestograms of gels

Starch-hydrocolloid slurries were analyzed in the Rapid Viscoanalyzer (RVA 4500; Perten Instruments, Hägersten, Sweden). Pasting performance and digestograms were examined following the method described by Santamaria et al. (2022a) with minor modifications. Three grams (14% mb) of starch plus hydrocolloid at different concentrations (0%–0.5% - 2.5%) were dissolved in 25 mL of distilled water. Slurries were exposed to heating and cooling cycles including 50 °C for 1 min, heating from 50 to 95 °C in 3 min 42 s, holding at 95 °C for 2 min 30 s, then cooling down to 37 °C in 4 min 90 s, stopping at 37 °C for 36 s to add the α-amylase solution (900 U/mL in 0.3 M sodium maleate buffer pH 6.9), and holding at 37 °C for 5 min. In the first stage during pasting performance, the parameters obtained were: onset (the time when viscosity started to increase), peak viscosity (highest viscosity during heating), trough (lowest viscosity when holding at 95 °C), breakdown (difference between the maximum and minimum viscosity), final viscosity at 37 °C, setback (difference among final viscosity and trough), and to obtain a representative parameter of the complete pasting performance, the area under the curve (AUC) was calculated.

In the second stage during de digestograms, kinetic constant (k) was calculated using a first-order equation (Eq. 2), where μ was the apparent viscosity (mPa s), μ_0 was the initial viscosity, μ_∞ was the final viscosity, k (min^{-1}) was the kinetic constant and t (min) was hydrolysis time. The Microsoft Excel Solver® was utilized to model first-order kinetic equations.

$$\mu = \mu_\infty + (\mu_0 - \mu_\infty)e^{-kt} \quad \text{Eq. (2)}$$

2.4. Statistical analyses

Three replicates were made for each sample. Experimental data were statistically analyzed by Statgraphics Centurion XVII software (Statistical Graphics Corporation, Rockville, MD, USA). Raw materials properties were examined using an analysis of variation (ANOVA). Multivariate analysis of variance (MANOVA) was used to evaluate pasting and hydrolysis parameters. The results were presented as mean ± standard deviation using Fisher's least significant differences test (LSD). Differences of $p < 0.05$ were considered significant. Furthermore, a principal component analysis (PCA) was made to explain the variability of the parameters. Pearson correlation and lineal regression were applied to identify possible correlations between pasting parameters (viscosity at 37 °C, setback and AUC) with kinetic constant (k).

3. Results and discussion

3.1. Raw materials characterization

Starches showed significant differences ($p < 0.05$) in their physicochemical properties (Table 1). Tuber starches (potato and cassava) had the lowest protein content, followed by cereals starches. Conversely, pea starch had the highest protein content (14.63 ± 0.08%). Similar protein content in starches has been reported by Aleixandre, Benavent-Gil, Moreira, and Rosell (2021). Amylose fraction was quantified, because it has been reported that it can interact with hydrocolloids, hindering the alpha-amylase accessibility. Amylose content ranged from 38.49% in the case of pea starch to 12.58% in rice starch. Cereals starches had lower amylose content than pulse starches (Bajaj, Singh, Kaur, & Inouchi, 2018). Corn starch, besides rice starch, showed the lowest average particle diameter of volume D (4,3), similarly to the value reported by Zhou et al. (2020). In opposition, cassava starch showed high average particle size value, which could be related to a less uniform milling. These results are in accordance with a previous study (Li et al., 2020). Regarding, the molecular weight (Mw) of the starches, the order was potato ($18.200{\cdot}10^6$ g/mol) > rice ($5.212{\cdot}10^6$ g/mol) > cassava ($3.841{\cdot}10^6$ g/mol) > wheat ($3.416{\cdot}10^6$ g/mol) > corn ($2.769{\cdot}10^6$ g/mol) > pea ($2.318{\cdot}10^6$ g/mol). Similar results were found by Ong, Jumel, Tokarczuk, Blanshard, and Harding (1994).

For the hydrocolloids' characterization, volume diameter D (4,3) and viscosity were considered (Table 1). Hydrocolloids presented higher volume diameter D (4,3). Guar gum and psyllium displayed the superior volume, 148.20 and 137.60 μm, respectively; they were also the hydrocolloids that resulted in more viscous suspensions.

3.2. Starch-hydrocolloid gels and digestograms analysis

To picture the performance of the binary combinations starches-hydrocolloids during pasting and also to predict their hydrolysis susceptibility to alpha-amylase, the method reported by Santamaria et al. (2022a) was followed. All the experimental parameters were statistically analyzed, and a principal component analysis (PCA) used to get the full picture of those combinations (Fig. 1). Two main components explained about 83.29% of the variation observed among results. Component 1 (PC1) explained 56.85% of the variation, being mainly defined by pasting parameters (peak, setback, and breakdown) and on the negative axis by the hydrolysis rate (k). Component 2 (PC2) explained 26.44% of the variation, being identified on the positive axis by the trough, viscosity at 37 °C and AUC. The analysis allowed discriminating starch source impact. Potato starch (−) had greater impact on pasting properties. Gularte et al. (2011) found higher viscosities during heating and cooling stages in potato starch gels than in corn-based ones. Besides, potato starch (−) was in the opposite corner from the kinetic constant (k), except when it was combined with xanthan gum (0.5 and 2.5%) or psyllium at 2.5%, those binary blends had lower impact than the other hydrocolloids, being characterized by trough or final viscosity at 37 °C. However, pea (+) and cassava (●) starches were closely related to the hydrolysis rate. Cereals starches did not show a clear tendency, corn (■) and rice (▲) starches were distributed along the two axes, and wheat starch (◆) was located at the negative abscissa axis at the opposite side of the pasting properties, but closer to the kinetic constant. This PCA shows that starch source dominated the clusters aggregation and not the different hydrocolloids or their concentrations. For deeper study of the *in vitro* hydrolysis of the gels, parameters representing each of the quartiles were selected, namely the setback, the AUC, the final viscosity at 37 °C and the kinetic constant (k).

Previous studies have reported the starch performance during pasting (Balet, Guelpa, Fox, & Manley, 2019), and in some occasions how hydrocolloids affected that according to the type or level of hydrocolloid added (Gularte et al., 2011). However, the rapid method applied in the present study allowed studying the influence of hydrocolloids and their concentration, on the hydrolysis of the different starches by α-amylase (Fig. 2). Once the α-amylase was added to the starch gels, as expected viscosity decreased due to the enzymatic action (Gasparre, Garzon, Santamaria, & Rosell, 2022). Control starch gels behave differently during the hydrolysis stage (Fig. 2 A). The RVA and digestograms parameters analyzed revealed statistically significant differences ($p < 0.05$) based on the factors (starch/hydrocolloid type) and cofactor (concentration), except the constant kinetic (k) that was not influenced by the hydrocolloid level added (Table 2). The RVA parameters obtained for potato starch were higher (Table 2), which agree with previous findings (Gularte et al., 2011; Liu et al., 2019). Sorba and Sopade (2013) explained that behavior based on the covalent binding induced by the presence of phosphorus. Cereals starches showed lower viscosities than potato starch, with corn having even lower kinetic constants than potato starch. Conversely, pea and cassava starches showed lower viscosity at 37 °C and faster hydrolysis (Fig. 2 A; Table 2). Santamaria et al. (2022a) found a negative correlation between peak viscosity and the hydrolysis rate of gelatinized starches. This inverse relationship was also observed by Fabek et al. (2014) in waxy corn starch matrices blended with several hydrocolloids.

The analysis of pasting parameters and gel hydrolysis of the different starches confirmed that they are dependent on the hydrocolloid type (Table 2). In general, the hydrocolloids concentration significantly affected the pasting behavior of starches but no the rate for their enzymatic hydrolysis (Table 2). Locust bean gum (LBG) at the different levels tested, increased viscosity at 37 °C, setback and AUC of the different starches, with the exception of the setback for wheat containing 2.5% LBG, and the AUC of the potato starch (Fig. 2 B and Table 2). Nevertheless, LBG only slowed down the hydrolysis rate of pea starch, which showed the lowest AUC, regardless the LBG concentration. The increase in the digesta viscosity induced by LBG has been used to explain the restricted accessibility of digestive enzymes and in consequence the slower digestion observed with high-amylose rice flour containing 0.5% LBG (w/w, DWB) (Jung et al., 2017). A low level of XG (0.5%) was enough to increase the viscosity of the starch gels after cooling (37 °C), except of potato, but higher XG level (2.5%) only increase that viscosity in corn, rice and pea starches (Fig. 2 C), which were the starches with the smaller granule size (Table 1). It is known the competency of starch granules and hydrocolloids for the water molecules (Rosell et al., 2011) likely, results could be related to the surface area of the starch granules. In general, XG increased the hydrolysis kinetic constant of the starch gels, except for wheat, pea and cassava, but the effect was dependent on the hydrocolloid concentration (Table 2). XG at 0.5% reduced the mean

Table 1
Physicochemical composition of starches and hydrocolloids.

Starch	Proteins [%]	Amylose [%]	D (4,3) [μm]
CO	0.79 ± 0.01^{c}	20.15 ± 0.13^{c}	18.34 ± 0.95^{e}
W	0.69 ± 0.01^{c}	23.98 ± 1.15^{b}	30.12 ± 1.05^{c}
R	1.44 ± 0.01^{b}	12.58 ± 0.29^{e}	19.06 ± 0.15^{e}
PO	0.54 ± 0.05^{d}	16.55 ± 0.18^{d}	41.82 ± 0.36^{b}
PE	14.63 ± 0.08^{a}	38.49 ± 0.80^{a}	25.37 ± 0.03^{d}
CA	0.58 ± 0.02^{d}	21.22 ± 1.48^{c}	310.53 ± 3.64^{a}
p-value	0.0000	0.0000	0.0000

Hydrocolloid	D (4,3) [μm]	Viscosity [mPa s]
LBG	119.38 ± 4.82^{c}	2495 ± 31^{c}
XG	54.31 ± 5.93^{e}	2521 ± 13^{c}
GG	148.20 ± 5.44^{a}	10956 ± 435^{b}
HPMC	108.39 ± 1.29^{d}	2166 ± 77^{c}
P	137.60 ± 0.36^{b}	12017 ± 763^{a}
p-value	0.0000	0.0000

Means within the same column followed by different letters indicate significant differences $p < 0.05$. Starches: corn (CO), wheat (W), rice (R), potato (PO), pea (PE) and cassava (CA); Hydrocolloids: locust bean gum (LBG), xanthan gum (XG), guar gum (GG), hydroxypropylmethylcellulose (HPMC) and psyllium (P).

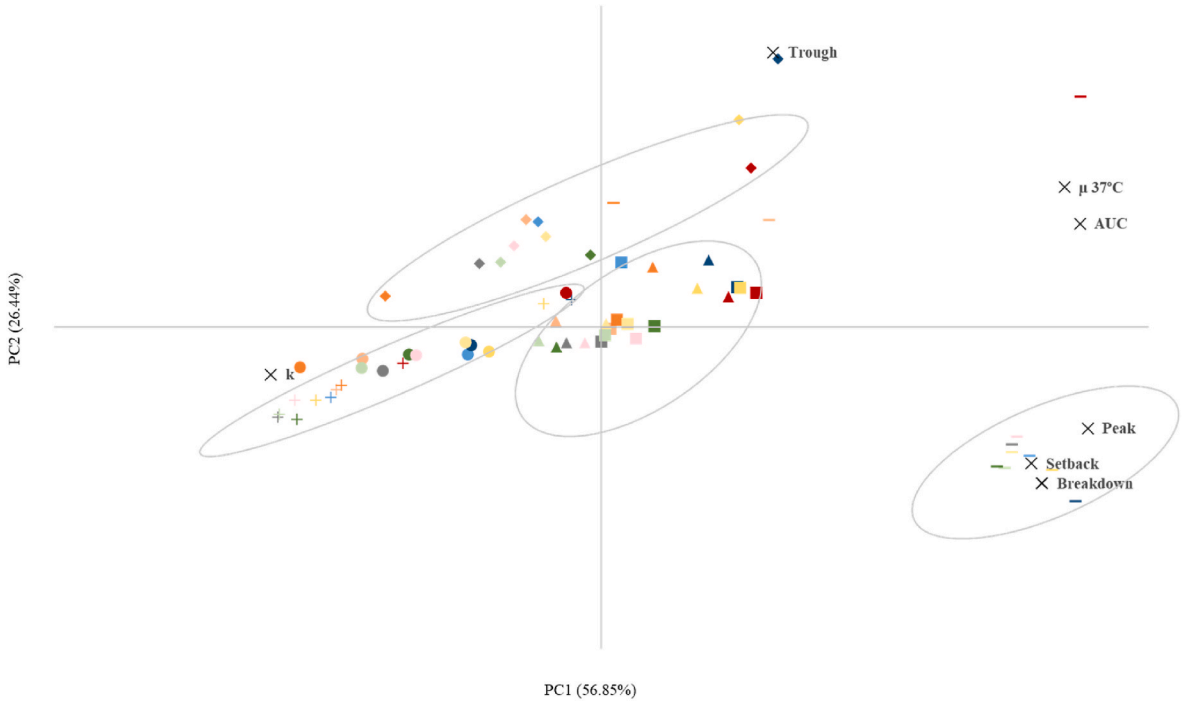

Fig. 1. Principal component analysis of the pasting properties and *in vitro* hydrolysis showed by individual starches and their binary blends with hydrocolloids at different concentrations. Starches: corn (■), wheat (◆), rice (▲), potato (−), pea (+) and cassava (●). Control (grey), locust bean gum (blue), xanthan gum (orange), guar gum (yellow), Hydroxypropylmethylcellulose (green) and psyllium (red). Hydrocolloid concentration was indicated by the symbol color intensity (0.5% lighter and 2.5% darker). Parameters: peak viscosity, trough, breakdown, final viscosity (μ 37 °C), setback, area under pasting curve (AUC) and hydrolysis rate (*k*).

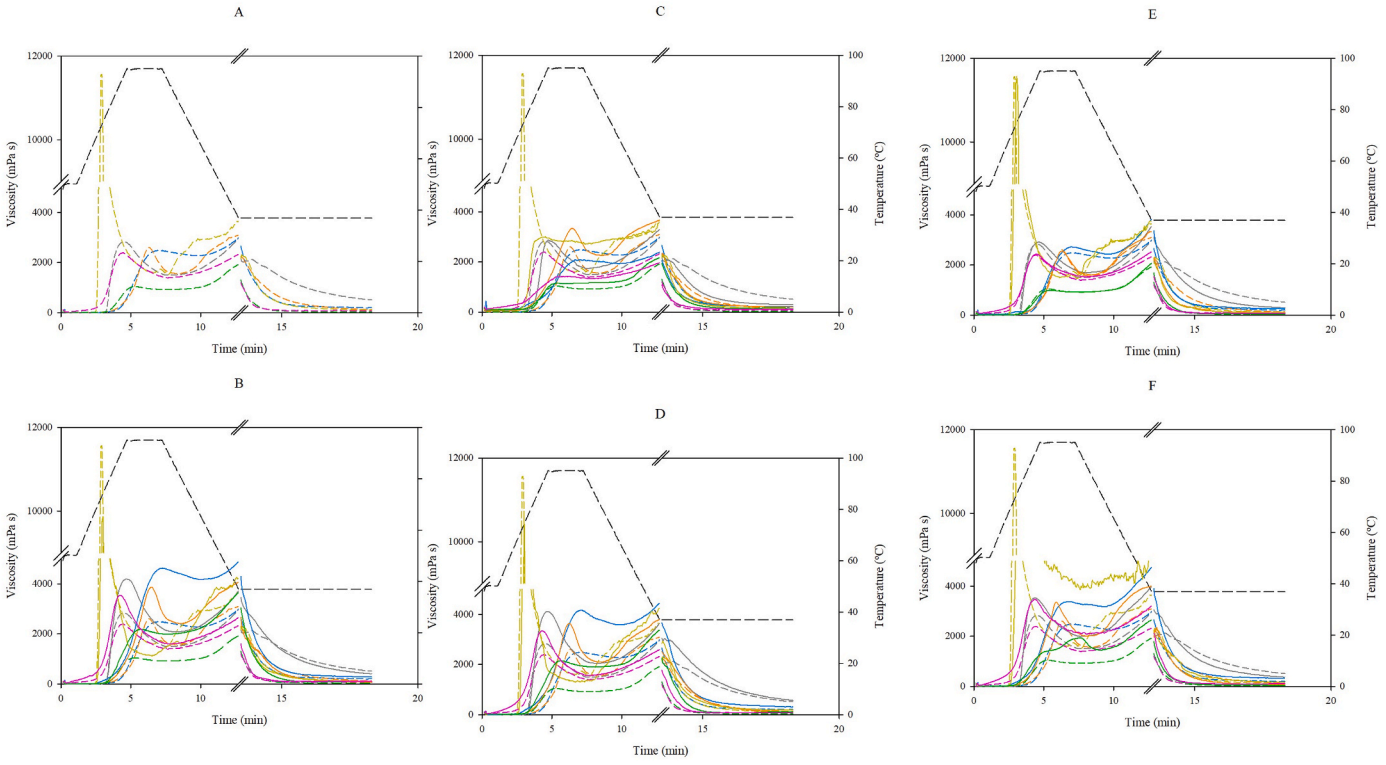

Fig. 2. Pasting and digestograms plots for each hydrocolloid with 0% (- -) and 2.5% (▬) blended with different starches. (A) Controls, (B) locust bean gum, (C) xanthan gum, (D) guar gum, (E) hydroxypropylmethylcellulose, and (F) psyllium. Starches: corn– wheat– rice– potato– pea– cassava–.

value of the hydrolysis constant of wheat, pea and cassava, meaning slower digestion respect to control samples, which might be related to its higher amylose content. Oh, Bae, and Lee (2018) observed a delay in the digestion of high amylose rice starch in the presence of 1% of XG. However, at the highest XG concentration tested (2.5%) only cassava and pea showed slower digestion (average value of *k*); undermining the

Table 2
Pasting performance parameters and hydrolysis rate based on starch, hydrocolloid, and concentration. Starches: corn (CO), wheat (W), rice (R), potato (PO), pea (PE) and cassava (CA); Hydrocolloids: locust bean gum (LBG), xanthan gum (XG), guar gum (GG), hydroxypropylmethylcellulose (HPMC) and psyllium (P). Parameters: area under pasting curve (AUC) and hydrolysis rate (k).

Starch	Hydrocolloid	%	Viscosity 37 °C (mPa s)	Setback (mPa s)	AUC	k (min^{-1})
CO		0	2963 ± 59	1471 ± 49	18976 ± 19	0.311 ± 0.020
W		0	3005 ± 13	739 ± 24	18464 ± 99	1.363 ± 0.172
R		0	3088 ± 90	1528 ± 92	16885 ± 262	0.764 ± 0.116
PO		0	3656 ± 30	2156 ± 204	30027 ± 555	0.799 ± 0.009
PE		0	1918 ± 1	996 ± 6	9529 ± 43	1.914 ± 0.055
CA		0	2316 ± 80	925 ± 30	17055 ± 885	2.127 ± 0.248
CO	LBG	0.5	3167 ± 11	1518 ± 5	20118 ± 50	0.493 ± 0.047
W	LBG	0.5	3450 ± 21	767 ± 97	21461 ± 288	1.543 ± 0.100
R	LBG	0.5	3394 ± 68	1671 ± 112	17719 ± 490	0.815 ± 0.050
PO	LBG	0.5	3869 ± 95	2385 ± 25	28935 ± 221	0.975 ± 0.519
PE	LBG	0.5	2217 ± 32	1124 ± 24	11121 ± 45	1.795 ± 0.103
CA	LBG	0.5	2656 ± 62	1062 ± 57	20680 ± 802	2.168 ± 0.043
CO	LBG	2.5	3724 ± 37	1642 ± 25	25736 ± 295	0.655 ± 0.026
W	LBG	2.5	4887 ± 110	721 ± 158	33050 ± 538	1.457 ± 0.079
R	LBG	2.5	4067 ± 6	1652 ± 4	24124 ± 99	1.215 ± 0.019
PO	LBG	2.5	4240 ± 34	3114 ± 21	27650 ± 108	1.132 ± 0.261
PE	LBG	2.5	3653 ± 134	1667 ± 74	19586 ± 519	1.633 ± 0.157
CA	LBG	2.5	2664 ± 52	972 ± 72	21428 ± 256	2.222 ± 0.033
CO	XG	0.5	3115 ± 70	1478 ± 49	19571 ± 317	0.479 ± 0.019
W	XG	0.5	3251 ± 36	607 ± 45	20600 ± 114	1.175 ± 0.218
R	XG	0.5	3135 ± 45	1327 ± 18	18389 ± 159	1.119 ± 0.154
PO	XG	0.5	3519 ± 0	888 ± 55	35138 ± 116	0.840 ± 0.185
PE	XG	0.5	2268 ± 88	1094 ± 49	11643 ± 372	1.837 ± 0.106
CA	XG	0.5	2274 ± 104	840 ± 52	16045 ± 247	1.970 ± 0.085
CO	XG	2.5	3289 ± 16	1552 ± 74	20193 ± 94	0.706 ± 0.120
W	XG	2.5	2390 ± 35	454 ± 21	16479 ± 437	1.437 ± 0.034
R	XG	2.5	3665 ± 86	1412 ± 148	23152 ± 155	0.996 ± 0.210
PO	XG	2.5	3565 ± 208	867 ± 30	27622 ± 379	1.298 ± 0.256
PE	XG	2.5	2159 ± 131	1021 ± 120	11682 ± 499	1.481 ± 0.039
CA	XG	2.5	1959 ± 127	640 ± 43	13895 ± 975	1.913 ± 0.046
CO	GG	0.5	3126 ± 23	1463 ± 1	20446 ± 192	0.372 ± 0.005
W	GG	0.5	3463 ± 11	911 ± 6	21067 ± 19	1.521 ± 0.019
R	GG	0.5	3361 ± 2	1613 ± 120	17616 ± 312	0.691 ± 0.003
PO	GG	0.5	3841 ± 20	2311 ± 38	29182 ± 419	1.175 ± 0.034
PE	GG	0.5	2156 ± 6	1078 ± 3	10895 ± 87	1.877 ± 0.066
CA	GG	0.5	2727 ± 180	1073 ± 116	20058 ± 4	2.017 ± 0.015
CO	GG	2.5	3654 ± 13	1607 ± 25	25067 ± 57	0.363 ± 0.026
W	GG	2.5	4468 ± 189	887 ± 86	29394 ± 943	1.124 ± 0.014
R	GG	2.5	3780 ± 101	1680 ± 33	22428 ± 420	0.765 ± 0.031
PO	GG	2.5	4233 ± 36	2939 ± 42	27862 ± 1547	0.990 ± 0.210
PE	GG	2.5	3368 ± 52	1456 ± 62	18567 ± 319	1.367 ± 0.088
CA	GG	2.5	2583 ± 91	1027 ± 37	20831 ± 568	1.709 ± 0.037
CO	HPMC	0.5	3122 ± 52	1534 ± 14	19480 ± 163	0.593 ± 0.112
W	HPMC	0.5	3204 ± 3	888 ± 8	18888 ± 70	1.502 ± 0.119
R	HPMC	0.5	3072 ± 129	1469 ± 58	16393 ± 665	1.012 ± 0.008
PO	HPMC	0.5	3656 ± 140	2240 ± 40	29680 ± 116	1.230 ± 0.162
PE	HPMC	0.5	1927 ± 4	984 ± 13	9703 ± 108	1.904 ± 0.008
CA	HPMC	0.5	2262 ± 54	838 ± 1	16690 ± 846	2.255 ± 0.036
CO	HPMC	2.5	3533 ± 163	1831 ± 132	20639 ± 330	0.774 ± 0.035
W	HPMC	2.5	3848 ± 165	1418 ± 120	20717 ± 740	1.675 ± 0.021
R	HPMC	2.5	3318 ± 146	1709 ± 207	17202 ± 383	1.425 ± 0.217
PO	HPMC	2.5	3737 ± 49	2363 ± 169	29983 ± 878	1.333 ± 0.283
PE	HPMC	2.5	2065 ± 251	1151 ± 142	9433 ± 1079	1.915 ± 0.161
CA	HPMC	2.5	2505 ± 116	977 ± 5	18247 ± 798	2.136 ± 0.151
CO	P	0.5	3241 ± 108	1682 ± 139	19853 ± 115	0.484 ± 0.136
W	P	0.5	3323 ± 90	849 ± 45	20119 ± 530	1.608 ± 0.007
R	P	0.5	3294 ± 109	1683 ± 85	17458 ± 303	1.010 ± 0.076
PO	P	0.5	3678 ± 28	2181 ± 49	32375 ± 237	0.897 ± 0.066
PE	P	0.5	2100 ± 42	1012 ± 33	11106 ± 205	2.104 ± 0.189
CA	P	0.5	2469 ± 159	947 ± 37	18441 ± 1343	2.057 ± 0.067
CO	P	2.5	3985 ± 60	1991 ± 14	24789 ± 305	0.595 ± 0.004
W	P	2.5	4764 ± 56	1588 ± 73	27789 ± 22	1.476 ± 0.148
R	P	2.5	3993 ± 64	1986 ± 122	22820 ± 14	0.763 ± 0.025
PO	P	2.5	5162 ± 28	1579 ± 170	46578 ± 360	0.605 ± 0.299
PE	P	2.5	2638 ± 134	1187 ± 60	15170 ± 881	2.035 ± 0.395
CA	P	2.5	3206 ± 23	1133 ± 7	24934 ± 86	1.875 ± 0.083
p-value						
Starch			**0.0000**	**0.0000**	**0.0000**	**0.0000**
Hydrocolloid			**0.0000**	**0.0000**	**0.0000**	**0.0000**
%			**0.0000**	**0.0041**	**0.0000**	0.6714

hypothesis that only amylose content could explain the starches comportment during hydrolysis. Jung et al. (2017) also observed that lower XG concentration (0.5%) had more impact on reducing glucose release, but at concentrations >0.7% a reverse action was observed regarding the hydrolysis rate associated to the swelling enhancement of starch granules. Therefore, the amount of XG added could play a significant role.

Overall, the addition of guar gum (GG) increased pasting behavior and in consequence, all pasting parameters for each starch (Fig. 2 D). Gasparre et al. (2022) observed more viscous gels with the binary association of guar gum - wheat starch, associating that with an increase in the swelling capacity of starch granules, hindering the amylose leaching out. This was related to the decrease in the hydrolysis constant rate (k), especially in rice (0.5%), wheat (2.5%), pea, and cassava starches (Table 2). It should be highlighted that wheat starch with 2.5% GG showed higher viscosity at 37 °C; and the increase in the GG concentration added to potato starch (from 0.5% to 2.5%) did decrease k, thus it could be related to the viscosity increase. In fact, gelatinized potato starch containing 5% of GG decreased blood glucose levels (Sasaki et al., 2015). Similarly, lower digestibility has been observed with the blends corn starch-guar, which have been related to the presence of a uniform layer covering the starch granules that could block the enzyme activity (Zhou et al., 2020). The addition of HPMC did barely modify the pasting behavior of starches (Fig. 2 E), as observed in previous studies (Gasparre et al., 2022), but, the kinetic constant increased in all starches, except in pea and cassava starches that was unchanged (Table 2). Similar results have been reported with cellulose derivative (carboxymethyl cellulose), that did not impact starch hydrolysis (Oh et al., 2018). In the case of psyllium (P) (Fig. 2 F), the addition of 2.5% increased starches viscosities. Furthermore, it was the only hydrocolloid that augmented the viscosity profile in potato and pea gels. Regarding hydrolysis, kinetic constants (k) of the starches were kept (corn and potato), decreased (cassava) or increased (wheat and rice) at 0.5%. It must be stressed the low k value obtained in potato starch that could be related to a higher viscosity at 37 °C (Table 2). Sevilmis and Sensoy (2022) observed a decrease in slowly digestible starch when psyllium fiber was incorporated into starches (wheat, potato and cassava), impeding the accessibility and interaction of digestive enzymes with starches during digestion.

To understand possible role of the viscosity on the starch hydrolysis a correlation matrix was built to identify any significant relationship between gels parameters (viscosity 37 °C, setback and AUC) and the hydrolysis behavior, taking the kinetic constant (k), of the binary starch-hydrocolloid mixtures (Table 3). The kinetic constant displayed a moderate negative correlation with viscosity 37 °C ($r = -0.5491$), setback ($r = -0.5036$) and AUC ($r = -0.4247$), considering all samples. Those correlations confirmed that the gels viscosities after cooling up to 37 °C and their whole viscosity performance during heating and cooling, indicated by AUC, did impact on the digestion rate. The pasting parameter with the highest negative correlation with the hydrolysis kinetic was the gel viscosity at 37 °C. This result also validates the use of the rapid test defined by Santamaria et al. (2022a) to predict the performance of starches on further enzymatic digestion. Furthermore, linear regressions were drawn with all the experimental results (Fig. 3). Although no pasting parameters presented a strong linear adjustment, a clear overall trend could be envisaged with the starches and hydrocolloids blends, which up to know have been only reported for individual associations of starches and hydrocolloids. These findings suggested that viscosity plays an important role in starch digestion, but it is not a single effect, but other factors, such as, starch source or hydrocolloid type must be considered (Fabek et al., 2014).

Table 3
Correlation matrix between pasting properties (final viscosity at 37 °C, setback, and area under pasting curve (AUC)) from gels development and hydrolysis constant (k). Hydrocolloids: locust bean gum (LBG), xanthan gum (XG), guar gum (GG), hydroxypropylmethylcellulose (HPMC) and psyllium (P).

Parameters			
Kinetic constant (min^{-1})	Viscosity 37 °C	Setback	AUC
$k_{\ all\ samples}$	**−0.5491*** **	**−0.5036*** **	**−0.4247*** **
$k_{\ Control}$	−0.7417**	−0.6556*	
$k_{\ LBG}$	−0.4112*	−0.4690*	
$k_{\ XG}$	−0.7462***	−0.5776**	−0.5581**
$k_{\ GG}$	−0.5306**	−0.4102*	
$k_{\ HPMC}$	−0.5973**	−0.5940**	
$k_{\ P}$	−0.6404***	−0.7973***	−0.5322**

Significant correlations: * indicates $p < 0.001$; ** indicates $p < 0.01$; * indicates $p < 0.05$.**

After the overall analysis of all the binary combinations of starches and hydrocolloids, a further analysis was carried out for the individual hydrocolloids (Table 3). Again, correlation coefficients for viscosity 37 °C and k were higher than for the other pasting indicators (setback and AUC), apart from LBG and psyllium. Therefore, the negative correlation of gel viscosity after cooling down to 37 °C with hydrolysis constant could be used as predictor of the starch gels susceptibility to enzymatic hydrolysis. This finding agrees with previously reported results, stating that viscosity greatly affects the cereal gels' digestibility (Santamaria, Montes, Garzon, Moreira, & Rosell, 2022b). Correlation coefficients between k and viscosity 37 °C of starches ($r = -0.7417$) were decreased in the presence of the individual hydrocolloids, except for XG (Table 3). Xanthan gum addition presented a strong negative correlation ($r = -0.7462$) between hydrolysis rate and viscosity at 37 °C. The starch combinations that mostly contributed to that effect were potato starch and 0.5% (XG) (viscosity of 3519 mPa s and k of 0.840 min^{-1}), or rice starch combined with 2.5% (XG) (viscosity of 3665 mPa s and k of 0.996 min^{-1}) (Table 2). Additionally, in psyllium containing gels, a strong negative correlation was observed between hydrolysis rate (k) and the setback ($r = -0.7973$). The binary combinations with utmost impact in that result were potato starch with 0.5%-P (setback of 2181 mPa s and k of 0.897 min^{-1}), potato starch with 2.5%-P (setback of 1579 mPa s and k of 0.605 min^{-1}). These results reveal that starch source and hydrocolloids type have a varied impact on alpha-amylase activity, but despite their varied functionality this study allowed drawing a relationship between viscosities and starch gels susceptibility to enzymatic hydrolysis.

4. Conclusions

A variety of starches and hydrocolloids have been included to understand possible relationship between viscosity and susceptibility of starches to enzymatic hydrolysis, independently on either the starch or hydrocolloid type. Cereals and potato gels showed higher viscosity and lower kinetic constant, but cassava and pea gels showed the opposite performance. Regarding hydrocolloids, their impact on starch enzymatic hydrolysis was greatly dependent on the type of starch and hydrocolloid, even the hydrocolloids concentration. A correlation matrix confirmed the negative correlations between hydrolysis rate (k) of gels and their viscosity at 37 °C, setback and AUC. This relationship could be used as predictor of either starch or starch-hydrocolloids susceptibility to enzymatic hydrolysis using a rapid viscosity test.

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Authors statement

Author Contributions: Credit roles: MS: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Roles/Writing -

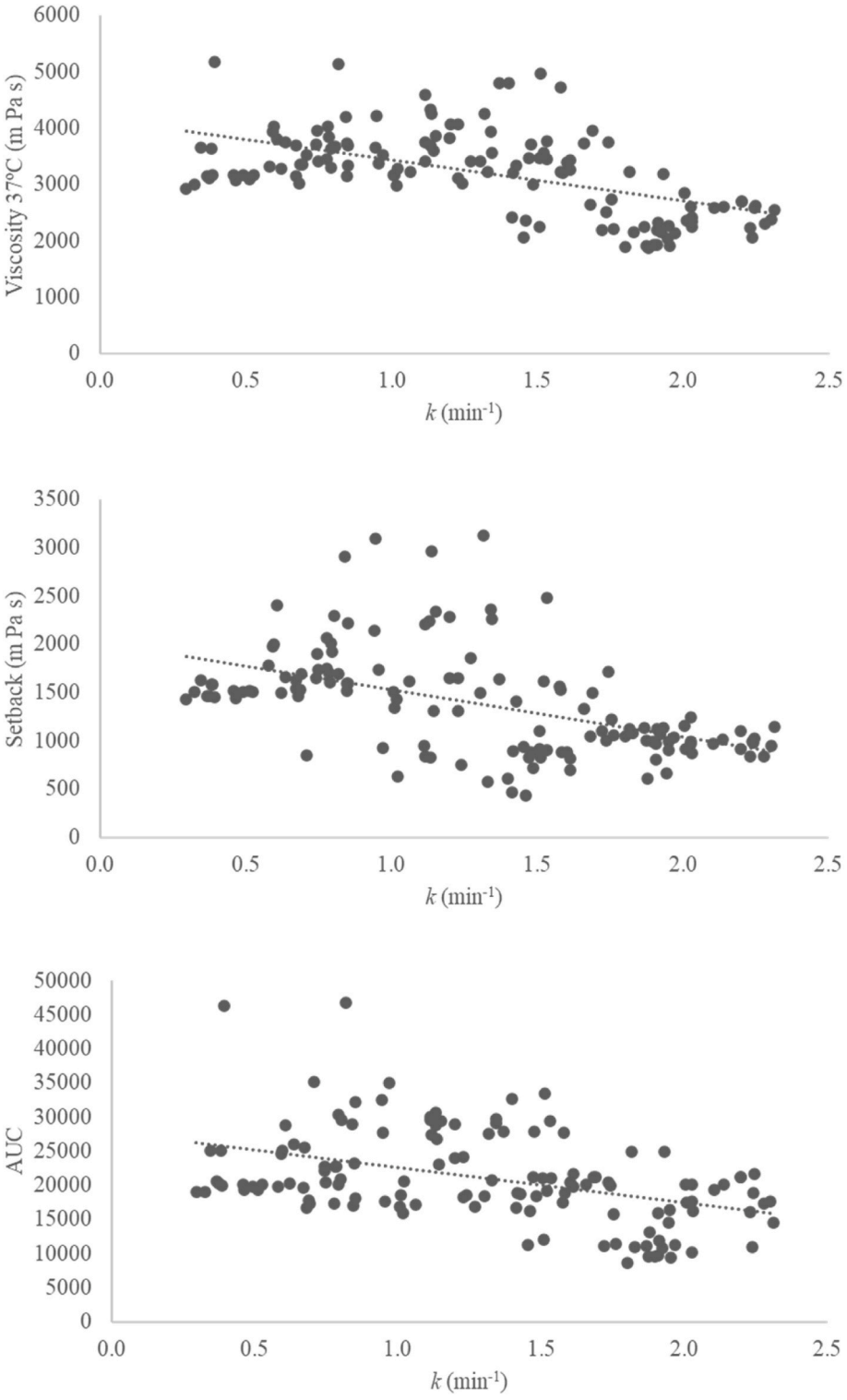

Fig. 3. Linear regression among pasting parameters (viscosity 37 °C, setback and AUC) and hydrolysis rate (*k*).

original draft; RG: Methodology; Supervision; Data curation; Writing - review & editing; CMR: Conceptualization; Funding acquisition; Investigation; Supervision; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2023.108764.

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