

## Research Article

# Viscoelastic and Textural Characteristics of Gels Obtained from Potato Starch Roasted under Several Temperature-Time Conditions

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The influence of roasting conditions on the potato starch (PS) composition, solubility, crystallinity, gel-forming thermal profiles, and texture of the corresponding gels was studied. Thermorheological testing of roasted starches with (RPS) and without (RPSI) the soluble fraction was conducted on a stress-controlled rheometer. Texture profile analysis (TPA) was used to determine the RPS final gel texture. Solubility tests showed equivalent effects of starch roasting for samples treated at 190°C for 8 h (RPS190-8), 210°C for 6 h (RPS210-6), and 230°C for 4 h (RPS230-4). The apparent amylose content of RPS linearly increased with the decreasing degree of crystallinity. Elastic ( $G'$ ) and viscous ( $G''$ ) properties of RPS depended markedly on apparent amylose content and crystallinity.  $G'_{\text{gel}}$  values of roasted starches linearly increased with the amylose content suggesting a promotion of the amylose breakdown with roasting temperature. Gels prepared with RPS roasted between 120 and 170°C exhibited intermediate strength and fully thermal reversible features. Roasting between 190 and 210°C favoured strong and fully thermal reversible gels. Although RPS230-4 gels exhibited similar strength to RPS190-8 and RPS210-4, no fully thermal reversible gels were obtained. The soluble fraction removal led to a drop the RPSI gels strength with increasing roasting temperature. No water syneresis was identified for RPS gels during one-week ageing, except for RPS230 gels. Relationships between textural parameters from TPA and viscoelastic gel properties determined by rheology were established.

## 1. Introduction

Potato starch (PS) is one of the most used biopolymers for industrial starch production, since the extraction procedure is simple in comparison to cereal starches [1]. This starch gains attention by its relatively low price, gluten-free features, abundance, and its renewable and biodegradability characteristics [2]. It is well known that native starches provide viscous, sticky, and cohesive pastes when their aqueous dispersions are heated and gels when above pastes are cooled down [3]. Native starches exhibit thermal decomposition and low shear stress resistance. Modified starches are designed to overcome the shortcomings of native starches, such as loss of viscosity and thickening power upon cooking and storage, syneresis, or retrogradation [4].

Starch modification can be made using physical, chemical, or biological methods [3]. Chemical or enzymatic modifications were extensively studied to extend the native starch applications, although physical modifications throughout the so-called “green chemistry” are currently preferred. The technological potential and industrial utility of native starches are enhanced by adequate modification [2]. Native and modified starches have been used as thickening agents in food processing [5] or in screen printing on textile [6], as glue in the adhesive industry [7], and as binding agents in pharmaceutical [8]. Roasted starchy materials could be an attractive alternative that have gained attention in the last years as the matrix of energy foods by high-performance ultrarunners and athletes [5]. Within nonfood applications, the use of roasted starches can be found in multiple industrial applications such as adhesives, inks, paper,

textiles, insecticides, and leather, among others [8, 9]. The roasting is the break down process to form dextrans by heating dry starch, alone or in the presence of an acid catalyst, until a desired conversion degree is obtained [8]. The solubility index has been reported as a simple method to follow the roasting process [10]. The main variables involved in starch roasting are the starch source used, the temperature applied (over the range from 100 to 230°C) and the conversion time (minutes to hours) [5]. Depending on the final use, starch must be roasted in such a way as to ensure that the structure fits the production process [8]. It should be remarked that these starch modifications require present industrial disadvantages from the economical point of view since these require thermal energy (expensive) and long-time processing. Consequently, achieving optimal temperature-time (i.e., energy consumption) operating conditions, depending on the properties required, is an important aspect for the industry.

The knowledge of the thermomechanical behaviour during the preparation of starchy-based gels offers essential information to select the optimum processing conditions to achieve well-defined and tailor-made final products, in particular, for gels from modified starches [5]. The rheology of native starch gels from different sources such as maize and potato starches was extensively studied [11]. Even correlations between gel rheology, structure, and final product quality were found for native starchy gelled systems. Fruit leathers incorporated with roasted sweet potato starch (between 150 and 250°C) have been proposed as a health alternative (low caloric) to sweet fruit snacks made with starch, high fructose syrups, and sugar [12]. In vitro digestibility, crystallinity, rheological, thermal, particle size distribution, and morphological characteristics of toasted ground white and blue maize flours were also comprehensively studied [13]. Nevertheless, the impact of roasting conditions in the absence of any added catalyst on the starch dispersions during gelatinization and on final mechanical gel behaviour needs to be determined [14]. Other starchy materials obtained from toasted ground maize (pinole) are widely consumed by different ethnic groups of Northern Mexico and Southern USA [13]. Latter authors explained that this toasted starchy matrix (about 250–270°C) can be combined with water, spices, or brown sugar; made into a drink and an oatmeal-like paste; or baked to form a more-portable “cake.” Given the specific starch functionalization, novelty products are unceasingly being developed and characterized, leading to a noteworthy potato starch value addition.

The effects of roasting of flour or isolated starches in physicochemical, mechanical, and morphological properties have been scarcely addressed. In this context, the main objective of this work is to study the effect of PS roasting conditions on its gel-forming thermal profiles (so-called gel-forming/maturation kinetics), final thermomechanical properties, and thermoreversible properties, which is critically relevant to the industrial processing. A comprehensive research on the thermorheology and texture of native PS and roasted PS (RPS) in a broad range of temperatures was carried out. Rheological testing at small amplitude oscillatory shear (SAOS) and texture profile analysis (TPA) was used to

evaluate the system structure evolution and the final gel texture, respectively. Fundamental chemistry (i.e., moisture content, total starch content, apparent amylose ratio, or damage starch), cold solubility, crystallinity, and particle size features of tested starches were also undertaken for further insight.

## 2. Materials and Methods

**2.1. Materials.** A commercial potato starch (PS) (CAS 9005-84-9, Panreac Química, S.A., Spain) was selected as a raw material for this research as it is a commonly used reference starch. All reagents used for the different tests were of analytical grade.

**2.2. Roasting Process.** Commercial PS (moisture content:  $24.3 \pm 0.3\%$ , dry basis (d.b.)) was dried at 40°C in a vacuum oven before roasting to reduce the moisture content (around  $6.1 \pm 0.8\%$ , d.b) to values commonly used in roasting starch processes [10]. Then, the starch samples (25 g) placed on a Petri dish in thin layer were roasted in an air convection oven (UFB500, Memmert, Germany) at different temperatures (120, 150, 170, 190, 210, and 230°C), labelled as RPS120, RPS150, RPS170, RPS190, RPS210, and RPS230, respectively, and times (2, 4, 6, 8, 16 and 24 h) to obtain a set of 36 roasted potato starches (RPS). Note here that time will be labelled as “– and the corresponding time” after temperature indication (RPS120-2, RPS120-4, ... , RPS230-24).

### 2.3. Proximate Physicochemical Properties

**2.3.1. Solubility Index.** The starch solubility index was obtained following a modified protocol [15]. Starch samples (around 0.2 g,  $M_0$ ) were dispersed in 10 mL distilled water and vortexed for 1 min. Starch dispersions were kept at room temperature for 30 min. Then, samples were centrifuged at 550 *g* for 15 min. The supernatant was decanted and dried at 110°C until constant weight ( $M_1$ ). The solubility index of the starch (g/100 g) was determined as  $M_1/M_0 \cdot 100$ .

**2.3.2. Composition.** Moisture content was determined according to the standard method (925.10) [16]. Total starch amount, apparent amylose content, and damage starch level were determined using enzymatic test kits (Megazyme Co., Wicklow, Ireland) following standard procedures [17].

**2.3.3. Crystallinity Degree.** The determination of the crystalline structure of tested potato starches was conducted on a diffractometer (X-ray PW1710, Philips, Netherlands) by means of  $\text{CuK}\alpha$  radiation ( $\lambda$ : 0.154 nm) operating at 20 mA and 40 kV. The starches were scanned at room temperature through the  $2\theta$  (diffraction angle) between 2 and 50° at a fixed scanning rate (4°/min). Roasted potato starch crystallinity evolution as a function of time of roasted potato starches was also determined. The relative degree of crystallinity was calculated from the ratio of diffraction peak and total diffraction area following the method previously detailed [18].

**2.3.4. Particle Size Measurements.** The particle size distribution and weight average particle diameter ( $D_w$ ) of the above-mentioned starches were determined following

standard sieving procedures [19]. Standard sieves (200, 125, 80, 63, and 40  $\mu\text{m}$ ) were employed. The fractions retained in each sieve were separated and weighed.

**2.4. Preparation of Samples for Textural and Rheological Measurements.** Starches were dispersed in distilled water (30%  $w/w$ , stirring at 3000 rpm for 15 min) on a magnetic stirrer at 25°C following the conditions previously selected for other starchy materials [20]. The selected starch content is in the range of those previously studied for concentrated starch gels (from 20 to 70%  $w/w$ ) [21]. In order to provide further insights on the effect of starch water insoluble fraction on the thermorheology of roasted potato starch (RPS) gels, aqueous dispersions made from roasted starches, where the soluble fraction was previously removed, were also prepared. The aqueous RPS dispersions were filtered and separated at 25°C into insoluble (RPSI) and soluble fractions. The soluble fraction was removed, and RPSI was washed several times with distilled water. After drying at 40°C, the corresponding dispersions were prepared as above-indicated.

For rheological measurements, aqueous starch dispersions (PS, RPS, and RPSI) were directly placed into the rheometer measuring system. This allows tracking of the starch gelatinisation in situ, avoiding further gel matrix disturbances. For texture measurements, stirred PS and RPS dispersions (3000 rpm for 15 min) prepared in cylindrical flasks (4.5 cm height and 2.5 cm diameter) were immediately heated up to 80°C as reported elsewhere [22]. Briefly, samples were held at 80°C for 60 min in order to prepare a set of gels. Then, samples were cooled at room temperature for 1 hour prior to being placed in a refrigerator (5°C) for 24 h in order to allow the full maturation of the gels before performing the texture assays.

**2.5. Rheology.** Rheological measurements (in terms of storage ( $G'$ ) and loss ( $G''$ ) moduli) were performed on a stress-controlled rheometer (MCR301, Anton Paar Physica, Austria) using a Couette geometry (cup diameter 26 mm and bob height 25 mm). Aqueous potato starch dispersions were placed into the Couette cup and sealed with paraffin oil to avoid water evaporation during tests. In order to define the linear viscoelastic region, stress sweeps were made on both starch dispersions and gels at different frequencies (0.1, 1, and 100 Hz) over the range of 0.1 to 1000 Pa. All temperature, time, and frequency sweeps were conducted within the linear viscoelastic region.

Potato starch dispersions were heated from 25 to 80°C at a rate of 1°C/min. In order to stabilise the samples, time sweep assays (0.1 Hz) were thereupon conducted at 80°C for 60 min. Samples were cooled down to 25°C (1°C/min). All the above-mentioned tests were performed at 0.1 Hz and 5 Pa. Gel maturation was monitored by time sweeps (1 Hz, 30 Pa) after cooling at 25°C for 60 min. Frequency sweeps (over the range of 0.01 to 100 Hz, 30 Pa) were thereupon conducted at 25°C without disturbing the gel. All these stages were repeated following an experimental protocol to study the thermal reversibility of obtained gels [23].

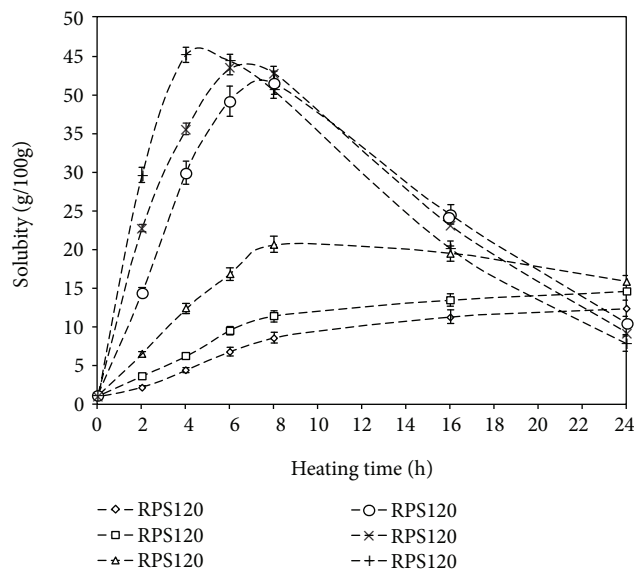


FIGURE 1: Influence of time-temperature roasting conditions on the solubility of potato starch (PS). Note here that in these subsequent plots, error bars are not included whether the uncertainty in data magnitudes is smaller than the symbol size.

**2.6. Texture.** Texture profile analysis (TPA) measurements were conducted on a texture analyser (TA-XT plus, Stable Micro Systems, UK) with a load cell of 5 kg as reported elsewhere [24]. For this purpose, starch gel samples prepared in cylindrical flasks filled up to 80% (4.5 cm height and 2.5 cm diameter) were submitted to a double penetration using a cylindrical probe P/05R (0.6 mm radius, 2 mm/s crosshead speed, and 5 mm penetration). Experiments were performed 24 h after sample preparation to allow full gel maturation. Before textural testing, samples were equilibrated for about 1 h at 25°C. Note here that hardness (peak force of the first cycle), adhesiveness (negative area of the first bite), springiness (related to elasticity), cohesiveness (ratio between the areas of both peak forces), and chewiness (hardness  $\times$  cohesiveness  $\times$  springiness) were determined.

**2.7. Syneresis.** Starch gel samples, prepared as those used in textural tests, were stored in centrifuge tubes in the fridge (5°C) for 7 days. Each sample was centrifuged (2200  $g$  for 15 min), and the percent of water release in relation to the gel weight represented the syneresis [15].

**2.8. Statistical Analyses.** All tests were performed in triplicate, and data sets were evaluated by means of one-way analysis of variance (ANOVA), using PASW Statistics (IBM SPSS Statistics 22.0.0). A Scheffé test was performed to distinguish means with 95% confidence ( $p \leq 0.05$ ).

### 3. Results and Discussion

#### 3.1. Physicochemical Features

**3.1.1. Solubility.** Figure 1 shows the solubility of potato starch after roasting at different temperature and time conditions. RPS120 and RPS150 exhibited the lowest solubility values,

TABLE 1: Proximate physicochemical features of tested potato starch (PS) (30% *w/w*) roasted at different temperatures (120, 150, 170, 190, 210, and 230°C) for the time corresponding to the highest solubility values for each tested roasting temperature. The corresponding gelatinization peak temperature ( $T_p$ ) is also displayed.

	PS	RPS120-8	RPS150-8	RPS170-8	RPS190-8	RPS210-6	RPS230-4
Roasting temperature	—	120	150	170	190	210	230
Roasting time, h	—	8	8	8	8	6	4
Initial moisture content, % d.b.	6.1 ± 0.8 <sup>a</sup>	7.1 ± 1.0 <sup>a</sup>	6.8 ± 1.3 <sup>a</sup>	6.6 ± 1.2 <sup>a</sup>	5.8 ± 0.6 <sup>a</sup>	5.5 ± 0.9 <sup>a</sup>	5.3 ± 1.2 <sup>a</sup>
Total starch content, % d.b.	98.7 ± 0.5 <sup>a</sup>	97.4 ± 0.4 <sup>b</sup>	97.1 ± 0.5 <sup>b</sup>	96.7 ± 0.5 <sup>b</sup>	93.5 ± 0.2 <sup>c</sup>	92.8 ± 0.4 <sup>c,d</sup>	92.4 ± 0.3 <sup>d</sup>
Apparent amylose content, %	21.6 ± 0.4 <sup>d</sup>	23.4 ± 0.3 <sup>c</sup>	23.6 ± 0.2 <sup>c</sup>	23.2 ± 0.4 <sup>c</sup>	29.3 ± 0.5 <sup>b</sup>	29.7 ± 0.3 <sup>a,b</sup>	30.6 ± 0.3 <sup>a</sup>
Damaged starch level, %	2.9 ± 0.6 <sup>a</sup>	2.9 ± 0.5 <sup>a</sup>	2.9 ± 0.5 <sup>a</sup>	3.0 ± 0.7 <sup>a</sup>	3.5 ± 0.4 <sup>a</sup>	3.7 ± 0.6 <sup>a</sup>	3.8 ± 0.5 <sup>a</sup>
Damaged/total starch, %	0.029 ± 0.003 <sup>b</sup>	0.030 ± 0.002 <sup>b</sup>	0.030 ± 0.002 <sup>b</sup>	0.031 ± 0.002 <sup>b</sup>	0.037 ± 0.001 <sup>a</sup>	0.040 ± 0.002 <sup>a</sup>	0.041 ± 0.002 <sup>a</sup>
Crystallinity level (30 days), %	22.6 ± 0.9 <sup>a</sup>	15.1 ± 0.2 <sup>b,C</sup>	14.6 ± 0.3 <sup>b</sup>	14.9 ± 0.3 <sup>b,C</sup>	6.7 ± 0.3 <sup>c,C</sup>	5.4 ± 0.1 <sup>c,d</sup>	5.3 ± 0.4 <sup>d,C</sup>
0 day*	—	17.7 ± 0.4 <sup>a,B</sup>	—	17.2 ± 0.2 <sup>a,B</sup>	10.4 ± 0.2 <sup>b,B</sup>	—	9.8 ± 0.1 <sup>c,B</sup>
1 day*	—	16.2 ± 0.2 <sup>a,A</sup>	—	16.2 ± 0.4 <sup>a,A</sup>	9.5 ± 0.2 <sup>b,A</sup>	—	8.6 ± 0.3 <sup>c,A</sup>
3 days*	—	15.2 ± 0.3 <sup>a,C</sup>	—	15.1 ± 0.5 <sup>a,C</sup>	6.9 ± 0.3 <sup>b,C</sup>	—	6.1 ± 0.3 <sup>c,C</sup>
$T_p$ (°C)	56.2 ± 0.5 <sup>a</sup>	50.5 ± 0.4 <sup>b</sup>	50.1 ± 0.3 <sup>b</sup>	49.6 ± 0.3 <sup>b</sup>	40.1 ± 0.4 <sup>c</sup>	39.9 ± 0.1 <sup>c</sup>	39.7 ± 0.3 <sup>c</sup>

Data are presented as mean ± standard deviation. Data values in a row with different superscript letters are significantly different at the  $p \leq 0.05$  level. \*Time-crystallinity dependence: measures were performed at different time periods after roasting processing. In this particular case, the significance was evaluated in columns and indicated with different ANOVA superscripts (u, v, and w).

except at 24 h where close values were identified for all samples. The first solubility increase was observed at temperatures between 170 and 190°C, becoming greater at 210 and 230°C. This solubility increase indicates that considerable roasting takes place for RPS190, RPS210, and RPS230. RPS230 gave the highest solubility (g/100 g) values (around 45 ± 0.5) of roasting closely followed by RPS210 and RPS190 (around 42.5 ± 1.0). Potato starch solubility curves featured induction periods in the roasting process, becoming gradually shorter as the roasting temperature increased (from 8 h for RPS120 to 4 h for RPS230). Earlier works [10] found similar induction times for roasted corn starches subjected at temperatures ranging from 150 to 213°C and times below 8 h, although with higher maximum solubility values (up to 80 g/100 g). These authors indicated that the solubility index is as a simple method to follow the roasting process directly related to the dextrin content. The solubility data suggests that the similar effect on starch roasting occurs for RPS190-8, RPS210-6, and RPS230-4. Thus, potato starches featuring the highest solubility values for each tested roasting temperature were selected for further physicochemical and mechanical analyses in order to observe clearer the roasting effect.

Solubility curves of RPS190, RPS210, and RPS230 displayed an initial step increase, and after the maximum the solubility is achieved, the plots showed a downward tendency. This solubility loss was slightly promoted at high temperatures. All RPS solubility curves tend to reach a common solubility value after 24 h (long time) subjected to roasting. This could be explained assuming that larger molecular weight glucans are formed from the fragments produced in the early starch roasting stages [25] or that the nonsolubilisation is owing to the formation of decomposition products and their noncarbohydrate nature polymers [10].

**3.1.2. Composition.** Composition experiments were carried out in roasted starches after the corresponding times that led to the largest solubility values. Table 1 collects the proximate physicochemical features of tested starches. The average moisture content of the starch before roasting was about 6.1 ± 0.8%, d.b. The average final moisture content (% d.b.) after roasting was around 2.5 ± 1.1, not exhibiting statistical differences. As expected, total starch content was relatively high in all cases, with a significant decrease with increasing roasting temperature. This result suggests that during roasting, starch is thermally degraded [26]. This is supported by the increase in the damaged/total starch ratio with rising roasting temperature, even though low damaged starch levels were observed in all cases. The determined damaged starch values are in the range of those reported for native starches extracted from gluten-free flours (below 3%) [5]. Apparent amylose content (%) exhibited intermediate values increasing significantly with increasing roasting temperatures. The largest apparent amylose content modifications (around 28%) were identified between RPS170 and RPS190, which suggest that the roasting process is favoured around 190°C [26]. The increase in apparent amylose content after roasting was reported for different starchy cereals and explained because heating promotes the formation of amylo-dextrins (linear dextrin or short chained amylose) [27].

**3.1.3. Crystallinity.** The degree of crystallinity (%) of tested starches is presented in Table 1. Crystallinity values statistically decreased with increasing crystallinity measurement times, achieving steady values after three days as evidenced by the negligible variation with those measured after one month. Analysing steady crystallinity values, it was noticed that crystallinity degree significantly decreased with increasing roasting temperature. The largest crystallinity drop was



identified between 170 and 190°C (around 36%). This is consistent with the amylose trends above-mentioned, since the crystallinity drop is expected to be related to amylopectin drop (responsible to the amorphous starch features) [25]. Crystallinity values exhibited a linear relationship (slope  $-0.56 \pm 0.05$ ,  $R^2 > 0.988$ ) with amylose content. This result agreed with those reported for native corn starches with different apparent amylose contents (from 0 to 40%), where a linear relationship (slope  $-1.01$ ) was observed between crystallinity and apparent amylose content, changing crystal type from A to C [24]. In our case, the characteristic B standard pattern of PS (with the strongest diffraction peak at around  $17^\circ 2\theta$ , a few small peaks at around  $2\theta$  values of  $20^\circ$ ,  $22^\circ$  and  $23^\circ$ , and an additional peak at  $5^\circ 2\theta$ ) evolves towards a more amorphous structure with increasing roasting temperature.

**3.1.4. Particle Size.** In all cases, the average particle size of tested starches was around  $61.2 \pm 2.4 \mu\text{m}$  without significant differences among the samples. The most important mass fraction (58.6%) was identified between 80 and  $63 \mu\text{m}$ . The second population (32.1%) was the particles with sizes from 63 to  $40 \mu\text{m}$ , followed by the fraction (9.3%) of particle sizes lower than  $40 \mu\text{m}$ . The above values are consistent with those (over the range from 5 to  $100 \mu\text{m}$ ) found for starches isolated from different potato varieties [28] and suggested as suitable for the gel formation [29].

## 3.2. Thermorheology

**3.2.1. Thermal Heating Profiles.** Roasted starch samples with the largest solubility values (i.e., RPS120-8, RPS190-8, and RPS230-4) for each roasting temperature were selected to the thermorheological assessment (Figure 2). The thermal heating profile (Figure 2(a)) of aqueous roasted starch dispersions did not show the inflection point corresponding to the initial gelatinization temperature ( $T_0$ ). This behaviour is usually observed in native starches [29]. Instead, in our work, it was identified as a rapid increase of both  $G'$  and  $G''$  moduli with increasing temperature achieving a peak around  $40.1 \pm 0.4^\circ\text{C}$  for RPS190-8, which represents the gelatinization peak temperature ( $T_p$ ), remaining practically invariant above this temperature.  $G'$  was larger than  $G''$  over the whole tested temperature range. Similar trends were obtained for all aqueous RPS dispersions, although the values of  $T_p$  were shifted to lower temperatures (from  $56.2 \pm 0.5^\circ\text{C}$  for PS to  $39.7 \pm 0.4^\circ\text{C}$  for RPS230-4) with rising roasting temperature, but without a uniform trend. The largest temperature drop (around  $9.5 \pm 0.3^\circ\text{C}$ ) was found between RPS170-8 and RPS190-8, which is consistent with physicochemical achievements, indicating that roasting conditions influence the gelatinization temperatures. The drop in gelatinization temperatures was also reported for roasted oat flours [30]. These authors indicated that this fact could be attributed to the presence of some pregelatinized starch in roasted systems. Here, no significant differences in  $T_p$  values were observed below RPS170-8 and above RPS190-8. The  $T_p$  values from RPS190-8 to RPS230-4 are similar to the initial gelatinization temperature ( $T_g$ )

identified for PS and lower than those  $T_p$  values reported for different native potato starches ( $45 \pm 1^\circ\text{C}$ ) [26]. Another relevant characteristic for RPS is the increase of the thermal stability after  $T_p$  (with  $G'$  and  $G''$  moduli almost parallel and constant with the increase of temperature) in comparison to other native starches evaluated at similar [21] and lower (<10%) [22] polymer content. RPS190-8 gels immediately attained  $G'$  and  $G''$  steady values after  $T_p$  and consequently exhibited the largest thermostability features. This is especially important for potato starches which are usually less thermostable than other commonly used native starches as maize or alternative sources such as chestnut [23].

**3.2.2. Thermal Cooling Profiles.** The thermal cooling profiles for RPS120-8, RPS190-8, and RPS230-4 gels are presented in Figure 2(b), as representative of tested systems. All samples were stabilised for 60 min at  $80^\circ\text{C}$  previously to cooling ramps, exhibiting  $G' > G''$  with constant values. During the cooling process, the values of both moduli of RPS gels rose for all gels. A moderate reinforcement of the gel structure during cooling was also reported for native maize starches [5] and other native starchy pastes [25]. This is consistent with the physicochemical features observed for roasted starches, since larger roasting temperatures involve lower crystallinity and consequently higher apparent amylose content favouring greater molecular entanglements and the easier formation of a gel network [31]. This behaviour could also justify the lowest reinforcement for systems formulated >RPS190-8, which exhibits the highest apparent amylose content.

**3.2.3. Maturation Profiles.** The maturation profiles in terms of the viscous and elastic modulus evolution with time for above RPS gels (i.e., RPS120-8, RPS190-8, and RPS230-4) are shown in Figure 2(c). The plot displays the  $G'$  and  $G''$  moduli evolution with time at  $25^\circ\text{C}$ , as examples of tested samples. Particularly, RPS190-8 reached dynamic gel network equilibration ( $G'$  and  $G''$  stability) instantaneously with steady values for  $G'$  (around  $1.6 \cdot 10^5 \text{ Pa}$ ) and  $G''$  (around  $2.4 \cdot 10^4 \text{ Pa}$ ). No differences (<1 min) in the time maturation were observed for gels formed between RPS190-8 and RPS230-4. Longer times (<10 min, RPS120-8, Figure 2(c)) were required for the structure maturation of gels prepared <RPS170-8, even though the maturation times of all RPS gels were much lower than those (around 30 min) reported for concentrated (between 10 and 40%  $w/w$ ) gels prepared with native starches from different sources [32].

In  $G'$  and  $G''$  magnitudes, the viscoelastic features of RPS gels depended notably on roasting conditions, increasing (around 7 times) the gel strength with rising roasting temperature ( $G'_{\text{gel}}$  (1Hz) from  $6.5 \cdot 10^4 \text{ Pa}$  for RPS120-8 to  $3.5 \cdot 10^5 \text{ Pa}$  for RPS230-4) achieving similar  $\tan \delta$  ( $G''/G'$ ) values in all cases. These moduli values are larger than those reported for gel maturation profiles made from modified potato starch (30%  $w/w$ ) under different gelatinization degrees, where  $G'_{\text{gel}}$  was in all cases below  $5.7 \cdot 10^4 \text{ Pa}$  [23].

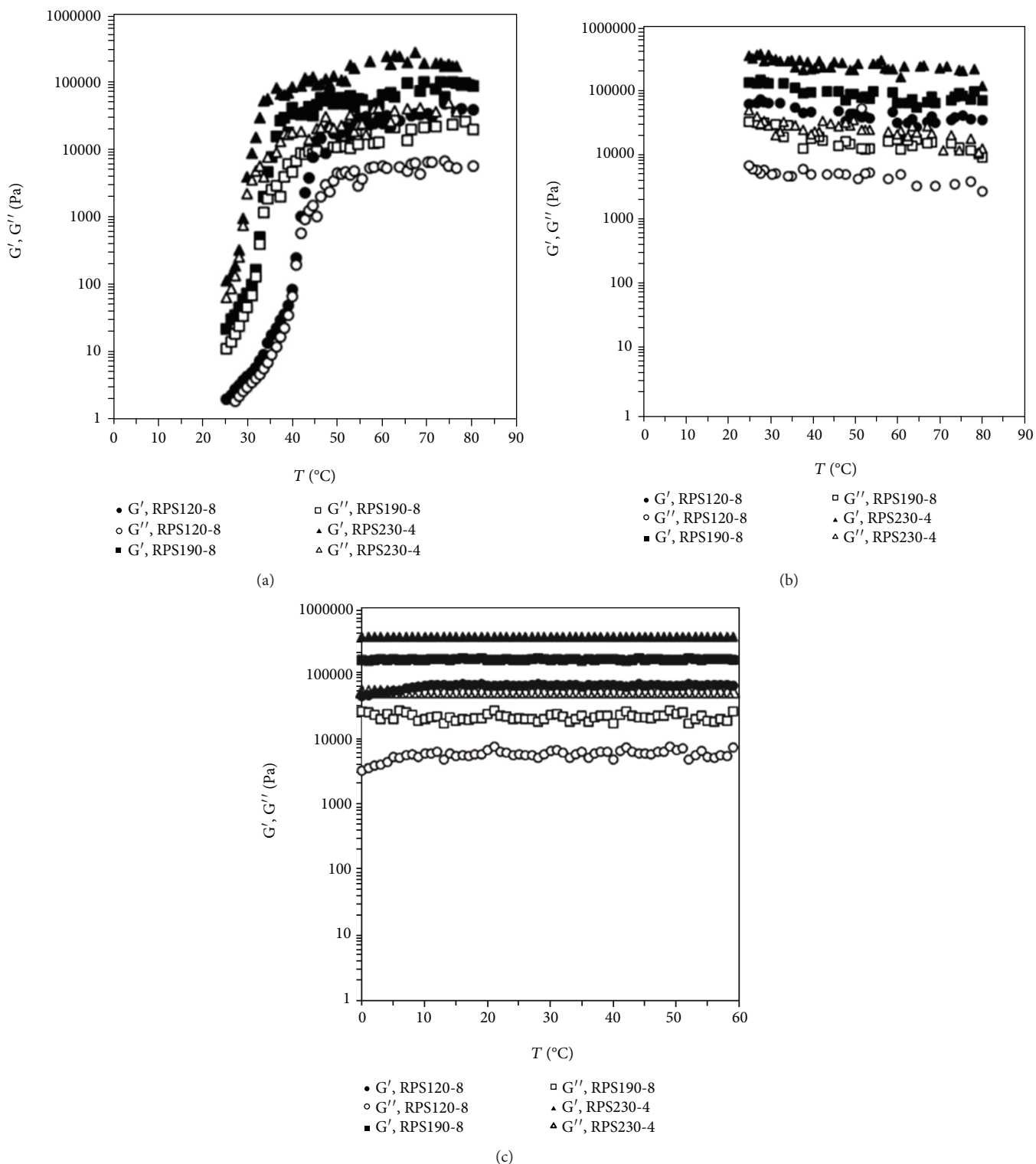


FIGURE 2: Thermorheological features of aqueous dispersions of potato starch (30%  $w/w$ ) roasted at 120  $^{\circ}\text{C}$  for 8 h (RPS120-8), 190  $^{\circ}\text{C}$  for 8 h (RPS190-8), and 230  $^{\circ}\text{C}$  for 4 h (RPS230-4): (a) temperature sweep on heating (from 25 to 80  $^{\circ}\text{C}$  at 1  $^{\circ}\text{C}/\text{min}$ ); (b) temperature sweep on cooling (from 80 to 25  $^{\circ}\text{C}$  at 1  $^{\circ}\text{C}/\text{min}$ ); and (c) time sweep (at 25  $^{\circ}\text{C}$ ).

3.2.4. *Mechanical Spectra.* Figure 3 shows the mechanical spectrum in terms of viscous and elastic modulus evolution with frequency above RPS gel obtained at 25  $^{\circ}\text{C}$ , as a

representative example. Note here that the mechanical spectra of untreated samples were previously reported for the authors [23]. All gels prepared exhibited a typical gel

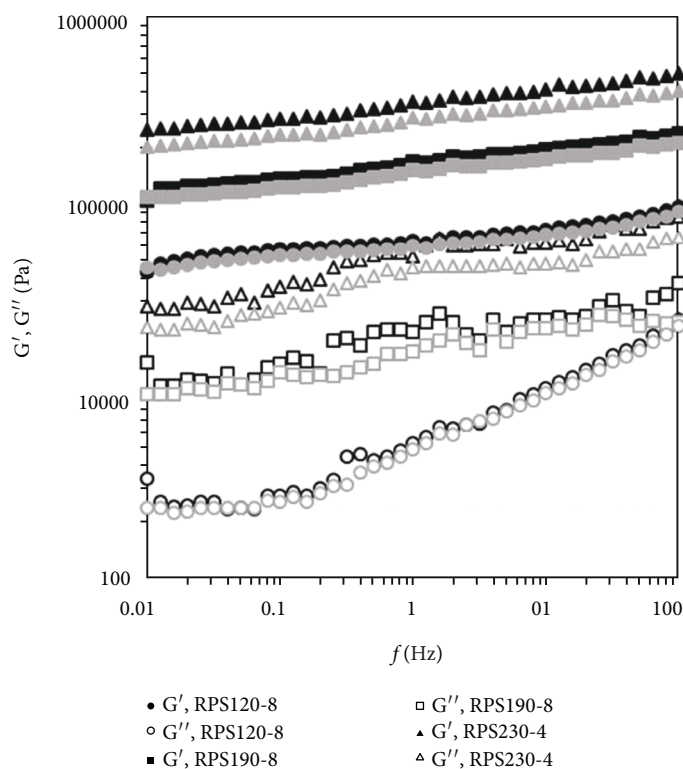


FIGURE 3: Mechanical spectra at 25°C of selected gels prepared from RPS120-8, RPS190-8, and RPS230-4. Note here that grey symbols correspond with the mechanical spectra data collected from the second heating/cooling cycle.

spectrum ( $G' > G''$  and both modulus frequency independent). This behaviour agrees with the solid characteristics found for other starchy gelled systems such as those made from maize, rice, or chestnut starches at lower starch content (<10%  $w/w$ ) [20, 22]. Concerning strength of RPS gels, the magnitude of  $G'$  and  $G''$  moduli at fixed angular frequency depended greatly on starch roasting temperature. A general strength evaluation of the obtained RPS gels can be given in terms of  $G'_{\text{gel}}$  (1 Hz) Figure 4(a).  $G'_{\text{gel}}$  increased with increasing roasting temperature, mainly above RPS190-8. The general behaviour agrees with those results found for gels formed from native corn or rice starches with different apparent amylose contents which occur here with RPS [33], explaining that higher apparent amylose content leads to stronger gels because of their greater molecular entanglements between linear polymer chains and less super globes that are easier to move than long linear chains. In the case of roasted starches above 190°C, the enhancement of the gel strength could be explained because roasting temperature favours the formation of short amylose chains. Synergistic effects on the viscous behaviour of gelled systems of potato starches prepared with fractionated amyloses have been previously reported [34]. A distribution of molecular weights promoted by temperature and acid hydrolysis has been also reported for potato starch and xanthan mixtures [35]. Viscoelastic values for PS and roasted starches from RPS120-8 to RPS170-8 are in the range of those found for food applications such as commercial savoury/sweet gelled

systems [22] or nonfood applications such as cosmetics and health personal care products [8]. RPS190-8, RPS210-6, and RPS230-4 exhibited viscoelastic values consistent with those reported for gelled formulations used in biofilm-based products [36].

Further insight on the behaviour of concentrated starch gels is critically relevant in order to improve the processing conditions of in multicomponent systems with high starch content as flour doughs. Figure 4(b) shows the  $G'_{\text{gel}}$  evolution for gels prepared with RPSI. The mechanical spectrum for RPSI190-8, as an example, is also included, exhibiting weaker gels than those formed with both fractions. It is clear that the RPSI gel strength decreased with increasing roasting temperature. The largest drop (around 45%) is observed between RPSI170-8 and RPSI190-8. The removal of the soluble fraction led to a drop in the apparent amylose content (%  $w/w$ ) ( $19.3 \pm 0.3$  for RPSI120-8,  $18.4 \pm 0.5$  for RPSI150-8,  $14.5 \pm 0.3$  for RPSI170-8,  $6.8 \pm 0.4$  for RPSI190-8,  $6.6 \pm 0.4$  for RPSI210-6, and  $5.4 \pm 0.4$  for RPSI230-4), which can be one of the main factors explaining the gel strength reduction. Note here that the  $G'_{\text{gel}}$  values exhibited a linear dependence with the apparent amylose content ( $R^2 > 0.98$ ). This behaviour supports the hypothesis that the roasting temperature promotes the breakdown of the apparent amylose because the shorter chains are solubilized and the largest ones remain in the insoluble fraction [33]. Therefore, the behaviour of the RPSI depends only on the apparent amylose content (without influence of apparent amylose modifications). Thus, the formulation of potato starch-

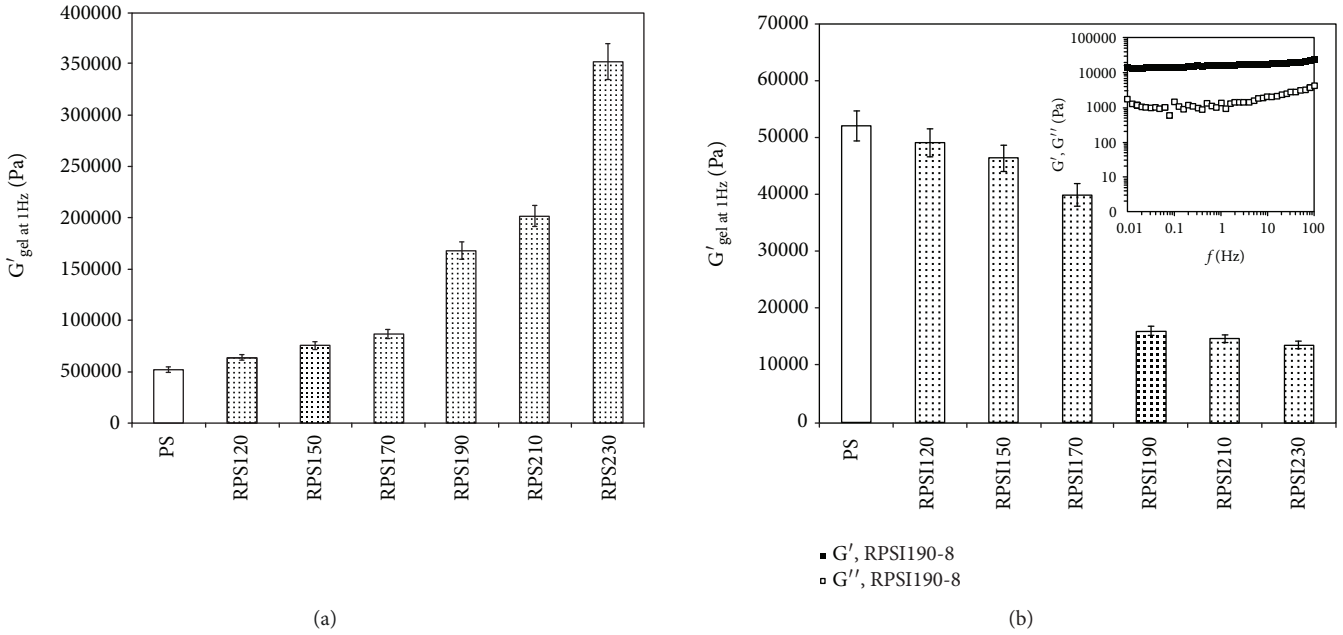


FIGURE 4: Influence of roasting conditions on the mechanical behaviour of the final potato starch gels ( $G'_{gel}$  at 1 Hz, Pa) without (a) and with (b) removal of the soluble fraction after starch roasting.

TABLE 2: Texture parameters of tested potato starch gels (30%  $w/w$ ) roasted at different temperatures (120, 150, 170, 190, 210, 230°C).

Gels	Hardness (kg)	Adhesiveness (kg s)	Springiness (-)	Cohesiveness (-)	Chewiness (kg)
PS	$2.74 \pm 0.08^c$	$0.04 \pm 0.01^b$	$0.69 \pm 0.01^c$	$0.29 \pm 0.03^b$	$1.70 \pm 0.12^e$
RPS120-8	$2.78 \pm 0.07^{b,c}$	$0.04 \pm 0.01^b$	$0.71 \pm 0.02^{b,c}$	$0.39 \pm 0.02^a$	$2.32 \pm 0.12^d$
RPS150-8	$2.83 \pm 0.08^{b,c}$	$0.04 \pm 0.01^b$	$0.73 \pm 0.01^{b,c}$	$0.39 \pm 0.02^a$	$2.43 \pm 0.11^{c,d}$
RPS170-8	$2.94 \pm 0.09^b$	$0.05 \pm 0.01^{a,b}$	$0.74 \pm 0.02^b$	$0.40 \pm 0.01^a$	$2.62 \pm 0.13^c$
RPS190-8	$3.25 \pm 0.06^a$	$0.07 \pm 0.01^a$	$0.84 \pm 0.04^a$	$0.41 \pm 0.02^a$	$3.38 \pm 0.08^b$
RPS210-6	$3.32 \pm 0.11^a$	$0.08 \pm 0.01^a$	$0.88 \pm 0.09^a$	$0.42 \pm 0.03^a$	$3.67 \pm 0.09^{a,b}$
RPS230-4	$3.38 \pm 0.10^a$	$0.08 \pm 0.01^a$	$0.93 \pm 0.10^a$	$0.42 \pm 0.02^a$	$3.98 \pm 0.12^a$

\*Data are presented as the mean  $\pm$  standard deviation. Data values in a column with different superscript letters are significantly different at the  $p \leq 0.05$  level.

based gels with a broad viscoelastic features range seems to be feasible combining commonly used separation techniques and roasting conditions. Weak gelling systems with viscoelastic features similar to those obtained in this work can be greatly valuable as basis of formulations for target population with specific requirements, such as puree-based baby or elder food [37].

**3.2.5. Thermal Reversibility.** Figure 3 shows thermal reversible features for RPS120-8, RPS190-8, and RPS230-4 gels, as an example of the behaviour observed in tested systems. The absence of differences between the mechanical spectra obtained at the end of the first and the second thermal cycle determined the strong thermal reversible characteristics of tested gels. The largest differences were observed for gels made from RPS230-4 (around 7.5% drop in both elastic and viscous moduli), indicating no complete thermal reversibility (Figure 3). Thermal stability characteristics were found for other native starches such as maize or wheat starches [38]; however, the authors are not aware that this rheological feature has been reported for other roasted starches. To

sum up, roasting temperatures between 120 and 170°C led to medium strength and fully thermal reversible gels, whereas temperatures between 190 and 210°C favour the formation of strong and fully thermal reversible gels (being the network structures formed in the sample more stable), with no completely thermal reversible gels at 230°C (Figure 3). These outcomes deliver a wide range of roasting conditions in terms of temperature (from 120 to 210°C) and time (from 4 to 8 h) for the potato starch gel processing without jeopardising the stability of the formulation.

**3.3. Texture.** Table 2 mentions the textural parameters determined for representative RPS gels. The macrostructure behaviour (textural features) was studied for the same selected formulations indicated in the rheological measurements. Hardness (kg) of gels statistically increased with increasing roasting temperatures. No significant variations were observed between RPS120-8 and RPS170-8 and between RPS190-8 and RPS230-4. Similar behaviour was identified for springiness, chewiness, and adhesiveness. No significant differences were noticed for cohesiveness of RPS



gels. These trends are consistent with those recently reported for chestnut starch isolated from roasted kernels [39], where starches from roasted chestnuts exhibited higher values of textural parameters when compared with those of fresh or boiled chestnuts. The textural parameters of modified starch gels depend strongly on the processing conditions [25]. Tested RPS gels exhibited larger hardness values (about the double) than those reported for gels prepared with acid-treated sweet potato starches at similar starch content [5], even though the values of textural features for all tested RPS gels were in the range of those reported for commercially offered savoury gelled systems and desserts [22].

The outcomes found from textural tests are related to those obtained from small deformation rheology. Hardness exhibited a linear relationship ( $R^2 > 0.98$ ) with the  $G'_{\text{gel}}$  (1 Hz) determined in the mechanical spectra for gels formed between RPS120-8 and RPS210-6. On the other hand, RPS230-4 gels featured higher hardness values related to the amylose breakdown above-discussed. Moreover,  $G'_{\text{gel}}$  (1 Hz) also showed a clear dependence with the ratio of the distances to each peak ( $D_1/D_2$ ) determined in TPA. An exponential dependence,  $G'_{\text{gel}} = 289.3 e^{5.1D_1/D_2}$  ( $R^2 > 0.99$ ), between both parameters was found. This outcome agrees with those reported for other food materials [15], where springiness (related to  $D_1/D_2$ ) was correlated with elastic material features.

**3.4. Syneresis.** The absence of water syneresis observed in the most RPS gels aged during one week at room temperature is a critically relevant feature in gels. Only gels prepared from RPS230-4 exhibited slight water syneresis (below 3% of the total gel). Negligible release of water was considered (<1%) for other concentrated starchy gelled systems as those formulated with sorghum starch [40]. The syneresis absence involves an important industrial advantage to other modified starchy [5, 26] gelling systems where water syneresis arises during the gel formation, suggesting that roasted starches feature more stable structures. Despite the increase of viscoelastic moduli of RPS gels with increasing starch roasting temperature, no gel syneresis was identified. It seems that these modified starches are more hydrophilic, the water is more structural, and then, no free water is available. It was reported [41] that the starch retrogradation rate (related to syneresis) is enhanced by the increasing of apparent amylose content, which is consistent with the results obtained here for RPS systems.

## 4. Conclusions

To conclude, it should be indicated that physicochemical features, the forming profiles of the gels, and the rheological and textural characteristics of the final gels for potato starch systems strongly depend on the roasting starch conditions. The largest physicochemical, rheological, and textural differences were identified between RPS170 and RPS190 systems. The adequate and almost equivalent solubility effect on starch roasting occurs for RPS190-8, RPS210-6, and RPS230-4. Temperatures below 170°C led to RPS gels with medium strength and fully thermal reversible gel formation, while

temperatures between 190 and 230°C promoted strong and fully thermal reversible gel formation, with no fully thermal reversible gels at 230°C. The critically relevant role of the starch soluble fraction was observed in the weakness of RPSI gels with increasing roasting temperature, intimately linked with the apparent amylose content reduction. Linear and exponential dependences were identified between  $G'_{\text{gel}}$  (1 Hz) and the hardness and springiness ratio ( $D_1/D_2$ ), respectively. The absence syneresis in RPS gels involves a very important industrial advantage. The  $T_p$  values from RPS190-8 to RPS230-4 could allow extending the functional potato starch features, to prepare new types of gelled products such as multicomponent gels or aerated gels where certain limitations (insufficient stability towards processing and environmental conditions or significant syneresis) may occur at large/low temperatures. Overall, this work provided a wide set of potato starches with potential gelling characteristics not only for food applications (PS, < RPS170) such as matrix for savoury/sweet gelatins or pastes, but also for non-food ones (between RPS190 and RPS230), arisen from different roasting starch conditions.

## Data Availability

All data generated or analysed during this study are included in this published article.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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