



Effect of formulation variables on rheology, texture, colour, and acceptability of apple jelly: Modelling and optimization



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ABSTRACT

The objective was to study and model the effect of the main formulation variables on the rheological and mechanical properties, colour and overall acceptability of apple jelly, and to optimize formulation variables in order to maximize overall acceptability. Formulation variables were juice proportion in the initial juice-sugar mix (J : 350–550 g/kg), product pH (2.8–3.6), concentration of added pectin (P : 0–10 g/kg), and final content of soluble solids (SS: 625–725 g/kg). Anova results showed that P was the main effect on all the rheological and mechanical properties. The strength of the pectin gel network increased at increasing values of P . Consequently, the jellies were more elastic and firm but more brittle, as well as more adhesive. Also, more work was required to disintegrate the jellies. Besides P , also J had a significant positive effect on storage modulus and adhesiveness, while SS had a significant positive effect on cohesiveness. Colour parameters were mainly affected by J . Overall acceptability was significantly affected by $J > \text{pH} > \text{SS}$, while P had no significant effect. The optimum was calculated to be at $J = 500$ g/kg, $\text{SS} = 700$ g/kg, $\text{pH} = 3.4$, and $P = 5$ g/kg.

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1. Introduction

Cooking jams, jellies and marmalades from fruits, sugar, pectin and edible acids is one of the oldest food preserving processes known to mankind, allowing fruit consumption in the off-season (Baker, Berry, & Hui, 1996). In this case food stabilization is achieved –besides the thermal treatment– by increasing the soluble solids content (reducing water activity), and increasing the acidity (reducing the pH). Also, these two parameters (soluble solids and pH) are of paramount importance for the texture, structure, and overall quality of fruit jams, since proper gelation of high methoxyl (HM) pectins is only achieved in narrow ranges of pH (2.8–3.5), and sugar content (~600–800 g/kg).

Industrial manufacture of fruit jams requires constant gel strength during production. Consequently, commercial pectin is added (0 to ~10 g/kg of the final product) to minimize the effect of the variability of fruit native pectin. Minimum soluble solids content required for the product depends on the legislation of each country, being 650 g/kg a typical limit (like in Argentine Food

Code). Maximum concentration allowed of added gelling agent also depends on the country, being 5 g/kg (without declaration in the label) in Argentina.

The main difference between jams, jellies and marmalades is the form in which their fruit component is incorporated, namely fruit juice, fruit pulp, pieces of fruit or whole fruit. Jellies are made from strained fruit juice. The minimum proportion of juice in the product also depends on the legislation of each country. In Argentina the legislation states that jellies should be manufactured by heat concentration of no less than 35 parts of filtered fruit juice, with a sweetener. In other words, the minimum ratio of ingredients to be cooked is 35 parts of juice in 65 parts of sugar and others ($J:S \geq 35:65$ g/g).

Besides determining general physical and chemical properties, many works have also performed sensory analysis of jams (Abdullah & Cheng, 2001; Basu, Shivhare, Singh, & Beniwal, 2011; Grigelmo-Miguel & Martín-Belloso, 1999; Singh, Jain, Singh, & Singh, 2009; Suutarinen et al., 2002), jellies (Acosta, Viquez, & Cubero, 2008; Khouryieh, Aramouni, & Herald, 2005; Moritaka, Naito, Nishinari, Ishihara, & Fukuba, 1999; Royer, Madieta, Symoneaux, & Jourjon, 2006), and marmalades (Egbekun, Nda-Suleiman, & Akinyeye, 1998; Yildiz & Alpaslan, 2012). Some of these studies and others have instrumentally measured the colour of jams (Dervisi, Lamb, & Zabetakis, 2001; Grigelmo-Miguel & Martín-Belloso, 1999; Singh et al., 2009; Suutarinen et al., 2002)

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and marmalades (Yildiz & Alpaslan, 2012). Several works have also studied the mechanical properties (texture) of jams (Basu et al., 2011; Singh et al., 2009; Suutarinen et al., 2002), and jellies (Khouryieh et al., 2005; Moritaka et al., 1999; Royer et al., 2006). A few studies have also determined the flow behaviour of these products (Costell, Carbonell, & Duran, 1993; Griguelmo-Miguel & Martín-Belloso, 1999; Yildiz & Alpaslan, 2012). The only justification of this type of destructive measurement in a structured product is the possibility to establish a quality control method for fruit derived products, based on the estimation of formulation/fruit content of the product from its viscometric properties (Fugel, Carle, & Schieber, 2005).

Remarkably, we just found a couple of works which studied the viscoelastic properties of jams (Basu et al., 2011; Dervisi et al., 2001). On the other hand, pectin gels have been much studied since the 60's and 70's (Barwal & Kalia, 1997; Doesburg & Grevers, 1960; Hinton, 1940; Smit & Bryant, 1968; Walter & Sherman, 1986). There are several studies about the effect of pectin concentration, pH, and type and concentration of cosolute, on the viscoelastic properties of HM pectin gels (e.g., Evageliou, Richardson, & Morris, 2000; Löfgren, Guillotin, Evenbratt, Schols, & Hermansson, 2005; Lopez da Silva, Gonçalves, & Rao, 1995; Tsoga, Richardson, & Morris, 2004). This may be attributed to the more complex structure and composition of jams, jellies and marmalades, compared to model pectin gels (pectin + sugar + acid + water). Genovese, Ye, and Singh (2010) tried to model the former systems by adding fruit particles to HM pectin gels, and studying the effect of particle size and concentration on the rheological and mechanical properties of these composite gels. However and as far as we know, the effect of composition on the viscoelastic properties of fruit jellies has not been studied yet.

The first objective of this work was to study the effect of formulation variables (juice proportion, added pectin concentration, and final soluble solids content), on the colour, rheological and mechanical properties, and overall acceptability of apple jellies. The last objective was to optimize the formulation based on acceptability results, and try to correlate this optimum with the physical properties of the jelly.

2. Materials and methods

2.1. Materials

Apples (*cv. Granny Smith*) were bought in a local market and stored at 5 °C during 48 h prior to juice extraction. High methoxyl pectin Genu Pectin Type 121 Slow Set (Cp Kelco, Brasil) was donated by Cp Kelco Argentina. Anhydrous citric acid Parafarm (Saporiti, Argentina) was used to regulate the pH. Food grade sucrose and potable bottled water, each from the same batch, were bought in the local market.

2.2. Juice extraction process

Only one batch of diluted apple juice was obtained and used to prepare the different jelly samples. To obtain this juice, apples were milled and the pulp mixed with water (1:1 w/w), blanched, press-filtered, and centrifuged. The diluted juice was bottled and frozen until use.

2.3. Jelly cook-concentration process

Required amounts of juice and sucrose were mixed in an open pan, heated up to the boiling point, and concentrated by evaporation until the desired concentration of soluble solids, which was monitored with a digital refractometer. The required amount of

pectin was separately dissolved in water with part of the sugar, and allowed to hydrate under agitation during 24 h before addition. In order to minimize pectin hydrolysis, this pectin solution was added to the juice-sugar mix towards the end of the concentration process. The desired pH was adjusted by adding a saturated solution of citric acid. To avoid pre-gelation, this solution was added just before the end of the process, and the pH was monitored with a digital pH meter (Altronix TPX II, Buenos Aires, Argentina) equipped with a high-temperature-resistant electrode (Broadley F-600, Irvine, USA). Finally, each sample was hot-filled at about 100 °C into three sanitized and labelled glass jars, which were sealed with their screw tops and stored for later measurements.

2.4. Rheological measurements

Viscoelastic properties of the jellies were determined by small deformation dynamic oscillatory measurements in a Paar Physica rheometer model MCR301 (Anton Paar GmbH, Austria), using a geometry of cone and plate (50 mm diameter, 1° cone angle), with peltier temperature control. Immediately after cook-concentration, an aliquot of the hot jelly was poured on the rheometer's lower plate, previously conditioned at 90 °C. The cone was lowered to the sample, excess sample was removed, and the exposed surface was covered with silicon oil to avoid sample dehydration during measurement. After thermal equilibrium was achieved, the measurement was initiated. Each measurement consisted in three successive steps, performed at an amplitude strain of 0.5%, namely: 1) Gelation: temperature ramp from 90 to 20 °C, at a cooling rate of 1 °C/min and a frequency of 1 rad/s; 2) Curing: time sweep of 180 min, at 20 °C and a frequency of 1 rad/s; and 3) Mechanical spectra: frequency sweep from 0.1 to 100 rad/s at 20 °C. Data obtained in each step were elastic modulus (G'), viscous modulus (G''), and derived parameters. Immediately after each measurement, a strain amplitude sweep (from 0.01 to 100%, at 20 °C and 1 rad/s) was performed to verify that the measurement was within the linear viscoelastic range (LVR).

2.5. Texture analysis

Mechanical properties of the jelly samples were obtained from a texture profile analysis (TPA) test using a TA-Plus texture analyzer (Lloyds Instruments, UK). Two containers (55 mm diameter) of each sample were stored for 1 month at room temperature, and conditioned at 20 °C in a controlled chamber during the last 48 h before measurement. The TPA test consists of two cycles of compression. In each cycle, the sample in each container was penetrated 20 mm by a cylinder probe (2.54 mm diameter), at a crosshead speed of 2 mm/s, and the probe was withdrawn from the sample at the same speed. Time and force exerted by the probe were measured during each test. Test settings followed a test procedure for marmalades (Genovese et al., 2010). Each sample was measured twice, once in each container.

From each force time curve of the TPA test a number of textural parameters can be extracted (Bourne, 2002). Hardness was obtained as the maximum peak force during the first compression cycle ($H = f_{\max}$). Fracturability was obtained as the force at the first significant break in the first compression cycle ($F = f_{\text{break}}$). Adhesiveness was calculated as the negative area under the force curve after the first compression cycle ($A = a_3$). Cohesiveness was calculated as the ratio of the positive force area during the second compression cycle to that during the first compression ($C = a_2/a_1$). Springiness was calculated as the ratio of the time elapsed during positive forces at the second compression, to that of the first compression ($S = t_2/t_1$). And gumminess was calculated as the product of hardness \times cohesiveness ($G = H.C$).

2.6. Colour measurement

Colour of jellies was measured in a HunterLab UltraScan XE tristimulus colorimeter (Hunter Associates Laboratory, Inc., Reston, VA). After 4 months of storage at room temperature, an aliquot of each sample was taken to fill a glass cuboid cell (10 mm thickness), and the total colour transmitted through the sample was measured at 10° observer angle with D65 illuminant. This procedure was repeated twice for each sample. Results were expressed as the Hunter Lab scale parameters L [lightness: 0 = black, 100 = white], a [greenness (–), redness (+)] and b [blueness (–), yellowness (+)].

2.7. Sensory evaluation. Acceptance test

A total of 100 untrained panellists (30 males and 70 females, 33 ± 11 years old) participated in the study. They were selected students and staff of Plapiqui Institute and Universidad Nacional del Sur (Bahía Blanca, Argentina), identified (in a survey previous to the test) as regular consumers of fruit jams, jellies and marmalades. Regular consumers were considered those who declared to consume these products at least 2 to 3 times per week, excluding those who only consumed light (reduced sugar) fruit jams. Samples were presented to the panellists coded and in random order. Plastic flat spoons and unsalted crackers were provided to the panellists as carriers. Unsalted crackers and/or drinking water were offered to the panellists to cleanse their palates between sample tasting. Panellists were instructed to consider taste, texture, spreadability (by spreading the jelly in the cracker with the spoon), and colour of the jellies, and based on these attributes they were asked to score overall acceptability of each sample on a 9-point Hedonic scale (1 = dislike extremely, 5 = neither like or dislike, 9 = like extremely). Each panellist evaluated 30 samples delivered in 3 sessions (10 samples per session, 1 session of ~30 min per day). A randomised complete block was the statistic design to analyze sensory results, where each panellist was considered a block. Data were subjected to analysis of variance (Anova) and Least Significant Differences (LSD) test to determine differences between jelly samples at a significance level of 5%.

2.8. Experimental design and statistical analysis

Response surface methodology (RSM), central composite experimental design (CCD) (Montgomery, 2005) was used to evaluate and model the effects of four independent formulation variables (factors) on the colour, rheological and mechanical properties, and sensory acceptance (responses) of apple jelly. Selected factors were juice proportion in the initial juice-sugar mix (J : 350–550 g/kg), added pectin (P : 0–10 g/kg), product pH (2.8–3.6), and final concentration of soluble solids (SS: 625–725 g/kg). Levels of each factor are listed in Table 1. The 4-factor CCD with 6 replicates at the central point consisted of 30 runs, whose coded factor levels are listed in Table 2. Selected apple jelly properties (responses) were plateau storage modulus at the end of curing

Table 1

Formulation variables of jellies: coded and actual levels of factors used in the central composite design, namely: g of juice per kg of initial juice-sugar mix (J), g of soluble solids per kg of final product (SS), pH of the final product, and g of pectin added per kg of final product.

Factor	–2	–1	0	1	2
J : Juice proportion (g/kg)	350	400	450	500	550
SS: Soluble solids (g/kg)	625	650	675	700	725
pH	2.8	3.0	3.2	3.4	3.6
P : Added pectin (g/kg)	0.0	2.5	5.0	7.5	10.0

(G'_{∞}), mechanical parameters hardness (H), fracturability (F), adhesiveness (A), cohesiveness (C), springiness (S), gumminess (G), colour parameters L , a , and b , and overall acceptability. Results were statistically analyzed with the Design Expert 7.0 software, at a significance level of 5%.

3. Results and discussion

Based on the results of the Anova (discussed later), 5 samples were selected to represent the results of the rheological and mechanical measurements, combining the 3 levels of pectin (P), the 3 levels of juice proportion (J), and the other two factors at their intermediate levels, namely pH = 3.2 and soluble solids SS = 675 g/kg.

3.1. Dynamic rheology

The elastic or storage modulus (G'), and the viscous or loss modulus (G'') of all samples were strain independent up to strain values of at least 1% (not shown). Then, all the measurements were carried out at a strain level of 0.5%, i.e. within the linear viscoelastic region. During the three steps of the rheological measurements (gelation, curing, and mechanical spectra), G' was higher than G'' for all jellies (except the sample without added pectin at high frequency, Fig. 3). This means that jellies showed predominantly solid-like behaviour, even at high temperatures. Consequently, G' was used to evaluate and compare the firmness/consistency of the jellies structure, which is determined by the gel strength.

Fig. 1a shows the increase of G' during cooling of the jellies. This increment represents the development and strengthening of the jellies structure due to pectin gelation. High methoxyl (HM) pectins form gels at low pH and high sugar concentration; this is why they are called sugar acid gels. The gelation mechanism of HM pectins is produced by non-covalent bonding of adjacent pectin chains, leading to an interconnected three-dimensional network. These bonds are produced in junction zones, which are stabilized by hydrogen bonds and hydrophobic interactions between the methyl-ester groups of the pectin chains. The sugar (or other co-solutes) reduces the water activity, promoting hydrophobic interactions. These interactions dominate at high temperatures. The acid releases H^+ , which neutralize the action of the $R-COO^-$ groups, reducing the electrostatic repulsion between pectin chains, and therefore favouring hydrogen bonding. This mechanism dominates at low temperature (Basu et al., 2011; Genovese et al., 2010; Kastner et al., 2014).

Fig. 1a shows how an increase in the added pectin concentration (P from 0 to 10 g/kg, at an intermediate juice proportion of $J = 450$ g/kg) produced a remarkable increase in both the absolute value of G' , considered as a measure of the strength of the gel structure, and the slope of the curves, considered as the structure development rate during gelation (Lopez da Silva et al., 1995). The increase of G' with P was attributed to the increase in the number of junction zones, resulting in an increase in the number of elastically active chains, which produced a firmer gel structure (Dervisi et al., 2001). It can also be observed how an increase in juice proportion (from 350 to 550 g/kg, at an intermediate pectin concentration of 5 g/kg) produced a modest increase in the elastic modulus. This was attributed to the increased contribution of native pectin from the juice. These effects were later supported by Anova results.

One traditional way to determine the sol-gel transition, gel point (GP), or gelatinization temperature of pectin gels during cooling, is from the point where G' becomes higher than G'' , also known as the crossover of the $G'-G''$ curves (Kastner et al., 2014; Löfgren et al., 2005; Lopez da Silva et al., 1995). However as previously mentioned, for all the jelly samples studied here G' was higher than

Table 2
Coded variable levels and responses of the central composite experimental design, namely: plateau storage modulus at the end of curing (G'_{∞}), mechanical parameters hardness (H), fracturability (F), adhesiveness (A), cohesiveness (C), springiness (S), gumminess (G), colour parameters L , a , and b , and overall acceptability. Each value of the physical properties is the average of at least two replicates. Overall acceptability is the average of 100 consumers scores.

Coded levels				G'_{∞} [Pa]	H [N]	F [N]	A [N.m] $\times 10^3$	C	S	G [N]	L	a	b	Overall acceptability ^a	
J	SS	pH	P												
-1	-1	-1	-1	100	1.08	1.27	-0.420	0.429	0.902	0.457	55.2	17.1	32.1	3.64a	
-1	-1	-1	1	592	2.69	2.11	-1.176	0.423	0.932	1.143	55.4	12.2	30.1	4.67b,c,d,e	
-1	-1	1	-1	83	1.08	1.24	-0.303	0.467	0.925	0.495	61.6	9.6	30.0	4.19b	
-1	-1	1	1	320	1.83	1.74	-0.482	0.451	0.937	0.826	65.2	8.2	30.3	4.99c,d,e,f,g,h	
-1	1	-1	-1	99	0.85	0.78	-0.395	0.517	0.912	0.438	54.4	16.1	31.3	4.94c,d,e,f,g,h	
-1	1	-1	1	372	2.40	2.10	-1.214	0.489	0.942	1.176	52.4	16.0	30.5	5.08e,f,g,h,i,j	
-1	1	1	-1	123	0.83	0.85	-0.188	0.506	0.927	0.420	63.2	10.4	32.1	5.21f,g,h,i,j,k	
-1	1	1	1	505	2.34	2.23	-1.193	0.403	0.919	0.947	63.6	9.6	31.1	5.15e,f,g,h,i,j,k	
1	-1	-1	-1	116	1.22	0.97	-0.288	0.469	0.923	0.570	57.4	13.5	31.8	4.83c,d,e,f,g	
1	-1	-1	1	646	3.12	2.33	-2.034	0.378	0.914	1.179	51.4	10.9	27.8	4.80c,d,e,f	
1	-1	1	-1	161	1.13	1.09	-0.221	0.422	0.910	0.473	49.0	16.5	28.8	5.29f,g,h,i,j,k	
1	-1	1	1	407	3.55	2.80	-1.411	0.388	0.932	1.378	46.8	17.1	27.9	5.34g,h,i,j,k	
1	1	-1	-1	222	2.09	1.55	-1.345	0.442	0.908	0.909	46.4	21.0	28.8	4.99c,d,e,f,g,h	
1	1	-1	1	551	2.38	1.91	-1.713	0.456	0.924	1.085	48.7	18.9	29.2	4.96c,d,e,f,g,h	
1	1	1	-1	131	0.93	0.79	-0.445	0.499	0.907	0.461	50.1	20.3	29.8	6.20m	
1	1	1	1	500	2.58	2.20	-1.981	0.484	0.923	1.251	44.1	20.0	27.1	5.54j,k,l	
-2	0	0	0	266	1.70	1.43	-0.287	0.465	0.941	0.789	62.0	10.5	31.6	4.53b,c,d	
2	0	0	0	360	1.48	1.50	-1.205	0.473	0.917	0.700	40.1	26.1	25.5	5.96l,m	
0	-2	0	0	197	1.90	1.48	-0.522	0.416	0.917	0.788	44.6	18.2	27.1	5.02d,e,f,g,h,i	
0	2	0	0	418	1.34	1.22	-0.925	0.459	0.921	0.613	55.1	17.1	31.4	5.40h,i,j,k	
0	0	-2	0	438	1.68	1.25	-0.721	0.531	0.945	0.912	44.7	21.2	27.2	4.95c,d,e,f,g,h	
0	0	2	0	292	1.85	2.09	-1.709	0.446	0.894	0.815	54.0	16.1	30.8	5.61k,l	
0	0	0	-2	36	0.65	0.94	-0.073	0.459	0.888	0.295	56.6	14.9	31.7	4.47b,c	
0	0	0	2	964	5.16	3.62	-2.015	0.366	0.935	1.898	46.9	14.0	26.8	5.14e,f,g,h,i,j,k	
0	0	0	0	393	1.17	0.97	-0.614	0.516	0.912	0.602	49.3	20.1	29.3	5.60j,k,l	
0	0	0	0	271	1.27	1.23	-0.655	0.467	0.942	0.593	54.0	16.6	31.2	6.03l,m	
0	0	0	0	371	1.51	1.42	-1.035	0.470	0.918	0.707	55.5	15.6	30.9	5.60j,k,l	
0	0	0	0	242	1.46	1.27	-0.345	0.480	0.956	0.702	58.1	13.2	31.3	5.53i,j,k,l	
0	0	0	0	380	1.56	1.55	-0.496	0.439	0.922	0.682	54.8	14.9	30.9	5.13e,f,g,h,i,j,k	
0	0	0	0	351	1.46	1.11	-0.364	0.491	0.948	0.714	54.5	16.5	31.5	4.68b,c,d,e	
Pooled Standard Deviation				72	0.39	0.27	0.449	0.028	0.020	0.201	2.3	1.0	1.1	2.08	

^a Means with a common letter are not significantly different ($p \leq 0.05$).

G'' (not shown) from the beginning of the cooling process. Consequently there was not $G'-G''$ crossover, and then the GP could not be determined in this way. An alternative method was suggested by Kastner et al. (2014) to obtain structuring parameters during pectin gelation, from the structure development rate (SDR), or structuring velocity plot. The SDR plot is obtained by plotting the first derivative of G' (dG'/dt) as function of the cooling temperature (T) (Lopez da Silva et al., 1995). According to this method, the initial structuring temperature (IST) is the temperature at which dG'/dt is different from zero for the first time, and the critical structuring temperature (CST) is the temperature of the first strong increase (Kastner et al., 2014).

Values of dG'/dt were calculated at temperature intervals of 5 °C during the cooling process. Fig. 1b shows the SDR plot obtained for the selected jelly samples. The jelly without added pectin showed a negligible SDR compared to the other jellies, which observed an increase of the dG'/dt during cooling up to a certain temperature where SDR reached a maximum, followed by a slight decrease upon further cooling. Calculated values of IST and CST are listed in Table 3. Both IST and CST decreased at decreasing concentration of added pectin (P), and at decreasing juice proportion (J). This indicates that the sol-gel transition range (in terms of temperature) decreased at decreasing the total pectin content of the jellies. The temperature of maximum dG'/dt was about 45 °C for the jelly with 10 g/kg added pectin, and 35–40 °C for the jellies with 5 g/kg added pectin.

An increase of the elastic modulus was observed at the beginning of the curing or ageing process (Fig. 2). This was attributed to the completion of the gelation process initiated in the previous step. This initial increase was followed by a gradual decrease of the elastic modulus, until it levelled off at an equilibrium or plateau

value towards the end of the 3 h curing process. The decrease was attributed to a relaxation of stresses developed in the pectin network during the previous gelation process. The last ten points of each curing curve were averaged and the value obtained was considered as the plateau elastic modulus (G'_{∞}) of each sample. Calculated values of G'_{∞} ranged from about 36 to 964 Pa (Table 2). Parameter G'_{∞} was selected as one of the responses of the DCC experimental design, and the effect of formulation variables on it will be analyzed in the Modelling Section (3.5).

Mechanical spectra (elastic and viscous moduli vs frequency) curves are shown in a log–log plot (Fig. 3). The selected jellies showed a gel-like behaviour with $G' > G''$, and a gentle linear increase of $\log(G')$ with $\log(\omega)$, which is typical of weak-gels (Genovese et al., 2010). The steeper slope of the jelly without pectin, and its $G'-G''$ crossover at high frequencies indicated the more liquid like character of this sample (Basu et al., 2011).

3.2. Texture

Texture profile analysis (TPA) consists of compressing a food sample twice, in a reciprocating motion that imitates the action of the jaw. Fig. 4 shows the resulting force–time curves obtained for the selected jellies. It can be observed how the increase in pectin concentration produced a remarkable increase in the resulting force profiles (both positive and negative) of the two cycles. Increasing juice proportion produced a similar but much more moderate effect. These results follow the trend of those obtained by dynamic rheology.

Textural parameters obtained from the force time curve have been described by Bourne (2002). Hardness (H) has been defined as

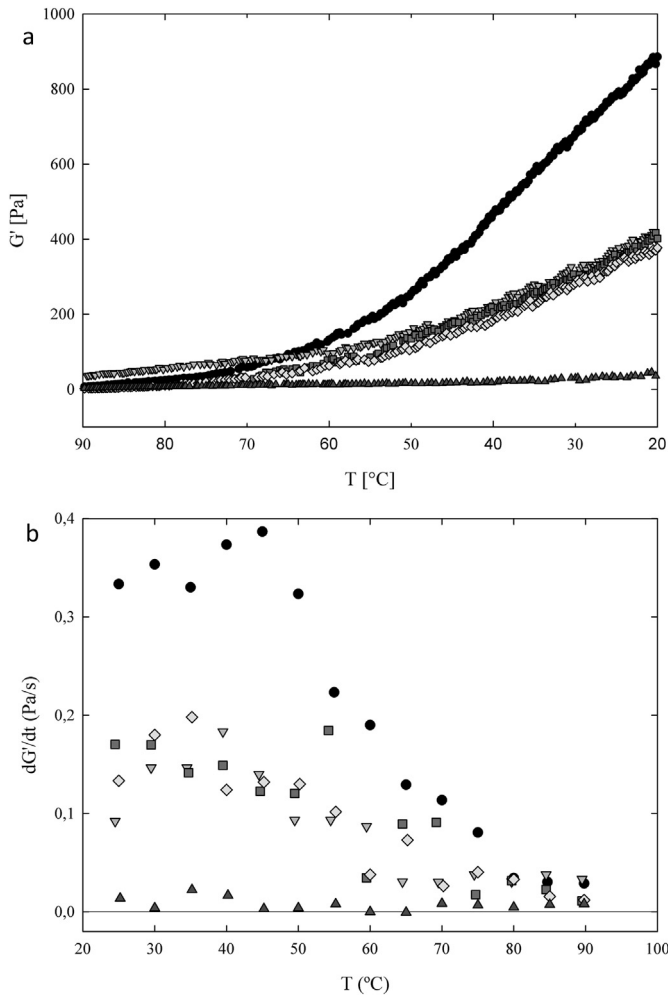


Fig. 1. Gelation: (a) Elastic modulus (G'), and (b) structure development rate ($SDR = dG'/dt$) as a function of temperature (T), during cooling of jellies. Five representative samples are shown, namely the jellies made with: Pectin 10.0 g/kg and Juice 450 g/kg (●), Pectin 5.0 g/kg and Juice 550 g/kg (▼), Pectin 5.0 g/kg and Juice 450 g/kg (■), Pectin 5.0 g/kg and Juice 350 g/kg (◇), and Pectin 0.0 g/kg and Juice 450 g/kg (▲). All these five samples had pH = 3.2 and soluble solids 675 g/kg.

the force necessary to attain a given deformation (sometimes called firmness). In sensory analysis, it is the force required to compress a food between molars in the first bite. Fracturability (F) has been defined as a measure of the ease with which a material fractures (sometimes called brittleness). Adhesiveness (A) represents the work required to pull the compressive probe away from the sample. In sensory analyses, it represents the work necessary to overcome the attractive forces between the surface of the food and the surface of the material with which the food comes into contact (e.g. tongue, teeth, palate). Cohesiveness (C) represents the strength of the internal bonds making up the body of the product. It is expected to be inversely proportional to the rate at which the material fractures under mechanical action. In other words, the lower the cohesiveness of a material, the more brittle it will be. Springiness (S) is related to the height that the food recovers during the time that elapses between the end of the first bite and the start of the second bite. It represents the rate at which a deformed material goes back to its undeformed condition after deforming force is removed (originally it was called elasticity). Gumminess (G) represents the energy required to disintegrate a semi-solid food product to a state ready for swallowing.

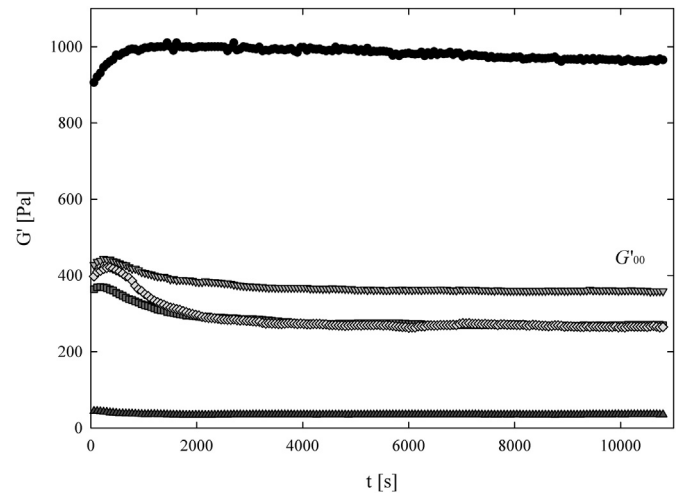


Fig. 2. Curing: Elastic modulus (G') as a function of time (t) during ageing of jellies. Five representative samples are shown, namely the jellies made with: Pectin 10.0 g/kg and Juice 450 g/kg (●), Pectin 5.0 g/kg and Juice 550 g/kg (▼), Pectin 5.0 g/kg and Juice 450 g/kg (■), Pectin 5.0 g/kg and Juice 350 g/kg (◇), and Pectin 0.0 g/kg and Juice 450 g/kg (▲). All these five samples had pH = 3.2 and soluble solids 675 g/kg.

Experimental values of these parameters are listed in Table 2, and their approximate ranges were H : 0.6–5.2 N, F : 0.8–3.6 N, A : -7.3×10^{-5} to -2.0×10^{-3} N m, C : 0.37 to 0.53, S : 0.89 to 0.96, and G : 0.30–1.90 N. Values of H , C , and S are in agreement with those reported for other fruit jams and jellies (Basu et al., 2011; Khouryieh et al., 2005; Royer et al., 2006; Singh et al., 2009). Parameters H , F , A , C , S , and G were selected as responses of the DCC experimental design, and the effect of formulation variables on them will be analyzed in the Modelling Section (3.5).

3.3. Colour

Experimental values of L ranged from about 40 to 65, values of a ranged from about 8 to 26 (reddish), and values of b ranged from about 26 to 32 (yellowish) (Table 2). These results reflected the

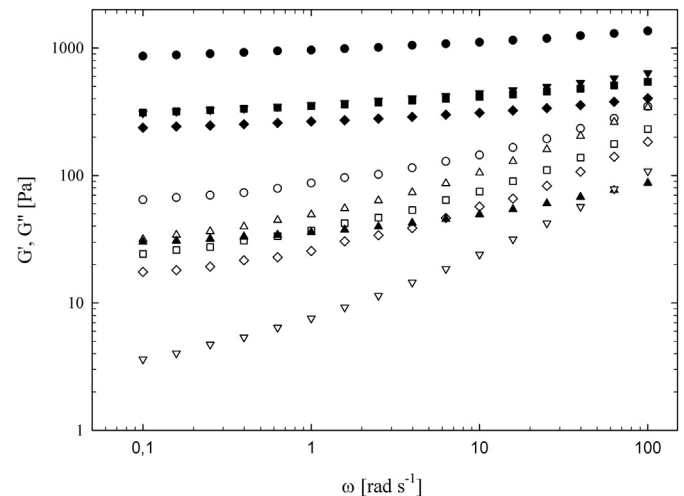


Fig. 3. Mechanical spectra: elastic modulus (G' , black symbols) and viscous modulus (G'' , open symbols) of jellies as a function of frequency (ω). Five representative samples are shown, namely the jellies made with: Pectin 10.0 g/kg and Juice 450 g/kg (●, ○), Pectin 5.0 g/kg and Juice 550 g/kg (▼, ▽), Pectin 5.0 g/kg and Juice 450 g/kg (■, □), Pectin 5.0 g/kg and Juice 350 g/kg (◇, ◇), and Pectin 0.0 g/kg and Juice 450 g/kg (▲, △). All these five samples had pH = 3.2 and soluble solids 675 g/kg.

Table 3

Initial structuring temperature (IST) and critical structuring temperature (CST) as function of added pectin (P) and juice proportion (J), for the five sample jellies selected for this analysis. Values obtained from the SDR curves (Fig. 1b).

P [g/kg]	J [g/kg]	IST [°C]	CST [°C]
10.0	450	90	80
5.0	550	90	65
5.0	450	85	60
5.0	350	80	60
0.0	450	–	–

orange-brown colour of our jellies. Parameters L , a , and b were selected as responses of the DCC experimental design, and the effect of formulation variables on them will be analyzed in the Modelling Section (3.5).

3.4. Sensory evaluation

Average scores of overall acceptability are reported in Table 2, and ranged from about 3.6 to 6.2 in the 9-point Hedonic scale. Anova results (not shown) indicated that there were significant differences between average scores of the samples, and also between average scores of the panellists. This means that panellists constituted a noise factor in the results. This effect was eliminated from the comparison between samples by considering the panellists as blocks in the statistic design. Significant differences observed between some replicates of the central point were attributed to the fact that each sample was made in a different batch.

The sample that scored the highest average acceptability (preferred sample) was the one with $J = 500$ g/kg, $\text{pH} = 3.4$, $\text{SS} = 700$ g/kg, and $P = 2.5$ g/kg. Overall acceptability was selected as the last response of the DCC experimental design, and the effect of formulation variables on it will be analyzed in the Modelling Section (3.5).

3.5. Modelling

Selected properties of the jellies (responses) were modelled in terms of the four formulation variables (factors) studied in this

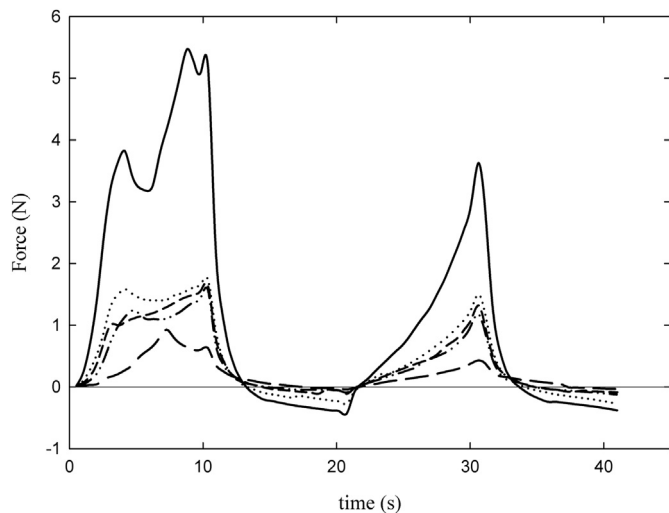


Fig. 4. Texture Profile Analysis: Force vs. time curves obtained during the two compression cycles performed on the jellies. Five representative samples are shown, namely the jellies made with: Pectin 10.0 g/kg and Juice 450 g/kg (—), Pectin 5.0 g/kg and Juice 550 g/kg (---), Pectin 5.0 g/kg and Juice 450 g/kg (····), Pectin 5.0 g/kg and Juice 350 g/kg (-·-·-), and Pectin 0.0 g/kg and Juice 450 g/kg (- - -). All these five samples had $\text{pH} = 3.2$ and soluble solids 675 g/kg.

work (Table 1). Results of the Box Cox diagnostic test indicated that plateau elastic modulus data required a square root transformation ($\sqrt{G_\infty}$) to meet the assumptions that make the Anova valid; hardness required an inverse square root transformation ($1/\sqrt{H}$), fracturability and gumminess required a log transformation ($\text{Ln}(F)$ and $\text{Ln}(G)$, respectively), and the other responses data did not require any transformation. Regression analyses suggested that the linear model was the most appropriate fit for all the responses, either transformed or not. In all cases, Anova results showed that each model was significant, lack of fit was not significant (except for G), adjusted and predicted R^2 were in reasonable agreement, and the signal to noise ratio was adequate, concluding that all the models obtained in this work were appropriate to navigate the design space.

Anova results showed that added pectin concentration (P) was the main effect on all the rheological and mechanical properties, while juice proportion (J) also had a significant effect on plateau storage modulus (G_∞) and adhesiveness (A). Both P and final concentration of soluble solids (SS) had a significant effect on cohesiveness (C). Remarkably, the pH had no significant effect on any of these properties. Following are the models obtained in terms of the actual factors, and the corresponding regression coefficients:

$$\sqrt{G_\infty} = -9.60 + 1.87 \cdot 10^{-2} \cdot J + 2.90 \cdot 10^{-2} \cdot \text{SS} - 3.86 \cdot \text{pH} + 2.26 \cdot P$$

$$(R^2 = 0.894, R^2_{\text{adj}} = 0.877, R^2_{\text{pred}} = 0.845)$$
(1)

$$1/\sqrt{H} = 5.53 \cdot 10^{-1} - 5.79 \cdot 10^{-4} \cdot J + 8.96 \cdot 10^{-4} \cdot \text{SS}$$

$$+ 8.28 \cdot 10^{-2} \cdot \text{pH} - 7.14 \cdot 10^{-2} \cdot P$$

$$\times (R^2 = 0.837, R^2_{\text{adj}} = 0.811, R^2_{\text{pred}} = 0.757)$$
(2)

$$\text{Ln}(F) = 3.66 \cdot 10^{-1} + 6.57 \cdot 10^{-4} \cdot J - 2.19 \cdot 10^{-3} \cdot \text{SS}$$

$$+ 1.50 \cdot 10^{-1} \cdot \text{pH} + 1.43 \cdot 10^{-1} \cdot P$$

$$\times (R^2 = 0.748, R^2_{\text{adj}} = 0.708, R^2_{\text{pred}} = 0.640)$$
(3)

$$A = 5.37 - 4.92 \cdot 10^{-3} \cdot J - 4.91 \cdot 10^{-3} \cdot \text{SS}$$

$$+ 8.03 \cdot 10^{-2} \cdot \text{pH} - 1.91 \cdot 10^{-1} \cdot P$$

$$\times (R^2 = 0.697, R^2_{\text{adj}} = 0.649, R^2_{\text{pred}} = 0.563)$$
(4)

$$C = 1.35 \cdot 10^{-1} - 1.12 \cdot 10^{-4} \cdot J + 7.60 \cdot 10^{-4} \cdot \text{SS}$$

$$- 3.17 \cdot 10^{-2} \cdot \text{pH} - 7.77 \cdot 10^{-3} \cdot P$$

$$\times (R^2 = 0.397, R^2_{\text{adj}} = 0.301, R^2_{\text{pred}} = 0.118)$$
(5)

$$S = 1.00 - 8.52 \cdot 10^{-5} \cdot J - 7.49 \cdot 10^{-6} \cdot \text{SS}$$

$$- 1.65 \cdot 10^{-2} \cdot \text{pH} + 3.42 \cdot 10^{-3} \cdot P$$

$$\times (R^2 = 0.331, R^2_{\text{adj}} = 0.224, R^2_{\text{pred}} = 0.101)$$
(6)

$$\text{Ln}(G) = -5.12 \cdot 10^{-1} + 1.25 \cdot 10^{-3} \cdot J - 4.72 \cdot 10^{-4} \cdot \text{SS}$$

$$- 2.70 \cdot 10^{-1} \cdot \text{pH} + 1.65 \cdot 10^{-1} \cdot P$$

$$\times (R^2 = 0.860, R^2_{\text{adj}} = 0.838, R^2_{\text{pred}} = 0.792)$$
(7)

The effect of P on all these properties (except C) was positive, which in terms of G'_{∞} and H means that increasing concentrations of added pectin increased the firmness or strength of the gels, with a reinforcing effect on the structure of the jellies. This was in agreement with the increase of G with P , which means that more work was required to disintegrate the jellies as more pectin was added. The effect of P on F was also positive, which means that the stronger were the gels at increasing pectin concentrations, the more brittle became the jellies. The increases of S and $G'_{\infty} \frac{n!}{r!(n-r)!}$ with P were consistent, meaning that the addition of pectin increased the elasticity of the jellies. The effect of J on G'_{∞} and A was also positive, which means that at higher juice proportions in the formulation, the more solid and adhesive were the jellies. Since A is a parameter with negative values, a positive effect means that the higher were P and J , the more negative was A . Contrarily to what we expected, final sugar content of the jellies (SS) had no effect on their adhesiveness. The effect of SS on C was positive, which means that increasing concentration of sugar increased the strength of the internal bonds of the jelly. This was attributed to the sugar reinforcing the bonds (through hydrophobic interactions) between the pectin chains making up the gel network. The effect of P on C was negative, which means that jellies fractured more easily (they were more brittle) at increasing pectin concentrations, in accordance with fracturability results.

Anova results also showed that juice proportion (J) was the main effect on the three colour parameters, while added pectin concentration (P) also had a significant effect on parameter b . The other two factors (pH and SS) had no significant effect on the colour parameters. Following are the models obtained in terms of the actual factors, and the corresponding regression coefficients:

$$L = 7.19 \cdot 10^1 - 1.01 \cdot 10^{-1} \cdot J + 3.02 \cdot 10^{-3} \cdot SS + 8.46 \cdot pH - 4.85 \cdot 10^{-1} \cdot P \quad (8)$$

$$\times (R^2 = 0.609, R^2_{\text{adj}} = 0.547, R^2_{\text{pred}} = 0.410)$$

$$a = -2.14 \cdot 10^1 + 5.84 \cdot 10^{-2} \cdot J + 4.18 \cdot 10^{-2} \cdot SS - 5.05 \cdot pH - 2.29 \cdot 10^{-1} \cdot P \quad (9)$$

$$\times (R^2 = 0.541, R^2_{\text{adj}} = 0.468, R^2_{\text{pred}} = 0.311)$$

$$b = 2.94 \cdot 10^1 - 2.35 \cdot 10^{-2} \cdot J + 1.63 \cdot 10^{-2} \cdot SS + 5.31 \cdot 10^{-1} \cdot pH - 3.42 \cdot 10^{-1} \cdot P \quad (10)$$

$$\times (R^2 = 0.565, R^2_{\text{adj}} = 0.496, R^2_{\text{pred}} = 0.366)$$

Factor J had a negative effect on L and b , and a positive effect on a . This means that at increasing proportions of juice in the formulation, the jellies obtained were darker, more reddish, and less yellowish. This was attributed to non-enzymatic (Maillard) browning during the concentration process, since higher juice proportions in the ingredients implicated longer cooking times. Factor P had a negative effect on b , which means that increasing concentrations of pectin produced less yellowish jellies. The reason for this is not clear. It is worth noting that the pH had no significant effect on any of the physical parameters.

On the other hand, overall acceptability was significantly affected by juice proportion (J), pH , and soluble solids (SS), in that order of importance, while pectin concentration (P) had no significant effect on it. Following is the model obtained in terms of the actual factors, and the corresponding regression coefficients:

$$\text{Acceptability} = -6.96 + 5.78 \cdot 10^{-3} \cdot J + 8.47 \cdot 10^{-3} \cdot SS + 1.11 \cdot pH + 4.30 \cdot 10^{-2} \cdot P$$

$$\times (R^2 = 0.537, R^2_{\text{adj}} = 0.463, R^2_{\text{pred}} = 0.374) \quad (11)$$

It can be observed that all factors J , pH , SS , and P had a positive effect on acceptability, although P was non-significant. Considering that P was the main effect on rheological and mechanical properties, this means that overall acceptability was mainly determined by the taste, and maybe the colour of the jellies (function of J), but not by their texture and spreadability. Regarding taste, it seems that consumers preferred fruitier, sweeter, and less acid samples.

3.6. Optimization

In order to obtain the optimum jelly formulation, acceptability was maximized within the experimental range studied, and respecting the legal limits for jellies in Argentina, namely: $J_{\text{MIN}} = 350$ g/kg, $SS_{\text{MIN}} = 650$ g/kg, and $P_{\text{MAX}} = 5$ g/kg. Maximum predicted acceptability (5.84) within these constraints was obtained at: $J = 500$ g/kg, $SS = 700$ g/kg, $pH = 3.4$, and $P = 5$ g/kg. It can be observed that these factor levels are the same as those of the preferred sample, except P which is higher. This was attributed to the fact that P had no significant effect on overall acceptability, but nevertheless has a positive effect on the model (Ec. 11). Calculated values of the other responses at this optimum are: $G'_{\infty} = 330$ Pa, $H = 1.47$ N, $F = 1.42$ N, $A = -1.21 \times 10^{-3}$ N m, $C = 0.464$, $S = 0.915$, $G = 0.733$, $L = 49.9$, $a = 18.7$, and $b = 29.2$. It can be observed that these values are intermediate in the range of each response. This means that maximum acceptability did not coincide with a maximum or minimum value of any of the physical parameters of the jellies. This implicates that the optimum values of these physical parameters should be determined by a descriptive sensory analysis of specific attributes of the jellies.

4. Conclusions

An important conclusion from rheological and mechanical results is that even though the addition of pectin reinforces the structure of the jelly, an excessive pectin dose will produce a jelly too brittle or breakable. Therefore, there must be an optimum concentration of pectin to give a jelly with an ideal structure. However, sensory analysis with untrained panellists (consumers) indicated that pectin concentration had no significant effect on overall acceptability of the jellies. In other words, texture, consistency, and/or spreadability were the less important attributes for consumers at the moment to judge the jellies as a whole. Instead, their preferences seemed to be based mainly on jellies taste, and maybe colour. To determine the best jelly structure, a descriptive sensory analysis with trained panellists shall be required.

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