HIGH METHOXYL PECTIN/APPLE PARTICLES COMPOSITE GELS: EFFECT OF PARTICLE SIZE AND PARTICLE CONCENTRATION ON MECHANICAL PROPERTIES AND GEL STRUCTURE

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ABSTRACT

In order to study the effect of fruit pulp on the structure of fruit jams, they were modeled as composites with a high-methoxyl pectin (HMP) gel matrix filled with apple particles. The effect of particle concentration (0, 1 and 2 wt%) and particle size (small: <125 μm, and large: 125–850 μm) on a pectin gel (0.5 wt% HMP, 65 wt% glucose, pH 3.0, 0.1 M citrate buffer) were studied. Rheological measurements showed that increasing concentration of small particles produced a significant increase in the elastic modulus of the composite gels. Penetration tests showed that 1 wt% small particles produced a significant decrease of gel strength, rupture strength, adhesiveness and brittleness. Increasing particle size produced a further decrease of these properties (only significant for gel strength). When concentration of small particles was raised to 2 wt%, these parameters (except brittleness) increased back to the control sample (0% particles) values.

PRACTICAL APPLICATIONS

Knowledge of the effect of fruit particles on the structure of pectin gels would allow controlling the rheological and mechanical properties of fruit jams in terms of the size and concentration of fruit pulp used in their formulation.

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INTRODUCTION

Fruit jams, jellies and marmalades are made by cooking fruit (pieces, pulp and/or juice) with sugars, gelling agents (usually pectin) and edible (usually organic) acids, and concentrating the mixture until a characteristic and suitable consistency is obtained (Fügel et al. 2005). This is one of the oldest processes used by mankind to preserve fruit for consumption in the off-season (Baker et al. 1996). The stability of these products is mainly provided by two factors: (1) low water activity, achieved by increasing the concentration of soluble solids to a minimum of about 65 wt%; and (2) low pH values, roughly between 2.8 and 3.5 (Royer et al. 2006), due to the natural acidity of fruits plus the addition of organic acids. When high-methoxyl pectin is used as gelling agent, those levels of soluble solids and pH (in combination with the type and concentration of pectin) are also of paramount importance for proper gel formation (or gelation).

In jellies, only strained fruit juice is used, while jams and marmalades are made with crushed ground fruit material (Baker et al. 1996). The form and concentration in which the fruit component is incorporated depends on the type of product, and on the legislation of each country. The minimum amount of fruit in the final product may vary from about 35–45 wt% (Fügel et al. 2005). Insoluble solids may range from 0.9 to 10 wt% (Egbekun et al. 1998). Modern manufacturing requirements for uniform gel strength and appearance preclude reliance on fruit native pectin, which may vary in content and quality, depending on fruit maturity and variety. Consequently, commercial pectin of known quality and gelling capacity is added to jam and jelly formulations to achieve the desired gel strength (Baker et al. 1996). The maximum amount of added pectin also depends on the legislation of each country, and may vary from 0.5 to 1.0 wt% of the final product.

Jams and marmalades (from now on, jams) may be regarded as filler–matrix composites consisting of fruit particles embedded in a continuous pectin gel. The dispersed phase or filler consists of insoluble solids of the fruit, of different sizes and shapes depending on the product (whole pieces, pulp or sieved pulp). The continuous phase or matrix is a pectin gel, which contains various solutes (sugars, pectin, organic acids and minerals), both native and added to achieve the appropriate gelation. Because of its complex nature, studies on jam’s structure are scarce and mostly empirical. Dervisi et al. (2001) studied the effect of pectin concentration on the rheological properties of jam.
of high hydrostatic pressure-treated jams. Royer et al. (2006) studied the effect of heating time, and initial concentrations of quince fruit and sugar on the mechanical properties of apple pomace and quince jelly.

On the other hand, mechanism of gelation and structure development of model pectin gels (namely water plus added pectin and co-solutes) have been widely studied (see for example Lopez da Silva et al. 1995; Evageliou et al. 2000; Löfgren et al. 2005). The various parameters that affect the rigidity of a filler–matrix composite have been modeled by the equation of Kerner (1956), and its modification by Lewis and Nielsen (1970). Food-grade matrices with different type of fillers have been studied (Brownsey et al. 1987; van Vliet 1988; Jampen et al. 2001; Kim et al. 2001; Manski et al. 2007; Wongsasulak et al. 2007; Mavrakis and Kiosseoglou 2008; Savary et al. 2008). Only one of these studies (Savary et al. 2008) analyzed a composite system where the matrix was a pectin gel (0.4 wt% low-methoxyl pectin, 35 wt% sucrose and an acidic buffer); the dispersed phase were cross-linked corn starch granules (1.4 wt%).

The aim of the present work was to study the effect of fruit pulp particles on the structure and mechanical properties of fruit jams. In order to do that, fruit jams were modeled as high-methoxyl pectin/microsized fruit particles composite gels. The specific objective was to analyze the effect of fruit pulp particle size and concentration on the microstructure, textural and rheological properties of these composite gels.

**MATERIALS AND METHODS**

**Materials**

High-methoxyl pectin powder (GENU pectin type 105 rapid set) was obtained from CPKelco (Lorong Chuan, Singapore). According to the manufacturer’s specifications, this pectin has a degree of esterification between 67% and 73%. A rapid set pectin was used in order to avoid sedimentation of the dispersed apple particles. Food-grade glucose syrup (20% water) was used as a co-solute. The concentration used is expressed on a dry-weight basis. A stock citrate buffer solution (pH 3.0, 0.1 M) was prepared from anhydrous citric acid and sodium citrate. Reverse-osmosis demineralized water was used throughout.

Apple pulp particles were obtained as follows. Apple sauce (IXL, Kyabram, Victoria, Australia) was purchased in a local supermarket. According to the manufacturer, this apple sauce had 99.8% apples, and 0.2% ascorbic acid. In order to remove natural sugars and other solutes, apple sauce was washed with hot water, centrifuged at 800 × g for 15 min, and the supernatant was removed. This procedure was repeated three times, when the supernatant
reached a soluble solids concentration of approximately 0.5°Brix. The washed pulp was freeze-dried and reduced to a powder in a coffee grinder. Apple powder was fractionated into two particle size classes, with the aid of sieves of two mesh sizes, 125 μm and 850 μm, shaken in a mechanical agitator. Particles that went through the 125 μm sieve were called small particles, while those retained between the 125 μm and 850 μm sieves were called large particles. Particles that could not go through the 850 μm sieve were not enough for analysis and were discarded.

Particle size Distribution

Aliquots of apple particles of each size class (small and large) were dispersed in water and allowed to hydrate for about 1 h under continuous stirring. Particle size distribution and mean size of these particle dispersions were determined by integrated light scattering (ILS) in a Malvern MasterSizer 2000 particle analyzer (Malvern Instruments Ltd, Worcestershire, U.K.). A refractive index of apple particles of 1.49 was used (Benítez et al. 2007). Measurements were done under sonication, in triplicate.

The ILS technique is based on the measurement of the steady intensity of light scattered by the particles at different angles. The angular dependence of the scattered light is defined by the wavelength of light, the index of refraction difference (contrast) and the shape and size of the scattering particles. Assuming that the particles are spherical, the instrument generates a volume distribution as the fundamental measurement, as well as the volume/surface and weight average diameters, $D_{3,2} = \sum n_i d_i^3 / \sum n_i d_i^2$ and $D_{4,3} = \sum n_i d_i^4 / \sum n_i d_i^3$, where $n_i$ and $d_i$ are the number percentage and average diameter of particles in each size interval, respectively. Most of the particles analyzed in this work were not spherical; consequently, each calculated value of $d_i$ was the equivalent diameter of a sphere producing the same light scattering pattern as the particle. Then, $D_{3,2}$ and $D_{4,3}$ were referred to as equivalent spherical diameters. These values were determined in order to quantify the difference in size of the two particle size classes. The same approximation has been done in other studies on composite gels, where particle size distribution and mean size of nonspherical particles like mastic gum (Mavrakis and Kiosseoglou 2008) and starch granules (Savary et al. 2008) were determined by ILS.

Preparation of the Hot Dispersions/Composite Gels

The required amounts of high methoxyl (HM) pectin, citrate buffer, apple particles and glucose syrup were weighed before mixing to achieve the desired final concentrations in the dispersion, namely: 0.5 wt% pectin, 65 wt% glucose and 0, 1 or 2 wt% particles. Pectin powder was dispersed in a beaker
with the buffer solution and stirred for 2 h at room temperature to allow the pectin to hydrate. Apple particles were added to this pectin-buffer dispersion during the last half hour of agitation. Glucose syrup was poured into a separate beaker, which, in turn, was put into a larger beaker with glycerin, and heated on a heating plate. Just before reaching the boiling point of the glucose, the beaker was removed from the bath and replaced by the beaker with the pectin-particles-buffer dispersion. The glucose syrup was immediately poured into this dispersion and stirred thoroughly to homogenize the mixture under heating. When the final dispersion reached the boiling point, the bath beaker (with the sample beaker still inside) was removed from the heating plate and immersed in an ultrasound bath to remove the bubbles from the dispersion. The foam formed on the surface was removed with a spatula. Subsequent cooling down of this hot dispersion induced gel formation, leading to the composite gel. Then, the purpose of leaving the dispersion into the hot glycerin bath during sonication was to avoid premature cooling and gelation.

Four different samples were prepared in this way, depending on the size and concentration of the dispersed apple particles, namely: 0 wt% particles (control), 1 wt% small particles, 2 wt% small particles and 1 wt% large particles. From now on, these samples will be referred to as 0%, 1%S, 2%S, and 1%L, respectively, where S and L stand for small and large, respectively. Each sample was prepared at least in quadruplicate.

Optical Microscopy

Two drops of each hot dispersion were placed in both hollow slides, and cooled down at room temperature until gelation. Optical microscopy images of the composite gels were obtained with a Nikon Eclipse E600 light microscope (Nikon Inc., Tokyo, Japan). Each composite gel was analyzed by duplicate, using a fresh sample each time.

Rheological Measurements

Rheological properties of the composite gels were determined by small deformation dynamic oscillatory measurements in an AR-G2 rheometer (TA Instruments, New Castle, DE), using a geometry of parallel plates (40 mm diameter, 1 mm gap). An aliquot of each hot dispersion was poured on the rheometer’s lower plate, previously conditioned at 90C. The upper plate was lowered and the surface of the sample was covered with silicon oil to avoid dehydration. Each measurement consisted of three successive steps, performed at an amplitude strain of 0.5%, namely: (1) a temperature ramp from 90 to 20C, at a cooling rate of 3C/min and a frequency of 1 Hz; (2) a time sweep of 10,800 s, at 20C and a frequency of 1 Hz; and (3) a frequency sweep from 0.01 to 10 Hz, at 20C. Immediately after each measurement, a strain amplitude
sweep (from 0.01 to 10%, at 20°C and 1 Hz) was performed to verify that the measurement was within the linear viscoelastic range (LVR). Each dispersion was measured at least in triplicate, using a fresh sample each time.

Measurement of Mechanical Properties

One of the most used large deformation tests in food gels is the uniaxial compression test (Brownsey et al. 1987; Kim et al. 2001; Manski et al. 2007; Wongsasulak et al. 2007; Mavrakis and Kiosseoglou 2008). However, this test was not appropriate for the composite gels analyzed in this work because they were not self-standing. Instead, a penetration test designed for marmalades (Anon 2000) was applied to the composite gels, using a TA-XTPlus texture analyzer (Stable Micro Systems, Surrey, U.K.) equipped with a 5 kg load cell. Each hot dispersion was poured into two cylindrical containers (42 mm inside diameter, approximately 40 mm sample height), cooled down at room temperature until gelation, covered with a screw tap and stored during approximately 20 h at 4°C for gel curing. After conditioning at room temperature, the sample container was placed centrally under the penetration probe (a 20 mm diameter cylinder), and the test was started. After a trigger force of 10 g was attained, the probe penetrated into the gel to a depth of 20 mm at a speed of 2.0 mm/s and, finally, the probe was withdrawn from the sample. Each composite gel was measured at least four times, using two containers of fresh sample each time.

Statistical Analysis

Experimental data were statistically processed by analysis of variance (ANOVA), and significant differences between means of the different samples were determined by the least significant difference (LSD) test ($P = 0.05$). The ANOVA and LSD tests were carried out using both Excel implementations developed by the Department of Mathematics of Universidad Nacional del Sur, Argentina.

RESULTS AND DISCUSSION

Size distributions (volume basis) of the apple particles of both size classes (small and large) are shown in Fig. 1. Both samples showed a monomodal distribution, with a small shoulder in the distribution of the large particles. According to these results, 54.5% v/v of the small particles was in fact bigger than 120 μm (approximately the size of the small sieve). The explanation on how these particles went through the sieve might be found in Fig. 2B, which shows a micrograph of sample 1%S. It can be observed that apple particles
were highly irregular in shape, and a high proportion of them were elongated. These rod or fiber shaped particles were able to go through the sieve because their shortest side was smaller than 125 \( \mu m \). However, their longest side was sometimes bigger than this, and, consequently, their equivalent volume diameter could be bigger than 125 \( \mu m \). Even a small number of these big particles would represent a high proportion in volume.

On the other hand, no particles bigger than 830 \( \mu m \) were found in the size distribution of the large particles (Fig. 1). However, these results indicate that 23.2\% v/v of these particles were smaller than 120 \( \mu m \). Figure 2D shows a micrograph of sample 1\% L. Indeed, particles smaller than this size range were observed in this and other micrographs of the same sample (not shown). One possible explanation for the presence of these small particles is that they came from aggregates bigger than 125 \( \mu m \) in the powder, which were dispersed by stirring during hydration, and/or by sonication during sample preparation and size measurement.
Volume/surface ($D_{3,2}$) and weight ($D_{4,3}$) equivalent spherical diameters were found to be $71.9 \pm 0.6$ and $145.6 \pm 1.3 \mu m$ for the small particles, and $114.2 \pm 0.8$ and $214.3 \pm 2.8 \mu m$ for the large particles, respectively. Although both characteristic diameters of the large particles were significantly higher ($P < 0.01$) than those of the small particles, the differences were less than expected because of the deviations explained earlier. Furthermore, particle size distributions showed a wide overlap of particle sizes (about 10–500 μm), with important volume percentages of particles with sizes around 150–200 μm (Fig. 1).

It should be noted at this point that the composite gels prepared in this work had both visual aspect and texture to the touch similar to a commercial fruit jam, as determined by visual and tactile inspection. It can be observed in micrographs at 2.5× magnification (Fig. 2A,C) that apple particles were uniformly distributed throughout the composite gels.

Considering the geometry used (parallel plates, 1 mm gap), rheological measurements were performed only on the composite gels with small particles. The elastic and viscous moduli, $G'$ and $G''$, were calculated from the

**FIG. 2. OPTICAL MICROPHOTOGRAPHS OF SAMPLE 1%S AT 2.5× (A) AND 5× (B) MAGNIFICATION, AND SAMPLE 1%L AT 2.5× (C) AND 5× (D) MAGNIFICATION**
measurements and used to characterize the rheological behavior of the composite gels. Results from the strain sweep tests (not shown) showed that the LVR of all samples were approximately between 0.02% and 1% strain, confirming that all measurements (performed at 0.5% strain) were within the LVR. Values of $G'$ were considered as an indicator of gel rigidity and used to statistically compare the different composites.

Gelation (sol–gel transition) of HM pectin solutions occurs by formation of junction zones between juxtaposed pectin chains. These junction zones are stabilized by hydrogen bonds and hydrophobic interactions between the ester methyl groups (Lopez da Silva et al. 1995; Rao 2007). Hydrogen bonds are favored at low pH due to suppression of electrostatic repulsion between pectin chains, and hydrophobic interactions are promoted by reduced water activity due to the presence of co-solute (Löfgren et al. 2005). Gelation occurs spontaneously during cooling from the solution-state at high temperature (Evageliou et al. 2000). Figure 3 shows the evolution of $G'$ and $G''$ of the HM pectin/apple particle dispersions during cooling from 90 to 20°C. In general, all samples experienced an approximately 1 fold increase in $G''$, and an approximately one to twofold increase in $G'$. The increase of $G'$ and $G''$ was a result of the increasing formation and density of junction zones into the pectin network (Rao 2007). It can be observed that gelation was a smooth process, with neither a $G'$–$G''$ crossover nor an onset temperature for gel formation. A similar behavior was reported for gelation of 0.5 wt% HM pectin with 65 wt% glucose at pH 3.0 (Evageliou et al. 2000).

Values of $G'$ of the different samples at the beginning and at the end of the temperature ramp are listed in Table 1. There were no significant differences between the values of $G'$ at the beginning of the cooling process ($G'$ at 90°C). This is reasonable because at this point the hot dispersions were in liquid state. During cooling, $G'$ increased more steeply for samples with particles (Fig. 3). This might indicate that particles had a favorable effect on the mechanism of gelation. Values of $G'$ at the end of cooling ($G'$ at 20°C) were significantly different, and increased with increasing concentration of particles (Table 1).

A common feature found in many biopolymer gelation processes, including HM pectin gels, is the nonequilibrium behavior even after aging for long periods. Typically, $G'$ continues to increase steadily as a result of a continuous reorganization of the network, involving the creation of new junction zones, or an increase in their extension (Rao 2007). The gel cure experiment is a typical test to determine the rate of structure development in physical gels. It is a time sweep in which $G'$ and $G''$ are measured under isothermal conditions (cure curves). Figure 4 shows the evolution of $G'$ and $G''$ during aging of the HM pectin/apple particle composite gels at 20°C for 3 h. In general, both $G'$ and $G''$ decreased rapidly at the beginning, and leveled off thereafter. This is not in agreement with previous observations (Lopez da Silva et al. 1995; Löfgren
FIG. 3. EVOLUTION OF $G'$ (FILLED SYMBOLS) AND $G''$ (OPEN SYMBOLS) OF SAMPLES 0% (CIRCLES), 1% S (TRIANGLES) AND 2% S (SQUARES), DURING COOLING FROM 90 TO 20°C

TABLE 1.
VALUES OF ELASTIC MUDULUS AT THE BEGINING OF THE TEMPERATURE RAMP ($G'$ AT 90°C), END OF TEMPERATURE RAMP AND BEGINING OF THE TIME SWEEP ($G'$ AT 20°C), END OF THE TIME SWEEP ($G'$ AT 3 h), AND BEGINING AND END OF THE FREQUENCY SWEEP ($G'$ AT 0.01 Hz AND $G'$ AT 10 Hz). LAST COLUMN INDICATES THE SIGNIFICANCE LEVEL OF THE ANOVA TEST

<table>
<thead>
<tr>
<th></th>
<th>0%</th>
<th>1% S</th>
<th>2% S</th>
<th>$P$ value</th>
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<tbody>
<tr>
<td>$G'$ at 90°C [Pa]</td>
<td>$83 \pm 58^a$</td>
<td>$32 \pm 12^a$</td>
<td>$70 \pm 40^a$</td>
<td>0.3594</td>
</tr>
<tr>
<td>$G'$ at 20°C [Pa]</td>
<td>$606 \pm 103^a$</td>
<td>$1,508 \pm 428^b$</td>
<td>$2,519 \pm 323^c$</td>
<td>0.0009</td>
</tr>
<tr>
<td>$G'$ at 3 h [Pa]</td>
<td>$483 \pm 59^a$</td>
<td>$1,195 \pm 393^b$</td>
<td>$2,160 \pm 184^c$</td>
<td>0.0006</td>
</tr>
<tr>
<td>$G'$ at 0.01 Hz [Pa]</td>
<td>$343 \pm 46^a$</td>
<td>$774 \pm 277^b$</td>
<td>$1,328 \pm 147^c$</td>
<td>0.0018</td>
</tr>
<tr>
<td>$G'$ at 10 Hz [Pa]</td>
<td>$706 \pm 75^a$</td>
<td>$1,780 \pm 516^b$</td>
<td>$3,282 \pm 240^c$</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Different letters (a–c) in a row indicate significant difference between the mean values ($P < 0.05$).

ANOVA, analysis of variance.
et al. 2005; Rao 2007). The reason might lie in the fact that the pectin used in this work was a rapid set pectin. Consequently, it seems that development and reorganization of the gel network was completed early during the gelation process (Fig. 3). Subsequent decrease of viscoelastic properties (Fig. 4) was attributed to relaxation of stresses developed during gel formation. Values of $G'/H_1$ at the end of the cure curves ($G'/H_1$ at 3 h) were listed in Table 1. These values were significantly different, and increased at increasing particle concentrations.

Gels can be classified into two type of systems: (1) those that are free-standing as a consequence of the development of a three-dimensional network, called true gels; and (2) those characterized by a tenuous gel-like network which is easily broken when submitted to a high enough stress, called weak gels. The difference can be easily established using mechanical spectra (Rao 2007), i.e., applying a frequency sweep and measuring $G'$ and $G''$. Figure 5
shows the mechanical spectra of the HM pectin/apple particle composite gels. All the samples showed a typical behavior of weak gels, which compared with true gels have a higher dependency on the frequency for the dynamic moduli, suggesting the existence of relaxation processes occurring even at short time scales, and lower difference between moduli values, indicating that a lower percentage of the stored energy is recovered (Rao 2007). The presence of particles did not change the shape of the curves, but shifted them up. Values of $G'$ at the beginning and at the end of the frequency sweep, $G'$ at 0.01 Hz and $G'$ at 10 Hz, for the different samples were listed in Table 1. These values were significantly different, and increased with increasing concentration of particles in the composite gels.

Overall, results indicate that increased concentrations of particles produced an increase of the rigidity of HM pectin/apple particles composite gels. This behavior might be attributed to one of two effects, or a combination of
them. The first one is based on the fact that particles replaced water in the final composition of the composite gels. Then, increasing amount of particles produced a decrease of water activity. This could have favored hydrophobic interactions between pectin chains, increasing the strength of the gel network. The second effect might be explained by the rheological behavior of filler–matrix composite gels. It has been found that the viscoelastic properties of such composite gels depend mainly on the rigidity of the matrix, the rigidity and volume fraction of the filler, and the interaction or affinity between the filler and the matrix (Rao 2007). It has been found that when the rigidity of the filler is higher than that of the matrix, and there is good adhesion or bonding between the filler and the matrix, increasing volume fractions of the filler produce a reinforcing effect on the gel (Brownsey et al. 1987; van Vliet 1988; Kim et al. 2001; Manski et al. 2007). Thus, the reinforcing effect of particles on the composite gels observed in this work might be explained by considering that apple particles were stiffer than the pectin gel, and that there was good adhesion between the particles and the gel network.

Figure 6 shows the force–time curves resulting from the penetration test performed on all the samples. During penetration, the force drops at the point where the gel breaks (Anon 2000). After this, the resulting force is due to continuing penetration up to the required depth. The maximum force, $F_{\text{max}}$ (i.e., the rupture point of the gel), is taken as the “rupture strength” (or “rupture force”). The distance that the probe penetrates before this break occurs, $d^*$ (i.e., the “distance at break”) gives an indication of the gel “brittleness,” i.e., the shorter this distance, the more brittle is the gel. When the probe withdraws from the sample, the total force to do this (area under the negative region of the curve) is recorded as the “adhesiveness,” $A$. An index of the “gel strength” is taken as the force, $F_e$, at a point in the initial stage of penetration, where little deformation has occurred (in this case 3 mm). These characteristic parameters obtained from the force–time curves were listed in Table 2. It must be noted that the force–time results obtained from this test (Fig. 6) depend on the size and shape of both the probe and the sample container. However, they normally show very good reproducibility (Anon 2000), and were considered to be useful for comparison between the samples used in this work. In order to qualitatively compare the trends obtained in this work with previous results on large deformation tests on composite gels, some analogies shall be proposed between the parameters obtained with the penetration test, and the ones obtained from uniaxial compression and tensile test, namely: $F_{\text{max}}$ – yield (or fracture) stress, $d^*$ – yield (or fracture) strain and $F_e$ – Young’s elasticity modulus.

It can be observed (Fig. 6) that the mechanical behavior (shape of the force–time curve) of sample 0% was remarkably different than the other samples. The rupture point of this gel (peak force) occurred at a low break distance, and afterwards the force continued to increase steadily until the probe
was removed from the sample. The composite gels with particles showed a smooth force peak at a significantly higher and approximately fixed break distance, $d^*$ (Table 2), without force recovery. In other words, the presence of particles significantly decreased the brittleness of the gels, in a magnitude that

![Force-Time Curves](image)

**FIG. 6. FORCE–TIME CURVES OF SAMPLES 0% (CIRCLES), 1%S (TRIANGLES), 2%S (Squares) AND 1%L (RHOMBUSES), OBTAINED FROM LARGE DEFORMATION PENETRATION TESTS**

<table>
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<tr>
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<th>0%</th>
<th>1%S</th>
<th>2%S</th>
<th>1%L</th>
<th>$P$ value</th>
</tr>
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<tbody>
<tr>
<td>$F_e$ [N]</td>
<td>1.65 ± 0.12$^a$</td>
<td>1.11 ± 0.22$^b$</td>
<td>1.67 ± 0.07$^a$</td>
<td>0.80 ± 0.10$^c$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$F_{max}$ [N]</td>
<td>2.76 ± 0.38$^a$</td>
<td>1.85 ± 0.36$^b$</td>
<td>2.62 ± 0.23$^a$</td>
<td>1.42 ± 0.24$^b$</td>
<td>0.0001</td>
</tr>
<tr>
<td>$d^*$ [mm]</td>
<td>5.05 ± 0.11$^a$</td>
<td>14.55 ± 1.51$^b$</td>
<td>13.91 ± 1.55$^b$</td>
<td>15.52 ± 2.22$^b$</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>$A$ [N * s]</td>
<td>-2.09 ± 0.22$^a$</td>
<td>-1.13 ± 0.15$^b$</td>
<td>-1.92 ± 0.18$^a$</td>
<td>-0.92 ± 0.15$^b$</td>
<td>&lt;0.0001</td>
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Different letters (a–c) in a row indicate significant difference between the mean values ($P < 0.05$).
was independent of particle size and concentration. This behavior has not been reported in previous studies: Kim et al. (2001) found no significant effect of the volume fraction of emulsion droplets and of droplet size on the fracture strain of soybean protein gels; Manski et al. (2007) found a decrease of the yield strain of sodium caseinate composites at increasing volume fractions of glass spheres (no significant effect of size), but no significant change of the yield strain when the filler were fat droplets; Mavrakis and Kiosseoglou (2008) reported a decrease of the fracture strain of various biopolymer composites in the presence of 6% mastic gum particles. In general, it seems that rigid particles decreased the yield or fracture strain, while deformable particles had no nonsignificant effect. However, Brownsey et al. (1987) showed that increasing binding between filler and matrix delayed the failure of the composites to higher strain values. This may be the only way to explain the fact that apple particles increased $d^*$ values of HM pectin gels.

The presence of 1 wt% of the small particles produced a significant decrease in the rupture strength, $F_{\text{max}}$, of the HM pectin gel, while 1 wt% of the large particles produced a further, but not significant decrease compared with the smaller particles (Table 2). Increasing the concentration of small particles to 2 wt% produced an increase of $F_{\text{max}}$ to values similar than those of the control sample. In other words, particle concentration had a significant effect on $F_{\text{max}}$ of the gels at 1 wt% (independent of particle size), but no significant effect at 2 wt%. Most of the studies on food composite gels reported an increase in the yield or fracture stress at increasing concentrations of filler, like Sephadex beads (Brownsey et al. 1987), oil droplets (Kim et al. 2001), cassava starch granules (Wongsasulak et al. 2007), glass spheres and palm fat droplets (Manski et al. 2007). However, Mavrakis and Kiosseoglou (2008) found that the effect of 6% mastic gum particles on the fracture stress of composites depended on the type of biopolymer conforming the matrix: it had a reinforcing effect on egg white gels, no significant effect on gelatin gels and a negative effect on polysaccharide (carrageenan and agar) gels, which was attributed to a complete lack of particle surface-network structure interaction. The importance of the filler–matrix interaction on the gel resistance against large deformations has been claimed by other authors (Brownsey et al. 1987; Kim et al. 2001; Manski et al. 2007). Other researchers (Kim et al. 2001; Manski et al. 2007; Mavrakis and Kiosseoglou 2008) showed that this effect of filler–matrix interaction, either positive or negative, increases with decreasing particle size, due to the higher specific surface area of the particles. Considering that previous results of the present work suggest a good affinity between apple particles and HM pectin gel, it is not clear why $F_{\text{max}}$ values of the composite gels with 1 wt% particles are lower than that of the gel without particles. One possible explanation is that the large deformation test used in this work actually might not be reliable for filler–matrix systems, and then neither for marmalades.
Gel strength, $F_e$, showed the same trend as $F_{\text{max}}$, with the only distinction that the difference between the values of samples 1% S and 1% L was significant (Table 2). Wongasulak et al. (2007) and Mavrakis and Kiosseoglou (2008) also reported the same trend of Young’s elasticity modulus compared with the fracture stress. Therefore, the previous discussion about the effect of filler on $F_{\text{max}}$ also seems to apply for $F_e$. It should be stated that $F_e$ was obtained at a point of the penetration test where the gel had only suffered a small deformation, supposedly still in the region of elastic response of the material. In this case, $F_e$ is expected to follow the same trend as $G'$, obtained from rheological measurements. Comparing the values of $F_e$ for samples 1%S and 2% S (Table 2), and for example $G'$ at 3 h (Table 1), it is evident that they did not follow the same tendency at increasing particle concentrations. One possible explanation is that at the point where $F_e$ was measured (3 mm depth), the deformation of the composite gels was no longer in the elastic region. This is supported by the fact that the portion of the curve before the point $F_e$ was not completely linear, as expected from the elastic region. It has been claimed (Brownsey et al. 1987; van Vliet 1988) that gel strength obtained under conditions of large deformation, may deviate from gel moduli obtained at small deformations, due to slip at the matrix-filler interface, and/or to uneven distribution of stress and strain throughout the material.

Adhesiveness ($A$) is defined as the work necessary to overcome the attractive forces between the product and a specific surface (Raikos et al. 2007), in this case a metallic probe, and is related to the breaking of cohesive bonds (Bonacucina et al. 2006). The presence of 1 wt% of the small particles produced a significant decrease in $A$ of the HM pectin gel, while 1 wt% of the large particles produced a further, but not significant decrease, compared with the smaller particles (Table 2). Increasing the concentration of the small particles to 2 wt% produced an increase of $A$ to values similar than those of the control sample. In other words, particle concentration had a significant effect on $A$ of the gels at 1 wt% (independent of particle size), but no significant effect at 2 wt%. Values of $A$ obtained in previous studies (Jones et al. 1997; Chang et al. 2009) using a similar penetration test, increased at increasing solids content of the gels. However, it is not clear why $A$ values of the composite gels with 1 wt% particles are lower than that of the gel without particles. Unreliability of the large deformation test, as suggested for $F_{\text{max}}$, might apply here as well to explain the apparently anomalous trend of $A$ values.

In general, increasing the concentration of small particles from 0 to 1 %wt produced a decrease in the magnitude of the mechanical properties (except $d^*$) of the composite gels, while increasing that concentration from 1 to 2 %wt produced an increase of those values (Table 2). On the other hand, increasing the particle size did not have a significant effect on the mechanical
properties (except $F_c$) of the composite gels (Table 2), at least within the size range studied in this work. One possible explanation is the wide overlap observed in the particle size distributions of both particle size classes (Fig. 1), resulting in similar mechanical properties of the corresponding composite gels. Nevertheless, other authors have claimed that the effect of particle size on mechanical properties of composite gels is minor (Manski et al. 2007), particularly when there is no filler-matrix interaction (Mavrakis and Kiosseoglou 2008). Overall, results showed that particle concentration had a more significant effect than particle size, on the mechanical behavior of HM pectin composite gels.

CONCLUSIONS

Assuming that fruit jams can be appropriately modeled as HM pectin/fruit particles composite gels, results obtained from rheological measurements indicate that increasing concentrations of microsized fruit pulp would have a reinforcing effect on the rigidity of fruit jams. Results obtained with the penetration test for marmalades showed some discrepancies compared with the results obtained with other large deformation tests in filler–matrix composite gels, and compared with the small deformation (rheological) measurements of this work. Nevertheless, it seems that the presence of microsized fruit pulp would have a significant effect on the mechanical behavior of fruit jams, and that increasing particle size would have a negative effect on their gel strength and adhesiveness, although nonsignificant in the size range studied here. Further work is required to extend particle size and concentration ranges to higher levels, and to explore other type of large deformation tests suitable for nonself-standing, filler/matrix composite gels.

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