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IMPACT OF BIOPOLYMERS ADDED TO A GRAPEFRUIT PUREE AND FREEZE-DRYING SHELF TEMPERATURE ON PROCESS TIME REDUCTION AND PRODUCT QUALITY

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Abstract

Freeze-drying provides high quality foods, despite the long time involved in the operation. Shortening the process time by increasing the heat supplied for sublimation to occur could affect the product quality. In this study, the impact of adding gum Arabic and bamboo fiber to a grapefruit puree and of raising the shelf temperature to 40 ºC during freeze-drying has been considered. The increase in temperature allows a 57.5% time reduction and promotes a porosity increase without any impact on the cake's color and vitamin C content. The addition of biopolymers does not affect the drying kinetics allow a crunchier and firmer cake to be obtained, despite the color changes and the fact that vitamin C becomes less available. In conclusion, raising the shelf temperature to 40°C significantly reduces the freeze drying time without noticeably impairing the product, and the addition of biopolymers improves the product characteristics without adversely impacting upon drying times.

Keywords: gum Arabic; bamboo fiber; porosity; mechanical properties; color, vitamin C.

1. Introduction

The growing consumer demand to expand the diversity of food products has led to a rapid development of the dehydrated food market. As most of these food products form part of the daily diet, the technologies involved in their production are growing in importance. This is because the quality and functionality of the processed products strictly depend on the efficiency of the production processes (Karam et al., 2016; Michalska et al., 2016).

The quality of a dehydrated product depends to a large extent on the drying conditions, as well as on the composition and physical properties (Hua et al., 2010; Karam et al., 2016). Within this context, freeze-drying emerges as a gentle dehydration technique that represents the ideal process for the production of high value dry products. This technique is known for its ability to maintain the quality of the product (color, shape, aroma and nutritional value) greater than many other drying methods, because of both its low processing temperature and the virtual absence of oxygen during the operation, which minimizes degradation reactions (Hammami and René, 1997). Other prominent factors include the structural rigidity exhibited by the previously frozen food, as well as the limited mobility of the frozen water, which prevents the collapse and contraction of the solid matrix when drying (Kasper and Friess, 2011; Nireesha et al., 2013). This opens the opportunity to take advantage of freeze-drying to obtain products with a crunchy and porous structure. From this point of view, the freeze-dried cake obtained from a fruit puree could be offered to the consumer as a healthy snack type product, avoiding, for example, steps such as frying. The negative part of freeze-drying is the use of low pressures and the long duration of the process, which makes the technique more expensive. However, a study that compares the industrial cost of using freeze-drying rather than spray-drying to obtain powdered fruit concludes that the cost of the latter can

be up to 2.5 times higher than that of freeze-drying because of its low product yield (Camacho et al., 2018). In this sense, it seems interesting to optimize the freeze-drying conditions so that the process time can be shortened while maintaining the quality of the obtained product. Increasing the temperature of the process can be an alternative in this regard.

The drying step in the freeze-drying process is governed by two transport mechanisms: (i) the transport of energy to transform the ice into water vapor (between -21 ºC and -30 ºC, approximately 2805 kJ/kg); and (ii) the transport of water vapor from the sublimation surface of the product being dried to the condensation system through the drying chamber (Hammami and René, 1997; Karam et al., 2016; Kasper and Friess, 2011; Nireesha et al., 2013; Oetjen and Haseley, 2003). The energy needed for sublimation can be supplied in four different ways: a) the radiation of heated surfaces, b) the conduction from heated plates or gases, c) the convection gas and d) the dielectric losses of ice in high frequency fields. After the ice has been sublimated (primary drying), the remaining adsorbed water is desorbed from the solid (secondary drying). This process is governed by laws other than those regulating primary drying. During secondary drying, energy transport does not play an important role, as the amount of remaining water usually represents less than 10% of the solids. However, secondary drying over time can be an important part of the total process and take half or the same length of time as the primary drying (Oetjen and Haseley, 2003).

As regards the stability of dehydrated products, important changes in their diffusional and physical properties will occur above the glass transition temperature (T_g) of its amorphous matrix. In this sense, the increase in molecular mobility when the temperature of the product is higher than the T_g may result in a loss of the porous structure developed while drying. When looking for a crunchy type product, this would eventually result in a

rejection of the product. From this point of view, on the one hand raising the temperature of the product during primary drying should be controlled in order to not exceed the T_g. On the other hand, the Tg of the product increases as the water content is lowered and higher molecular weight solutes are added. In this sense, it is necessary to point out the low T_g exhibited by the dried fruit products due to their large amount of both low molecular weight carbohydrates, such as sucrose, fructose and glucose, and organic acids (Telis and Martínez-Navarrete, 2010; Fongin et al., 2017). For this reason, the addition of high molecular weight biopolymers trying to rise the T_g is recommended for the purposes of preventing collapse phenomena (Telis and Martínez-Navarrete, 2010).

The aim of this study was to determine the impact of both adding high molecular weight gum Arabic and bamboo fiber and increasing the shelf temperature to 40 ºC during the freeze-drying of a grapefruit puree in order to obtain a cake that could be offered as a crunchy snack-type product. The effect on the drying kinetics, volumetric and surface porosity, color, mechanical properties and vitamin C content of the obtained cake has been studied.

2. Materials and methods

2.1. Sample preparation

The citrus grapefruit (*Citrus paradisi*) of the pigmented variety Star Ruby was purchased in a local market (Valencia, Spain). The fruits were selected according to their size, firmness and absence of physical damage. Complex carbohydrates of high molecular weight, that henceforth we will refer as biopolymers, were used to stabilize the powdered product: Gum Arabic (GA, Scharlab, Spain) and Bamboo Fiber (BF, Vitacel® BAF 200, Spain).

The peel, albedo and central axis were detached manually from the grapefruit before being crushed (Thermomix Vorwerk TM-21, Spain, working at speed 4 for 40 s, followed by speed 9 for 40 s) as to ensure an homogeneous batch to carry out all the experiments. Two samples of grapefruit puree were prepared: one without the addition of biopolymers (G) and another one with the addition of 4.2 g GA and 0.58 g BF /100g puree (GB) (Thermomix Vorwerk TM-21, Spain, working at speed 2 for 300 s) (Agudelo et al., 2017). Both samples were characterized as to the water (vacuum oven JP Selecta, 60 ± 1ºC and pressure <100 mm Hg) and soluble solid (Mettler Toledo 30PX refractometer, Spain) content. Samples G and GB were placed in aluminum trays of 5.8 cm in diameter, 1 cm thickness (≅27 g) and after they were frozen (Liebherr LGT 2325, Germany) at -45 ºC for 6h.

2.2. Process conditions and freeze-drying kinetics

The frozen samples were freeze-dried for different times, from 1.5 to 21 h, in a Telstar Lyo Quest-55 (Spain) freeze-dryer provided with a standard cylindrical acrylic chamber (∅ 215x300mm) with three heated shelves. The samples were placed only on the central shelf. Two different conditions were used: the pressure of the chamber (0.09 mbar) was maintained in both of them and the temperature of the shelves was varied: without applying any heat to the shelves (samples RT, room temperature) or controlling to40 °C (samples 40). In this way, four samples were processed: G(RT), G(40), GB(RT) and GB (40). For each sample, four replicates of the freeze-drying (FD) process were carried out at each time. Samples obtained at the different FD times were weighed, with an accuracy of 0.0001 g (Mettler Toledo XS204, Spain). No mean values were considered for any sample, but each of the 4 pieces of data obtained at each FD time were considered together for the drying kinetics study.

The drying kinetics was studied on the basis of the sample mass loss. The residual water content present in the obtained samples was calculated based on Eq. (1) and used to obtain the moisture ratio (MR) evolution (Eq. 2).

$$X_{wt} = \frac{m_o * X_w^o - (m_o - m_t)}{m_o * (1 - X_w^0)} \qquad (1)$$

where X_{wt} is the water content of the freeze-dried sample at each process time (g water / g freeze-dried sample, db); m_o and X_w^o are the mass (g) and the water content (g water / g sample, see section 2.1) of the sample that enters the freeze-dryer, respectively; m_t is the mass of the freeze-dried sample (g).

$$MR = \frac{X_{wt} - X_{we}}{X_{wo} - X_{we}} \approx \frac{X_{wt}}{X_{wo}} \qquad (2)$$

Where X_{wt}, X_{wo} and X_{we} indicate the water content (g water / g sample, db) at time t, time 0, and at equilibrium, respectively. The equilibrium water content values are usually very low, and Eq. (2) is often simplified, assuming X_{we}= 0 without a significant change in the MR value (Azzouz et al., 2002; Calín-Sánchez et al., 2014; Simal et al., 2005; Simpson et al., 2017).

Trying to find an empirical equation that adequately reproduced our experimental data the Page model (Eq. 3) was selected. This model has been previously reported for slices of orange, black aronia (*Aronia melanocarpa*) or whole plums (Michalska et al., 2016; Calín-Sánchez et al., 2014). The MATLAB R2015b software was used to fit the drying model. For each sample, the 4 MR values (Eq. 2) obtained at each FD time were fitted to the model.

$$MR = a * e^{-k*t^n} \quad (3)$$

Where k, n and a are the parameters of the model and t the freeze-drying time (h).

2.3. Quality of the freeze-dried samples

Taking into account the kinetic results, the time needed to obtain freeze-dried samples with 2 g water/100 g sample (db) was calculated. Each of the four studied samples was prepared as described in section 2.1 and freeze-dried in duplicate as described in section 2.2 just for the corresponding calculated time. The obtained samples were weighed, with an accuracy of 0.0001 g, and their water content was analyzed as described in Section 2.2.(Eq. 1). Immediately afterwards, two images per sample were taken using a Canon EOS 350D (Spain) digital camera with a focal aperture of 55 mm (Lens EFS 18-55) and in automatic mode. The camera was placed in a Kaiser RS2XA support (Germany), at 23 cm from the sample, and illuminated with a standard white light (6500K). As described below, the images were submitted to posterior image analysis so as to characterize the superficial porosity by means of the pore number and size distribution. The volumetric porosity, color, mechanical properties and vitamin C content of the cakes were also characterized.

2.3.1. Volumetric porosity

The porosity (ε) of the samples was estimated from both the apparent (ρ_{app}) and the real (ρ) density by using Eq. (4-6) (Datta, 2007). To determine the apparent density (Eq. 5), a 12 mm radius (r) cylindrical punch was used to obtain, in triplicate, a piece of each sample, whose height (H) was also measured in triplicate with a Vernier caliper CM (0.02

mm; 1/1000") and weighed (W) using an analytical balance (Mettler Toledo XS204, Spain).The real density of each sample was estimated from the mass fraction and density at 20 ºC of water (X_w, w/w; ρ_w=0.9976 g/cm^3) and carbohydrates (X_{CH}, w/w; ρ_{CH} 1.4246 g/cm^3) (Eq. 6, Choi and Okos, 1986).

$$\varepsilon = 1 - \frac{\rho_{app}}{\rho} \qquad (4)$$

$$\rho_{app} = \frac{W}{\Pi * r^2 * H} \qquad (5)$$

$$\frac{1}{\rho} = \frac{X_w}{\rho_w} + \frac{X_{CH}}{\rho_{CH}} \qquad (6)$$

2.3.2 Superficial porosity. Number and pore size distribution

The pore size distribution was based on the area of the superficial pores formed in the samples. This area was analyzed from the images taken as described earlier. Images were analyzed by means of the software image J, 1.51, which uses the contrast between the two phases (pore and solid part) in the image (Broeke et al., 2015; Russ, 2005; Sahin and Gülüm, 2006). The calibration used was 1 mm = 53.5 pixel. The color image was transformed into a gray scale (8bit) (Fig. 1.a) in order to then apply a thresholding process (Fig. 1.b), which allowed the measurement of the area of the pores formed. The frequency or number of pores formed of each size was established based on a geometric distribution of the areas containing the minimum and the maximum values found from the image analysis and considering 30 area intervals. From this data, the mean area of the pores was also calculated (Eq. 7).

198 $$\overline{A} = \frac{\sum_i (A_i * F_i)}{\sum_i F_i} \quad (7)$$

199

200 Where $\overline{A}$ is the mean area (mm^2), A_i is the greatest area of the corresponding area
201 range (mm^2), F_i is the pore frequency at each area range.

202

203 *2.3.3. Color*

204 The color of the samples was measured in triplicate 15 min after leaving the
205 freeze-dryer using a MINOLTA CM 2600-D color spectrophotometer (Japan), coupled
206 with a measuring window of 8 mm in diameter, and placing a reflective glass over the
207 sample. The CIE L*a*b* coordinates were obtained using the D65 illuminant and the 10º
208 observer as reference. The hue angle (h_{ab}*), chroma (C_{ab}*) and total color difference
209 (ΔE*) were obtained (Eq. 8-10, Hutchings, 1999).

210

211 $$h_{ab}^{*} = arctan\frac{b^{*}}{a^{*}} \quad (8)$$

212

213 $$C_{ab}^{*} = \sqrt{a^{*2} + b^{*2}} \quad (9)$$

214

215 $$\Delta E^{*} = \sqrt{(\Delta L^{*})^2 + (\Delta a^{*})^2 + (\Delta b^{*})^2} \quad (10)$$

216

217 *2.3.4. Mechanical Properties*

218 Mechanical compression tests were performed at 20 ºC using a texture analyzer
219 TA-XT Plus (Stable Micro Systems, Ltd., United Kingdom), provided with a cylindrical
220 probe (P/1KD) of 10 mm diameter. The same pieces of each sample obtained for the
221 apparent density measurement were uniaxially compressed along the vertical axis to 80%

of their thickness at a test speed of 1 mm/s. The analysis of the force vs. distance curves was performed using the Exponent 6.1.11.0 software. Each sample was measured in triplicate. The force-distance curves were analyzed as to obtain the fracture, when available, and the deformability of the samples. Fracture point was provided by the texture analyzer software program which was fitted to a force threshold of 0.049 N. The deformability of the samples was obtained from the slope of the straight line at the beginning of the curve.

2.3.5. Vitamin C

Vitamin C (VC) was determined by high-performance liquid chromatography (HPLC) (Jasco, Italy). For the analysis, 0.075 g of powder was used. The procedure employed was the reduction of dehydroascorbic acid to ascorbic acid, using DL-dithiothreitol (Scharlab S.L, Spain) as the reductant reagent, and extraction with oxalic acid (Scharlab S.L, Spain) (Igual et al., 2014; Xu et al., 2008). The HPLC conditions were: KROMAPHASE100-C18, 5mm (4.6x250mm) column (Scharlab S.L, Spain); mobile phase 0.1 % oxalic acid, volume injection 20 μL, flow rate 1mL/min, detection at 243 nm (detector UV-visible MD-1510) and at 25 ºC. A standard solution of L(+) ascorbic acid (Scharlab S.L, Spain) solution was prepared. The vitamin C content was calculated as mg of ascorbic acid per 100 g of the grapefruit's own solutes (mg AA/100gGS, Agudelo et al., 2017).

3. Results and discussion

3.1. Drying kinetics

The water and soluble solute contents of the grapefruit puree used in the study were 87.6 ± 0.4 g water/100 g sample and 11.47 ± 0.12 ºBrix, respectively. They changed to

83.0 ± 0.1 g water/100 g sample and 15.23 ± 0.06 ºBrix after GA and BF addition. For each sample, this water content was considered the corresponding X_w^o (Eq. 1). The evolution of MR (Eq. 2) throughout the freeze-drying of the different processed samples is presented in Fig. 2. As can be observed, the drying time was greatly reduced when a shelf temperature of 40 ºC was applied, with no apparent effect of the incorporation of Bp on the drying rate. It was not the mean value that was used but rather each of the 4 replicates of the kinetic data for each sample and FD time which was fitted to the modified Page model (Eq. 3, Table 1). The high R^2 value obtained in each of the 4 samples, over 0.9803, allows the model to be used as to predict with some certainty the drying time needed to achieve a desired final water content in the product.

Table 1 shows the predicted drying time needed to achieve a target water content of 0.02 g water/g sample, assumed to be a normal water content for this kind of product. As no important differences were observed in the model parameters as a result of biopolymer addition, considering the standard deviation, a mean time value was taken into account to process the two samples freeze-dried with no shelf heating and another one for the two treated at 40 ºC on the shelf, this being 23.9 h and 10.15 h, respectively. It has been established that simply heating the shelves to 40 ºC during freeze-drying considerably shortens the process time by more than 50 %. New samples were processed at these times and characterized so as to analyze the product quality change due both to the presence of GA and BF and the heating of the shelves. The obtained results are discussed in the next section.

3.2. Quality of the target freeze-dried samples

The experimental water content of the freeze-dried samples was 0.030±0.001, 0.025±0.004, 0.013±0.002 and 0.018±0.007g water/g sample for G(RT), GB(RT), G(40), GB(40), respectively, these values being within the error limits of the considered model.

3.2.1. Porosity

The porosity of a freeze-dried product will be conditioned by the ice number and crystal sizes that occur during the freezing step. The porosity (Table 2) of the G(RT) and G(40) samples was greater than that shown by the corresponding GB(RT) and GB(40) samples, with added biopolymers. This could be related with the lowest water content of GB samples and to the cryoprotective effect of the biopolymers, decreasing the amount of ice formed (Telis and Martínez-Navarrete, 2010). Raising the shelf temperature also promotes an increase in porosity, which is counteracted by the biopolymer effect. This could be explained considering that at a lower temperature, sublimation would occur at a lower speed. This could mean a certain collapse of the structure that would render in a smaller pore size. The presence of GA and BF in this case seems to exert an effect on the degree of contraction of the sample during the freeze-drying process, enhancing the union between the fruit's own solutes and those added.

3.2.2 Superficial porosity. Number and pore size distribution

Fig. 3 shows the number of superficial pores in each area range considered. A similar pore number distribution was observed for each of the four samples. The total number of pores formed was similar in the samples without added biopolymers, G(RT) and G(40), with 415 and 419 pores, respectively. A lower number of superficial pores appeared in GB(RT) and GB(40) samples with 312 and 270, respectively. This coincides with the porosity results (Table 2) and could be related with the cryoprotective effect of the

biopolymers and the formation of a more structured matrix, as commented on previously. The freeze-drying temperature was not observed to have any clear effect on the number of pores formed.

The mean pore size was calculated for each sample (Fig. 4), together with the median and mode of the pore size distribution. Each of the three properties behaved similarly. As can be observed, the samples freeze-dried at 40 ºC exhibited a greater mean pore size than when processed at room temperature, especially when no biopolymers were added. In this sense, the G(40) sample was the one in which more and bigger pores were formed, which agrees with the greater porosity exhibited (Table 2).

3.2.3. Color

The color co-ordinates and attributes (Fig. 5) varied significantly ($p < 0.05$) as a consequence of the incorporation of biopolymers. The luminosity (L*) and the hue angle (h*) increased and the chroma (C*) decreased. The addition of biopolymers has led to similar behavior described by other authors (Raj et al., 2018; Lachowicz et al., 2018; González et al., 2018). Heating the samples to 40 °C during the FD process does not affect the color of the cake. To quantify the global color differences between freeze-dried samples, ΔE was calculated. When the color of the samples with and without biopolymers was compared without taking the temperature into account, the ΔE were found to lie between 8.71 and 9.87. Nevertheless, the ΔE was 0.66 or 1.24 for GB(RT)-GB(40) and G(RT)-G(40) samples, respectively. From these results, it may be observed that it is the biopolymers that exert the predominant effect on the color change of the sample during FD rather than the temperature. As has been mentioned, ΔE values of ≤ 3 are not perceived by the human eye (Bodart et al., 2008; Buvé et al., 2018).

3.2.4. Mechanical properties

Fig. 6 shows, as an example, the force-distance curves obtained from the compression test. Two different behaviors were observed for the samples with or without added biopolymers. Every sample with added biopolymers showed greater force values and multiple fracture peaks from the beginning of the test, while a mild increase in the compression force was observed in the samples without GA and BF. This behavior may be related with the T_g of the samples, greater when high molecular weight solutes are present (Roos, 1995). In this way, at the temperature at which the mechanical test was carried out, the G(RT) and G(40) samples may be expected to have a more rubbery state. It is known that the degree of fracture serves as a measurement of crunchiness (Hackl and Ermolina, 2016).

Every force-distance curve (Fig. 6) shows an initial force increase related to the deformability of the sample; the higher the slope, the lower the deformability. The sample's surface is deformed until a significant fracture (samples GB) or yield point (samples G) is observed. From this moment, the fracture of the internal part of the GB samples continues and no more force increase is observed until the fractured sample remaining under the probe is compressed, which leads to a sharp increase in the force. In the case of the G samples, the less fracturable behavior leads to an initial mild, continuous force increase until the compression under the probe is clearly observed at which point the force increases sharply.

The beginning of the curve, visually selected, was considered so as to evaluate the fracture force or yield point (Fx). When no fracture exists, the yield point was provided by the linear behavior change. To evaluate the deformability (d) of the sample, the slope of the straight line fitted from the origin to Fx was considered. Fig. 6 shows, as an example, the procedure used to analyze the Fx and d values. The obtained values appear

346 in Table 2. As can be observed, the added biopolymers result in less deformable and more
347 resistant to fracture samples ($p<0.05$), in line with what is expected in the glassy state.
348 Heating the samples during FD led to the obtained cake exhibiting a greater resistance to
349 fracture and the samples with added biopolymers ($p<0.05$) having a greater degree of
350 deformability. A correlation was observed between the mechanical properties and the
351 porosity of the samples (Table 2). Thus, the GB(RT) and GB(40) samples, which were
352 those with the lowest porosity, were also the crunchiest and the firmest. Bearing in mind
353 both this mechanical behavior and also the significantly shorter process time involved
354 when freeze-drying at 40 °C, it is recommended to add biopolymers and to heat the freeze-
355 dryer shelves for the purposes of obtaining a crunchy snack-type product.
356
357 *3.2.5 Vitamin C*
358 As to compare the content of vitamin C across all samples, avoiding the dilution
359 effect of adding the biopolymers, it was evaluated per unit mass of grapefruit solids in the
360 sample and not per total mass of solids (Table 2). The samples with added GA and BF
361 had a significant ($p <0.05$) lower vitamin C content. This may be due to the fact that
362 biopolymers help to create a network that exerts a retention-protection effect which
363 hinders the extraction of the vitamin (Agudelo et al., 2017). On the other hand, heating
364 the shelves to 40 ºC does not significantly affect ($p <0.05$) the vitamin C content of the
365 samples (Table 2). In other studies, carried out on apple or mango purees, it has also been
366 described how the vitamin C content is not affected in processes carried out at up to 80
367 ºC (Herbig et al., 2017; Xanthakis et al., 2018).
368
369 **4. Conclusions**

When the freeze-drying process is used to obtain a grapefruit snack-type product, heating the shelves just to 40 ºC during freeze-drying considerably shortens the process time (by 57.5 %), leaves the color and vitamin C content of the product unaffected and promotes samples with a greater mean pore size. Although the presence of GA and FB in the fruit puree does not affect the drying kinetics, they do change the color and interact with the grapefruit puree matrix. This interaction makes it more difficult to extract vitamin C and results in a less porous, crunchier and firmer structure of the freeze-dried cake. Raising the shelf temperature to 40 ºC counteracts the biopolymer effect. These conclusions allow us to recommend both incorporating GA and FB into the grapefruit puree and also heating the freeze-dryer shelves to 40 ºC in order to shorten the process time and obtain a firm, crunchy cake that could be consumed as a snack.

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FIGURE CAPTIONS

Figure 1. Example of gray-scale transformation (a) and thresholding (b) of an image belonging to a sample without added biopolymers and freeze-dried at room temperature for 9 h.

Figure 2. Mean experimental data and predicted (modified Page's model) moisture ratio (MR) evolution throughout freeze-drying. G(RT): grapefruit puree freeze-dried at room temperature; GB(RT): grapefruit puree with added biopolymers and freeze-dried at room temperature, G(40): grapefruit puree freeze-dried at 40 ºC on the shelf, and GB(40): grapefruit puree with added biopolymers and freeze-dried at 40 ºC on the shelf.

Figure 3. Number of pores (frequency) formed in each area range considered. G(RT): grapefruit puree freeze-dried at room temperature; GB(RT): grapefruit puree with added biopolymers and freeze-dried at room temperature, G(40): grapefruit puree freeze-dried at 40 ºC on the shelf, and GB(40): grapefruit puree with added biopolymers and freeze-dried at 40 ºC on the shelf.

Figure 4. Mean area of the pores formed. Median and mode of the pore size distribution. G(RT): grapefruit puree freeze-dried at room temperature. G(RT): grapefruit puree freeze-dried at room temperature; GB(RT): grapefruit puree with added biopolymers and freeze-dried at room temperature, G(40): grapefruit puree freeze-dried at 40 ºC on the shelf, and GB(40): grapefruit puree with added biopolymers and freeze-dried at 40 ºC on the shelf. Different (a-c) letters by property indicate non-homogeneous groups established by the ANOVA ($p<0.05$) using Fisher's test.

Figure 5. CIE L*a*b* color co-ordinates, chroma (C*) and hue angle (h*). G(RT): grapefruit puree freeze-dried at room temperature; GB(RT): grapefruit puree with added biopolymers and freeze-dried at room temperature, G(40): grapefruit puree freeze-dried at 40 ºC on the shelf, and GB(40): grapefruit puree with added biopolymers and freeze-dried at 40 ºC on the shelf. For each co-ordinate and attribute, different (a, b) letters indicate non-homogeneous groups of samples, established by the ANOVA ($p<0.05$) using Fisher's test.

542 Figure 6. Example of a compression force (N) vs. distance (mm) curve for one of the
543 samples obtained under the different process conditions: at room temperature (RT) and at
544 40 ºC on the shelf (40), without (G) and with (GB) the addition of polymers. The circle
545 drawn with the continuous line indicates the data considered to evaluate the fracture or
546 yield force (value indicated by the arrows) and the one with the dashed line represents the
547 data used for deformability analysis.

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