LWT - Food Science and Technology 127 (2020) 109415

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Use of different biopolymers as carriers for purposes of obtaining a freeze-dried orange snack

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ARTICLE INFO

Keywords:
Gum Arabic
Maltodextrin
Modified and native starch
Pea and bamboo fibre
Crunchiness

ABSTRACT

In addition to colour, one of the most important qualities of a snack-type product is its crunchy texture. A freeze-dried fruit snack is characterised by its low water content, which creates the problem of a loss of crunchiness related to its low glass transition temperature (Tg). In this sense, a common technique with which to increase the Tg of these types of products is to add different biopolymers. However, these compounds can, at the same time, affect the colour and texture of the product. In this study, different biopolymers have been tested in order to discover their similarities or differences in terms of hygroscopicity, antiplasticising character, colour and impact on the mechanical properties of a freeze-dried orange snack formulated from their different mixtures. Gum Arabic, maltodextrin, starch modified with octenylsuccinic anhydride, pea fibre, bamboo fibre and native corn starch have been selected as biopolymers. The impact of any of them on the studied properties can be confirmed, without any of them being more or less effective than the others.

1. Introduction

The consumption of fruit is part of a healthy diet and it is recommended as a way of improving our health and well-being (WHO, 2018). With the intention of promoting the consumption of fruit among the population, there is continuous interest in offering consumers new products that stimulate this consumption (Telis & Martínez-Navarrete, 2012). To this end, there exists the possibility of obtaining a snack from freeze-dried orange puree.

The final water content of the freeze-dried fruit will condition its characteristics, especially its optical and textural properties, and the expected shelf life under given conditions (Telis & Martínez-Navarrete, 2012). During the processing of typical snacks, a low water content is determinant for their characteristic brittleness, crispness or crunchiness. The plasticising effect of water on the mechanical properties of the food systems is well known (Roos, 1995). The primary mechanical effect of a plasticizer is that of weakening or breaking intermolecular bonds, thus decreasing its mechanical resistance and increasing its deformability, gumminess or sogginess (Pittia & Sacchetti, 2008). The impact of water content change on the mechanical behaviour of a food has been related to its physical state (Roos, 1995). Dehydrated fruits obtained by freeze-drying are normally in an amorphous state. Above the glass transition temperature (Tg), the change from the glassy state, more stable, to the rubbery occurs. The much lower viscosity of the rubbery state determines the aforementioned product softening, so that the typical crunchiness is lost. For this reason, it is of great importance to ensure the glassy state of a crispy product. To this end, it should be processed and stored at temperatures below its Tg. Likewise, it is important to know, at a specified storage temperature, the critical water content (CWC) and the critical water activity (CWA) of the product in order to ensure the glassy state. As in the low water content range, a small increase in the food water content leads to a significant decrease in the corresponding Tg, the storage relative humidity (RH) has to be strictly controlled. The state diagram of a food is one tool with which to predict and control the phase transitions. According to different authors, it is the right tool for the purposes of finding out the relationships between Tg and the water content in order to design efficient processes to obtain high-quality products and also to optimize storage conditions (Fabra, Talens, Moraga, & Martínez-Navarrete, 2009; Rahman, 2006; Roos, 1995; Roos & Karel, 1991).

Freeze-dried fruit pulps, such as sugar–rich foods, present structural problems of stickiness, caking and collapse. The Tg of freeze-dried fruit products present very low values, between 25 °C and −38 °C for a water content of between 3.3 and 25% (Telis & Martínez-Navarrete, 2010). Therefore, it is fairly easy to find these products in a rubbery state under the usual storage conditions. One way to prevent this, is, for example, the addition of biopolymers of high molecular weight that contribute to increasing the value of Tg or that even play a steric role

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https://doi.org/10.1016/j.lwt.2020.109415
Received 15 September 2019; Received in revised form 8 April 2020; Accepted 9 April 2020
Available online 14 April 2020
0023-6438/

delaying the structural collapse. Biopolymers, such as gums (gum Arabic, xanthan), maltodextrins, proteins (whey protein concentrate), starches (octenyl succinic anhydride, waxy starch) and natural fibres (bamboo fibre), have been used as drying carriers to obtain stable dehydrated products (Agudelo, Igual, Camacho, & Martínez-Navarrete, 2017; Bhusari, Muzaffar, & Kumar, 2014; Cano-Chauca, Stringheta, Ramos, & Cal-Vidal, 2005; Da; Fongin, Kawai, Harnkarnsujarit, & Hagura, 2017; González, García-Martínez, Camacho, & Martínez-Navarrete, 2019; Martínez-Navarrete, Salvador, Oliva, & Camacho, 2019; Da Silva et al., 2013; Telis & Martínez-Navarrete, 2009). However, the addition of biopolymers may cause unintended effects in other properties, such as changes in the colour or texture of the final product. Non-enzymatic browning reactions, such as Maillard reactions and caramelization, may stem from heating or occur during the long-term storage of foods containing carbohydrates, especially reducing sugars (BeMiller & Whistler, 1996; Telis & Martínez-Navarrete, 2012). Since the biopolymers differ as to their composition and nature, their interactions with the food matrix may vary, causing different water-solid interactions. According to Acevedo, Schebor, and Buera (2008), there is a correlation of the effects of water–solid interactions and water mobility on the non-enzymatic browning rates in freeze-dried potato. Some authors have studied the effect of different storage vapour pressure atmospheres on the stability of fruit powders containing biopolymers. They have found that the mechanical properties of the dried food are closely dependent on the a_w (Pérez-Alonso, Beristain, Lobato-Calleros, Rodríguez-Huezo, & Vernon-Carter, 2006; Telis & Martínez-Navarrete, 2009).

In this study, different biopolymers, gum Arabic, maltodextrin, starch modified with octenylsuccinic anhydride, pea fibre, bamboo fibre and native corn starch, have been tested in order to evaluate the possible advantages or disadvantages of each one of them when added to an orange puree for the purposes of freeze-drying and obtaining a snack.

2. Materials and methods

2.1. Raw materials

2.1.1. Fruit

The oranges (*Citrus x sinensis* var. Navel) used in this study were bought from a local supermarket in the city of Valencia (Spain). The fruit pieces were chosen by visual inspection based on the size, homogeneity, colour and good physical integrity.

2.1.2. Biopolymers

The carriers used to obtain the dehydrated orange samples were gum Arabic (GA, Scharlab, Sentmenat, Spain), maltodextrin (MD, Roquette, France), starch modified with octenylsuccinic anhydride (OSA, Roquette, France), pea fibre (PF, Roquette, France), native corn starch (NCS, Roquette, France) and bamboo fibre (BF, VITACEL®, Germany). These biopolymers were selected to avoid structural collapse of the dehydrated product, GA, MD and OSA for its ability to increase Tg and BF, NCS and PF because of its steric role avoiding the formation of interparticle bridges.

2.2. Samples preparation

In order to obtain the orange puree, the fruit was washed, peeled, cut and triturated in a bench top electrical food processor for 40 s at speed 4 (2000 rpm) followed by 40 s at speed 9 (91000 rpm) (Thermomix TM 21, Vorwerk, Spain). The orange puree was mixed (10 min at speed 3 (1000 rpm) with the biopolymers (Table 1) to obtain five different formulated samples to be freeze-dried, in addition to the orange puree with no biopolymers (O) that was also considered. The ratio orange puree:biopolymers was selected to ensure the physical stability of the dried product (Agudelo et al., 2017).

Table 1
Sample code as a function of the corresponding formulation.

Sample	Biopolymers added and concentration	
	5g/100 g orange puree	1g/100 g orange puree
GA + BF	gum Arabic	bamboo fibre
MD + PF	maltodextrin	pea fibre
MD + NCS	maltodextrin	native corn starch
OSA + PF	starch modified with octenylsuccinic anhydride	pea fibre
OSA + NCS	starch modified with octenylsuccinic anhydride	native corn starch

For freeze-drying purposes, each of the samples was distributed on two aluminium plates, 10.5 × 7.8 cm, 0.5 cm thickness, and immediately frozen at −45 °C (Liebherr LGT 2325, Germany) and then dried (Telstar Lioalfa-6, Spain), at 0.05 mbar, −45 °C on the condenser and 40 °C on the shelves for 20 h, to obtain two cakes from each of the six different freeze-dried cakes (O, GA + BF, MD + PF, MD + NCS, OSA + PF, OSA + NCS). One cake from each sample was crushed manually with a mortar to obtain the corresponding powder.

2.3. Sorption experiments

The freeze-dried cake and the powder from each of the six samples were placed at 20 °C in hermetic chambers containing saturated salt solutions (BrLi, ClLi, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, the corresponding relative humidity (RH) ranging between 6% and 53% (Greenspan, 1977). The samples were weighed every week in order to determine the equilibrium condition with the surroundings ($\Delta m < \pm 0.001$ g) (Kaymak-Ertekin & Gedik, 2004). In this moment, the water activity of each sample was assumed to be equal to the corresponding RH/100. The time needed to reach equilibrium was approximately two months.

2.4. Analytical determination

2.4.1. Water content (x_w)

The mass fraction of water (x_w) was obtained by drying the equilibrated powdered samples in a vacuum oven (Selecta®, Vaciotem-T, J.P. Selecta S.A., Spain) at 60 °C ± 1 °C under p < 100 mm Hg until constant weight (AOAC, 1990). Three replicates were carried out on each of the six equilibrated freeze-dried samples and the mean value was considered as the corresponding x_w.

2.4.2. Glass transition temperature (Tg)

The Tg of the powdered samples conditioned at different water contents was determined by differential scanning calorimetry (DSC 220CU-SSC5200, Seiko instruments Inc., Japan). Approximately 15 mg of each sample were placed into DSC pans (P/N SSC000C008, Seiko Instruments Inc., Japan). The heating rate was 5 °C/min and the temperature range varied between −80 °C and 80 °C, depending on the water activity of each sample. The onset, midpoint and endpoint of the glass transition were obtained from each thermogram.

2.4.3. Fitted models

In order to predict the water sorption behaviour of the samples, the linearized BET model (Eq. (1)) was used to predict water sorption up to $a_w \approx 0.5$ (Brunauer, Emmett, & Teller, 1938).

$$\frac{a_w}{(1-a_w)\,W_e} = \frac{1}{W_0\,C} + \frac{C-1}{W_0\,C}.\,a_w \tag{1}$$

Where W_e is the equilibrium water content (g water/g dry solute), W_o is the monolayer water content value (g water/g dry solute), C is the energy constant related to the sorption heat and a_w is the water activity.

In order to predict glass transition temperatures, experimental Tg - x_w data were fitted to the linearized Gordon and Taylor (1952) equation (Eq. (2)) considering the onset, midpoint and end of the transition.

$$T_g = T_{g(s)} + k\frac{x_w \cdot (T_{g(w)} - T_g)}{(1 - x_w)} \quad (2)$$

Where Tg is the glass transition temperature (°C), $Tg_{(s)}$ is the glass transition temperature of the anhydrous solids (°C), k is the Gordon y Taylor constant model, x_w is the mass fraction of water (g water/g product) and $Tg_{(w)}$ is the glass transition temperature of amorphous water: 135 °C (Roos, 1995).

The relationship between Tg - a_w is given by the linear regression proposed by Roos (1995) (Eq. (3)), where Y and Z are the constants of the model.

$$T_g = Ya_w + Z \quad (3)$$

2.4.4. Mechanical properties

The mechanical behaviour of the equilibrated samples was registered using a texture analyser TA-XT2i (Stable Micro Systems, UK). Portions of 20 × 20 mm of the freeze-dried cakes were compressed using a cylindrical probe of 10 mm diameter applying a strain of 80% with a test speed of 1 mms^{-1}. Five replicates were performed per sample. The parameters analysed in the test were the maximum force (F), expressed in Newtons.

2.4.5. Colour measurements

CIE L*a*b* colour space was selected as a uniform and objective method with which to specify the colour of equilibrated freeze-dried cake samples. The L* coordinate denotes lightness on a 0–100 scale from black to white; a*, (+) red or (−) green; b*, (+) yellow or (−) blue. Colour coordinates (10° observer and D65 illuminant) were obtained from the reflectance spectrum using a spectrophotometer (Minolta, CM 3600D, Japan). The colour was measured at four different points of the whole cake and the mean value was considered. From the colour coordinates, the hue angle (h*, Eq. (4)), and chroma or saturation (C*, Eq. (5)) were obtained. Measurements were taken with the specular component excluded.

$$h^* = \text{arctg}(b^*/a^*) \quad (4)$$

$$C^* = (a^{*2} + b^{*2})^{0.5} \quad (5)$$

3. Results and discussion

3.1. Sorption behaviour

The obtained sorption isotherms predict the relationship between w_e and a_w of the different freeze-dried orange purees at 20 °C (Fig. 1). As can be observed, all the added biopolymers reduced the hygroscopicity of the orange cake over the whole a_w range of, OSA seeming to be the most effective for this purpose.

The experimental data of each sample were fitted to the BET model (Table 2). The BET monolayer water content (W_o) was in the range of 0.0619–0.0742 g water/g dry solid, the highest value being that of the orange sample without biopolymers and the lowest that of the orange with OSA ones. The W_o indicates the amount of water that is tightly adsorbed in specific sites on food surfaces, which has been related with a security water content below which the product stability is guaranteed (Choudhury, Sahu, & Sharma, 2011; Telis & Martínez-Navarrete, 2010; Wan et al., 2018). The values of constant C, the other BET parameter, varied between 2.25 and 2.96, which allows these sorption isotherms to be classified as type II (Brunauer, Deming, Deming, & Teller, 1940). In order to evaluate the significant differences in the sample's sorption behaviour, the BET equation fitted to each sample and that fitted to different groups of samples were statistically compared through the values of the statistic E, which was compared with tabulated F – Snedecor (Moraga, Martínez-Navarrete, & Chiralt, 2004). The obtained results permitted a twofold confirmation: that there were no differences between the formulated samples (P > 0.05) and that all of them were different to the O sample (P < 0.05). In this way, the capacity of any of the biopolymers used to reduce the hygroscopicity of the freeze-dried orange snack can be confirmed, without any of them being more or less effective than the others.

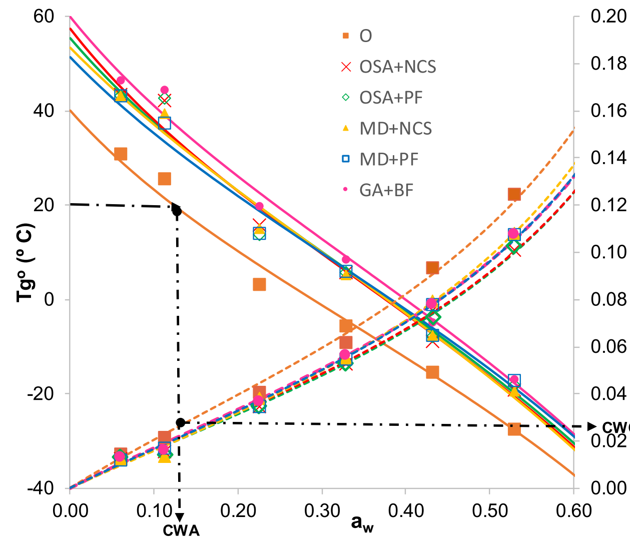

Fig. 1. Water content (w_e) - water activity (a_w) – onset glass transition temperature (Tg^0) relationships of freeze-dried orange puree (O) and that formulated with: starch modified with octenylsuccinic anhydride and native corn starch (OSA + NCS) or pea fibre (OSA + PF); maltodextrin with native corn starch (MD + NCS) or pea fibre (MD + PF); gum Arabic with bamboo fibre (GA + BF). The continuous lines represent the Tg-a_w fitted model, the discontinuous lines predict x_w-a_w data obtained from the BET fitted model and the points correspond to experimental data. The black dashed lines show, for the O sample, how to obtain the critical water activity and water content (CWA and CWC, respectively) for glass transition at 20 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Parameters of the BET (W_o, C) and linear (Y, Z) models fitted to experimental water content-water activity (Eq. (1)) and mid-point glass transition temperature-water activity (Eq. (3)) data, respectively. The sample codes can be identified in Table 1.

Sample	C	W_o (g water/g dry solids)	R^2	Y	Z	R^2
O	3,0	0,074	0,911	−124,4	36,8	0,981
OSA + PF	2,7	0,062	0,708	−137,8	51,9	0,969
OSA + NCS	2,8	0,062	0,837	−140,5	52,7	0,981
MD + PF	2,6	0,066	0,901	−130,4	49,3	0,982
MD + NCS	2,3	0,071	0,580	−136,2	50,9	0,985
GA + BF	2,8	0,066	0,827	−140,2	55,6	0,987

R^2: adjusted determination coefficient.

3.2. Glass transition temperature-water content-water activity relationships

The glass transition temperature of dried foods is extremely important as a means of predicting the conditions of a proper drying process and product storage (Roos & Karel, 1991). Nevertheless, glass transition is a state transition that is developed over a temperature range. That is why the onset (Tg^o), mid-point (Tg^m) and end-point (Tg^e) of glass transition can be characterized (Fig. 2). The majority of studies published take Tg^m as the characteristic Tg value (Goula, Karapantsios, Achilias, & Adamopoulos, 2008; Khalloufi & Ratti, 2003; Roos, 1995;

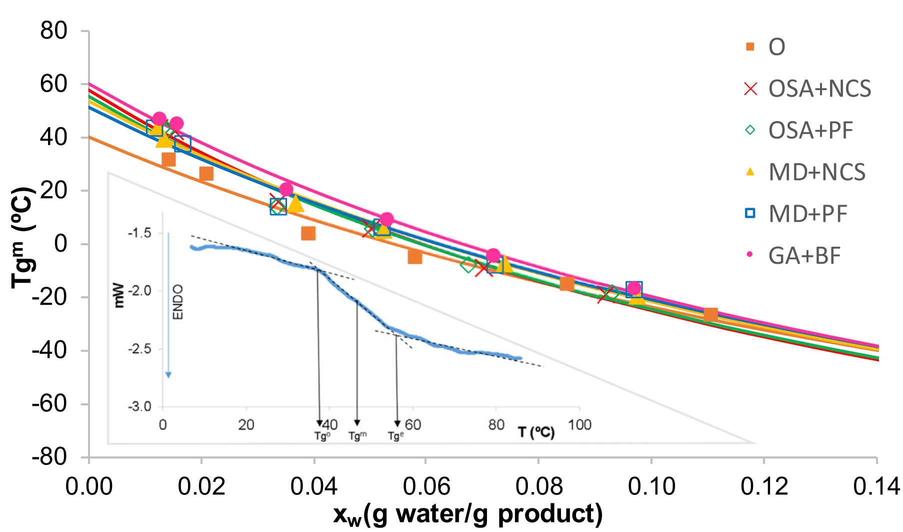

Fig. 2. Mid-point glass transition temperature (Tg^m)-water content (x_w) relationship of freeze-dried orange puree (O) and that formulated with: starch modified with octenylsuccinic anhydride and native corn starch (OSA + NCS) or pea fibre (OSA + PF); maltodextrin with native corn starch (MD + NCS) or pea fibre (MD + PF); gum Arabic with bamboo fibre (GA + BF). The lines represent the Gordon and Taylor fitted model and the points correspond to experimental data. The inner graph shows an example of one of the DSC thermograms obtained with GA + BF sample with a_w = 0.06. The dashed lines and arrows indicate the way to obtain the temperature at the onset (Tg^0), mid-point (Tg^m) and end-point (Tg^e) of glass transition. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Gordon and Taylor parameters (K and Tgs) obtained when fitting the experimental onset, midpoint and end point of the glass transition temperature (Tg^0, Tg^m and Tg^e, respectively) - water content relationship (Eq. (2)). The sample codes can be identified in Table 1.

		O	OSA + PF	OSA + NCS	MD + PF	MD + NCS	GA + BF
Tg^o	K	5,69	6,93	7,24	6,16	6,52	6,62
	Tgs	37,2	48,6	50,6	45,1	47,7	52,6
	R^2	0,985	0,972	0,981	0,970	0,984	0,985
Tg^m	K	5,19	6,56	6,81	5,74	6,02	6,28
	Tgs	40,0	55,4	57,5	51,4	53,4	60,0
	R^2	0,958	0,963	0,982	0,964	0,989	0,988
Tg^e	K	4,86	6,22	6,44	5,36	5,56	5,97
	Tgs	44,8	62,3	64,4	57,8	59,2	67,3
	R^2	0,953	0,951	0,981	0,957	0,985	0,991

R^2: adjusted determination coefficient.

Table 4
Values of the critical water content (CWC) and critical water activity (CWA) for the onset (°) and end (e) point of the glass transition at 20 and 4 °C. The sample codes can be identified in Table 1.

		O	OSA + PF	MD + PF	OSA + NCS	MD + NCS	GA + BF
20 °C	CWA^o	0,095	0,170	0,160	0,165	0,169	0,190
	CWA^e	0,165	0,279	0,275	0,275	0,275	0,302
	CWC^o	0,019	0,026	0,026	0,026	0,026	0,031
	CWC^e	0,032	0,042	0,044	0,042	0,043	0,049
4 °C	CWA^o	0,213	0,293	0,289	0,285	0,295	0,311
	CWA^e	0,305	0,404	0,409	0,400	0,405	0,425
	CWC^o	0,040	0,044	0,046	0,044	0,046	0,050
	CWC^e	0,057	0,063	0,067	0,063	0,067	0,071

Wu, Sun, & Liu, 2019). However, the change in the food properties associated with glass transition, could start from the moment in which the transition begins or might not become patent until the entire amorphous matrix has changed to the rubbery state, at the end of the Tg. For this reason, it may be interesting to consider Tg^o and Tg^e as being related to the physical properties (Rahman, 2006; Wan et al., 2018). The samples considered in this study showed a Tg amplitude of about 5–15 °C and, as expected, the Tg fell as the water content increased (Fig. 2). The orange sample without biopolymers presented lower Tg values than the samples with added biopolymers, especially in the lower water content range (approximately up to 0.07g water/g product). From this value, the added biopolymers do not seem to have so much influence on the Tg. The GA + BF sample seems to be the one that most increases the Tg over the entire water content range. Each one of the 3 characteristic values of the Tg of each sample was related to the corresponding water content by fitting the Gordon and Taylor model (Eq. (2)). Table 3 shows the corresponding k and $Tg_{(s)}$ parameters. The value of these parameters confirms the above comments. In this sense, the lowest $Tg_{(s)}$ was that of the O sample and the highest that of the GA + BF sample, the amplitude of the corresponding Tg ranging between 7.6 and 14.7 °C, respectively. Again, the statistical comparison among the different Gordon and Taylor fittings, performed through comparing the values of statistic E with the tabulated F-Snedecor, showed that only the O sample was different as regards the water plasticization behaviour. No significant differences ($P > 0.05$) were detected among the formulated samples.

As shown in Fig. 1, Tg-a_w-w_e relationships may be plotted together to construct the stability map, which is a tool that permits an easy identification of the critical processing or storage conditions (temperature and relative humidity) for glass transition (Fabra et al., 2009). Table 4 shows the critical water content (CWC) and critical water activity (CWA) values that have to be exceeded for the glass transition to take place, both at 20 and 4 °C, common room and refrigeration temperatures. The freeze-dried orange cake with added biopolymers showed higher values of CWC and CWA than the O sample, related to the greater capacity of these samples to maintain the more stable glassy state. It is remarkable that, despite the great microbiological and chemical stability of the dehydrated products, decreasing the storage temperature appreciably increases the CWC and CWA of all the samples. In this regard, at 20 °C for instance, the glass transition of the GA + BF sample will take place, at a surrounding RH in the range of 19.0–30.2%, this increasing to 31.1–42.5% at 4 °C. This increase in the critical values may be related to the physical stability of the products in terms of aspects such as the texture or colour of the snack.

On the other hand, in order to obtain a tool that makes it easy to relate both temperature and RH storage conditions for glass transition, Tg and a_w were related using the linear relationship (Eq. (3)) proposed by Roos (1995). Table 2 shows the results of this fit, where a very good and useful linear relationship can be observed.

3.3. Colour and mechanical properties

The addition of biopolymers led to an increase in L* and a decrease in a* and b*, so that the chroma of the samples decreased and the hue angle increased (Fig. 3). This colour change is related to the colour of the biopolymers themselves and to the dilution of the orange pigments in the formulated samples (Telis & Martínez-Navarrete, 2009). The whitish colour of the biopolymers contributes to the increase in lightness, the colour becoming yellower and less pure. The most significant colour change in every sample was observed at water activities between 0.328 and 0.432. At this a_w, the amorphous matrices of all the samples are already in a totally rubbery state (Table 4), and the water content is enough for enzymatic and non-enzymatic oxidation and browning reactions to occur. From this water activity, the greater amount of water present in the samples exerts a dilution effect of the components responsible for the colour, which means that the change in colour is no longer so marked.

The variation in the mechanical properties of the studied snacks was evaluated from the force–deformation curves. Fig. 4 shows the typical shape of the force–distance curves obtained from the different studied samples with several a_w. For the purposes of clarity, only one of the replicates at each a_w was selected for the Figure. In every case, the increase in the water content dramatically affected the shape of the curve, so that a change from a jagged to a smooth and regular trend of the force–deformation relationship was observed. This change is related to the material transformation from hard and brittle (or crunchy and crispy) when dried to soft and ductile at a higher water content (Martínez-Navarrete et al., 2019). The loss of crispness in the orange sample without added biopolymers was evident at water activities between 0.113 and 0.225, while in the samples with added biopolymers it was in the range of 0.225–0.328. In every case, the number of fracture peaks observed at the lower a_w decreased when the water content rose. These results point to the fact that any of the studied biopolymers may be used to protect the mechanical properties of the snack over a wider water content range, although there is still a limit to the gain of water if the quality of the product is to be ensured.

As a measurement of the strength of the samples with different a_w and so different water contents, the maximum force achieved in the mechanical test (Fmax) was characterized from the force–distance curves (Fig. 5). Significant differences ($p < 0.05$) were observed between samples and a_w. In order to confirm the impact of the physical state of the snack matrix on the measured mechanical response, the CWA for the glass transition of every sample (Table 4) was related with Fmax. Fig. 5 shows CWA for the onset and end point of the Tg (CWA^o

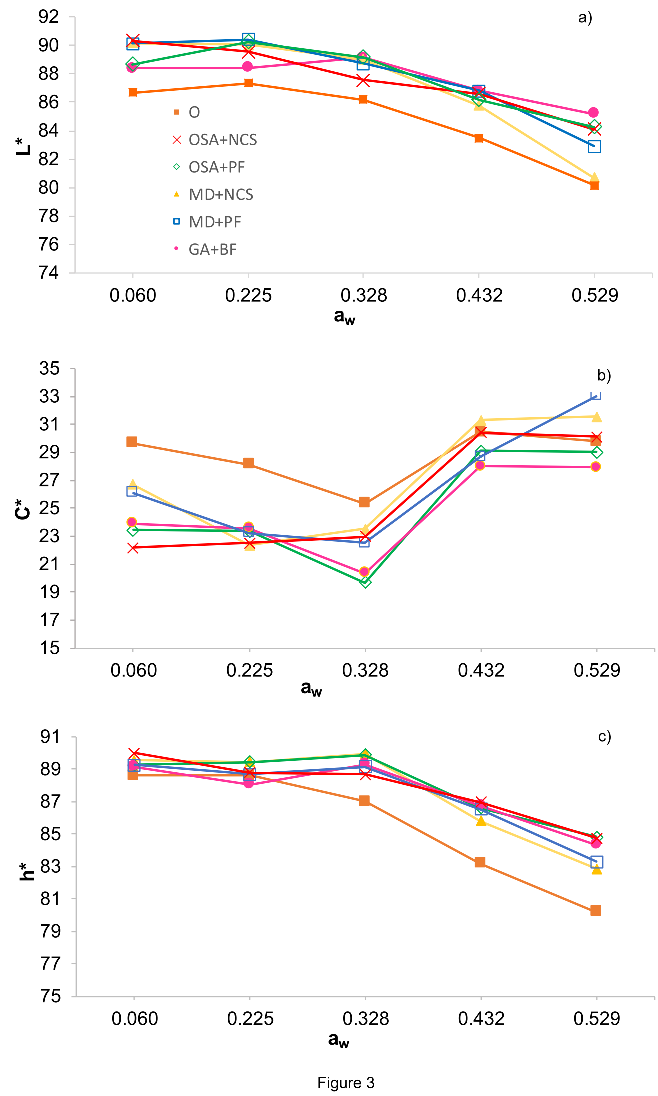

Fig. 3. Values of a) luminosity (L*), b) chroma (C*) and c) hue angle (h*) of freeze-dried snack obtained from orange puree (O) and that formulated with: starch modified with octenylsuccinic anhydride and native corn starch (OSA + NCS) or pea fibre (OSA + PF); maltodextrin with native corn starch (MD + NCS) or pea fibre (MD + PF); gum Arabic with bamboo fibre (GA + BF), conditioned at different water activity (a_w). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and CWA^e, respectively) of the O and GA + BF samples, and also those of the OSA + PF sample, whose values were genuinely close to the rest of the samples. As may be observed, the values of Fmax remain low below CWA^o, while all the product matrix is in the glassy state. Fmax sharply increases while the transition from the glassy to the rubbery state occurs (between CWA^o and CWA^e) and sharply decreases again when the rubbery state is fully achieved, above CWA^e. The small differences observed in the Tg-x_w-a_w relationships of the different samples containing biopolymers, despite not being significant ($P > 0.05$), were enough to ensure a significantly ($P < 0.05$) higher Fmax value of the GA + BF sample at a_w = 0.328 compared to the other samples, MD + PF having intermediate values.

The decrease in Fmax is related with the plasticising effect of water in the fully rubbery state. In this state, the amount of water in the sample is enough to ensure all the primary interactions with the matrix and there is still water available to contribute to the softening of the sample by weakening intermolecular bonds. The increase in Fmax at

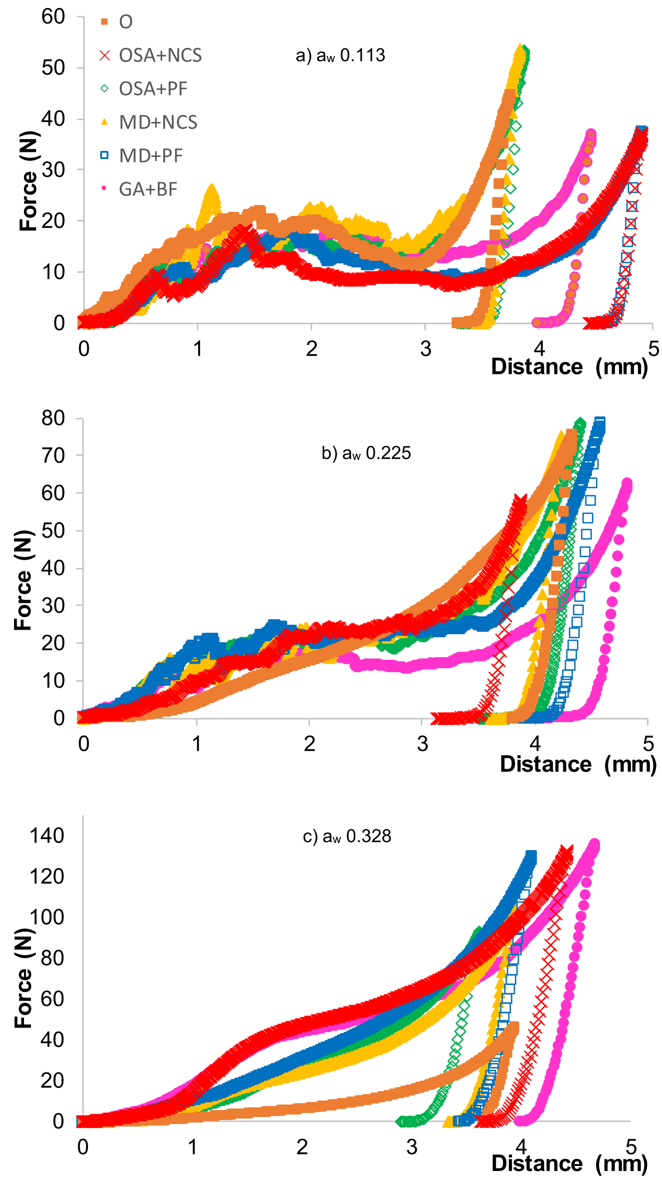

Fig. 4. Force (F) – distance (d) curves obtained with freeze-dried snack obtained from orange puree (O) and that formulated with: starch modified with octenylsuccinic anhydride and native corn starch (OSA + NCS) or pea fibre (OSA + PF); maltodextrin with native corn starch (MD + NCS) or pea fibre (MD + PF); gum Arabic with bamboo fibre (GA + BF), conditioned at different water activity (a_w). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the lowest a_w, also observed in other studies (Chang, Cheah, & Seow, 2000; Moraga, Talens, Moraga, & Martínez-Navarrete, 2011; Sogabe, Kawai, Kobayashi, Jothi, & Hagura, 2018), has been called the anti-plasticization effect of water and it has been related with an increase in the cohesiveness of the glassy food matrix that increases its rigidity and firmness (Pittia & Sacchetti, 2008). This offers a greater resistance upon force application and more energy is needed to compress the sample. For these authors, the anti-plasticization effect could be considered as a mere hardening or 'toughening' effect. This hardening limit the number of fractures when a_w increases over this low a_w range. In fact, it seems that the loss in the number of observed multiple fracture peaks occurs at the same a_w from which Fmax starts to decrease (Fig. 4-c and 5), when the whole matrix is in the rubbery state.

The above results indicate the need to keep the orange snack in a completely glassy state to ensure a crispy texture and adequate colour.

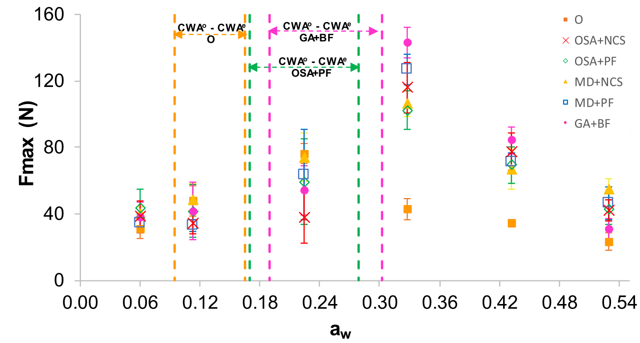

Fig. 5. Values of maximum force (Fmax) obtained in the mechanical test carried out with the freeze-dried snack obtained from orange puree (O) and that formulated with: starch modified with octenylsuccinic anhydride and native corn starch (OSA + NCS) or pea fibre (OSA + PF); maltodextrin with native corn starch (MD + NCS) or pea fibre (MD + PF); gum Arabic with bamboo fibre (GA + BF), conditioned at different water activity (a_w). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Despite the fact that the W_o value has frequently been considered as a secure water content below which product stability is guaranteed (Choudhury et al., 2011; Telis & Martínez-Navarrete, 2010; Wan et al., 2018), in this study, the CWC that ensured the glassy state of the studied snack was lower than W_o (Tables 2 and 4). In this sense, regardless of whether W_o may be considered an optimum value for the purposes of preventing processes such as oxidative deterioration (Goula et al., 2008), it is not only a_w but also Tg data that may be considered as complementary tools with which to ensure the stability of some products.

4. Conclusions

Any of the biopolymers studied permit a reduction in hygroscopicity and an increase in the glass transition temperature of the freeze-dried orange snack, without any of them being more or less effective than the others. The typical crunchy characteristics of the snack are lost at the onset of glass transition, while the colour changes are evident at its end. This indicates the need to keep the snack at temperatures below its Tg, depending on its water content. In this sense, it is recommended that the orange puree be formulated with any of the biopolymers studied and, although unnecessary from the perspective of chemical and microbiological stability, stored in refrigeration.

CRediT authorship contribution statement

Marilu Andrea Silva-Espinoza: Formal analysis, Funding acquisition, Investigation, Methodology, Writing - original draft, Writing - review & editing. **María del Mar Camacho:** Conceptualization, Funding acquisition, Methodology, Project administration. **Nuria Martínez-Navarrete:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors have no competing interests to declare.

Acknowledgments

The authors thank the Ministerio de Economía y Competitividad for the financial support given through the Project AGL 2017-89251-R (AEI/FEDER-UE) and the Ministerio de Educación for the FPU grant (FPU14/02633) awarded to Ms. Andrea Silva.

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