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Additional Information

36 **INTRODUCTION**

37

38 In recent years, several nutritional studies recommend a higher consumption of
39 foods rich in carbohydrates and fiber. To ensure these needs, the food companies
40 have introduced new products in the market. An example is the wide variety of
41 breakfast cereals and granola bars with dried fruit pieces that can be found on the
42 market. The multicomponent system created by the addition of dried fruits to cereals
43 offers new flavors, colors and textures, and new products rich in vitamins, minerals
44 and fiber. These products are an interesting alternative for people of all ages who
45 want to make breakfast, lunch, or a light meal between regular meals, more
46 attractive, varied, nutritious, and with new flavors. When dried fruits and cereals are
47 mixed, a new food system is created. However, the multicomponent system created
48 is not in thermodynamic equilibrium because their components are not in stationary
49 states (Sapru and Labuza, 1996) due to the differences in water activity values that
50 exist between dried fruits and cereals. When both components are mixed together
51 there is a water transfer between the component that has a higher water activity, the
52 dried fruit, with the component with the lower water activity, the cereals, until the
53 system reach the equilibrium. The water migration ceases when the difference in
54 water activity no longer exists (Risbo, 2003). This moisture migration can result in
55 undesirable physical and chemical changes in the system, affecting its quality and
56 shelf life. The crunchiness or crispness, an essential property in the breakfast cereals
57 quality, is lost when the cereals exceed values from 0.60 to 0.68 water activity
58 (Sauvageot and Blond, 1991; Peleg, 1994; Martínez-Navarrete *et al.*, 1998), resulting
59 in the rejection by consumers (Nielsen, 1979). On the other hand, dried fruits require
60 higher water content than cereals to give rise to a right texture, becoming

61 unacceptable when they reach water activity values lower than 0.5 to 0.3 (Labuza
62 and Contreras-Medellin, 1981, Talens *et al.*, 2010). Several factors influence the
63 amount and rate of moisture migration in multicomponent foods. Water activity
64 equilibrium (thermodynamics) and rate of diffusion (dynamics of mass transfer) are
65 the two main factors (Labuza and Hyman, 1998). In order to control the migration,
66 several principles can be utilized. One possibility is formulating the components to
67 obtain as close as possible water activity parallelism through the use of selected
68 solutes. For example, try to adjust as close as possible the water activity of the
69 intermediate-moisture fruit and the dry cereal in order to reduce the driving force of
70 the moisture migration. The cereal does not pick up much moisture and loses
71 crispness. Another possibility for controlling moisture migration is to add an edible
72 barrier between components (Talens and Fabra, 2011). Nowadays, most industries
73 solve the problem using the thermodynamic approach by drying or freeze-drying the
74 fruit to levels close to those of cereals, causing in most cases a decrease in the fruit
75 quality and a reduce in its attractiveness to the consumer. The use of partially
76 dehydrated fruit, obtained by osmotic dehydration and vacuum impregnation
77 processes, and the application of an edible coating on it, could solve the problem
78 increasing the quality of these kinds of products. In fact, the use of osmotic
79 dehydration and vacuum impregnation has been used in the dehydration of fruits due
80 to the advantages of this technique to preserve the product flavor and other sensory
81 properties obtaining good yields by increasing the kinetics of entry of soluble solids
82 (Barat *et al.*, 2002).

83 The application of edible films based on chitosan or caseinates is interesting because
84 of its high nutritional quality, excellent sensory properties, and adequate protection

85 of food products from their environment (Vargas *et al.*, 2006; Pinotti *et al.*, 2007;
86 Vargas *et al.*, 2009; Fabra, *et al.*, 2009; Pereda, *et al.*, 2010; Mendes de Souza *et al.*,
87 2010).

88 The main objective of this work was to evaluate the effectiveness of edible films,
89 based on caseinates or chitosan, and the application method, in partially dehydrated
90 pineapple for its use in dry fruit-cereal systems. The objective was achieved by (1)
91 identifying the water activity-moisture content-glass transition relationships for the
92 cereals, (2) preparing partially dehydrated pineapples by osmotic dehydration and
93 vacuum impregnation, (3) evaluating the application method of the caseinate or
94 chitosan films on the pineapple samples, (4) evaluating the effectiveness of the
95 combined method (partially dehydration and application of edible films) by storing
96 coated and uncoated pineapple samples with cereals under controlled conditions and
97 temperature.

98

99 **MATERIALS AND METHODS**

100 **Moisture sorption isotherm and glass transition of breakfast cereals**

101 Commercial breakfast cereals (Corn flakes) were purchased in a local supermarket
102 in Valencia (Spain). According to the producer's specifications, the composition of
103 corn flakes was (g/100g): 84g of carbohydrates, 7g of proteins, 0.9g of lipids, 3g of
104 fibre, 0.5g of sodium and 1.3g of salt. Likewise, the ingredients specified on the label
105 were maize, sugar, barley malt flavouring, salt, niacin, iron, vitamin B6, vitamin
106 B12, riboflavin (B2), thiamine (B1), folic acid, vitamin D. The cereals were
107 conditioned immediately after opening at different relative humidities. Sorption
108 experiments were carried out by triplicate at 20 °C. For moisture conditioning, the

109 cereals (approximately 10g) were placed at 20 °C in hermetic chambers containing
 110 saturated salt solutions with different relative humidities (LiCl: 0.113, CH₃COOK:
 111 0.230, MgCl₂: 0.330, K₂CO₃: 0.430, Mg(NO₃)₂: 0.520, CuCl₂: 0.680, NaCl: 0.755
 112 and KCl: 0.845, Greenspan, 1977). The sample weights were controlled till a
 113 constant value assumed as equilibrium was reached ($\Delta\text{weight} < \pm 0.0005$ g) (Spiess
 114 and Wolf, 1983). At this moment, the water activity of each sample was assumed to
 115 be equal to the corresponding relative humidity/100. Initial moisture content of
 116 cereals was determined by triplicate using a Vaciotem, J.P. Selecta vacuum oven (60
 117 ± 1 °C and at a pressure <100 mm Hg). In each equilibrated sample, the final
 118 moisture content was calculated using the initial moisture content and the final
 119 registered weight. These values were used to construct the sorption isotherms. In
 120 order to predict the water sorption behaviour of the samples, the GAB (Guggenheim,
 121 Anderson and de Boer) (Van den Berg and Bruin, 1981) model was used (Equation
 122 1).

$$123 \quad w_e = \frac{w_o C K a_w}{(1 - K a_w)(1 + (C - 1) K a_w)} \quad (\text{Eq.1})$$

124 Where: w_e : water content (g water/ g dry solids); a_w : water activity; w_o : monolayer
 125 value (g water/ g dry solids); C: constant related to monolayer sorption heat and K:
 126 constant related to multilayer sorption heat.

127 To determine the glass transition temperature of the samples, a differential
 128 scanning calorimeter (DSC) 220CU-SSC5200 (Seiko instruments Inc., Tokyo, Japan)
 129 was used. About 10 mg of each equilibrated sample were placed into DSC pans (P/N
 130 SSC000C008, Seiko Instruments Inc., Tokyo, Japan) sealed and analysed. Heating
 131 rate was 5 °C/min and temperature range varied between -100 and 100 °C, depending
 132 on sample moisture content.

133 Experimental glass transition temperature-mass fraction of water data were fitted
134 to the Gordon and Taylor model (1952) (Equation 2).

$$135 \quad T_g = \frac{(1 - x_w)T_{g(as)} + kx_w T_{g(w)}}{(1 - x_w) + kx_w} \quad (\text{Eq.2})$$

136 Where: x_w : mass fraction of water (g water/ g product); T_g : glass transition
137 temperature (°C); $T_{g(w)}$: glass transition temperature of amorphous water (-135 °C);
138 $T_{g(as)}$: glass transition temperature of anhydrous solids (°C) and k: constant model.

139 **Preparation of coating forming solutions**

140 Materials

141 High molecular weight chitosan (CH), with a deacetylation degree of 82.7 % and
142 a viscosity of 0.919 Pa·s at 1 wt %, in 1 wt % acetic acid solution (Batch 14624DB,
143 Sigma-Aldrich Química, Madrid, Spain), 98 % glacial acetic acid, 1 N NaOH, oleic
144 acid (OA), Tween 80 (Panreac, Barcelona, Spain) and food-grade methylcellulose
145 (MC) with a substitution degree of 1:9 (Methocel A-15, Dow Chemical Co, Midland,
146 USA) were used to obtain the film-forming dispersions of chitosan.

147 Alanate-110 sodium caseinate (NaCas), Alanate-310 calcium caseinate (CaCas)
148 (98% of purity, Llorella, SA, Barcelona, Spain), Beeswax (BW) (Brillocera, SA,
149 Valencia), oleic acid (OA) and Glycerol (Gly) (Panreac Química, SA, Castellar Del
150 Vallés, Barcelona, Spain) were used to obtain the film-forming emulsion of
151 caseinate.

152 Preparation of chitosan-based film-forming emulsions.

153 Two different emulsions of CH-MC (Emulsion E1) and CH-OA (Emulsion E2)
154 were prepared. Chitosan (1 wt %) was dispersed in an aqueous solution of glacial
155 acetic acid (1 % v/w), at 40 °C. Tween 80 at 0.1 % (v/w) was added to improve
156 wettability. MC or OA were added to the CH film until reach a final concentration of

157 1 wt % and 2 wt % respectively. The mixtures were emulsified at room temperature
158 using a rotor-stator homogenizer (Ultraturrax DI 25 basic-Yellowline, Janke and
159 Kunkel, Staufen, Germany) at 13,500 rpm for 4 minutes. The pH of all film-forming
160 emulsions was adjusted to 5.2 with NaOH 1N.

161 Preparation of casinate-based film-forming emulsions

162 Two different emulsions of NaCas-BW-OA (Emulsion E3) and NaCas-CaCas-
163 BW-OA (Emulsion E4) were prepared. Pure NaCas (8 w/w) for the emulsion E3 and
164 a mixture of NaCas:CaCas (1:0.5 mass ratio) for the emulsion E4 were dispersed in
165 an aqueous solution of distilled water. In both emulsions the protein:glycerol ratio
166 was 1:0.3 and the protein:lipid ratio was 1:0.5. The lipid fraction was composed of
167 OA:BW (70:30 mass ratio). After glycerol was added to aqueous solutions of
168 caseinates, all dispersions were heated till 85 °C and the amount of beeswax required
169 was incorporated whereas melted in the hot solution. Afterwards, it was
170 homogenized at 85 °C for 1 min at 13,500 rpm, followed by 1 min at 20,500 rpm.
171 The emulsions were cooled at room temperature and oleic acid was added in the
172 amount required. Each emulsion was homogenized again with a vacuum high-shear
173 probe mixer (Ultraturax T25, Janke and Kunkel, Germany) for 2 min at 20,500 rpm.
174 Finally, they were degasified at 7 mbar at room temperature with a vacuum pump
175 (Wertheim, Germany).

176 **Preparation of dehydrated pineapple samples**

177 Fresh pineapple (*Ananas comosus* var. Golden Sweet) purchased in a local market
178 in Valencia (Spain) was used in the experiments. A metallic core borer was used to
179 obtain 2 cm diameter cylinders. The cylinders were sliced obtaining samples with 1
180 cm of thickness. The cylinders were submitted to vacuum impregnation (VI),

181 osmotic dehydration (OD) and air dried (AD) process. The samples were immersed
182 in a sucrose osmotic solution of 35 °Brix and were submitted to a VI operation in the
183 first step by using a grid to keep them immersed in the osmotic solution for 30 min,
184 applying 50 mbar of pressure for 10 minutes and restoring afterwards the
185 atmospheric pressure for 20 minutes. As a second step, the samples were introduced
186 into a sucrose osmotic solution of 65 °Brix and stirred in a bath for 48 hours in order
187 to achieve the equilibrium condition. In both cases, the experiments were carried out
188 at 25 °C and the ratio of the weight of osmotic solution:sample was high enough
189 (20:1) to avoid any significant change in the osmotic solution concentration.

190 In the third step, the samples were submitted to an air drying (AD) process at 30
191 °C till the same concentration level (water activity of 0.752 ± 0.007) was reached in
192 all samples. The AD processing was carried out before or after the application of the
193 coating depending on the treatments.

194 **Coating of pineapple samples**

195 Four application techniques were used for coating the pineapple samples, method
196 I, sample drying until $a_w = 0.75$ and afterwards dipping at atmospheric pressure in
197 the film-forming solutions for 5 minutes, with the subsequent coating drying at room
198 temperature; method II, sample dipping at atmospheric pressure in the film-forming
199 solutions for 5 minutes before drying until $a_w = 0.75$; method III, sample dipping at
200 atmospheric pressure in the film-forming solutions two times (5 min and 5 min,
201 respectively) before drying until $a_w = 0.75$; and method IV, sample dipping in the
202 film-forming solutions applying a vacuum impregnation operation before drying
203 until $a_w = 0.75$. The vacuum impregnation operation consisted of applying a vacuum
204 pulse (50 mbar for 3 min) to the immersed sample, afterwards restoring the

205 atmospheric pressure while the sample remains immersed for 2 min more. Control
206 samples followed the same treatments but were dipped in distilled water.

207 **Sample analysis**

208 Water activity, soluble solids, and moisture content of fresh and processed
209 pineapple samples were determined. The water activity was determined using a dew
210 point equipment (Decagon®, model Aqualab CX2, Decagon Devices, Inc., Pullman,
211 Wash., U.S.A.) at 25 °C. The soluble solids were determined using a refractometer
212 (Atago, NAR T3, Japan) at 20 °C. Moisture content was determined by vacuum
213 drying the samples to constant weight at 60 °C (method 20.013 AOAC, 1980).

214 Rheological behaviour of the film-forming dispersions was characterized in
215 triplicate at 25 °C. The shear stress was measured as a function of the shear rate from
216 0 to 512 s⁻¹ by means of a rheometer (HAAKE Rheostress 1, Thermo Electric
217 Corporation, Karlsruhe, Germany) using coaxial cylinders, sensor type Z34DIN Ti.

218 The surface solid density (SSD), as an indicator of the coating's average
219 thickness, was estimated by Equation (3). The surface drying time of coated samples
220 was set to eliminate all the solvent content from the adhered coating through their
221 weight control.

$$222 \quad SSD = \frac{M_{FA} \cdot x_S}{A_S} \quad (\text{Eq.3})$$

223 Where: SSD (g/m²): surface solid density; M_{FA} (g): mass of coating solution adhered
224 to surface of pineapple obtained by weighing the samples before and after coating;
225 x_S: mass fraction of solids in the coating solution; A_S (m²): surface area of pineapple
226 slices, measured using a digital caliper.

227 In order to determine the water vapour resistance, coated and non-coated samples
228 were kept in desiccators where a 22.5% of RH was generated using saturated

229 potassium acetate solutions. Desiccators were placed in a temperature controlled
230 chamber, Hot-Cold M4000668 (P-Selecta, Barcelona, Spain), at 20 °C. Eight
231 repetitions were performed for each coated pineapple sample including uncoated
232 control samples. Samples were kept stored for 12 days and were weighed 2 times a
233 day during the first 5 days and 1 time each day during the remaining time with an
234 electronic balance (± 0.00001 g) (ME36S Sartorius, Germany). Water vapour
235 resistance (WVR) was calculated using a modified equation of the First Fick Law
236 (Equation 4), as described by Avena- Bustillos *et al.* (1994).

$$237 \quad WVR = \frac{a_w - \frac{\%RH}{100} \cdot P_{wv}}{R \cdot T} \times \frac{A_s}{J} \quad (\text{Eq.4})$$

238 Where: WVR: water vapour resistance (h/m), J : slope of the weight loss curve in
239 stationary conditions (mol/h), A_s : sample area (m²), a_w : water activity of the samples,
240 RH: relative humidity inside of the desiccator, P_{wv} : saturated vapour pressure (Pa), T :
241 absolute temperature (K), R : the universal constant of gasses (8.314472 J/mol K).

242 The dimensions of the pineapple samples at initial and final control time were
243 used to calculate the average surface area.

244 **Storage study of the cereal-pineapple system.**

245 To predict how long the cereal-pineapple system can maintain its quality, coated
246 and uncoated samples of pineapple were stored with breakfast cereals in sealed
247 polyethylene bags at a ratio fruit:cereal 30:70 (w/w) under a controlled temperature
248 of 20 °C. Both components were weighed weekly until 6 months.

249

250 **RESULTS AND DISCUSSION**

251 **Moisture sorption isotherm and glass transition of breakfast cereals**

252 Corn flakes are cereals whose crispness is considered a primary textural attribute,
253 highly affected by the product's physical state (glassy or rubbery). The physical state
254 of breakfast cereals may change from a solid glassy state to a liquid-like rubbery one
255 when the glass transition temperature (T_g) is reached. As the T_g is dependent on
256 water content, a change from a glassy to a rubbery state can also occur as a
257 consequence of an increase in the product water content during its processing or
258 storage. In order to establish the critical values of water content and water activity
259 that induces the glass transition in the product matrix (which can alter the texture of
260 the product) the water activity-moisture content-glass transition relationships for the
261 corn flakes have been studied. The moisture content analysed in the commercial
262 breakfast cereals was $3.5 \pm 0.1\%$, which agrees with the compositional data specified
263 on the product's label, where the main solids content was 96.7%. Equilibrium
264 moisture contents (w_e) at the different water activity (a_w) of the samples are plotted
265 in Figure 1, which shows the sorption isotherm of corn flakes at 20 °C. In order to
266 predict the water sorption behaviour of the samples, the experimental sorption data
267 were fitted to GAB model (Equation 1). Table 1 shows the parameter values obtained
268 for the GAB fitted model and Figure 1 shows the predicted sorption isotherm
269 obtained from the fitted model. The observed behaviour is typical of a product with
270 high-sugar content which adsorbs relatively small amounts of water at low-water
271 activities but high quantities of water at higher water activities. This effect can be
272 explained by the sorption effect that mainly occurs at low-water activities on the
273 product matrix formed by biopolymers (basically polysaccharides and proteins) and
274 due to the prevailing effect of solute-solvent interactions associated to sugar
275 dissolution at high-water activities (Tsami *et al.*, 1990; Vazquez *et al.*, 1999).

276 To analyze the water plasticization effect on the corn flakes, the glass transition
277 temperature of the samples was determined using a differential scanning calorimeter
278 as it is described in materials and methods section. Table 1 shows the values of the
279 glass transition temperature for the corn flakes with different moisture content. As
280 expected, for this kind of products, as the water activity or moisture of the samples
281 increased, the glass transition temperatures decreased. The Gordon and Taylor model
282 (equation 2) was used to fit the experimental Tg-Moisture data. This model considers
283 food materials as binary mixtures of solids and water and it has been proved to be a
284 reliable predictor of the glass transition temperatures of sugars at various water
285 contents (Roos, 1995). Table 1 shows the parameter values obtained for the Gordon
286 and Taylor fitted model. A combined plot showing the experimental sorption (x_w - a_w)
287 and glass transition (Tg- a_w) data and the corresponding GAB and Gordon and Taylor
288 fitted models (Figure 2) was used to determined the critical values of water content
289 (CWC) and water activity (CWA) at 20 °C. These values were 9.1 g of water/100 g
290 of product and 0.60, respectively. The level of critical water activity after which
291 products with similar characteristics to corn flakes lose their crispness has been
292 stated as 0.36–0.51 for potato chips, saltines, or popcorn (Katz and Labuza, 1981),
293 0.50–0.57 for krispies (Roos *et al.*, 1998), 0.60 for biscuits (Hough *et al.*, 2001),
294 0.60–0.68 for breakfast cereals (Sauvageot and Blond, 1991; Peleg, 1994; Martínez-
295 Navarrete *et al.*, 1998) and 0.58 for wafers (Martinez-Navarrete *et al.*, 2004). In the
296 commercial product, with 0.035 water mass fraction, glass transition will occur at
297 52.94 °C. As the predicted CWC at 20 °C was 9.1 %, this will imply that samples
298 with greater moisture content will be in a rubbery state at this temperature. This
299 value coincides with the moisture limit (0.1g of water/g of dry solids) in the sorption

300 isotherm (Figure 1) from which point onwards the ascending tendency is observed,
301 which is related to the beginning of solute-solvent interactions in the system. The
302 low water content value of the commercial studied product makes it very sensitive to
303 becoming damp at the usual environmental relative humidity. This implies the
304 requirement of a water impermeable packaging and the subsequent precautions
305 during product manipulation to avoid it becoming rubbery, thereby losing its typical
306 textural characteristics.

307 **Coating of pineapple samples**

308 Table 2 shows the water activity, mass fraction of water (x_w) and mass fraction of
309 soluble solids (x_{ss}) values of fresh and processed pineapple samples. It can be
310 observed that the samples used in the study had a similar composition. Mean values
311 of mass fraction of water and mass fraction of soluble solids in the fresh pineapple
312 were 0.830 ± 0.020 and 0.154 ± 0.021 respectively, with a_w value of 0.987 ± 0.005 .
313 During the osmotic step, pineapple samples reached between 61 and 62 °Brix in their
314 liquid phase, in agreement with their practical equilibrium with the solution used in
315 the long osmotic step. After the air drying process, very close values of water activity
316 were obtained in all treatments for each sample, the mean values being 0.752 ± 0.007 .

317 Table 3 shows the mass of film-forming dispersion adhered to pineapple samples
318 after coating application, expressed as percentage of the sample initial mass
319 (M_{FA}/M_0), the surface solid density (SSD) values, and the viscosity of the film-
320 forming dispersions used for the coating of pineapple samples. The amount of film-
321 forming dispersion adhered to the pineapple surface, related with the thickness of the
322 wet layer retained in the sample surface after the immersion step, was significantly
323 higher ($p < 0.05$) when the viscosity of the film-forming dispersions was high

324 (emulsion1) and when the coatings were applied by a two-step dipping process
325 (method III) or applying a vacuum impregnation operation before drying the sample
326 (method IV). The vacuum impregnation process promotes the exchange of gas or
327 liquid phase in the pineapple tissue for the external solution increasing the mass of
328 film-forming dispersion adhered to the sample. Similar effects were observed by
329 other authors working with carrot, using coatings made from hydroxypropyl
330 methylcellulose (Villalobos *et al.*, 2009) or chitosan (Vargas *et al.* 2009). The SSD
331 values reached after drying the coating were obtained as an indicator of the applied
332 film thickness. As expected, SSD values increased with the solid concentration of the
333 film-forming dispersions (emulsion 3 and emulsion 4) for all the application
334 methods. Among the application methods, as occurred with the M_{FA}/M_0 values, the
335 methods III and IV were more effective than the methods I and II. Both, I and II
336 methods, significantly increased the SSD values, except for the first film-forming
337 dispersion, probably due to the high viscosity of the formulation that limit the gain of
338 external liquid by capillary action (Chafer *et al.*, 2001, Talens *et al.*, 2002, Talens *et*
339 *al.*, 2003).

340 The direct measurement of the product water vapour resistance, under controlled
341 environmental conditions, would make it possible to determine *in situ* if the coating
342 shows the required properties for a specific combination of storage conditions
343 (Amarante and Banks, 2001). The values of WVR of the coated pineapples are
344 shown in table 3. When the samples are coated with the film forming dispersions
345 based on caseinates (emulsion3 and emulsion4) show higher WVR values than when
346 they are coated with chitosan (emulsion1 and emulsion2). This effect can be due,
347 firstly, to the highest surface solid density that the caseinate forming dispersions

348 have, resulting in a thicker coating, and secondly, to the lower water vapor
349 permeability values that the caseinates films have compared to the chitosan films
350 (Fabra *et al.*, 2008, Vargas *et al.*, 2009). The values obtained for the uncoated
351 samples were 71±16 s/cm, 188±35 s/cm, 211±61 s/cm and 140±30 s/cm for the
352 methods I, II, III and IV, respectively. Differences can be attributed the different
353 batch or to the different surface wetting degree of the sample when immersed in
354 distilled water to simulate the coating processes. So, in order to compare each of the
355 different application methods, minimizing this variability, relative values of water
356 vapor resistance (WVR_r) were calculated (Equation 5) for each application method.

$$357 \quad WVR_r = \frac{WVR_{ri} - WVR_C}{WVR_C} \quad (\text{Eq.5})$$

358 Where, WVR_{ri} is the water vapor resistance of the sample coated by the different
359 emulsions and WVR_C is the water vapor resistance of respective uncoated samples.
360 Figure 3 shows the mean values (and LSD intervals) of WVR_r values for all the
361 coated samples by the different methods. Despite the different values of M_{FA}/M_0 and
362 SSD presented in Table 3, Figure 3 shows that when coatings were applied under
363 atmospheric pressure (methods I, II and III), there were no improvement in terms of
364 water vapour resistance values as compared to non-coated samples for all film-
365 forming dispersions. However, with the exception of the samples coated with
366 emulsion2, when coatings were applied by using vacuum impregnation (method IV)
367 the resistance of water vapour transmission of samples significantly increased ($p <$
368 0.05). This effect can be attributed to the significant increase in surface solid density
369 when a vacuum pulse is applied, associated with the penetration of the film-forming

370 dispersions into the empty pores of the sample surface, thus affecting the final
371 thickness and structure of the coating (Vargas *et al.*, 2009; Villalobos *et al.*, 2009).

372 **Storage study of cereal-pineapple mixtures.**

373 Figure 4 shows the changes in pineapple and cereal weight throughout the storage
374 time, mixed in the plastic bag. These changes are related with the water loss of
375 pineapple samples and with the water gain of cereals. In general, an asymptotic
376 development for weight loss and weight gain is observed. Faster changes in sample
377 weight were observed at the beginning of the storage, due to the highest differences
378 in the water activity values of pineapple and cereal samples, which implies a higher
379 driven force for the water transfer. Throughout the storage time there is progressive
380 decrease in this driven force in line with decrease of the differences of their water
381 activity values. To analyze the kinetics of water loss of pineapple samples stored
382 with cereals, a mathematical model proposed by Peleg (1979) was used. Eq. (6)
383 describes the application of this model to a determined variable U (in this case, the
384 weight loss), where U_0 is the initial value and U_t at time t. This equation properly
385 describes asymptotic curves and yields two parameters, K_1 and K_2 , inversely related
386 to the rate and degree of change of U, respectively. The asymptotic value of U (U_e)
387 can be determined using Eq. (7) (Peleg, 1988).

388
$$\frac{t}{U_t - U_0} = K_1 + K_2 t \quad (\text{Eq.6})$$

389
$$U_e = U_0 + \frac{1}{K_2} \quad (\text{Eq.7})$$

391 Peleg's model parameters K_1 and K_2 , as well as the corresponding equilibrium
392 values (calculated with Eq. (8)) are shown in Table 4. The values obtained using
393 Peleg's equation show that samples coated by method I have the highest water losses

394 while samples coated by method IV show the lowest water losses. Samples coated by
395 the methods II and III show intermediate water losses between those shown by
396 samples coated by methods I and IV. It is remarkable that, except for the method IV,
397 the equilibrium weight loss of coated samples with the different formulations are in
398 the order, or even greater, than that obtained for the corresponding uncoated samples.
399 Nevertheless, when the method IV is applied, an important reduction of weight loss
400 is obtained for caseinate formulations (emulsion 3 and 4), which indicates that the
401 water barrier effect of coating and the interactions developed with the product
402 surface (affected by the application method), greatly determine the coating
403 effectiveness to control the water migration in this kind of systems. In this sense, the
404 final air drying of the product, after the coating application, has a positive effect due
405 to the fact that the coating become more dried in the product surface and so their
406 water vapor permeability decrease due to its lower water content and lesser
407 plasticization degree. The protein-based films have better barrier properties than the
408 polysaccharide-based films and, in both cases, these were reduced when the film
409 moisture increases (Cao, Fu & He 2007).

410 To analyze the effect that water transfer between components has on the quality
411 and shelf life of cereals, the changes on the moisture content of cereals during the
412 storage time was determined from the initial moisture content of cereals and weight
413 change at each time (Figure 5). The illustrated line showed in Figure 5 indicates the
414 critical value of water content for cereals determined previously by their water
415 activity-moisture content-glass transition relationships (Figure 2). When cereals
416 reach the critical water content (9.1 g of water/ 100 g of product) turn from the solid
417 glassy state into a rubbery state losing their crunchy characteristics and so their

418 quality. Figure 5 shows that cereals stored with the coated pineapple according to
419 methodo I, use to turn into rubbery state before those stored with the control
420 pineapple and moreover, it happen gradually according to the hydrophobicity of the
421 coating (E1, E2, E3, and E4). This effect could be due, as has been previously
422 mentioned, to the coating application that was applied after hot air drying of the
423 pineapple that wet the surface of the product that resulted in a higher gradient of
424 water activity between the components of the pineapple-cereal system. However, the
425 effectiveness of the coating increases in the samples in which the coating has been
426 applied before the drying step (methods II to IV). In general, cereals stored with
427 pineapple samples coated using these methods with caseinate coatings reach the
428 rubbery state later than that stored with control pineapple samples, whereas no
429 notable differences with respect the control is observed for chitosan coatings. These
430 results agree with those commented for the pineapple weight losses and can be
431 attributed to the lower water vapour permeability of caseinate-based coatings in
432 comparison to chitosan-based coatings (Fabra *et al.*, 2008, Vargas *et al.*, 2009) and to
433 the better effectiveness achieved when coating was applied by vacuum impregnation
434 and sample was dried after coating application. During the sample drying, coatings
435 become also more dried, thus increasing their water barrier properties (Villalobos *et*
436 *al.*, 2009).

437 These differences are emphasized in samples coated using vacuum impregnation
438 technique (method IV) due to the entry of the coating solids into the pores of the
439 sample surface which could block pineapple porous areas from where the water
440 vapour transfer used to happen. In fact, for samples coated with caseinate
441 formulations by using method IV, the critical moisture content of cereals is not

442 reached in the tested time while a practically constant value (equilibrium) was
443 reached from about 80 days onwards.

444

445 **CONCLUSIONS**

446 The water activity-moisture content-glass transition relationships for the commercial
447 breakfast cereals analysed at 20 °C using Gordon and Taylor's equation to model the
448 water plasticization effect, and GAB equation to model the sorption effect, indicates
449 that values of water activity higher than 0.60 and water contents higher than 9.1 g
450 water/ 100 g of product would result in the looseness of cereal's crispness.

451 When intermediate moisture pineapple samples are mixed with cereals these values
452 are easily reached, affecting the quality of the new multicomponent system. Coating
453 the fruit with caseinate based films applying vacuum impregnation and subsequent
454 drying of the samples to a_w 0.75 greatly extend the shelf-life of the pineapple-cereal
455 system in comparison to other tested methods. Chitosan based coatings were not
456 enough effective to avoid the cereals to reach the critical moisture content in a
457 reasonably long storage period.

458

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463

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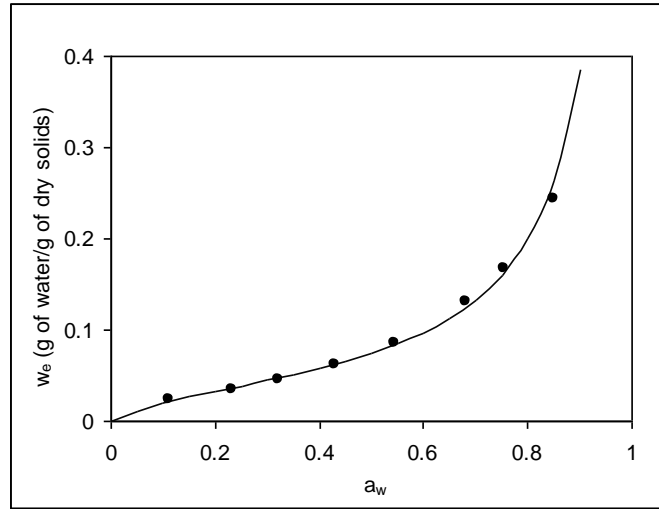
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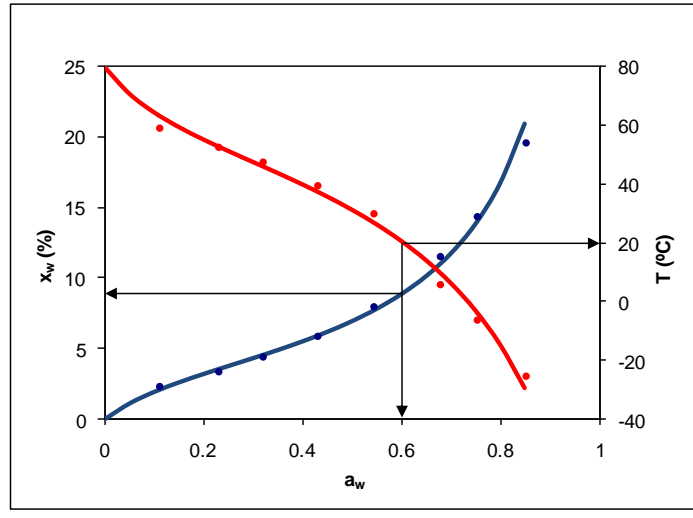
- 1 List of figures:
- 2 Figure 1. Water sorption isotherm of corn flakes, at 20 °C. Experimental points (·)
- 3 and GAB fitted model (-).
- 4
- 5 Figure 2. Water activity-moisture content-glass transition relationships for corn
- 6 flakes. Experimental points (·) and fitted models (-). Arrows show the critical water
- 7 content and water activity at 20 °C.
- 8
- 9 Figure 3. Mean values (and LSD intervals) of relative water vapor resistance (WVR_r)
- 10 for all the coated samples by the different methods.
- 11
- 12 Figure 4. Changes in pineapple and cereal weight throughout the storage time for
- 13 fruit samples coated with the different coating formulations by method I (a), method
- 14 II (b), method III (c) and method IV (d) and for control samples.
- 15
- 16 Figure 5. Changes in cereal water content throughout the storage time for fruit
- 17 samples coated with the different coating formulations by method I (a), method II
- 18 (b), method III (c) and method IV (d) and for control samples. The illustrated line
- 19 indicates the critical value of water content for cereals.

1 **Figure 1**



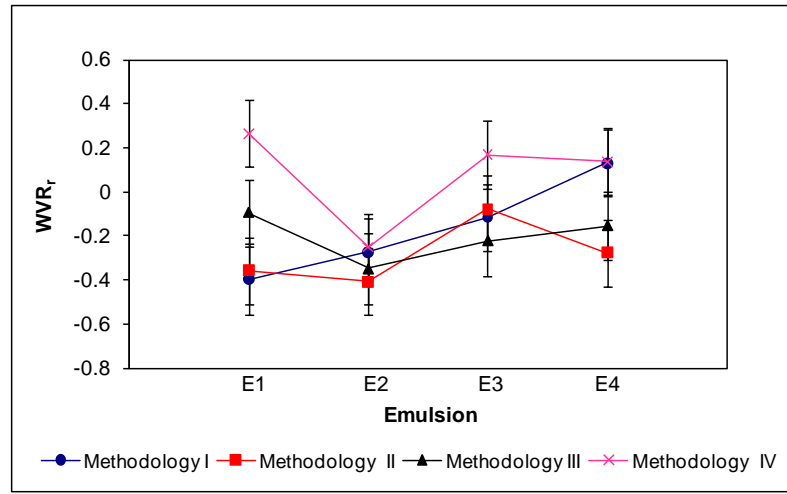
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1 Figure 2

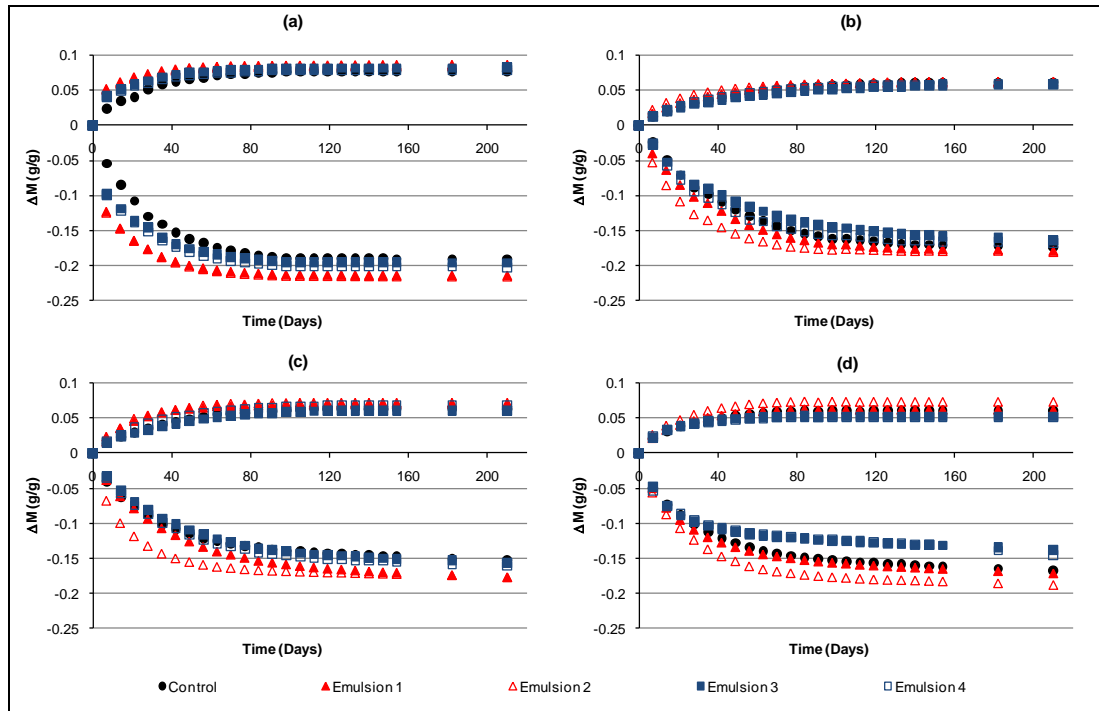


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1 **Figure 3**

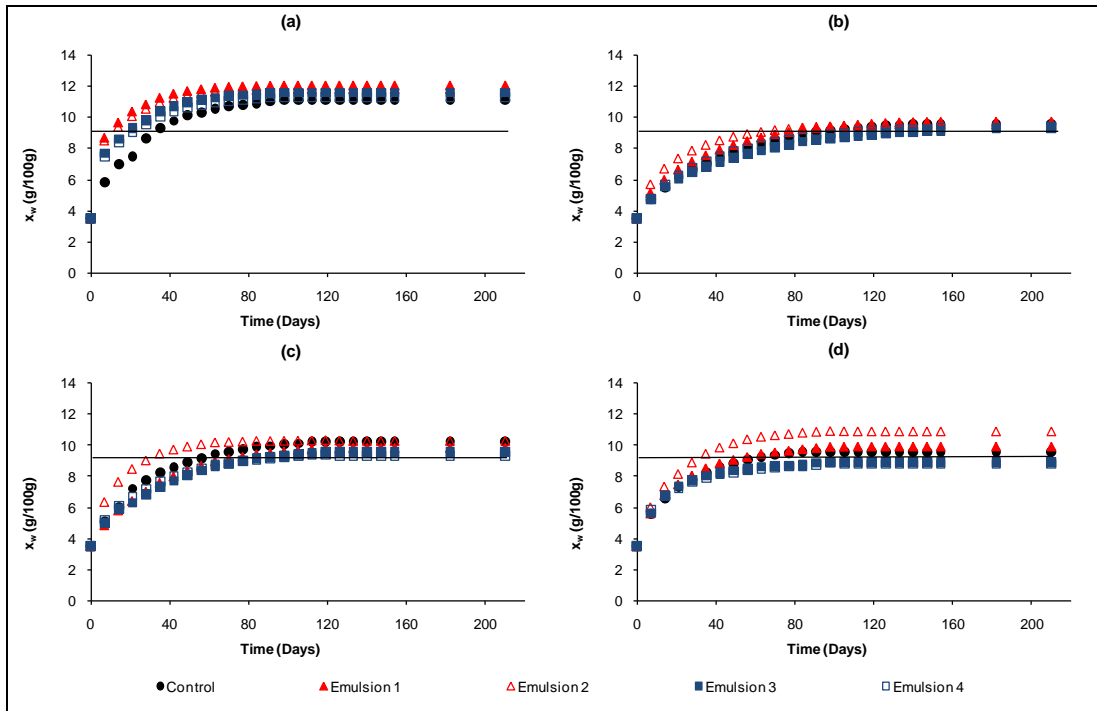


1 Figure 4
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3
4

1 Figure 5
2



3

1 **Table 1. Glass transition temperature for corn flakes with different moisture**
 2 **content and parameter values obtained for the GAB and Gordon y Taylor fitted**
 3 **models.**

Glass transition temperature for corn flakes								
Salt solution	LiCl	CH₃COOK	MgCl₂	K₂CO₃	Mg(NO₃)₂	CuCl₂	NaCl	KCl
Water activity	0.113	0.230	0.330	0.430	0.520	0.680	0.755	0.845
Moisture (g/gProduct)	0.023	0.034	0.044	0.059	0.079	0.116	0.144	0.196
Tg (°C)	58.9	52.6	47.6	39.6	29.8	5.6	-6.3	-25.6
Parameters of the GAB Model								
w₀ (g water/g dry solids)	C			K		r²		
0.044	6.146			0.987		0.949		
Parameters of the Gordon & Taylor Model								
Tg of anhydrous solids (°C)					K		r²	
79.6					3.916		0.991	

4

1 **Table 2. Values of water activity, mass fraction of water (x_w) and mass**
 2 **fraction of soluble solids (x_{ss}) of fresh and processed pineapple samples for the**
 3 **different batches used for each coating application method. Mean values and**
 4 **standard deviation (in brackets).**

	Application Method	a_w	x_{ss}	x_w
Raw Pineapple	I	0.985 (0.001)	0.142 (0.002)	0.835 (0.001)
	II	0.992 (0.001)	0.177 (0.001)	0.805 (0.004)
	III	0.990 (0.001)	0.131 (0.005)	0.852 (0.002)
	IV	0.980 (0.001)	0.164 (0.001)	0.827 (0.001)
After Osmotic dehydration process	I	0.877 (0.003)	0.629 (0.006)	0.360 (0.002)
	II	0.889 (0.001)	0.612 (0.003)	0.387 (0.001)
	III	0.875 (0.001)	0.604 (0.004)	0.361 (0.003)
	IV	0.884 (0.001)	0.601 (0.002)	0.338 (0.005)
After Air Dried process	I	0.749 (0.002)	0.805 (0.004)	0.172 (0.014)
	II	0.749 (0.004)	0.813 (0.006)	0.169 (0.017)
	III	0.762 (0.013)	0.812 (0.002)	0.171 (0.009)
	IV	0.749 (0.001)	0.795 (0.002)	0.202 (0.006)

5

1 **Table 3. Mass of film-forming dispersion adhered to pineapple samples after**
 2 **coating application, expressed as percentage with respect to the sample initial**
 3 **mass (M_{FA}/M_0), surface solid density (SSD), resistance to water vapour**
 4 **transmission (WVR) and viscosity of the coatings formulations.**
 5

Properties	Coating	Coating application method			
		I	II	III	IV
M_{FA}/M_0	E1	6.9 (1.4) ^{a,y}	5.8 (1.3) ^{a,y}	9.3 (0.9) ^{b,y}	5.8 (1.4) ^{a,y}
	E2	2.7 (0.4) ^{a,z}	2.1 (1.0) ^{a,z}	4 (2) ^{b,z}	3.4 (1.2) ^{b,z}
	E3	2.4 (1.4) ^{a,z}	1.3 (0.6) ^{b,z}	4.3 (0.7) ^{c,z}	2.9 (1.0) ^{a,z}
	E4	3.2 (1.5) ^{a,z}	1.1 (0.3) ^{b,z}	3.5 (0.6) ^{c,z}	3.2 (1.0) ^{c,z}
SSD (g/m ²)	E1	4.0 (0.4) ^{a,y}	4.2 (1.0) ^{a,x}	6.7 (1.0) ^{b,x}	4.7 (1.3) ^{a,y}
	E2	2.4 (0.4) ^{a,y}	1.8 (0.9) ^{a,y}	4 (2) ^{b,y}	3.8 (1.4) ^{b,y}
	E3	9 (4) ^{a,z}	6 (3) ^{a,z}	19 (2) ^{b,z}	15 (6) ^{b,z}
	E4	11 (2) ^{a,z}	6 (2) ^{b,z}	18 (2) ^{c,z}	17 (6) ^{c,z}
WVR (s/cm)	E1	43 (5) ^{a,y}	121 (31) ^{b,y}	131 (46) ^{b,x}	137 (42) ^{b,x}
	E2	51 (10) ^{a,z}	100 (20) ^{b,z}	138 (53) ^{b,x}	105 (18) ^{b,y}
	E3	62 (12) ^{a,z}	150 (25) ^{b,y}	164 (22) ^{b,y}	164 (33) ^{b,z}
	E4	80 (27) ^{a,z}	136 (44) ^{b,y}	185 (11) ^{b,z}	159 (19) ^{b,z}
Viscosity (100 s ⁻¹) Pa·s	E1	0.392 (0.005)			
	E2	0.141 (0.003)			
	E3	0.044 (0.007)			
	E4	0.020 (0.004)			

6 Mean values and standard deviation (in parenthesis). E1: Emulsion 1; E2: Emulsion 2; E3:
 7 Emulsion 3; E4: Emulsion 4. ^{a,b,c} Different letters in the same row imply 95% significant
 8 differences due to the method of coating application. ^{x,y,z} Different letters in the same column
 9 imply 95% significant differences among coatings.
 10

1 **Table 4. Values of parameters of Peleg's equation fitted to the weight loss data**
 2 **of uncoated and coated pineapple samples in contact with cereals.**

Application method	Coating	K2	K1	R2	Equilibrium values
I	Control	-4.7	-73.8	0.996	-0.211
	E1	-4.5	-24.6	1.000	-0.223
	E2	-4.5	-25.0	1.000	-0.224
	E3	-4.8	-41.3	0.999	-0.207
	E4	-4.7	-40.6	0.999	-0.214
II	Control	-4.6	-187.7	0.989	-0.219
	E1	-4.8	-127.9	0.996	-0.210
	E2	-5.1	-71.6	0.997	-0.197
	E3	-5.0	-196.3	0.997	-0.199
	E4	-5.0	-154.3	0.994	-0.200
III	Control	-5.9	-136.2	1.000	-0.171
	E1	-4.9	-148.9	0.999	-0.206
	E2	-5.4	-55.4	1.000	-0.186
	E3	-5.5	-174.8	0.999	-0.183
	E4	-5.4	-155.1	0.999	-0.186
IV	Control	-5.4	-113.9	1.000	-0.185
	E1	-5.3	-102.6	1.000	-0.187
	E2	-4.9	-79.6	0.999	-0.205
	E3	-6.9	-97.8	1.000	-0.145
	E4	-6.7	-115.1	0.995	-0.148

3