

Document downloaded from:

<http://hdl.handle.net/10251/77472>

This paper must be cited as:

Mosquera, L.H.; Moraga Ballesteros, G.; Fernández De Córdoba Castellá, P.J.; Martínez Navarrete, N. (2011). Water content-water activity-glass transition temperature relationships of spray-dried borjón as related to changes in color and mechanical properties. *Food Biophysics*. 6(3):397-406. doi:10.1007/s11483-011-9215-2.



The final publication is available at

<https://dx.doi.org/10.1007/s11483-011-9215-2>

Copyright Springer Verlag (Germany)

Additional Information

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44

**WATER CONTENT-WATER ACTIVITY-GLASS TRANSITION
TEMPERATURE RELATIONSHIPS OF SPRAY-DRIED BOROJÓ AS
RELATED TO CHANGES IN COLOR AND MECHANICAL PROPERTIES**

45 Luz Hicela Mosquera; Gemma Moraga; Pedro Fernández de Córdoba; Nuria Martínez-
46 Navarrete.

47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

ABSTRACT

49 The water content-water activity-glass transition temperature relationships of
50 commercial spray-dried borojó powder, with and without maltodextrin, have been
51 studied as related to changes in color and mechanical properties. The GAB and Gordon
52 and Taylor models were well fitted to the sorption and glass transition data,
53 respectively. The Boltzman equation adequately described the evolution of the
54 mechanical parameter characterized in the samples with the difference between the
55 experimental temperature and the glass transition temperature (T_g) of the sample. The
56 color of the samples showed a sigmoid change with water activity. The changes in the
57 mechanical properties of borojó powder related to collapse development started when
58 the sample moved to the rubbery state and began to be significant at about 10 °C above
59 T_g . The increase in the molecular mobility from this point on also favors browning
60 reactions. Maltodextrin presence slows the caking kinetics but induces color changes to
61 spray-dried borojó powder.

62
63
64
65

Key Words: powdered borojó, maltodextrin, sorption isotherms, glass transition, compression test, CIEL*a*b* coordinates.

66 INTRODUCTION

1
2 67 Borojó represents one of the major consumer products in the department of
3
4 68 Chocó (Colombia) and in much of South America, where the functional properties
5
6
7 69 conferred by the traditional use of the fruit has encouraged its introduction in some
8
9
10 70 international sectors. It is characterized by a high energy and nutritional capacity,
11
12 71 especially a high fiber content, as well as the supposed properties attributed by the
13
14 72 indigenous and black groups in the region who use it as medicine, to embalm cadavers
15
16
17 73 and to prepare aphrodisiacal beverages. Current developments focus on the
18
19 74 commercialization of borojó as energy drinks, jellies or jams, as the appearance and
20
21
22 75 weight of the fruit (700 - 1000 g) make it difficult to distribute as a fresh product,
23
24 76 besides its pulp is quite acid and viscous¹. Extracts and juices obtained from plants and
25
26
27 77 fruits are used more and more in both the pharmaceutical and the food industry for the
28
29 78 manufacture of a large number of products. On the other hand, freeze-drying and spray-
30
31
32 79 drying are used to obtain products in powdered form, which highly preserve the
33
34 80 majority of the natural components present in the fresh products. Nevertheless, the
35
36
37 81 presence of compounds such as sugars makes it difficult to dry these products by spray
38
39 82 due to their adherence to the inner surfaces of the equipment, which leads to a poor
40
41 83 performance when obtaining the final product². The use of inert additives such as starch,
42
43
44 84 cyclodextrin, lactose or maltodextrin favors the product recovery, acting as interveners
45
46 85 of the drying³.

47
48
49 86 The deteriorative phenomenon that occurs most frequently in the powdered
50
51
52 87 products has been associated with the transition from a glassy to rubbery state. In these
53
54 88 products, when a critical temperature, related to the glass transition temperature, is
55
56
57 89 reached, a sequence of deleterious events occur⁴. Initially, stickiness is developed due to
58
59 90 the formation of an incipient liquid state of lower viscosity on the particle surface. The
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

91 caking of sticky powders takes place because of interparticle bridging, eventually
92 forming agglomerations⁵. The extension of this phenomenon in the matrix leads to
93 structure collapse. To prevent the occurrence of this undesirable phenomenon, it is
94 important to keep the amorphous matrix in a glassy state⁴. The glass transition
95 temperature (T_g) of an amorphous matrix defines the temperature at which the
96 glassy/rubbery change occurs and depends on its water content; the greater the water
97 content, the lower the T_g . For this reason, during the processing, handling, storage and
98 distribution, powdered products may experience a deteriorative evolution due to
99 changes in temperature and environmental relative humidity. An increase in the product
100 temperature above the T_g will lead it to the unstable rubbery state. On the other hand, an
101 increase in the environmental relative humidity surrounding the powder of over 100
102 times its water activity will lead to the hydration of the powder, thus decreasing its T_g .
103 If the T_g falls below the storage temperature, the product will again change into the
104 rubbery state. The relationship between the water activity and the water content is given
105 by the water sorption isotherm. Structural changes caused by powder collapse, together
106 with the water content, may affect some physical properties such as color or mechanical
107 behavior⁶⁻⁷. From this point of view, it is important to maintain the glassy state in these
108 products.

109 The solid composition also affects the T_g , the greater the average molecular
110 weight, the greater the T_g . The carbohydrates present in fruits are normally low
111 molecular weight sugars, thus implying low T_g values in this kind of foods. For this
112 reason, high molecular weight solutes are usually added to fruit prior to spray-drying, to
113 improve not only the drying process but also the product stability of the obtained
114 powder. The effect of adding a solute will depend on the amount used and its average
115 molecular weight as related to that of the solids present in the fruit.

116 This work focused on studying the effect water uptake had on the stability of
117 spray-dried borojó, with and without added maltodextrin, related both to glass transition
118 and to changes in the mechanical properties and color.

119

120 MATERIAL AND METHODS

121 1. Sorption isotherms and glass transition.

122 The commercial products *Boroj3 Powder, Spray Dried* (B) and *Boroj3 Powder,*
123 *Spray Dried (Maltodextrin)* (BM) were acquired from Ecoflora Ltda. (Medell3n,
124 Colombia). B and BM water content was 0.044 and 0.043 g water/100g product,
125 respectively and water activity was 0.315 and 0.312, respectively.

126 For sorption experiments, both B and BM spray-dried powder samples were
127 placed at 20°C in hermetic chambers containing saturated salt solutions (LiCl,
128 CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, CuCl₂, NaCl₂ and KCl₂). Three replicates of
129 about 2 g each were placed in each chamber with different relative humidities (RH)
130 ranging between 11- 85 %⁸. The sample weights were controlled till a constant value
131 ($\Delta m < \pm 0.0005$ g) was reached, where the equilibrium between the sample and the
132 environment was assumed⁹. In this moment, the a_w of each sample was assumed to be
133 equal to the corresponding RH/100. In each equilibrated sample, the final water content
134 was obtained from both the initial water content data and the change in the registered
135 weight till the equilibrium. The initial water content of the samples was determined
136 from the loss of mass when drying the samples at 60 ± 1 °C under a pressure of < 100
137 mm Hg until constant weight. Water content (dry basis) and a_w values were used in
138 order to construct the sorption isotherms. Calorimetric analyses were carried out in each
139 equilibrated sample in order to determine the glass transition temperature (T_g) by means

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

140 of differential scanning calorimetry (DSC). About 10 mg of each sample were placed
141 into DSC pans (P/N SSC000C008, Seiko Instruments, Inc., Japan), sealed and analyzed
142 using a DSC 220CU-SSC5200 (Seiko instruments, Inc., Japan). The heating rate was 5
143 °C/min and the temperature range varied between -100 and 200°C, depending on the
144 sample water content and the kind of sample. The mid-point of the glass transition was
145 considered as the characteristic temperature of the transition.

146

147 **2. Mechanical properties and color analyses**

148

149 Different samples of about 1 g of B and BM were placed in cylindrical vials and
150 stored in hermetic chambers at relative humidities of between 23 % and 85 %, following
151 the same procedure described for sorption experiments. Every 3 days, for a period of 4
152 weeks, a vial of B and BM was weighed and its water content, mechanical properties
153 and color analyzed. The water content was calculated from the initial moisture content
154 and the sample mass change. For the analysis of the physical properties, the powder was
155 placed in a circular aluminum sample holder of 11 mm in diameter and 5.5 mm in
156 height. A reflectance glass (CR-A51, Minolta Camera, Japan) was placed between the
157 sample and the spectrophotometer lens (Colorimeter Minolta mod. CM-3600d, Japan.).
158 The measurement window was 6 mm in diameter and D65 illuminant/10° observer were
159 selected to obtain CIE L*a*b* color co-ordinates. After color measurement, a
160 mechanical compression test with a cylindrical probe of 10 mm in diameter was carried
161 out using a texture analyzer TA-XT Plus (Stable micro Systems, Ltd., UK). The sample
162 was compressed at a fixed distance of 3 mm at a constant rate of 0.05 mm/s. The

163 maximum force attained during the test was recorded as Fmax. Each color and
164 mechanical property measurement was carried out in quadruplicate.

165

166 3. Fitted models and statistical comparison of the different experimental series

167

168 In order to predict the water sorption behavior of samples, the GAB
169 (Guggenheim, Anderson and de Boer)¹⁰ model (Eq. 1) was used.

170

$$171 \quad w_e = \frac{w_o \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 + (C - 1) \cdot K \cdot a_w)} \quad \text{Eq. 1}$$

172 where:

173 w_e : water content (g water/ g solids).

174 a_w : water activity.

175 w_o : monolayer water content (g water/ g solids).

176 C: constant related to monolayer sorption heat.

177 K: constant related to multilayer sorption heat.

178

179 Experimental T_g (mid-point)–water content (g water/g product) data were fitted
180 to the Gordon and Taylor model¹¹, (Eq. 2).

181

$$182 \quad T_g = \frac{(1 - x_w) \cdot T_{g(as)} + k \cdot x_w \cdot T_{g(w)}}{(1 - x_w) + k \cdot x_w} \quad \text{Eq. 2}$$

183 where:

184 x_w : mass fraction of water (g water/ g product).

185 T_g : glass transition temperature (°C).

186 $T_{g(w)}$: glass transition temperature for amorphous water: -135 °C⁴.

187 $T_{g(as)}$: glass transition temperature for anhydrous solids (°C).

188 k: model constant.

189

190 The Boltzman function was fitted to correlate the sigmoid behavior described by
191 the mechanical parameter of samples with a different water content, referred to the
192 sample mass, (Fmax/m) as a function of its glass transition temperature (Eq. 3). In this
193 equation, F1 and F2 are the values of Fmax/m at the initial (upper) and final (lower)
194 asymptotes, respectively, λ_F is a parameter that describes the shape of the curve between
195 the upper and lower asymptotes, and ΔT_F is the value of T-T_g at which Fmax/m attains
196 the average value between F1 and F2¹².

197

$$198 \quad F \text{ max/ } m = \frac{F1 - F2}{1 + e^{(\Delta T - \Delta T_F) / \lambda_F}} + F2 \quad \text{Eq. 3.}$$

199

200 To evaluate the differences between sample behavior (a_w or T_g changes with x_w
201 and Fmax/m with ΔT_F) as a function of the presence of maltodextrin (MD), the models
202 were fitted to each individual data series (B and BM) and to all the grouped data (B +
203 BM). The obtained results were statistically compared through the values of statistic E

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

204 (Eq. 4) which was compared with tabulated F-Snedecor as a function of the values of
205 DFDR and SFDR_i at 99% significance level¹³.

206

$$E = \frac{(RSS_g - \sum_{i=1}^n RSS_i) / DFDR}{\sum_{i=1}^n RSS_i / \sum_{i=1}^n FDR_i}$$

207

Eq. 4

208 where:

209 RSS_g: residual square sum of the function fitted to a group of series.

210 RSS_i: residual square sum of the function fitted to an individual series.

211 FDR_g: freedom degrees of the residuals of the function fitted to a group of series.

212 FDR_i: freedom degrees of the residuals of the function fitted to an individual series.

213 DFDR: difference between freedom degrees of the residuals of the function fitted to a
214 group of series (FDR_g) and the sum of freedom degrees of the residuals of the
215 individual fittings of the series involved in the group ($\sum FDR_i$),

216

217 **RESULTS AND DISCUSSION**

218 **1. Sorption isotherms and plasticizer effect of the water.**

219 Wall depositions of sticky products are a frequent problem during the spray-
220 drying of fruit juices, as the low molecular weight of the sugars present prevents
221 products from being obtained with a water content of under 5 %. The convenience of
222 adding maltodextrin to decrease the higroscopicity of fruit powders, thus improving the
223 handling during spray-drying, has been widely studied. Moreover, the high T_g value of
224 maltodextrins provides a good stability in powdered products^{14, 15}.

225 Figure 1 shows the sorption isotherm of B and BM. Experimental sorption data
226 were well fitted to the GAB model (table 1). On the other hand, the decrease in the T_g
227 observed when increasing the water content of the samples (figure 2) was fitted to the
228 Gordon and Taylor model (table 1). A non-linear fitting procedure (CHI^2)¹⁶ using
229 OriginPro 6.1 software was applied. Both models were fitted individually to the B and
230 BM samples and to all the B+BM data. The statistical analysis performed by means of
231 the Snedecor test showed no significant differences either between the sorption behavior
232 of B and BM or in $T_g - x_w$ relationships (table 2), which suggests that adding
233 maltodextrin has no effect. The parameters of these models fitted to all the grouped data
234 appear in table 1.

235 The fact that this study found that maltodextrin had no significant effect on
236 water sorption and T_g do not coincide with what has been found when working on other
237 fruits, such as pineapple, camu camu or grapefruit^{17,18,12} and even freeze-dried borojó.
238 This may be related to the different soluble solid composition of borojó as compared to
239 the other fruits and also to the amount of maltodextrin added to our product. Mosquera
240 et al.¹ have pointed to the high carbohydrate content of borojó (about 30 g / 100 g
241 borojó). Fructose, glucose and sucrose account for a very small fraction of these
242 carbohydrates (7.3 g / 100 g borojó), so the rest may be attributed to high molecular
243 weight carbohydrates, bearing in mind the total analyzed dietary fiber (23.58 g / 100 g
244 borojó) and pectin (2.62 g / 100 g borojó) content. Carbohydrates in pineapple and
245 grapefruit represent about 10 % of the fruit weight, being almost all of them sugars.
246 From this point of view, the average molecular weight of the solids present in borojó is
247 much greater and so its adsorption capacity is lower and its T_g is higher. So a greater
248 amount of maltodextrin will be needed to affect these aspects. Silva et. al.¹⁸ noted that
249 the addition of 0.88 kg of maltodextrin (20 DE) / 1 kg of total solids can reduce the

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

250 moisture content in freeze-dried camu camu pulp from 15.8 % to 6.5 % (dry basis) and
251 increase the T_g . A similar effect was observed by Gabas et al.¹⁷ and Telis & Martínez-
252 Navarrete¹² studying freeze-dried powdered pineapple pulp and freeze-dried grapefruit
253 when adding 0.2 and 1kg of maltodextrin / kg of total solids, respectively.

254 Mosquera et al.¹ also suggested the use of 0.55 kg of maltodextrin (16.5 - 19.5
255 DE) or arabic gum for each kg of total solids in freeze-dried borojó to significantly
256 affect the sorption behavior and T_g , although this effect was not so noticeable as in the
257 other fruit powders with high amount of low molecular weight carbohydrates. In our
258 study, as no effect of MD on water sorption and T_g of borojó was observed, the amount
259 of maltodextrin added to the fruit (not specified on the label) must be supposed to be
260 lower than 0.55 kg maltodextrin / kg total solids in the sample and not enough to reduce
261 the hygroscopicity of the powder and to increase the glass transition temperature. On
262 the other hand, in the mentioned study of Mosquera et al.¹, the critical water content
263 (CWC) for the glass transition of freeze-dried borojó at 20 °C was increased from 0.059
264 to 0.085 when maltodextrin was added, which significantly improves the handling of
265 the powder. In our work, when considering the information of B and BM samples
266 together, the combined analysis of water sorption and T_g data, allowed us to obtain the
267 T_g - a_w - x_w relationships (figure 3). From this analysis, CWC and critical water activity
268 (CWA) for the glass transition at 20 °C were determined, these being 0.046 g water /g
269 product and 0.319, respectively. As deduced from this value and the measured water
270 content in newly spray-dried borojó products used as raw matter in the study (see
271 Material and methods section), both of them were in a glassy state at this temperature,
272 although very near to the critical values. The greater CWC of freeze-dried borojó as
273 compared to that of spray-dried borojó may be related to the different structure of the
274 obtained products. As referred by Haque and Roos¹⁹, spray-dried particles are spherical

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

275 and of low porosity, while freeze-dried particles appear as porous flakes with a greater
276 surface area available for water adsorption. Therefore a spray-dried material may have
277 less hydrogen-bonding sites available for water molecules in sorption than freeze dried
278 materials. In our case, sorption and T_g behavior of freeze-dried and spray-dried borjón
279 powder seems to be different. The lower stability of the powders obtained by spray-
280 drying would recommend a greater amount of high molecular weight solute to be added
281 to them as compared to freeze-dried products.

282

283 **2. Mechanical properties and color**

284 As referred to in the introduction section, the collapse of food powders includes
285 time dependent structural changes related to four stages: bridging, agglomeration,
286 compaction and liquefaction²⁰. Caking and/or stickiness of powdered products
287 developed during this process occur as a result of the viscous flow caused in the product
288 at over T_g and it lead changes in the mechanical properties²¹. The rate of caking is a
289 function of T_g , relative humidity and time. Relative humidities that allow the product to
290 be maintained in a glassy state at storage temperature do not provoke caking, while a
291 RH that implies a decrease of T_g to below the storage temperature does lead to caking;
292 the higher the RH, the faster the observed changes⁵. When a system is above its T_g , the
293 kinetics of caking and related phenomena, such as collapse and stickiness, vary as $10^{\Delta T}$,
294 where $\Delta T = T - T_g$ ^{20,22}.

295 The analysis of the shape of the curve force-distance and the maximum force
296 attained during the mechanical compression test used in this study have been proposed
297 by Telis and Martínez-Navarrete⁷ as a simple, rapid method, sensitive enough to
298 quantify the effect of water uptake on the mechanical properties of food powders that

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

299 may be related to the development of stickiness. Figure 4 shows the maximum force
300 evaluated in the compression test carried out on borjón samples at different RH and
301 storage times. In this figure, some of the force-distance curves obtained during the test
302 have also been included. The analysis of these curves allowed us to detect changes in
303 the mechanical properties which seem to be related to the caking process that
304 characterizes the beginning of the collapse.

305 Force-distance curves obtained in both newly processed B and BM samples and
306 those stored at RH lower than 43%, showed fracture peaks during the entire period
307 under study as corresponds to a free flowing powder, with no caking problems and easy
308 to compact. The ratio of the maximum force attained during the compression test to the
309 sample weight (F_{max}/m) on newly processed samples was not affected by maltodextrin
310 addition and they underwent no noticeable change as a consequence of storage time
311 when stored at RH 23 and 33 %. Samples stored at RH of over 52% did not show these
312 fracture peaks at any time, as occurs when the caking process is fully developed; the
313 greater the water content, the lower the force needed to compact the liquefied sample. In
314 B and BM samples stored at RH 68, 75 and 85 %, a sharp decrease in F_{max}/m was
315 observed from the third storage day onwards. Force-distance curves obtained in BM
316 samples stored at 43% RH showed fracture peaks for up to 14 days, while BM samples
317 stored at 52% RH only showed them for up to 3 days. However, B samples under the
318 same storage conditions did not show any fracture peak during the entire storage period
319 under consideration. The differences observed between these samples could be
320 associated with a protective effect of maltodextrin that slows the caking kinetic in BM
321 samples. Caking phenomena started in B samples stored at 43 and 52% RH before 3
322 storage days, and progresses at a slower rate than samples stored at RH 68 %, while BM
323 samples needed more time. The caking process starts with the formation of inter-particle

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

324 bridges over a certain amount of water which implies an increase of the force needed to
325 compact the sample²³. For this reason, there was an observed increase in F_{max}/m for
326 BM samples stored at 43% and 52% RH, not shown for B samples, at the beginning of
327 the storage period when compared to samples stored at 23 and 32% RH. At the end of
328 the storage period, caking was fully developed and the trend of F_{max}/m was in line with
329 the rest of the BM samples.

330 From the water content calculated for each sample at each storage time, a_w and
331 T_g were predicted by applying the GAB and Gordon and Taylor fitted models,
332 respectively. The change of the mechanical parameter evaluated with a_w and with the
333 difference between the temperature at which the mechanical analysis was carried out
334 and the glass transition temperature of the sample ($\Delta T = T - T_g$) appears in figures 5 and
335 6, respectively. A similar trend, sigmoid in behavior, was observed in both cases. At an
336 a_w greater than CWA, which means the samples are in the rubbery state ($\Delta T > 0$), a sharp
337 decrease in F_{max}/m was observed, related with a softening of the samples in this
338 physical state. The Boltzman equation was fitted to F_{max}/m vs. ΔT (OriginPro 6.1
339 software) separately for samples with and without maltodextrin and to all the grouped
340 data (table 1). As no significant differences were observed between the fittings (table 2),
341 no effect of MD on the mechanical properties of borj6 powder can be assumed as
342 related to glass transition temperature This was expected, since the presence of MD had
343 no observed effect on T_g . In this way, figure 6 shows the trend of the predicted behavior
344 by using the corresponding model parameters. From the fitted parameters, it was
345 possible to determine that 20% of the transition between the upper and lower
346 asymptotes occurred at a value of $\Delta T = 12.19$ °C, whereas 80% of the transition was
347 attained at $\Delta T = 36.12$ °C. As suggested by Foster et al.²⁴, this result allows us to
348 conclude that important changes in the mechanical properties of borj6 powder related

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

349 to collapse development occur at about 10 °C above T_g. The magnitude of the
350 temperature differences obtained in this study coincides with the results obtained by
351 Foster et al.²⁴, when studying the cohesiveness of different freeze-dried sugar powders.
352 The T_g of samples that led to a ΔT equal to 12.19 and 36.12 °C were 7.81 and -16.12 °C
353 and the corresponding a_w were 0.445 and 0.631.

354 For color measurement, CIEL*a*b* system coordinates was selected. In this
355 system, L* denotes lightness on a 0 to 100 scale from black to white; a*, (+) red or (-)
356 green; and b* (+) yellow or (-) blue. The total color difference (ΔE*) with respect to the
357 newly spray-dried borjón was obtained (Eq. 5).

358

$$359 \quad \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \text{Eq. 5}$$

360

361 Figure 7 shows the L*a*b* values for samples, with and without maltodextrin,
362 in the range of the studied relative humidity during the storage time. Color coordinates
363 of samples remained more or less stable over time when stored at relative humidities
364 lower than 43-52 %. From this value, L* and b* decreased and a* increased over time;
365 the greater the RH surrounding the sample, the greater the observed change. When the
366 data were plotted vs. a_w (figure 8), the addition of maltodextrin was observed to have an
367 effect. This involved an increase in L* and b* and a decrease in a*, related to an
368 increase in the lightness of the product and in the hue angle due to the development of
369 yellowness. In both samples, as the water activity increased, lightness and b*
370 coordinates decreased and a* increased, in a sigmoid way. The abrupt change of the
371 coordinates was observed when the a_w was in the range of 0.5 to 0.6 and it provoked a

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

372 darkness in the samples and an important change in the hue angle and chrome that
373 turned the samples browner. The afore mentioned a_w range was near to that established
374 when 20-80% of the change in the mechanical properties with ΔT was calculated,
375 indicating that the decrease in the viscosity which takes place at about ten degrees above
376 the glass transition favors color changes. These color changes may be attributed to
377 optimum conditions for enzymatic and non-enzymatic browning reactions. Some
378 authors have pointed out that both kinds of reactions occur mainly at intermediate water
379 activities²⁵⁻²⁸. The Maillard, or non-enzymatic browning reaction, is most likely to occur
380 in low-moisture systems (a_w 0.3-0.7), as the removal of water allows the solid content to
381 be concentrated and, hence, leads to an increase in the interactions between the reducing
382 sugars and amino acids in the fruit. On the other hand, water activity values of 0.430
383 have been pointed out as the limit above which the rate of food enzymatic browning
384 rises. Nevertheless, water dilution that takes place at water activity values which are too
385 high may prevent these processes.

386 The color difference with respect to newly spray-dried borojó was calculated at
387 each storage period and RH (Figure 9). As can be observed, three groups of samples can
388 be identified. The first one, with color differences lower than about six units ($\Delta E < 6$),
389 appeared at a_w values lower than 0.5. The second one was found in the range of a_w from
390 0.5 to 0.7, where a sharp increase in ΔE values from approximately 5 to 22 was observed.
391 From this water activity onwards, ΔE remained stable. Color changes that occur in
392 borojó at a_w values lower than 0.5 could be more related with the development of
393 Maillard reactions, while those which take place from a_w 0.5 could be more closely
394 related to enzymatic browning. The presence of maltodextrin does not prevent browning
395 reactions.

396

397 **CONCLUSIONS**

398 The critical water content and critical water activity for the glass transition of
399 borojó at 20 °C was 0.046 g water/g product and 0.319, respectively. The water content
400 of the newly spray-dried borojó powders used in this study were in the range of this
401 CWC, so the use of high molecular weight solutes should be recommended to increase
402 the T_g of the product and, therefore, its stability. Nevertheless, the amount of solute
403 added must be optimized by taking both the product composition and the process used
404 to obtain the powder into account. Otherwise, no significant effect could be detected, as
405 occurred in this study. Changes in the mechanical properties of borojó powder related to
406 collapse development started when the sample moved to the rubbery state and began to
407 be significant at about 10 °C above T_g . The increase in the molecular mobility from this
408 point on also favors browning reactions. Maltodextrin presence slows the caking
409 kinetics but induces color changes to spray-dried borojó powder.

410

411 **References**

- 412 1. L.H. Mosquera, G. Moraga, N. Martínez-Navarrete, J. Food Eng. 9, 72 (2010).
413 doi: 10.1016/j.jfoodeng.2009.09.017
- 414 2. V. Truong, B. R. Bhandari, T. Howe, J. Food Eng. 71, 55 (2005). doi:
415 10.1016/j.jfoodeng.2004.10.017
- 416 3. B. Bhandari. *Glass transition in relation to stickiness during spray drying*
417 (Academic press, Sterling Publication, London, 2001), pp 64
- 418 4. Y. Roos. *Phase transitions in foods* (Academic Press, New York, 1995), pp. 360.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

419 5. P. Saragoni, J.M. Aguilera, P. Bouchon, *Food Chem.* 104, 122 (2007). doi:
420 10.1016/j.foodchem.2007.11.066

421 6. C.K. Pua, N. Sheikh Abd. Hamid, C.P. Tanm, H. Mirhosseini, R. Abd. Rahman,
422 G. Rusul, *J. Food Eng.* 89, 419 (2008). doi: 10.1016/j.jfoodeng.2008.05.023

423 7. V.R.N. Telis, N. Martínez-Navarrete, *LWT – Food. Sci. Technol.* 43, 744 (2010).
424 doi:10.1016/j.lwt.2009.12.007

425 8. L. Greenspan, *J. Res. Nat. Inst. Stan.* 81, 89 (1977). IDS: DM875

426 9. W.E.L. Spiess, W.R. Wolf, ed. by F. Escher, B. Hallstrom, H.S. Mefert, W.E.L.
427 Spiess, G. Woss. *Physical Properties of foods* (Applied Sci. Publisher, New York, 1983),
428 p. 65

429 10. C. Van den Berg, S. Bruin, ed. by L.B. Rockland, G.T. Stewart. *Water Activity*
430 *and its Estimation in Food Systems: Theoretical Aspects* (Academic Press, London/New
431 York, 1981), p. 43

432 11. M. Gordon, J.S. Taylor, *J. Appl. Chem.* 2, 493 (1952).
433 doi:10.1002/jctb.5010020901G

434 12. V.R.N. Telis, N. Martínez-Navarrete, *Food Biophysics.* 4, 83 (2009) doi:
435 10.1007/s11483-003-9104-0

436 13. G. Moraga, N. Martínez-Navarrete, A. Chiralt, *J. Food Eng.* 62, 315 (2004). doi:
437 10.1016/S0260-8774(03)00245-0

438 14. C.I. Beristain, E. Azuara, E.J. Vernon-Carter, *J. Food Sci.* 67, 211.2002. IDS:
439 522JP

440 15. B.R. Bandhari, R.W. Hartel, ed. by . C. Onwulata, R.P. Konstance. *Encapsulated*
441 *and food powder.* (Marcel Dekker, New York, 2005), p. 216

442 16. N. William, *Estadística para Ingenieros y Científicos* (MacGraw-Hill, Mex.,
443 2006), pp 120

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- 444 17. A.L. Gabas, V.R.N. Telis., P.J.A. Sobral, J. Telis-Romero, J. Food. Eng. 82, 246
445 (2007). doi: 10.1016/j.jfoodeng.2007.02.029
- 446 18. M.A. Silva, P.J.A. Sobral, T.G. Kieckbusch, J. Food. Eng. 77, 426 (2006). doi:
447 10.1016/j.jfoodeng.2005.07.009
- 448 19. Md. K. Haque, Y. H. Ross, Innovative Food Science & Emergin Technologies.
449 7,1-2,(2006) doi:10.1016/j.ifset.2004.12.004
- 450 20. J.M. Aguilera, J.M. del Valle., M. Karel, Trends Food Sci. Technol. 8, 149
451 (1995). doi:10.1016/S0924-2244(00)89023
- 452 21. H. Levine, L. Slade, Cryoletters 9, 21 (1988) IDS: M1923
- 453 22. Y.H. Ross, J. Food Eng. 24, 339 (1995b) doi:10.1016/0260-8774(95)90050-L
- 454 23. G. Barbosa-Canovas, E. Ortega-Rivas, P. Juliano, & H. Yan. (2005). *Food*
455 *powders: physical properties, processing and functionality*. (Kluwer Academic/Plenum
456 Publisher New York, N.Y) p.372
- 457 24. K.D. Foster, J.E. Bronlund., A.H.J. Paterson, J. Food Eng. 77, 997 (2006). doi:
458 10.1016/j.jfoodeng.2005.08.028
- 459 25. E. Venir, M. Munari, A. Tonizzo, E. J. Maltini, Food Eng. 81, 27 (2007) doi:
460 10.1016/j.jfoodeng.2006.10.004
- 461 26. N. C. Acevedo, C. Schebor., P. Buera, J. Food Eng. 77, 1108 (2006). doi:
462 10.1016/j.jfoodeng.2005.08.045
- 463 27. N. C. Acevedo, C. Schebor., P. Buera, Food Chem. 108, 900 (2008). doi:
464 10.1016/j.foodchem.2007.11.057Ahmed, U.S. Shivhareb, P. Singhc, Food Chem. 84,
465 605 (2004). doi: 10.1016/S0308-8146(03)00285-1
- 466 28. L. Hang-Ing Ling, J. Birch, M. Lim, Int. J. Food. Sci. Tech. 40, 921 (2005).
467 doi:10.1111/j.1365-2621.2005.00996

Legends

1
2
3 Fig.1. Amount of water adsorbed (g water/g dry solids) in function of water activity of Boroj3
4 Powder, Spray Dried (solid line) and Boroj3 Powder, Spray Dried (Maltodextrin) (dashed line)
5 products (experimental points, \circ and \bullet , respectively, and predicted behavior by GAB fitted
6 model).
7
8
9

10
11
12 Fig.2. Glass transition temperature (T_g) in function of water content of Boroj3 Powder, Spray
13 Dried (solid line) and Boroj3 Powder, Spray Dried (Maltodextrin) (dashed line) products
14 (experimental points, \circ and \bullet , respectively, and predicted behavior by Gordon and Taylor
15 fitted model).
16
17
18
19
20

21
22
23
24
25 Fig.3. Glass transition temperature (T_g) – water activity (a_w) (\blacksquare) and water content (x_w : g
26 water/g product)– water activity (\square), relationships of Boroj3 Powder, Spray Dried and Boroj3
27 Powder, Spray Dried (Maltodextrin) products (experimental points and predicted behavior by
28 GAB and Gordon and Taylor model fitted to all the experimental data together).
29
30
31
32
33
34
35
36
37

38 Fig.4. Maximum force attained per mass unit in the compression test carried out at different
39 relative humidity and storage time of (a) Boroj3 Powder, Spray Dried and (b) Boroj3 Powder,
40 Spray Dried (Maltodextrin) products.
41
42
43
44
45
46
47
48

49 Fig.5 Change in the maximum force attained per mass unit in the compression test carried out as
50 a function of a_w in Boroj3 Powder, Spray Dried (\circ) and Boroj3 Powder, Spray Dried
51 (Maltodextrin) (\bullet) products. The line indicates the critical water activity.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Fig.6. Change in the maximum force attained per mass unit in the compression test carried out in Boroj3 Powder, Spray Dried and Boroj3 Powder, Spray Dried (Maltodextrin) products, as a function of $T-T_g$. Experimental points (\circ and \bullet , respectively) and predicted behavior by the fitted Boltzman equation to all the experimental data together.

Fig.7. $L^*a^*b^*$ color coordinates of (a) Boroj3 Powder, Spray Dried (Maltodextrin) and (b) Boroj3 Powder, Spray Dried products, at different relative humidity and storage time.

Fig.8. $L^*a^*b^*$ color coordinates of Boroj3 Powder, Spray Dried (\circ) and Boroj3 Powder, Spray Dried (Maltodextrin) (\bullet) products, as a function of water activity.

Fig.9. Color difference of Boroj3 Powder, Spray Dried (\circ) and Boroj3 Powder, Spray Dried (Maltodextrin) (\bullet) products, stored at every relative humidity with respect to newly spray-dried boroj3.

Figure 1

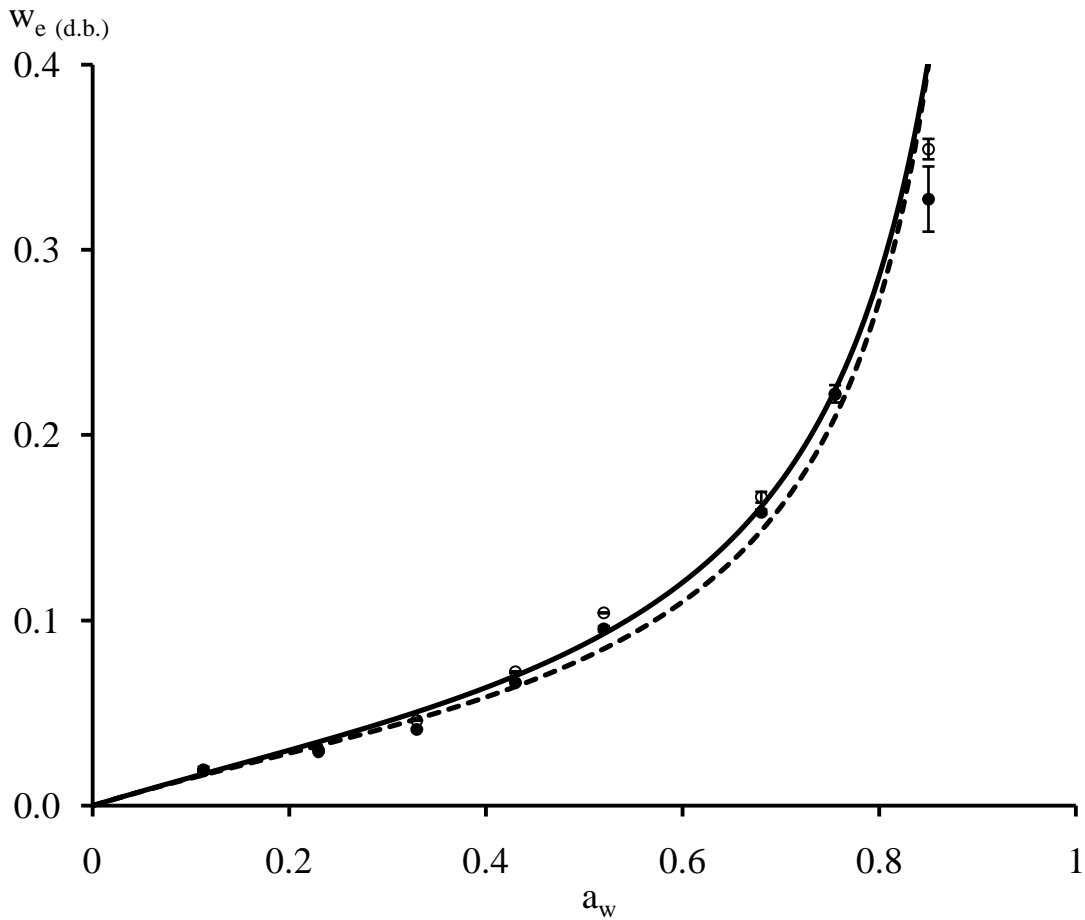


Figure 2
 T_g ($^{\circ}\text{C}$)

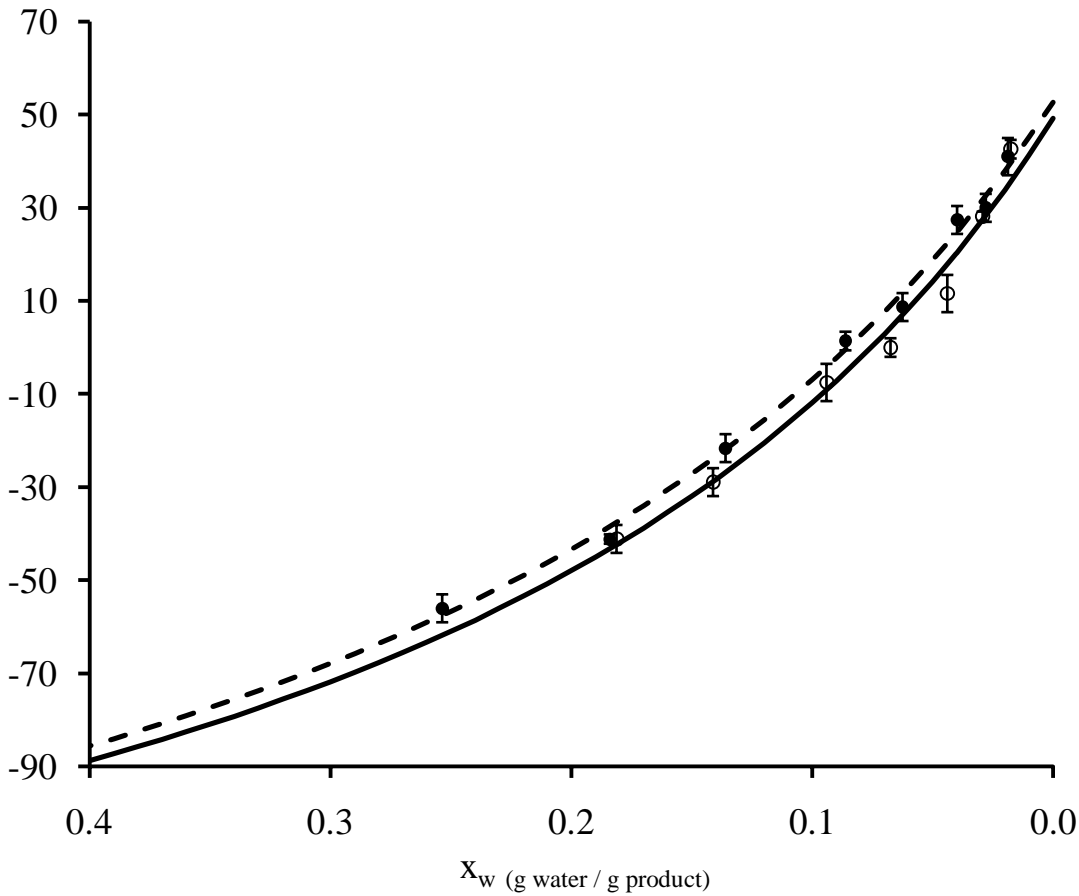


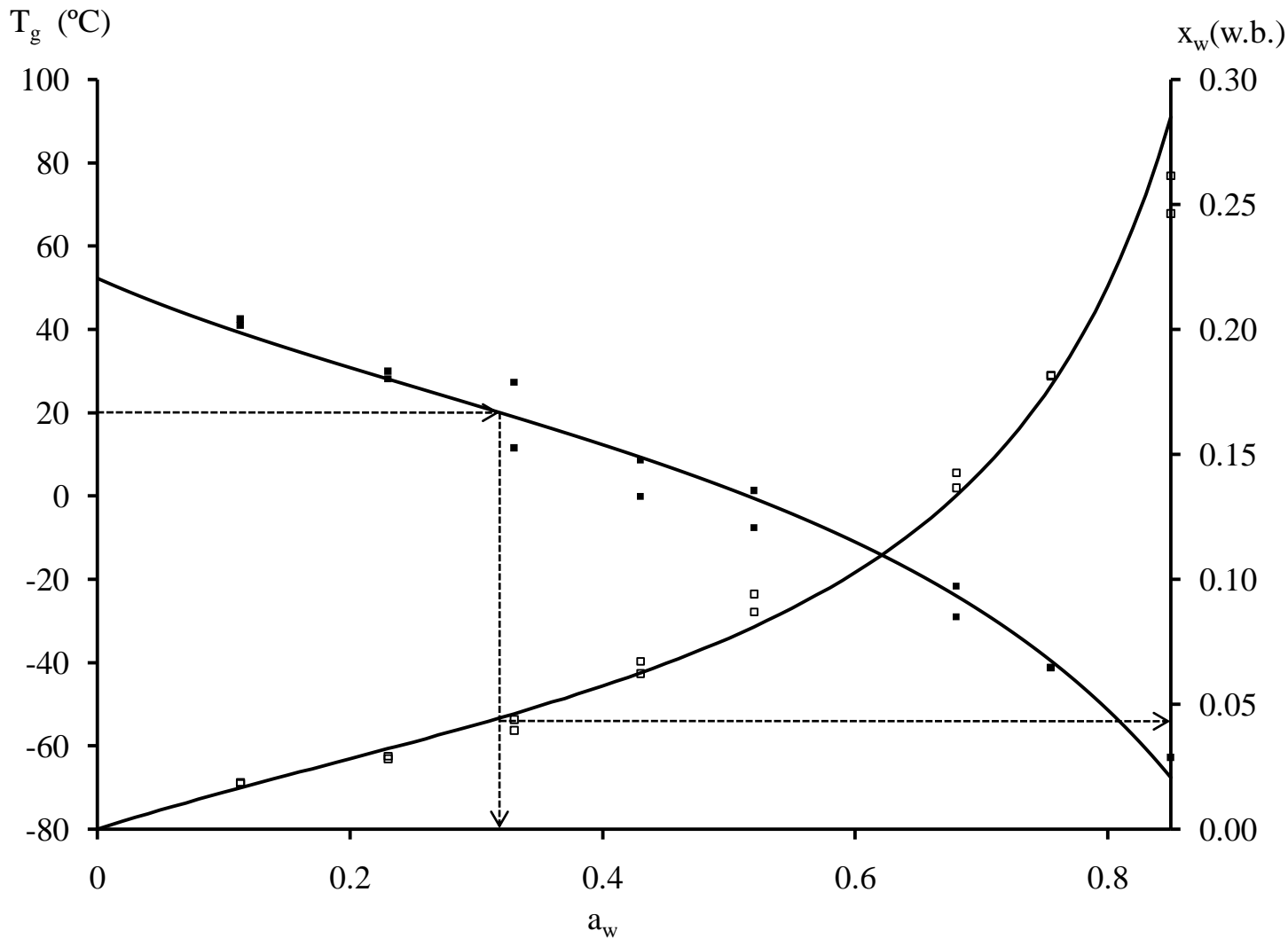
Figure 3

Figure 4a
x

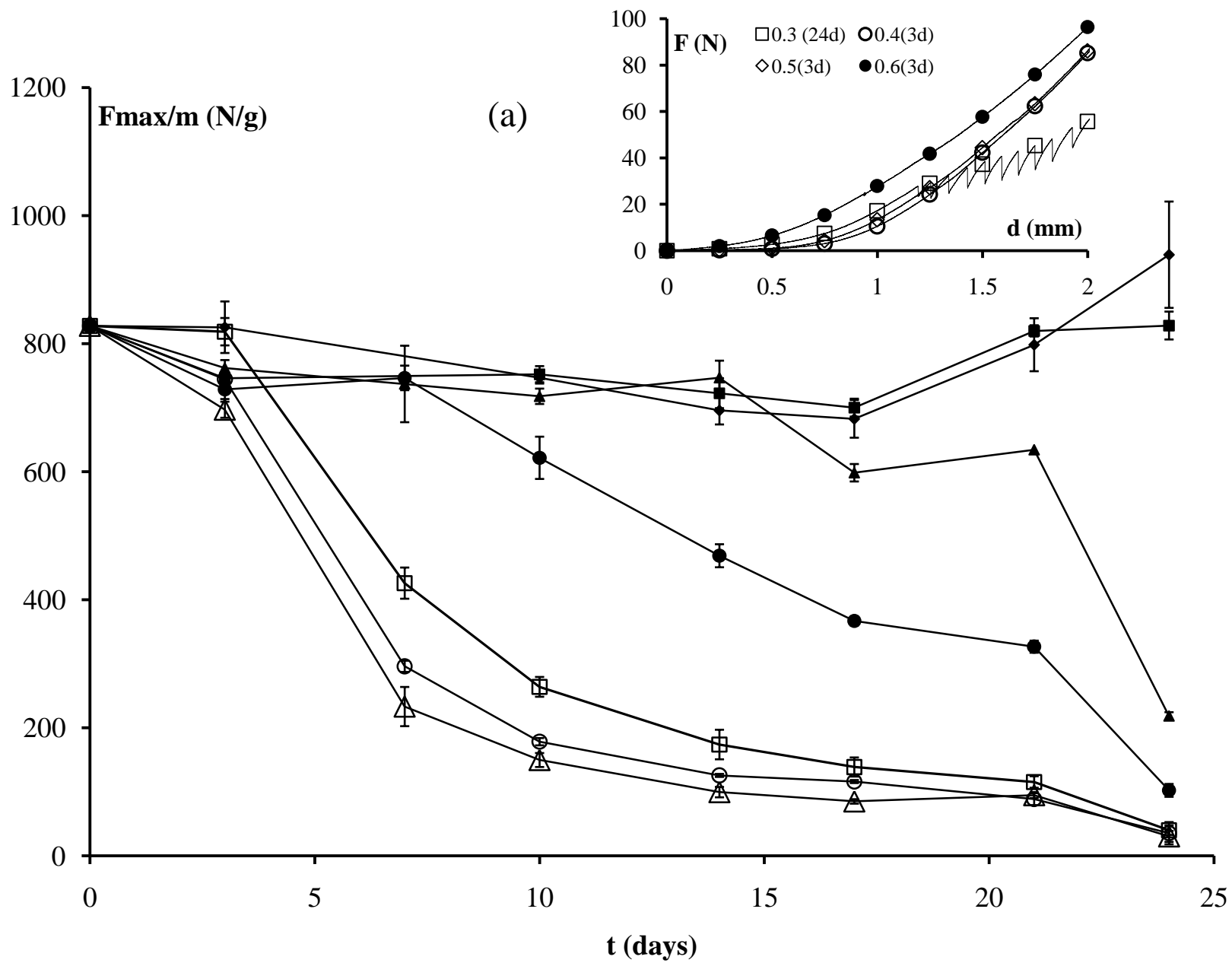


Figure 4b

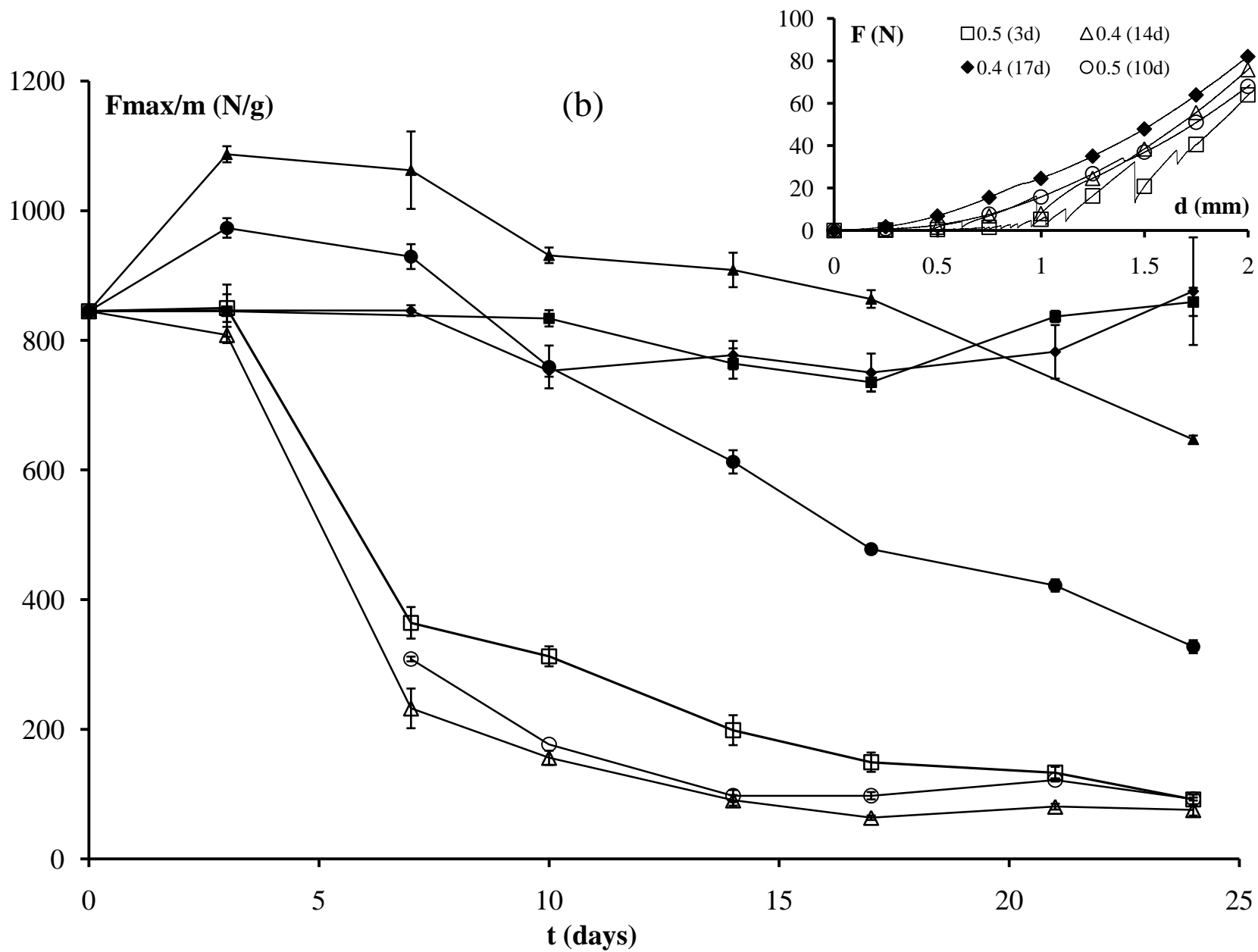


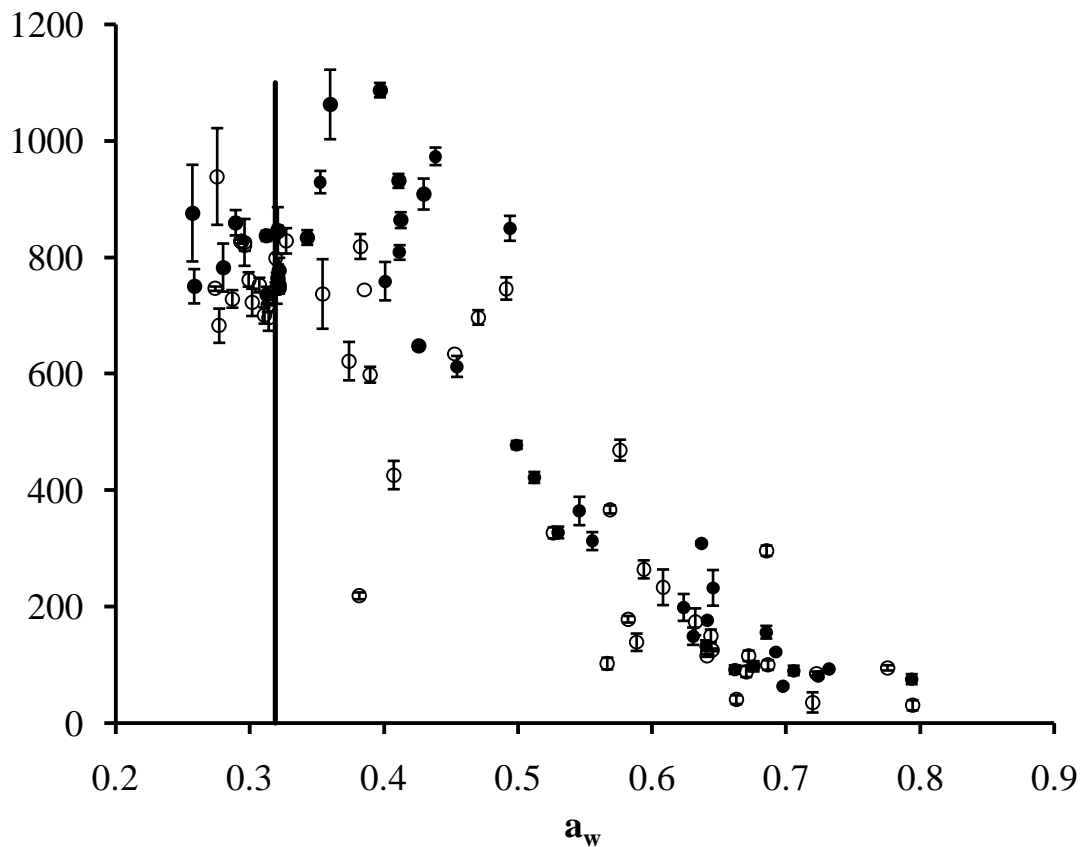
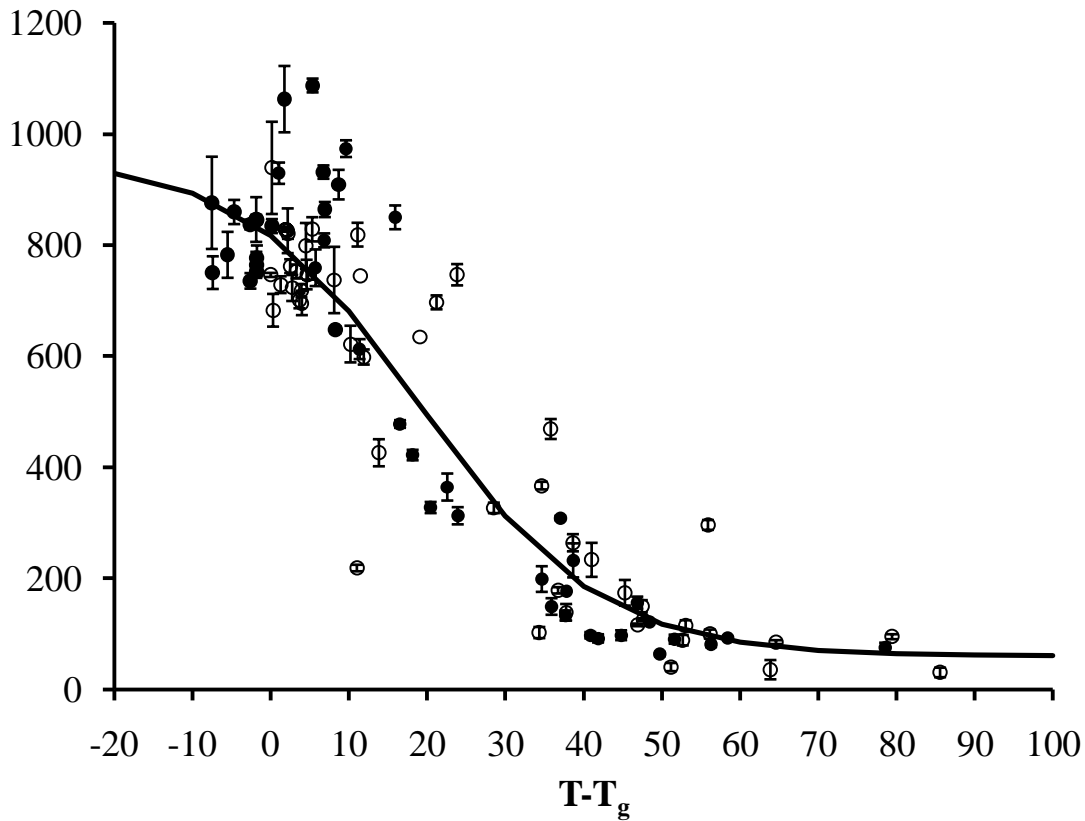
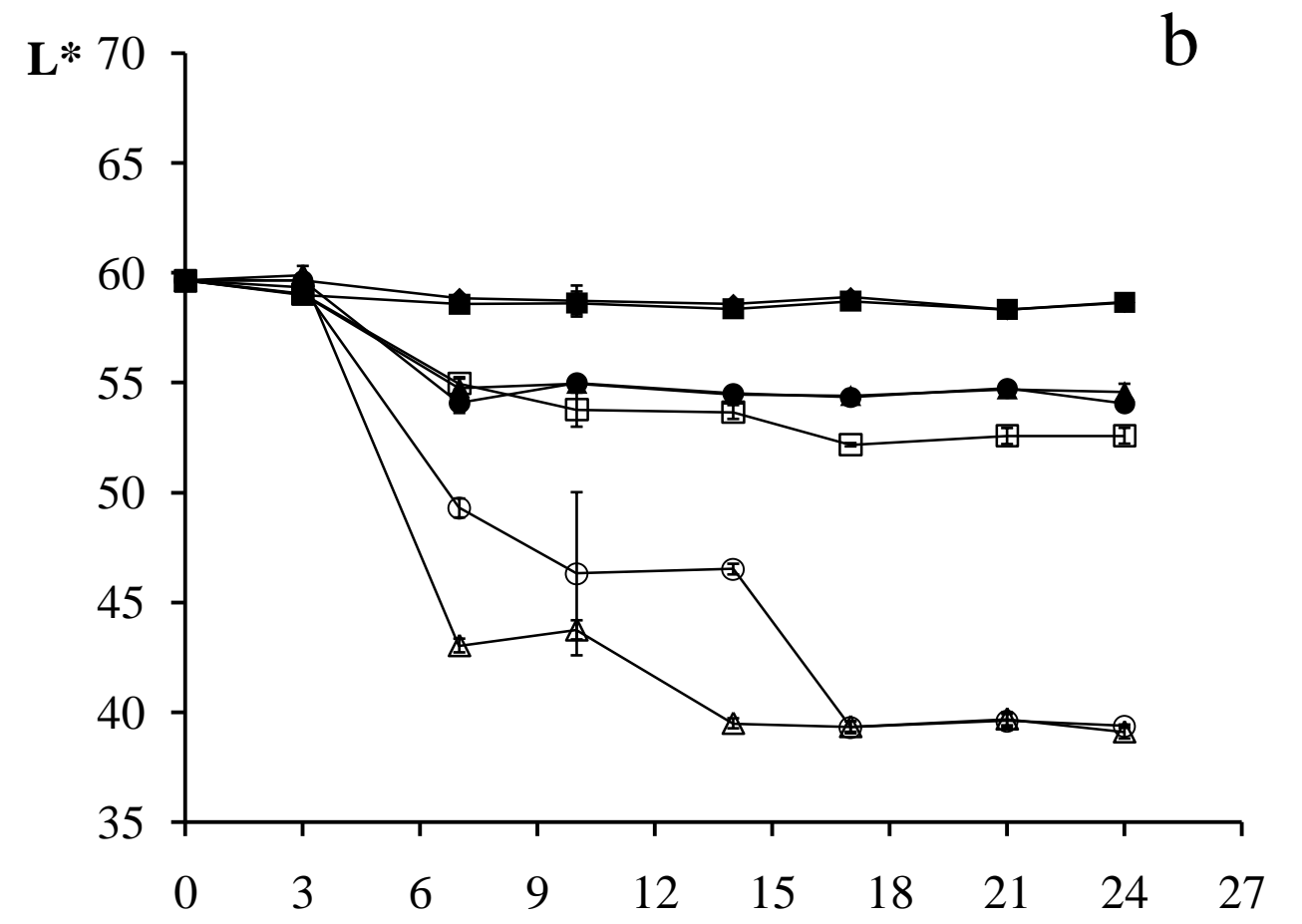
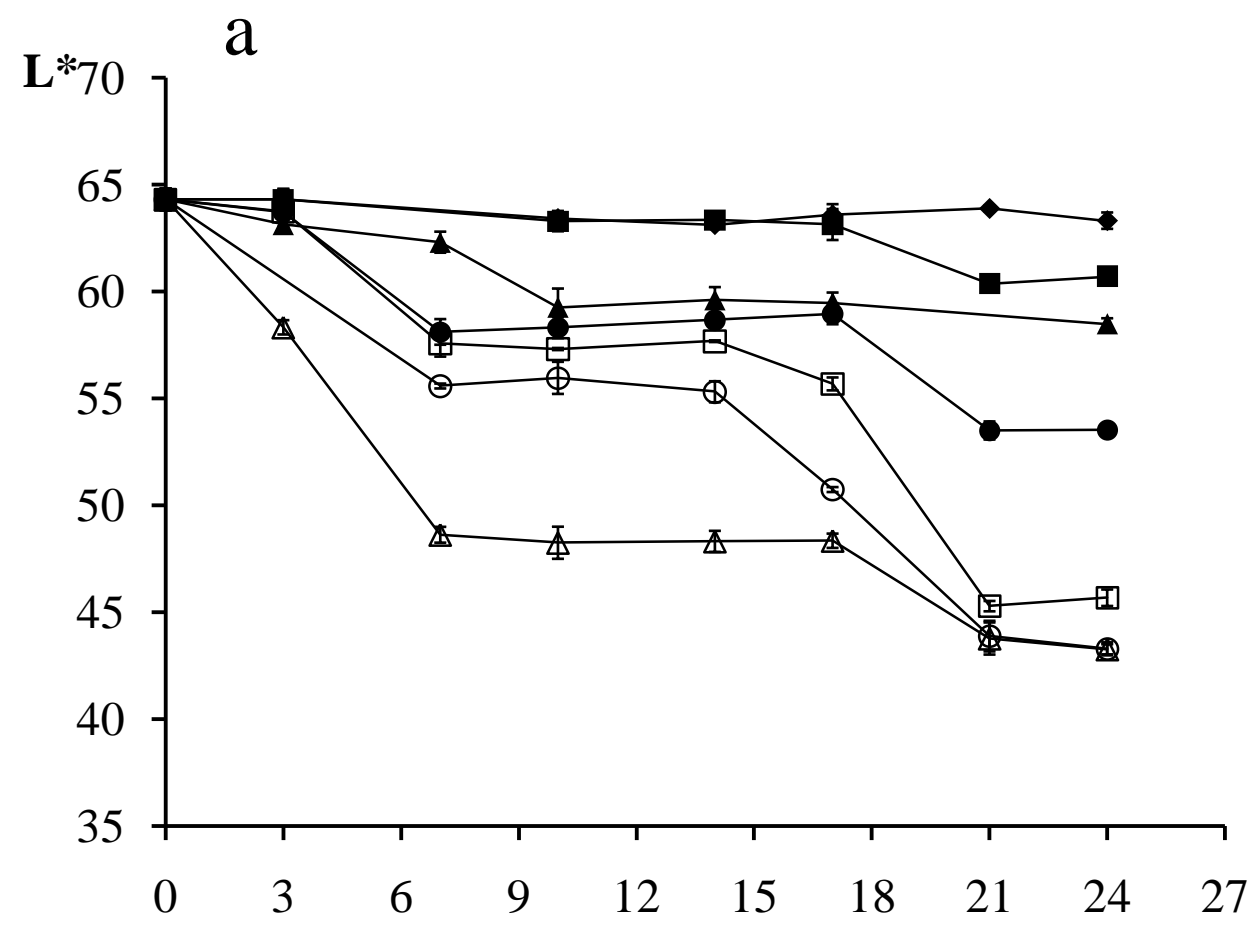
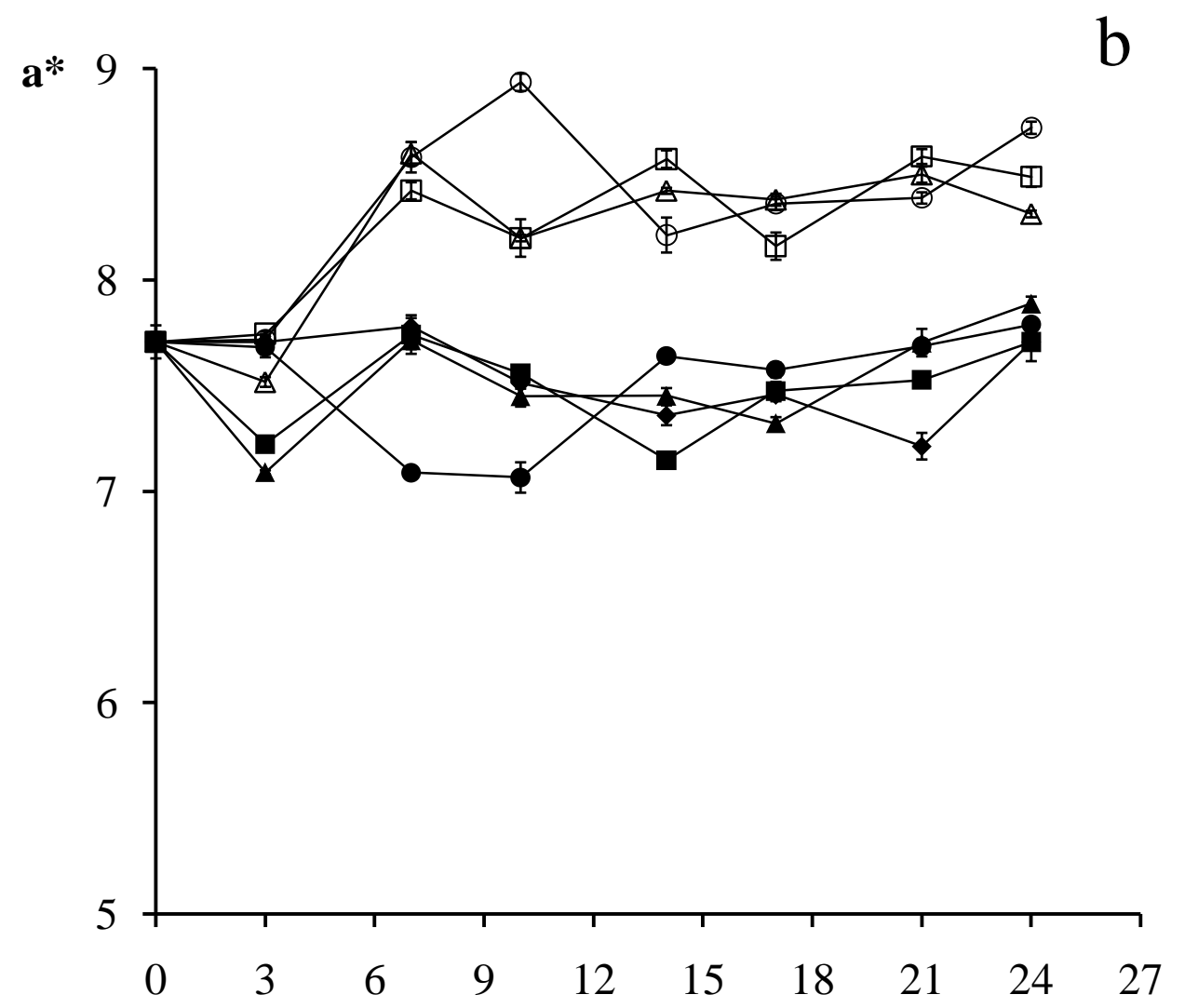
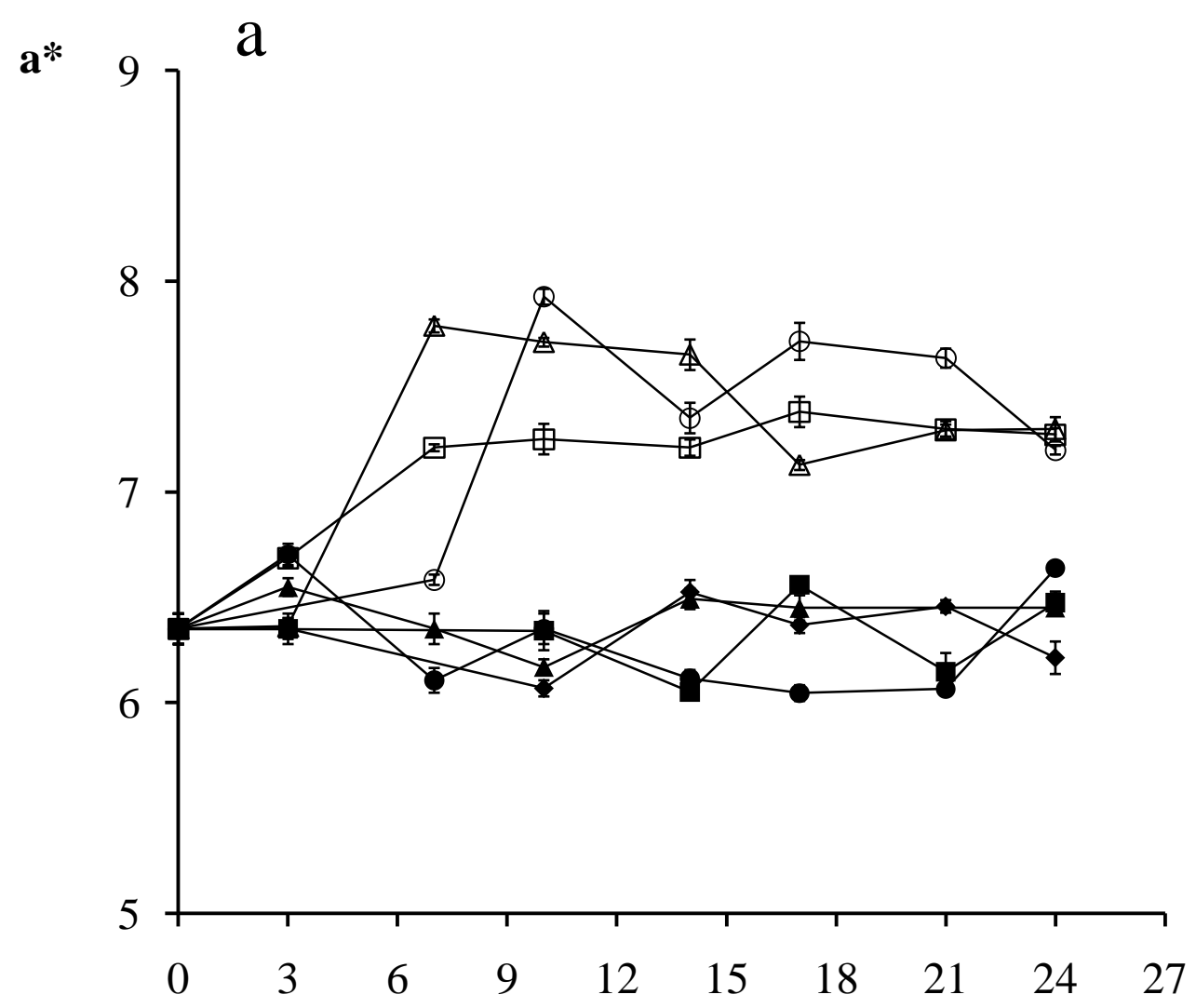
Figure 5**Fmax (N/g)**

Figure 6**Fmax (N/g)**

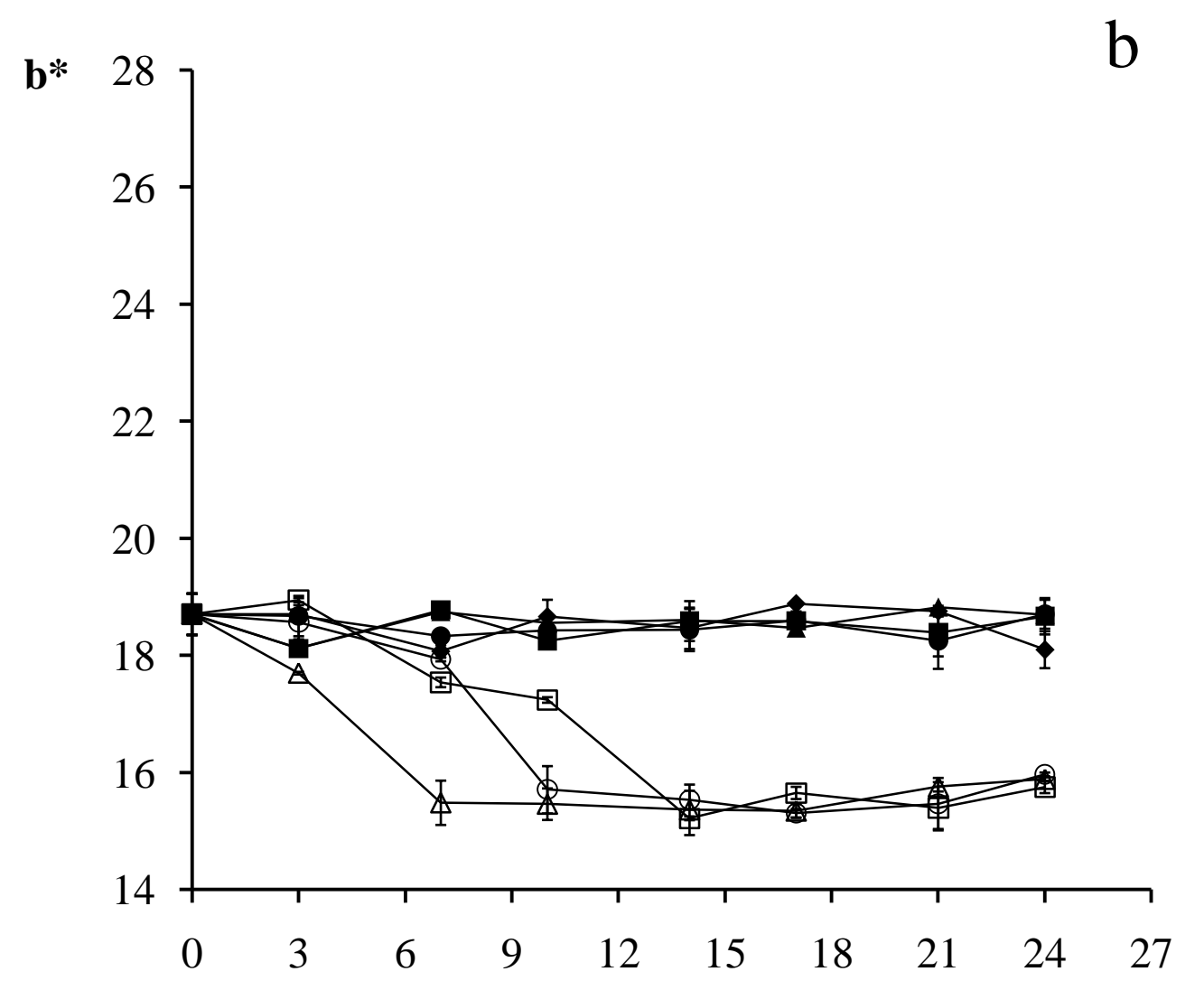
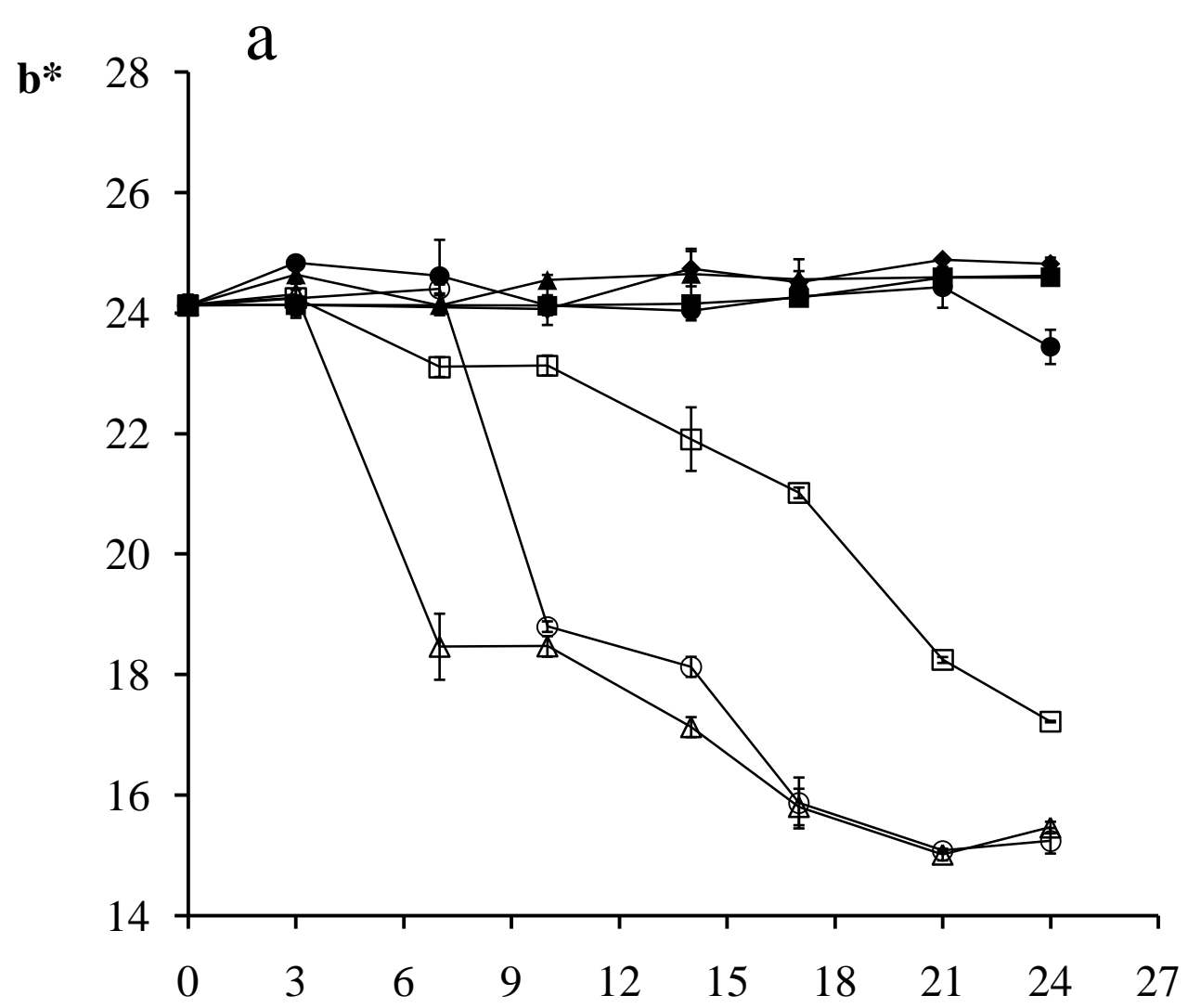
◆ 23% ■ 33% ▲ 43% ● 52% ◻ 68% ○ 75% △ 85%



t (days)



t (days)



t (days)

Figure 8

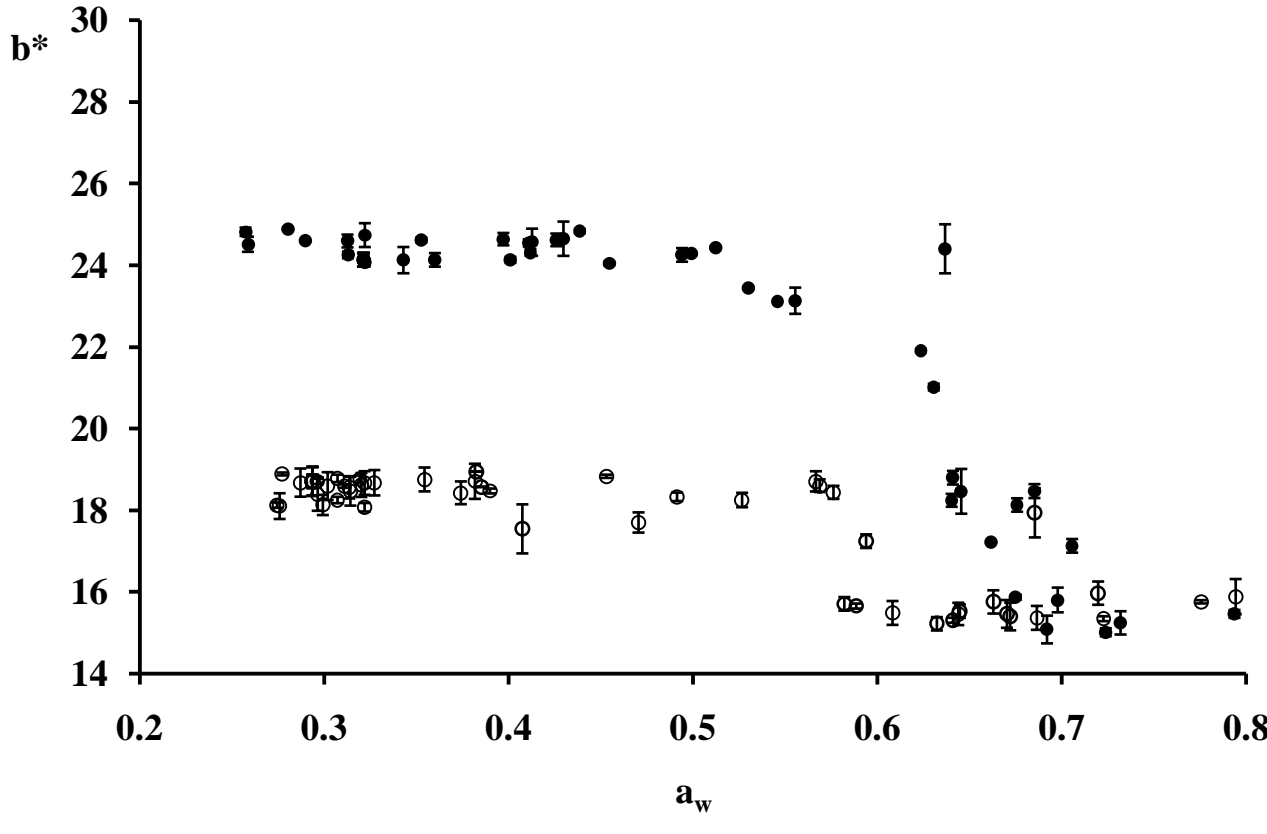
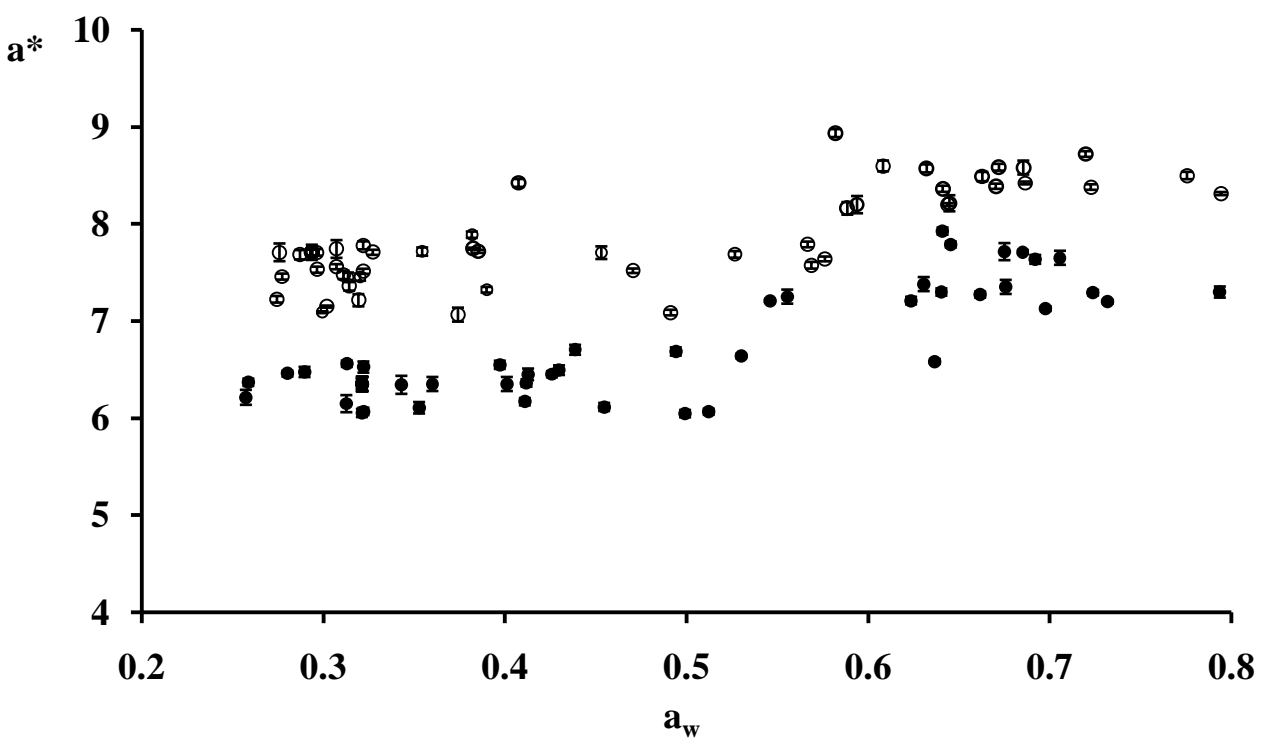
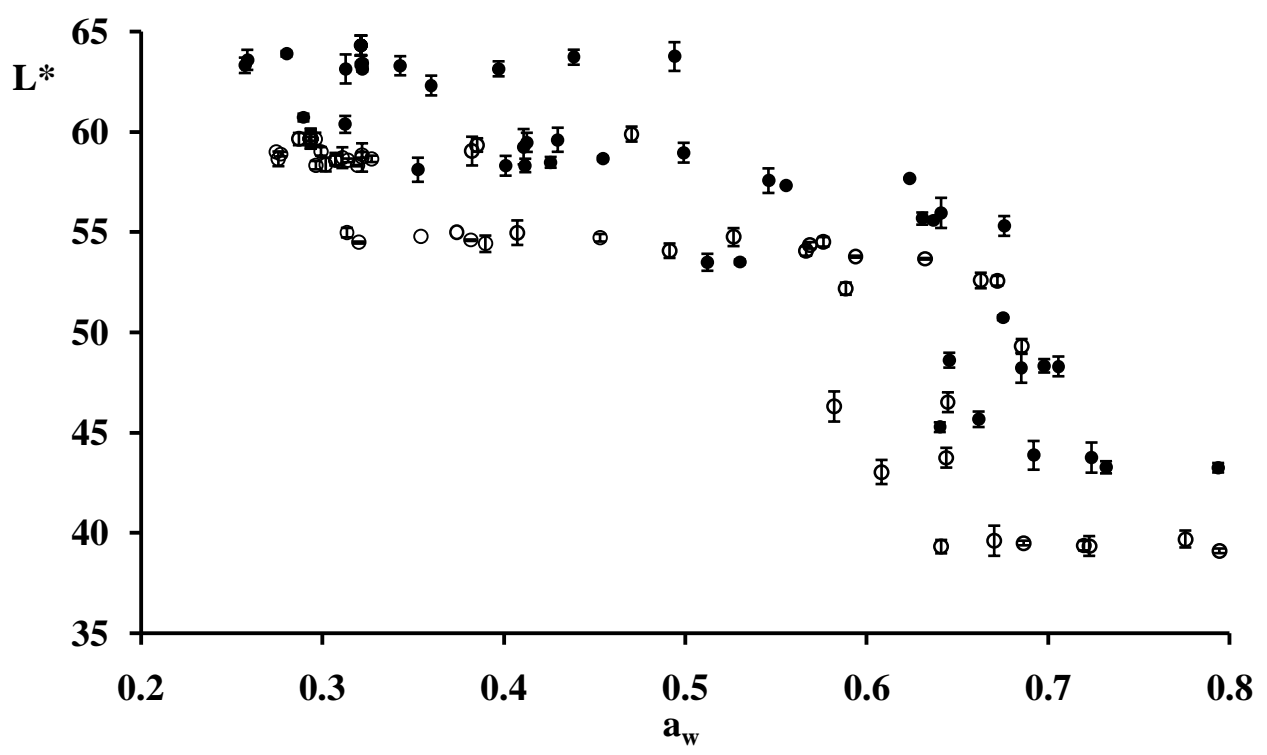


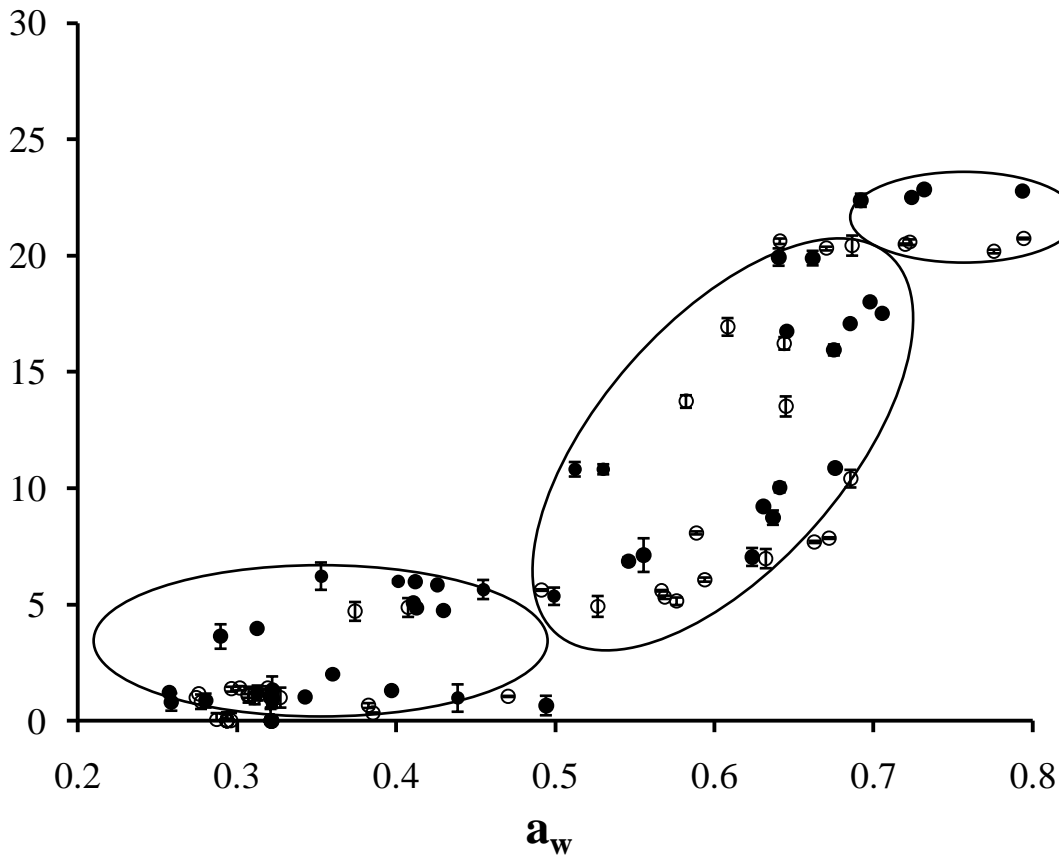
Figure 9 ΔE^* 

Table 1. Values of the obtained parameters when fitting experimental data to the GAB, Gordon and Taylor and Boltzman equations: of Boroj6 Powder, Spray Dried (B) and Boroj6 Powder, Spray Dried (Maltodextrin) (BM) products.

Fitting	B	BM	B + BM
GAB			
<i>k</i>	1.016	1.036	1.027
<i>C</i>	2.739	3.155	2.947
<i>w₀</i>	0.058	0.050	0.053
<i>R</i> ²	0.895	0.888	0.882
Gordon & Taylor			
<i>T_{gs}</i>	51.1 ±3	53.3 ±2	52.3 ±2
<i>k</i>	4.6 ± 0.3	4.2 ± 0.1	4.4 ± 0.2
<i>R</i> ²	0.987	0.995	0.986
Boltzman			
<i>F₁</i>	929.82	870.22	956.49
<i>F₂</i>	35.93	118.27	59.53
ΔT_F	23.03	17.77	19.28
λ_F	13.17	5.92	11.43
20%	28.63	9.97	12.19
80%	47.32	25.87	36.12
<i>R</i> ²	0.870	0.967	0.908

Table 2. Statistical comparison between Boroj3 Powder, Spray Dried (B) and Boroj3 Powder, Spray Dried (Maltodextrin) (BM) products, in terms of the fitted models.

	GAB	Gordon and Taylor	Boltzman (Fmax/m)
RSSg	12.07	420.20	901814.00
ΣRSSi	11.04	243.20	799817.00
FDRg	29	13	95
DFDR	3	2	4
ΣFDRI	26	11	91
E	0.81	4.00	2.90
F (99%)	5.53 ^(n.s)	7.28 ^(n.s)	3.95 ^(n.s)

^(n.s) Non-significant differences ($\alpha > 0.01$)