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Accepted Version

Sharma, N., Goyal, S. K., Alam, T., Fatma, S. and Niranjana, K. (2018) Effect of germination on the functional and moisture sorption properties of high pressure processed foxtail millet grain flour. *Food and Bioprocess Technology*, 11 (1). pp. 209-222. ISSN 1935-5130 doi: <https://doi.org/10.1007/s11947-017-2007-z> Available at <https://centaur.reading.ac.uk/73581/>

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To link to this article DOI: <http://dx.doi.org/10.1007/s11947-017-2007-z>

Publisher: Springer

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1 **Effect of germination on the functional and moisture sorption properties of high**
2 **pressure processed foxtail millet grain flour**

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10 **Abstract** Foxtail millet is one of the commonly cultivated, nutritionally competitive
11 source of protein, fibre, phytochemicals and other micronutrients, as compared to major
12 cereals like wheat and rice. Considering the potential of these grains, the high pressure
13 processed flours of germinated (GFMF) and non-germinated foxtail millet (NGFMF) grains
14 were studied for its functional, moisture sorption and thermodynamic properties. Germination
15 and high pressure processing of foxtail millet grains significantly improved the functional
16 properties of the flour. Apart from this, the moisture sorption isotherms of both the flours
17 were determined at 10, 25 and 40 °C and the sorption data was fitted to Guggenheim-
18 Anderson-De Boer (GAB) sorption model. The monolayer moisture content for NGFMF and
19 GFMF ranged between 3.235 - 2.364 g g⁻¹ and 2.987 – 2.063 g g⁻¹, respectively. The isosteric
20 heat of sorption ranged between -76.35 kJ mol⁻¹ to -38.23 kJ mol⁻¹ for NGFMF and 172.55 kJ
21 mol⁻¹ to -34.02 kJ mol⁻¹ for GFMF at a moisture range of 0 to 36%, whereas, the integral
22 entropy of sorption for NGFMF ranged between -0.404 to -0.120 kJ mol⁻¹ K⁻¹ and for GFMF
23 between -0.667 to -0.383 kJ mol⁻¹ K⁻¹. Along with the validation of the compensation theory,
24 the values of spreading pressures lied in the range of 0 – 0.078 J m⁻² for NGFMF and 0 –
25 0.124 J m⁻² for GFMF, while, the glass transition temperatures ranged between 82.25 to 28.67
26 °C for NGFMF and from 51.11 to 11.83 °C for GFMF at all three temperatures.

27 **Keywords** Foxtail millet flour, germination, high pressure processing, functional
28 properties, moisture sorption isotherms, thermodynamic properties

29

30 **Introduction**

31 Water sorption characteristics are necessary for predicting the shelf life and determining the
32 moisture content and critical activity for acceptability of products that deteriorate, mainly due
33 to moisture gain, and also for drying, packaging and storage (Katz and Labuza 1981). A food
34 moisture sorption isotherm describes the relationship between the moisture uptake in food
35 and the relative humidity of the air with which the food is in equilibrium at a constant
36 temperature (Lagoudaki et al. 1993). Thermodynamics has been reported as an approach to
37 understand the properties of water and calculate the energy requirements of heat and mass
38 transfer in biological systems (Rizvi and Benado 1983; Fasina et al. 1997; Fasina et al. 1999).
39 Properties such as isosteric heat of sorption, net integral enthalpy and entropy and spreading
40 pressures are important for understanding the energy requirement during dehydration, the
41 food microstructure, physical phenomena on the food surfaces and sorption kinetic
42 parameters (Rizvi and Benado 1983). Also, the glass transition temperature is an important
43 physical parameter, which serves to explain the physical and chemical behaviour of food
44 systems (Bell and Labuza 2000), and it is defined as the temperature at which the material
45 changes from the glassy to the rubbery state for a given heating rate.

46 Foxtail millet (*Setaria italica* (L.) P. Beauv.) is the sixth highest yielding grain amongst all
47 the millet varieties and has been identified as a major millet in terms of worldwide production
48 (Sharma et al. 2017). Foxtail millet ranks second in the total world millet production of
49 around 29 million tonnes (in 2015-16 season). It originates in the Yellow River Basin
50 country, which makes China a leading foxtail millet producer holding 80% of world
51 production, followed by India with 10% of world production (Zhang et al. 2017). Foxtail
52 millet is one of the oldest cultivated cereal grains belonging to the *Setaria* genus, of *Poaceae*
53 family and subfamily *Panicoideae*. Sharma et al. (2017) have discussed the versatility of
54 foxtail millet as a food source and its potential to address food and nutrition security. These
55 authors have reviewed the effects of various processing techniques on the properties of
56 foxtail millet grains.

57 It has been recognised that non-thermal processing techniques like high hydrostatic pressures
58 (HHP), can potentially inactivate anti-nutritional factors like phytate and tannin content in
59 cereal grains and preserve their constituents and quality (Estrada-Girón et al. 2005; Yu et al.
60 2015; Zhang et al. 2017). In addition to high pressure processing, germination, is one of the
61 traditional approaches used to supplement the bio-accessibility of nutrients in plant-based

62 diets. The process of germination in cereal grains results in an increase in enzymatic activity,
63 soluble protein content and break down of starch into simple sugars, resulting in the
64 formation of typical colours and flavours (Barreiro et al. 2003). Moisture sorption properties
65 have also been studied for various cereals and its products like various cereal grains and
66 legumes (Al-Mahasneh et al. 2014), milk-foxtail millet powder (Simha et al. 2016), two
67 millet grain varieties (Aviara et al. 2016), tef (*Eragrostis tef* (Zucc.) Trotter) grain flour
68 (Abebe and Ronda 2015), bulgar (Erbaş et al. 2015), Greek durum wheat semolina (Pollatos
69 et al. 2013), RTE breakfast cereal formulation (Sandoval et al. 2009), oat and rice flour (Brett
70 et al. 2009), maize meal and millet flours (Ikhu-Ornoregbe and Chen 2005). In general, very
71 limited moisture sorption data is available for germinated cereals, especially for high pressure
72 processed and germinated millet grains. This study was therefore conducted to assess the
73 effect of germination on the functional, moisture sorption and thermodynamic properties of
74 high pressure processed foxtail millet grain flour.

75 **Materials and methods**

76 **Sample collection**

77 Foxtail millet (*Setaria italica* L.) grains were procured from authorized grain centres. All
78 procured grains were a month old since harvesting and were tested for viability using
79 tetrazolium chloride test (Lakon 1949). The moisture content of the native grains was found
80 to be $8.41 \pm 0.45\%$, following which the grains were stored in polythene bags at 4 °C until
81 further use. The chemicals used for analysis were procured from Sigma-Aldrich Chemical
82 Co., (St. Louis, Mo, USA).

83 **Germination of foxtail millet grains**

84 The foxtail millet grains were washed using 1.5% formaldehyde solution to prevent any
85 contamination. To remove the traces formaldehyde, the grains were then washed thoroughly
86 with distilled water and tested for any residues using the ferric chloride method described by
87 VICH Steering Committee (2002). Prior to germination, the foxtail millet grains were first
88 soaked in deionised water for 15h and then were subjected to germination in a controlled-
89 environment growth cabinet. The temperature was maintained at 25 ± 2 °C and the relative
90 humidity was controlled at 50%; these conditions were based on the work reported by
91 Sharma et al. (2015). Following the method described by Elkhalfa and Bernhardt (2010), the
92 activities of alpha amylase and protease were monitored at regular intervals of 12 hours, and

93 the germination period of 72h represented the time taken for their activities to reach a
94 maximum value., as. The maximum alpha amylase and protease activity was found to be
95 attained after 72h (Fig. 1). The germinated foxtail millet grains were dried to a final moisture
96 content of 7 – 8%, packed and stored in air-tight containers at 4 °C until further analysis.
97 Non-germinated foxtail millet grains were used as a control.

98 **High pressure soaking**

99 Both germinated and non-germinated foxtail millet grains (25g each) were subjected to high
100 hydrostatic pressures in a temperature-controlled pressure vessel system (vessel dimensions:
101 37mm diameter and 246mm length, Food LAB 900, Stansted Fluid Power Ltd., Stansted,
102 UK). A blend of castor oil and ethanol in a ratio of 80:20 v/v was used as a medium to
103 transmit pressure to the packed samples in the pressure vessel chamber. The foxtail millet
104 grains were treated at a pressure of 400 MPa for 60 mins at a temperature of 60 °C. For this,
105 25g foxtail millet grain samples were suspended in 150ml of deionised water and sealed with
106 virtually no headspace polyethylene pouches of dimensions 3cm × 20cm by employing
107 Cryovac™. All the experiments were triplicated.

108 After high-pressure processing under specified conditions of pressure and temperature for a
109 stipulated time, the water was completely drained from the pouches and the water occluding
110 to the grains separated, was then blotted using a tissue paper. The processed grains were then
111 subjected to freeze drying and were finally milled into fine flour passing through sieves of
112 mesh sizes ranging between 100 and 200µm, using vibratory sieve shaker (Fritsch Analysette
113 3, Germany). The resulting flour was packed and stored in air-tight containers at 4 °C until
114 further analysis.

115 **Determination of functional properties**

116 The bulk density, porosity and flowability of the optimized foxtail millet flour, as the angle of
117 repose (as a static measure for flowability), were determined by the method of Sjollem
118 (1963). The occluded air content was determined by the methods used by Jha et al. (2002).
119 The wettability was determined by the method given by Muers and House (1962). The
120 dispersibility of the optimized baby food was determined by the method described by the
121 American Dry Milk Institute (ADMI 1965). The insolubility index was determined by the
122 modified ADMI method described by Jha et al. (2002). The water, oil absorption capacity
123 and swelling capacity of the product were determined by the method described by Sodipo and

124 Fashakin (2011). The emulsion activity, emulsion stability, foaming capacity and foaming
125 stability were determined using the methods described by Elkhalfa and Benhardt (2010).

126 Finally, the gelatinization temperatures were determined using Differential Scanning
127 Calorimetry, where a suspension of the resulting flour in deionised water was prepared in a
128 ratio of 1:3; equilibrated for 15-18 h at ambient temperature; and presented to the differential
129 scanning calorimeter, equipped with a built-in software (Model Q 2000a TA Instruments,
130 New Castle, U.S.A.). A 10-12 mg suspension sample was weighed precisely in an aluminium
131 sample pan and hermetically sealed. A similar empty pan was used as a reference for the
132 analysis. A temperature range of 10 to 140 °C was used for scanning the sample in the pan at
133 a heating rate of 10 °C min⁻¹. The resulting thermogram gave the values of onset (T_o), peak
134 (T_p) and conclusion temperatures (T_c) in °C.

135 Sorption studies

136 Gravimetric method described by Lang et al. (1981), was used to determine the sorption
137 isotherms for processed foxtail millet flour. The saturated salt solutions of eight reagent-grade
138 salts, namely, lithium chloride, magnesium chloride, potassium carbonate, magnesium nitrate,
139 sodium chloride, potassium chloride, potassium nitrate, and potassium sulfate, were chosen as
140 mentioned by Greenspan (1977) to cover the water activity range from 0.11 to 0.97. It is
141 important to note that the water activity values for these salts can show slight variations at
142 different temperatures. Therefore, different water activity values of these salts at temperatures
143 10, 25 and 40 °C were used in this study. These saturated solutions were placed in air tight,
144 wide mouth glass jars. Approximately 1 g of sample was weighed into a glass beaker placed
145 on glass bead support inside the glass jar. The glass beakers were equilibrated for three days
146 with the humid atmosphere before placing the sample. Then the moisture sorption
147 characteristics were studied at 10, 25 and 40 °C (± 2 °C) by placing the sample containing
148 glass jars in incubators for equilibration. These conditions were chosen in this study, as they
149 represent the possible storage conditions for cereals like rice (Ondier et al. 2012) The samples
150 in bottles were weighed at a regular interval of 3 days till a constant weight was attained.
151 Equilibrium was considered to have accomplished when the weight difference between two
152 successive weighing was less than 1 mg. Experiment was conducted in triplicates for all the
153 samples at each relative humidity and temperature conditions. After the equilibrium has been
154 attained, the moisture content of the samples was determined and was expressed in gram per
155 litre (g/L). The average standard deviation between the replicates was calculated to be less

156 than 1% of the mean of the three values. These average values of equilibrium moisture
157 content were then plotted against relative humidities or water activities to obtain moisture
158 sorption isotherms.

159 *Sorption model*

160 Various approaches have been used to describe sorption isotherms of foods. Amongst which,
161 Guggenheim-Anderson-De Boer (GAB) (Pérez-Alonso et al. 2006) is mostly used to study
162 the correlation between the equilibrium moisture content (M) and water activity (a_w) for
163 various foods. The following linearized form of GAB model were used for evaluating the
164 best fitted values of model constants using linear regression:

165 GAB

$$166 \quad W = W_o \frac{Gka_w}{(1-ka_w)(1-ka_w+Gka_w)} \quad (1)$$

167

168 The GAB model could be rearranged into a second-degree polynomial equation as given
169 below:

$$170 \quad \frac{a_w}{W} = aa_w^2 + ba_w + c \quad (2)$$

171 where, a , b and c are model constants and significantly depend on type of regression analysis.
172 A nonlinear regression analysis of a_w/W v/s a_w yields a polynomial equation of the second
173 order. The coefficients a , b and c were thus obtained from this polynomial equation and then
174 substituted to obtain GAB constants W_o , G and k . W_o is the moisture content corresponding to
175 saturation of all primary adsorption sites by one water molecule, G is the Guggenheim
176 constant and k is the factor correcting for properties of multilayer molecule with respect to
177 the bulk liquid.

178 *Thermodynamic properties*

179 The integral enthalpy, also known as, net isosteric heat of sorption was determined using
180 Clausius-Clayperon equation (Rizvi 1986; Bell and Labuza 2000):

$$181 \quad \frac{\partial(\ln a_w)}{\partial(\frac{1}{T})} = \frac{Q_{st}}{R} \quad (3)$$

182 where, T is the absolute temperature (K), Q_{st} is the net isosteric heat of sorption (kJ mol^{-1})
183 and R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$).

184 The calculation procedure assumed that net heat of sorption was independent of temperature
185 change. The slope of the plot of $\ln(a_w)$ versus $1/T$ at constant moisture content gave the net
186 isosteric heat of sorption (Eq. 3). Adding the latent heat of vaporization of pure water at 10,
187 25 and 40 °C to the net isosteric heat of sorption (Q_{st}), gave the values of isosteric heat of
188 sorption. A cubic spline interpolation was used to determine a_w values at various
189 temperatures for a given moisture content (M).

190 Substituting free Gibbs energy in the Gibbs- Helmholtz equation (McMinn and Magee 2003;
191 Kaya and Kahyaoglu 2005), the differential entropy was calculated using the following
192 equation:

$$193 \quad -\ln(a_w) = \frac{-(Q_{st} + \lambda)}{RT} - \frac{\Delta S}{R} \quad (4)$$

194 where, λ is the latent heat of vaporization of pure water ($44.045 \text{ kJ mol}^{-1}$ at 25 °C), and ΔS is
195 the integral entropy of sorption ($\text{kJ mol}^{-1} \text{ K}^{-1}$). The maximum storage stability point is when
196 the water activity and temperature gives the minimum value of integral entropy (Alpizar-
197 Reyes et al. 2017).

198 From the intercept of the plot of $\ln(a_w)$ versus $1/T$ at specified moisture levels of eq. (4), the
199 integral entropy was evaluated.

200 *Isokinetic theory*

201 A linear relationship between the isosteric heat of sorption (differential enthalpy) and
202 differential entropy established the enthalpy- entropy theory (McMinn and Magee et al.
203 2003; Arslan and Togrul 2006):

$$204 \quad Q_{st} = T_{\beta} \Delta S_d + \alpha \quad (5)$$

205 where, Q_{st} is the isosteric heat of sorption (kJ mol^{-1}), T_{β} is the isokinetic temperature (K), and
206 α is the constant or Gibb's free energy (kJ mol^{-1}).

207 The isokinetic temperature (T_{β}) is a characteristic property of the material surface (Aguerre et
208 al. 1986), and it represents the slope of the enthalpy- entropy linear relationship (Eq. 5).

209 Linear regression of Q_{st} with ΔS_d evaluated T_β . A statistical test proposed by Krug et al.
 210 (1976) verified the enthalpy- entropy compensation theory by defining the harmonic mean
 211 temperature (T_{hm}) as:

$$212 \quad T_{hm} = \frac{n}{\sum_1^n \left(\frac{1}{T}\right)} \quad (6)$$

213 where, T_{hm} is the harmonic mean temperature (K), and n is the number of temperature levels.
 214 Linear enthalpy- entropy compensation theory applies only when $T_\beta \neq T_{hm}$; the process is
 215 enthalpy driven if $T_\beta > T_{hm}$ and entropy driven if $T_\beta < T_{hm}$ (Leffler and Grunwald 1963). Eq.
 216 (6) shows that T_{hm} is a function of temperature levels selected for the experiment and is
 217 independent of the material considered. Analyses were conducted with $\alpha = 0$ to evaluate the
 218 effect of temperature on the sorption behaviour by introducing a temperature correction factor
 219 (Aguerre et al. 1986) as:

$$220 \quad -\ln(a_w) = \frac{Q_{st}}{R\left(\frac{1}{T} - \frac{1}{T_\beta}\right)^{-1}} \quad (7)$$

221 *Spreading pressures*

222 Spreading pressure was evaluated based on the analytical procedure described by Iglesias et
 223 al. (1976) and Fasina et al. (1999). Spreading pressure is given by the following equation:

$$224 \quad \pi = \frac{KT}{A_m} \int_0^{a_w} \frac{x}{x_m a_w} \quad (8)$$

225 where, π is the spreading pressure (J m^{-2}), K is the Boltzman constant ($1.380 \times 10^{-23} \text{ J K}^{-1}$)
 226 and A_m is the surface area of a water molecule ($1.06 \times 10^{-19} \text{ m}^2$).

227 This integral becomes indeterminate at $a_w = 0.0$. Therefore, spreading pressure was evaluated
 228 by dividing the total limit (0.0 to a_w) into a very small interval of 0.0 to 0.05 and the
 229 remaining 0.05 to a_w . The integral in the first infinitesimal a_w range (0.0 to 0.05) was
 230 evaluated assuming a linear relationship (Henry's law) between m and a_w with usual notations
 231 (Fasina et al. 1999) as:

$$232 \quad \pi = \frac{KTx}{A_m x_m} \quad (9)$$

233 The integral in the second a_w range (0.05 to a_w) was evaluated after fitting isotherm data (m ,
 234 a_w) to the GAB model equation and the spreading pressure was obtained by integrating the
 235 equation in the second interval of 0.05 to a_w (Iglesias et al. 1976):

$$236 \quad \pi = \frac{KT}{A_m} \ln \left[\frac{1+cka_w-ka_w}{1-ka_w} \right]_{0.05}^{a_w} \quad (10)$$

237 Adding the results of the two selected a_w intervals produced the spreading pressures at any
 238 studied temperature and water activity combination.

239 *Glass transition temperature*

240 Differential scanning calorimetry was used to determine the glass transition temperature. A
 241 suspension of processed foxtail millet flours and deionised water was prepared in a ratio of
 242 1:3 and equilibrated for 15-18 h at ambient temperatures and were analysed using a TA
 243 Instruments model Q-2000 differential scanning calorimeter, equipped with a built-in
 244 software (TA Instruments, Newcastle, U.S.A.). For this, 10-12 mg of flour, equilibrated at a
 245 range of water activities (0.11 – 0.85) and temperatures (10, 25 and 40 °C) were weighed in
 246 an aluminium sample pan and hermetically sealed. A similar empty pan was used as a
 247 reference for the analysis. A temperature range of -50 to 150 °C was used for scanning the
 248 sample in the pan with a heating rate of 2 °C min⁻¹ (Alpizar-Reyes et al. 2017). The resulting
 249 thermogram gave the values of onset (T_o), peak (T_p) and conclusion temperatures (T_c) in °C
 250 and gelatinisation enthalpies (ΔH) in kJ kg⁻¹. The final values obtained were an average of
 251 three replicates for each sample, with a maximum deviation of less than 1.5%. The midpoint
 252 of the baseline shift obtained using DSC was taken as the glass transition temperature (T_g).
 253 The measurements were made in triplicates. Further, to deduce the plasticizing effect of water
 254 on T_g , the DSC data was put in the Gordon-Taylor equation:

$$255 \quad T_g = \frac{W_1 T_{g1} + K W_2 T_{g2}}{W_1 + K W_2} \quad (11)$$

256 Where, W_1 and W_2 are the mass fractions of the flours and of water, respectively, T_{g1} is the T_g
 257 value of flour at zero moisture content and T_{g2} is the T_g value of water (-135 °C), and K is a
 258 constant.

259

260

261 **Statistical analysis**

262 The differences amongst the samples were determined using one-way analysis of variance
263 (ANOVA) using Minitab 17.0 software. Using the Duncan's test the differences were
264 considered statistically significant at p-value ≤ 0.05 . The degree of fitness of the model was
265 evaluated using determination coefficient (R^2).

266 **Results and discussion**

267 **Functional properties of the flours**

268 The functional properties of the processed germinated foxtail millet flour (GFMF) as well as
269 non-germinated foxtail millet flour (NGFMF) are shown in **Table 1**. Germination of foxtail
270 millet increased the values of porosity, occluded air content, water and oil absorption
271 capacity, dispersibility, swelling capacity, wettability, flowability, **gelatinization enthalpy,**
272 **emulsification activity and stability**; while decreased the values of bulk density, insolubility
273 index, **foaming capacity and stability**. Albarracín et al. (2016) reported that the water
274 absorption and water solubility values were higher for germinated brown rice samples as
275 compared to the control brown rice samples. Similar results were also stated by Chinma et al.
276 (2009) for varieties of germinated tigernut flour; Devisetti et al. (2014) for millet flours and
277 Elkhailifa and Bernhardt (2010) for germinated sorghum flour.

278 **Moisture sorption characteristics**

279 The effect of germination was studied for the stability of the high pressure processed foxtail
280 millet flours.

281 *Equilibrium moisture content- water activity*

282 The relationship between the EMC and water activity (a_w) at a constant temperature forms the
283 MSI. Therefore, foods with different moisture content have different water activity, thus they
284 form their own sorption isotherm (Alpizar-Reyes et al. 2017). **Fig. 2 (a, b)** shows the
285 experimental isotherms for NGFMF and GFMF at 10, 25 and 40 °C, respectively, with which
286 the thermodynamic functions related to moisture sorption in porridge flours were determined.
287 Both figures depict that the EMC increased with increasing water activity ranging from 0.11
288 to 0.97 at a constant temperature. A constant linear increase in EMC at lower water activities
289 ranging from 0.11 to 0.55 was observed for NGFMF and from 0.11 to 0.76 for GFMF, which

290 could be due to the ability of the flour to lower the vapour pressure, with the decrease in the
291 relative humidity. While, a rapid increase in EMC at higher water activities from 0.55 to 0.97
292 for NGFMF (Fig. 2(a)) and an impulsive increase (Fig. 2(b)) in the EMC from 0.76 to 0.97
293 for GFPMF could be attributed to the high sorptive capacity of hydrophilic starch in foxtail
294 millet flours consisting of a large number of free hydroxyl sites (Pollatos et al. 2013). This
295 impulsive increase in the case of GFPMF could be because of elevated enzyme activity and
296 breakdown of complex sugars into simple sugars during germination (Wu et al. 2013).
297 Barreiro et al. (2003) also found similar results for malted barley flours. Therefore, it could
298 be concluded from the results that GFPMF would require improved storage conditions with
299 relative humidity not exceeding 76% and NGFMF not exceeding 55%.

300 The increase in temperatures did not have a significant effect on the moisture sorption
301 behaviour of both the flours. Though it was observed that for NGFMF, the EMC decreased
302 with the increase in temperatures for a given water activity, showing a less hygroscopic
303 behaviour of NGFMF at higher temperatures. This is because high temperatures increase the
304 kinetic energy of the water molecules, thus increasing the distance between them and causing
305 easy binding of these water molecules to the surface of the flours (Pollatos et al. 2013;
306 Alpizar-Reyes et al. 2017). On the other hand, an opposite trend was depicted by GFPMF,
307 which could be attributed to the higher content of sugars due to germination, thus increasing
308 the active sites for the sorption of water by proteins (Barreiro et al. 2003; Pollatos et al.
309 2013). In addition to this, the MSI's of both NGFMF and GFPMF were of the characteristic
310 sigmoidal shape (BET II type), which is likely found in all types of dry foods rich in starch
311 and sugars.

312 *Sorption models*

313 The experimental sorption data for both the flours were fitted using GAB model, with R^2
314 value of more than 0.998 at all temperatures and RMSE value of less than 0.051. The model
315 parameters were determined using non-linear regression method. Table 2 and 3 shows the
316 model parameters for NGFMF and GFPMF, respectively. MSIs of both the flours can be
317 divided into an: (1) initial monolayer region (a_w less than 0.2), where the water molecules are
318 strongly absorbed as critical moisture content that starts the chemical reactions in foods. It is
319 also a measure of the availability of active sorption sites; (2) an intermediate multilayer
320 region (a_w in the range of 0.2-0.6), that causes lipid oxidation and physical changes in foods,
321 and (3) a final condensed water region (a_w greater than 0.6), which ascertains the microbial

322 growth (Labuza and Altunakar 2007). The values of monolayer moisture content (W_o) for
323 both NGFMF and GFMF decreased with the increase in temperatures from 10 to 40 °C, as
324 expected by the theory of physical sorption (Pollatos et al. 2013). The values for W_o for
325 NGFMF and GFMF ranged between 3.235 - 2.364 g g⁻¹ and 2.987 – 2.063 g g⁻¹, respectively.
326 The composition and nature of the product was responsible for the difference in the values of
327 the monolayer moisture content in germinated and non-germinated flours. Thus, NGFMF
328 being a starch rich flour was found to be more hygroscopic and GFMF being a sugar rich
329 flour due to germination, was found to be less hygroscopic.

330 The constant G is related to the monolayer sorption heat which associates the chemical
331 potential difference with the superior layers of moisture in the flour structure. It has been
332 established that low temperatures assist the formation of strong adsorbent and adsorbate
333 interactions, thus causing an increase in the G values with the increase in temperature
334 (Alpizar-Reyes et al. 2017). While, this study reported a decrease in the G values on
335 increasing the temperature from 10 to 25 °C and then an increase in the G values on further
336 increasing the temperature from 25 to 40 °C, for both NGFMF and GFMF. Thus, it suggested
337 that the flour-water interactions in both NGFMF and GFMF decreased as follows: 10 °C > 40
338 °C > 25 °C. These results agreed with Pollatos et al. (2013) and Simha et al. (2016).

339 Another constant k is related to the enthalpy of water multilayer sorption indicating a measure
340 of the interactions between multilayer molecules and adsorbent. When, k values are in the
341 range of 0.24 to 1.0, GAB model best describes the sigmoid shaped isotherms (Lewicki
342 1997). For NGFMF and GFMF, the k values were in the range of 0.780 – 0.881 and 0.852 –
343 0.944, respectively. Since the values $k \ll 1$, so it was inferred that the flours comprised of a
344 structured state of adsorbate in the adjacent layers to the monolayer (Alpizar-Reyes et al.
345 2017).

346 *Thermodynamic properties*

347 Dried foods like the flours that have been studied here, undergo various changes during
348 storage due to the processes like crystallization, dissolution, diffusion, swelling, etc.
349 Therefore, various thermodynamic properties like integral enthalpy and entropy determines
350 the condition of maximum food stability.

351

352 Net isosteric heat of sorption

353 The degree of bound water in the flour estimates the variation in the integral enthalpy which
354 is also known as net isosteric heat of sorption (Q_{st}). It indicates the interaction of water
355 vapour with solid substrates in the flours, thus explaining the endothermic or exothermic
356 nature of the interaction (Pushpadass et al. 2014). Fig. 3 (a, b) shows the relationship between
357 Q_{st} and the moisture content at constant temperature for both NGFMF and GFMF. The
358 negative values of Q_{st} in the graph indicated the exothermic nature of sorption for both flours.
359 Strong water-substrate interactions were suggested at low moisture contents, as the water
360 binding capacity of the flours increased with the increase in the negative values of Q_{st} . The
361 values of Q_{st} ranged between $-76.35 \text{ kJ mol}^{-1}$ to $-38.23 \text{ kJ mol}^{-1}$ for NGFMF and 172.55 kJ
362 mol^{-1} to $-34.02 \text{ kJ mol}^{-1}$ for GFMF at a moisture range of 0 to 36%. At the higher moisture
363 contents, the value of Q_{st} became close to the values of heat of sorption of pure water, thus
364 indicating the excess moisture bounded to the flours or condensation in the capillaries of flour
365 particulates. The difference in the Q_{st} of both flours at low moisture contents indicated that
366 the degree of binding of water molecules was higher for GFMF as compared to the NGFMF.
367 This could be because of the availability of the higher energy polar sites on the surface in the
368 initial stages of sorption of GFMF, causing water molecules to form a monomolecular layer.
369 In addition to this, as the moisture content further increased for both the flours, the
370 availability of these sites decreased and sorption occurred at less active sites, yielding lower
371 heats of sorption (Lagoudaki and Demertzis 1994). Similar findings were observed for
372 chestnut and wheat flours (Moreira et al. 2010); Japanese durum wheat flour (Chuma et al.
373 2012); whole wheat flour (Martín- Santos et al. 2012) and Greek durum wheat semolina
374 (Pollatos et al. 2013).

375 Integral entropy

376 The integral entropy of sorption (ΔS) for NGFMF ranged between -0.404 to -0.120
377 $\text{kJ mol}^{-1} \text{ K}^{-1}$, with a minimum value at 4% moisture content and 40 °C temperature and for
378 GFMF between -0.667 to $-0.383 \text{ kJ mol}^{-1} \text{ K}^{-1}$, with a minimum value at 8% moisture content
379 and 10 °C temperature. Fig. 4 (a, b) shows the integral entropy as a function of moisture
380 content at 10, 25 and 40 °C for both flours. These findings were in accordance with Simha et
381 al. (2016). The minimum ΔS value was observed for GFMF as compared to NGFMF, thus
382 interpreting that GFMF is more stable than NGFMF at a temperature range of 10 to 40 °C.
383 This stability is because the water molecules in the flour forms more ordered arrangement,

384 bond between adsorbate and adsorbent being the strongest. Therefore, less moisture is
385 available for spoilage reactions. The subsequent increase in the values of ΔS with the increase
386 in moisture content for both the flours, reflected the formation of multi-layers and freely held
387 molecules of water (Rizvi 1986). The increasing temperatures also had a great impact on the
388 integral entropy of both the flours. With the increase in temperature from 10 to 40 °C, the
389 values of ΔS decreased for NGFMF and increased for GFMF, suggesting that NGFMF was
390 more stable at higher temperatures, while GFMF was more stable at lower temperatures. This
391 could be attributed to the composition of the flours.

392 *Enthalpy-entropy compensation theory*

393 The isokinetic theory or the enthalpy-entropy compensation theory determines the existence
394 of true compensation by comparing the difference between the harmonic temperature (T_{hm})
395 and isokinetic temperature (T_{β}) ($T_{hm} \neq T_{\beta}$). This theory helps in evaluating the sorption
396 reactions, confirming if the reactions are enthalpy driven or entropy driven. According to
397 Leffler and Grunwald (1963), if $T_{\beta} > T_{hm}$ the process is enthalpy driven, while if $T_{\beta} < T_{hm}$ the
398 process is considered to be entropy controlled. The T_{hm} values were found to be 297 K and
399 303 K at all three temperatures for NGFMF and GFMF, respectively. The results of this study
400 showed that the T_{β} values were greater than T_{hm} at all three temperatures, therefore it was
401 concluded that the sorption reactions for both NGFMF and GFMF were enthalpy-controlled
402 processes in the studied moisture content range. This further confirmed the predominance of
403 mesopores in the interactions between water-flour (Azuaara and Beristain 2006). These values
404 were calculated by fitting the data in Eq. 7. Fig. 5 (a, b) depicts the enthalpy-entropy
405 compensation obtained by plotting the integral properties of both flours at constant
406 temperatures of 10, 25 and 40 °C. The linear relationship between the two thermodynamic
407 properties confirmed the existence of compensation theory, which has been already justified
408 for various foods by Fontan et al. (1982).

409 *Spreading pressures*

410 The spreading pressures (π) represents the excess of free energy at the surface of the flours,
411 and provides an indication of the increase in surface tension at free sorption sites due to
412 adsorbed molecules (Fasina et al. 1999). The spreading pressure isotherms for both NGFMF
413 and GFMF were plotted against the water activity at 10, 25 and 40 °C (Fig. 6 (a, b)). The
414 values of π lied in the range of 0 – 0.078 J m⁻² for NGFMF and 0 – 0.124 J m⁻² for GFMF,

415 indicating higher surface tension on the surface of GFMF at high water activities. The graph
416 showed that the value of π increased with increasing water activity and decreased with
417 increasing temperatures. While, at water activities above 0.76 the values of π significantly
418 increased with increasing temperatures. Similar trend was observed for cassava flour (Ayala-
419 Aponte 2016) and milk-foxtail millet powder (Simha et al. 2016).

420 *Glass transition temperatures*

421 DSC thermograms obtained for both NGFMF and GFMF at a range of water activities
422 between 0.11 to 0.97 at 10, 25 and 40 °C, gave the values of glass transition temperatures
423 (T_g). T_g was obtained from the midpoint of the typical heat capacity change in the
424 thermogram line over a range of temperatures (Sandoval et al. 2009). Increasing temperatures
425 did not have any significant effect on the T_g values of both flours. Fig. 7 (a, b) shows the
426 relationship between T_g and water activity at constant temperature. It was observed that as the
427 water activity increased the values of T_g decreased linearly for both the flours, ranging
428 between 82.25 to 28.67 °C for NGFMF and from 51.11 to 11.83 °C for GFMF at all three
429 temperatures. The lower values of GFMF could be attributed to the conversion of starch into
430 sugars and other compounds due to germination of foxtail millet flours. The low molecular
431 weight of sugars and other compounds formed of germination, have been reported to cause
432 plasticizing effect of small molecules on starchy products (Chen and Yeh 2000). While, the
433 decrease in T_g values with increasing temperatures and water activities could be explained by
434 the plasticizing effect of water. Increasing temperatures causes decrease in the attractive
435 forces, thereby causing slow motion of water molecules, that gets easily adsorbed on the flour
436 surfaces, thus decreasing the T_g values. Whereas, increasing water activities, increases the
437 moisture content in the flours that acts as plasticizers, thus changing the glassy material into
438 rubbery state (Alpizar-Reyes et al. 2017).

439 The experimental values of T_g for NGFMF and GFMF stored at different water activities and
440 temperatures were fitted in Eq. 3.8.12 with a R^2 value of 0.991. The estimated values of T_g
441 were found to be 124.36 °C for NGFMF and 101.82 °C for GFMF. This difference in the
442 result could be due to erratic decrease in the experimental T_g values with increasing water
443 activity, predominantly in NGFMF as compared to GFMF. Similar justification was provided
444 for lower T_g values of dry amorphous materials in comparison to pure starch materials by
445 Sandoval et al. (2009).

446 **Conclusion**

447 The germinated and non-germinated flours obtained from high pressure processed foxtail
448 millet grains were studied for their moisture sorption characteristics to understand the
449 interdependence between the water and the foxtail millet grain components. Thus, the
450 moisture sorption isotherms provided information regarding the stability of these flours in
451 any environment. Apart from this, the thermodynamic properties were also studied that gave
452 information on the changes that took place in the flours during storage. Sorption moisture
453 isotherms showed a sigmoidal type II shape. Experimental data for these isotherms at 10, 25
454 and 40 °C fitted satisfactorily to the GAB model. Sorption properties of processed
455 germinated and non-germinated foxtail millet flour indicated that the percent of bound water
456 decreased for NGFPPF and increased for GFPPF, as the temperature increased, confirming that
457 the availability of active sites decreased due to a reduction in the total sorption ability for
458 NGFPPF and vice-versa for GFPPF. This work also suggested that the moisture sorption,
459 thermodynamic properties, spreading pressures and glass transition temperatures can be
460 related to obtain conditions guaranteeing maximum stability for storage of the flours.

461 **Acknowledgement** Nitya Sharma gratefully acknowledges the support provided by the
462 Commonwealth Scholarship Commission (INCN-2015-124).

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638 **TABLES**639 **Table 1** Functional properties of processed foxtail millet flours

Property	GFMF	NGFMF
Bulk density (g l ⁻¹)	592±12.2 ^b	732±10.4 ^a
Porosity (% volume)	67.8±0.5 ^a	53.4±0.6 ^b
Occluded air content (ml 100ml ⁻¹)	105.3±2.0 ^a	94.6±1.8 ^b
Water absorption capacity (g 100g ⁻¹)	157.4±1.8 ^a	148.2±2.3 ^b
Oil absorption capacity (g 100g ⁻¹)	98.0±0.5 ^a	80.4±1.1 ^b
Dispersibility (%)	82.2±0.5 ^a	75.4±0.3 ^b
Insolubility index (ml)	3.1±0.2 ^b	4.7±0.1 ^a
Swelling capacity (ml g ⁻¹)	5.2±0.2 ^a	4.0±0.3 ^b
Wettability (s)	58.0±1.0 ^a	52.0±1.0 ^b
Flowability (θ)	70.1±0.4 ^a	62.3±0.9 ^b
Emulsion activity (%)	64.5±0.1 ^a	48.2±0.0 ^b
Emulsion stability (%)	82.4±0.2 ^a	66.5±0.1 ^b
Foaming capacity (%)	5.2±0.4 ^b	8.8±0.5 ^a
Foaming stability (%)	57.8±0.7 ^b	78.8±0.9 ^a
Gelatinization properties:		
1. Onset temperature (°C)	70.05±0.92 ^a	70.05±1.03 ^a
2. Peak temperature (°C)	73.16±1.11 ^a	73.01±1.13 ^a
3. Conclusion temperature (°C)	77.25±0.88 ^a	77.13±0.98 ^a
4. Gelatinization enthalpy (J/g)	2.306±0.110 ^a	1.563±0.099 ^b

640 Values are mean of three replications (n=3) and expressed as mean ± standard deviation.

641 Means with different superscript within the same row are significantly different at p ≤ 0.05.

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648 **Table 2** Estimated parameters of GAB sorption model for NGFMF

<i>T</i> (°C)	<i>W_o</i> (%)	<i>G</i>	<i>k</i>	R²
10	3.235±0.100 ^a	43.171±0.150 ^a	0.780±0.020 ^a	0.99
25	2.662±0.150 ^b	28.260±0.200 ^b	0.820±0.020 ^a	0.99
40	2.364±0.090 ^b	32.720±0.190 ^c	0.881±0.025 ^a	0.99

649 Values are mean of three replications (n=3) and expressed as mean ± standard deviation.

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651 **Table 3** Estimated parameters of GAB sorption model for GFMF

<i>T</i> (°C)	<i>W_o</i> (%)	<i>G</i>	<i>k</i>	R²
10	2.987±0.090 ^a	42.701±0.220 ^a	0.852±0.025 ^a	0.99
25	2.476±0.095 ^a	28.912±0.150 ^b	0.896±0.030 ^a	0.98
40	2.063±0.090 ^a	33.661±0.150 ^c	0.944±0.010 ^a	0.99

652 Values are mean of three replications (n=3) and expressed as mean ± standard deviation.

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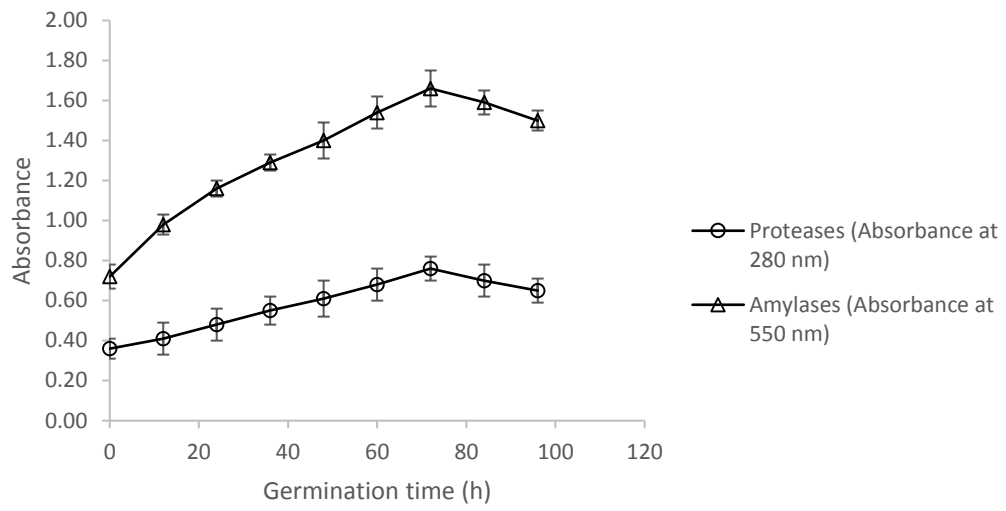
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667 **FIGURES**



668

669 **Fig. 1** Protease and amylase activity variation during the germination of foxtail millet
670 grains (Temperature= 25±2 °C; RH=80%)

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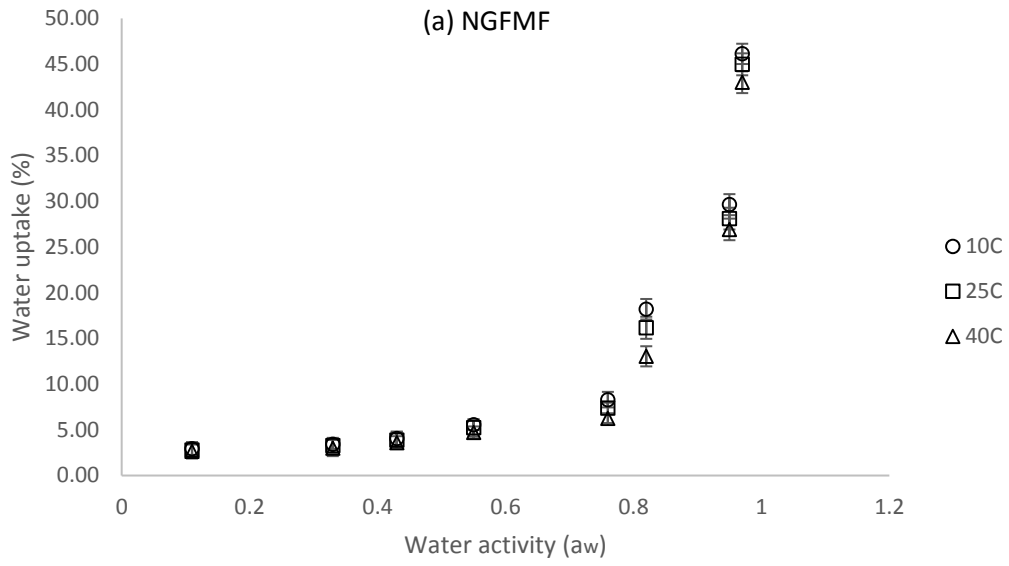
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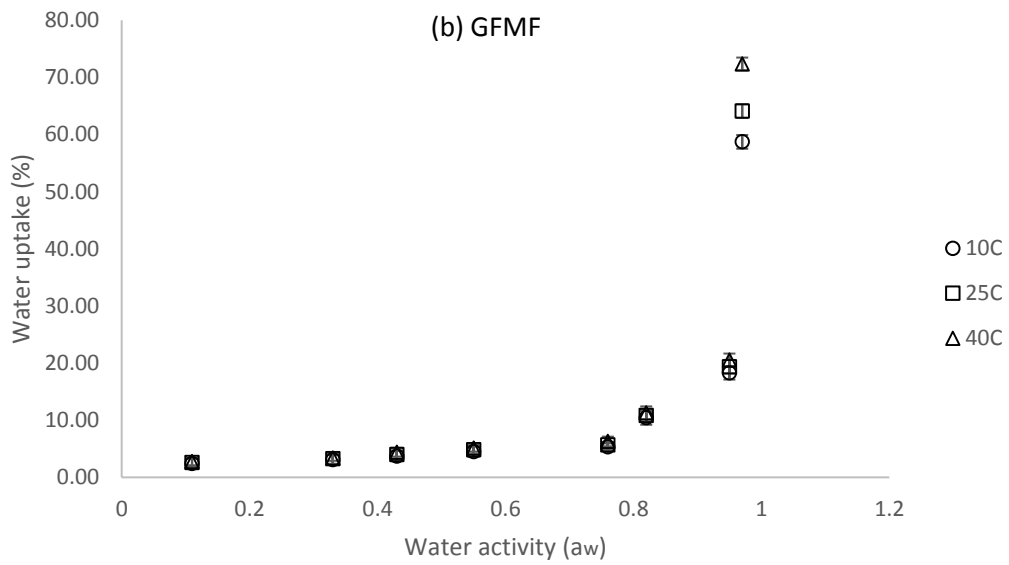
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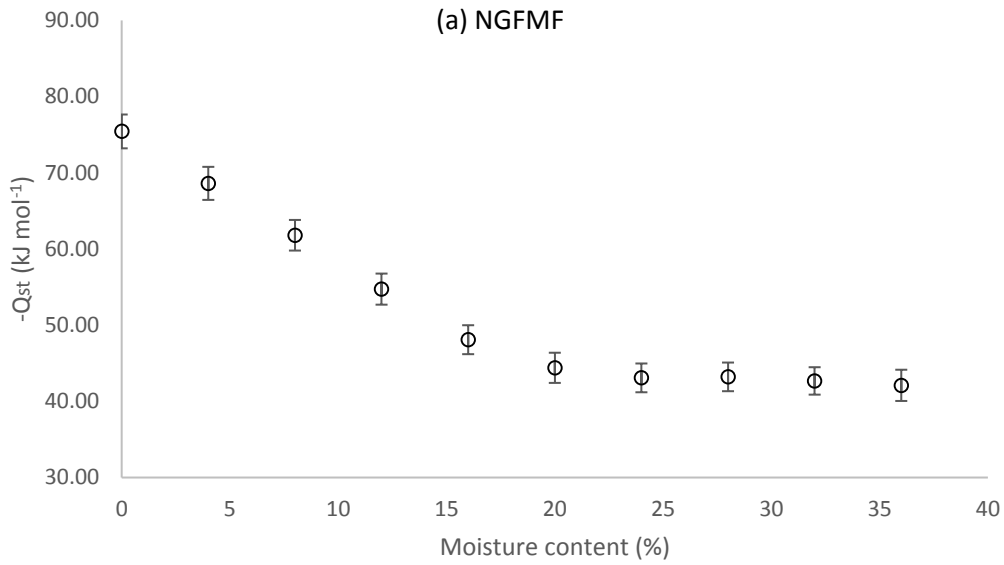
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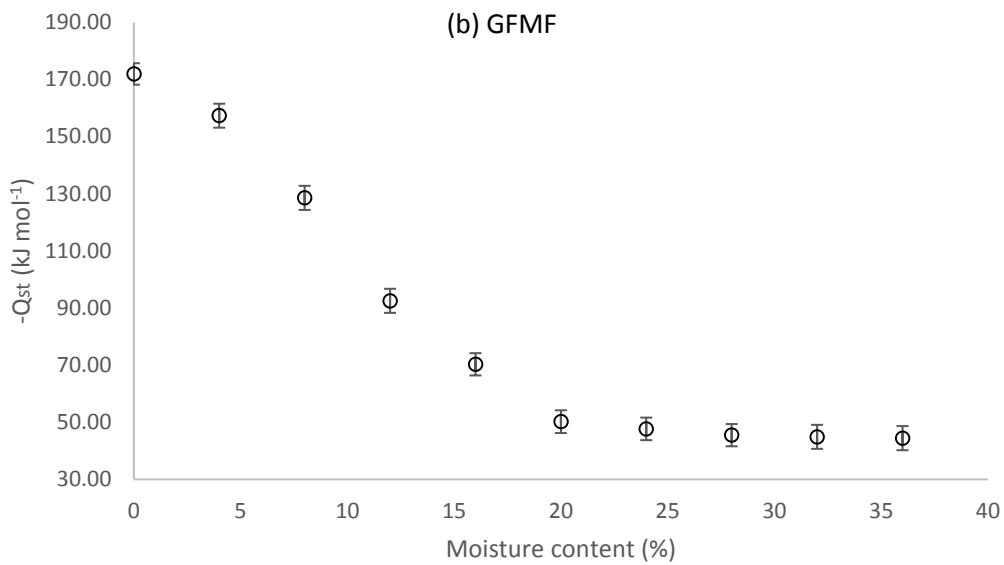
680 **Fig. 2** Moisture sorption isotherms for (a) NGFMF and (b) GFMF at 10, 25 and 40 °C
 681 obtained by static gravimetric method

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686 **Fig. 3** Net isosteric heat of sorption (Q_{st}) as a function of moisture content for (a)
 687 NGFMF and (b) GFMF. The isosteric heat of sorption at any temperature can be
 688 obtained by adding the latent heat at that temperature to the Q_{st} values.

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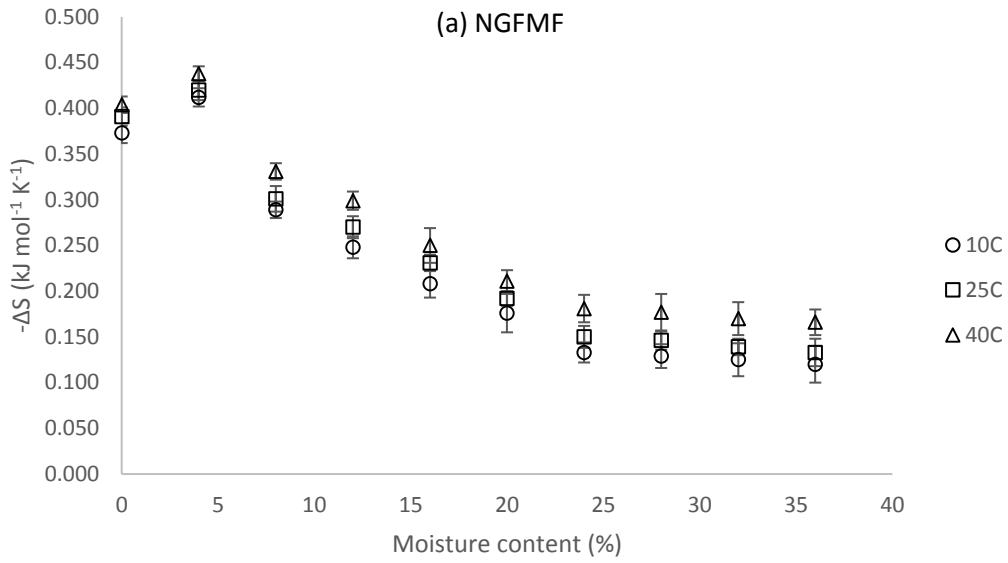
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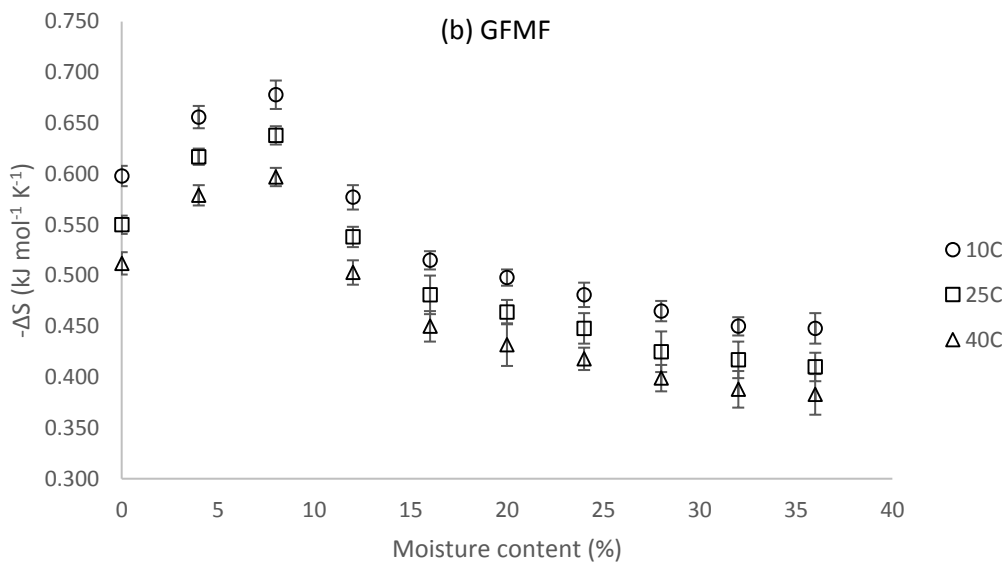
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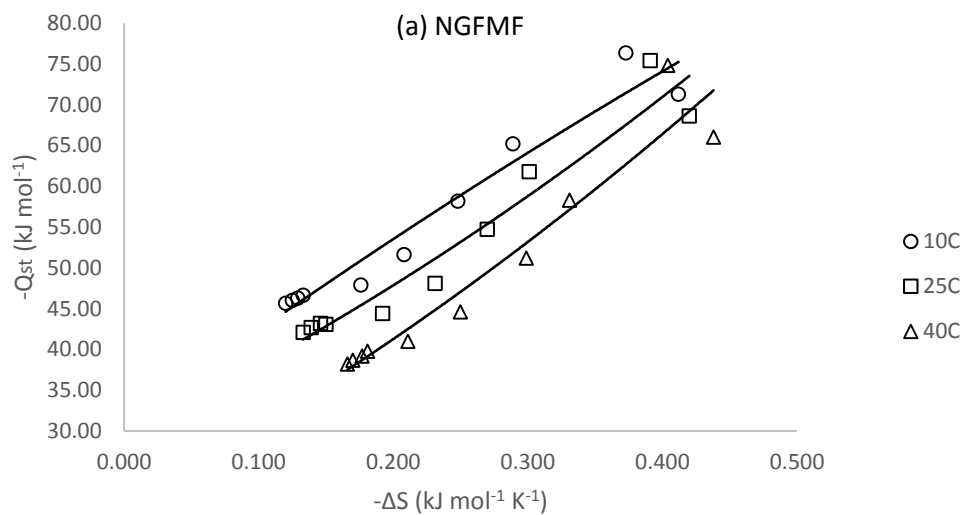


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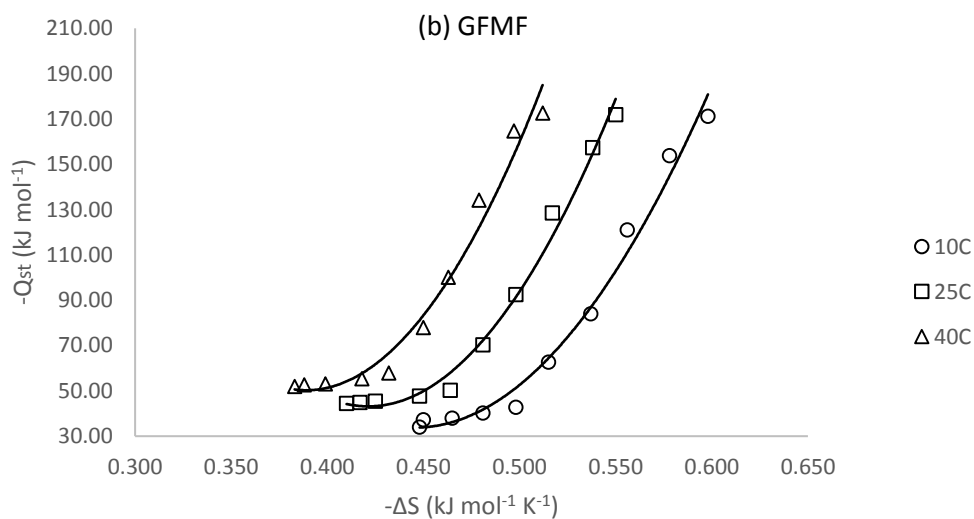
699 **Fig. 4** Integral entropy (ΔS) as a function of moisture content of (a) NGFMF and (b)
700 GFMF

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705 **Fig. 5** Integral enthalpy-integral entropy compensation for (a) NGFMF and (b) GFMF

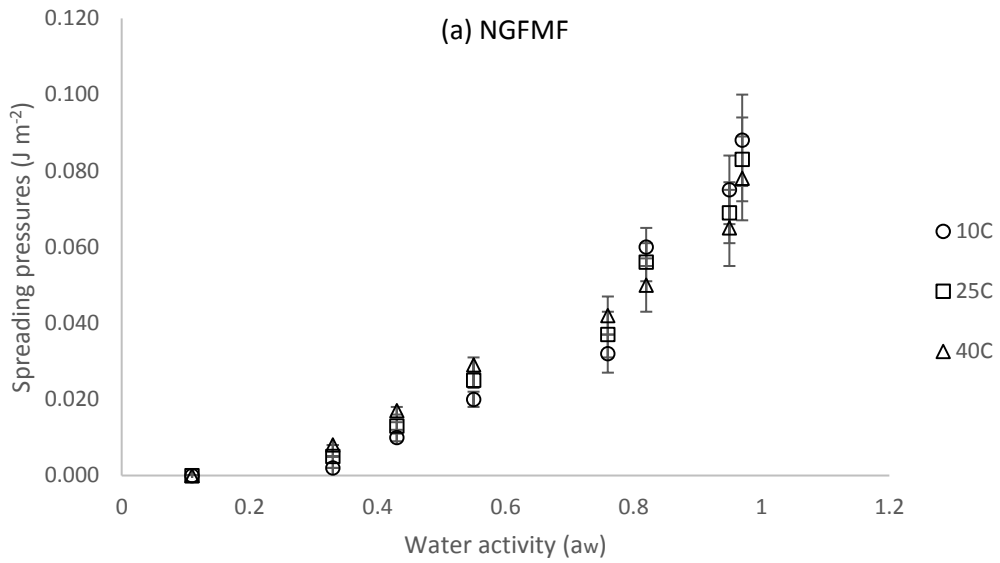
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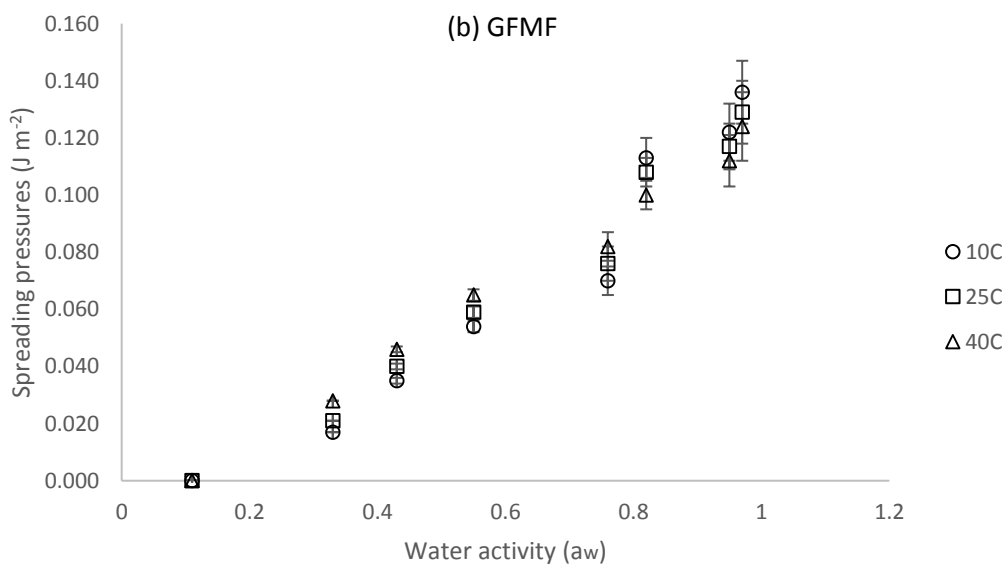
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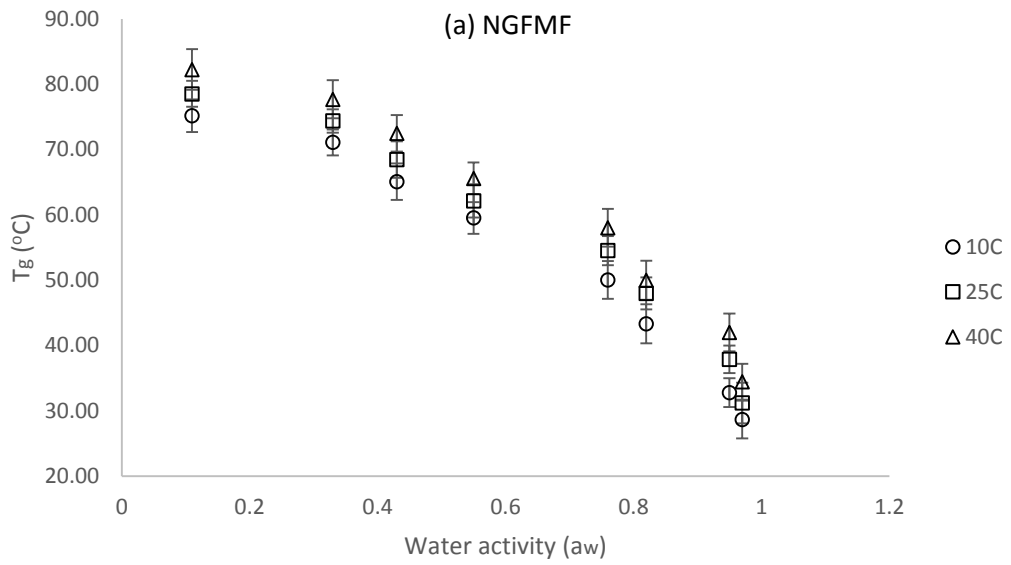
714 **Fig. 6** Spreading pressure isotherms as a function of water activity of (a) NGFMF and
 715 (b) GFMF

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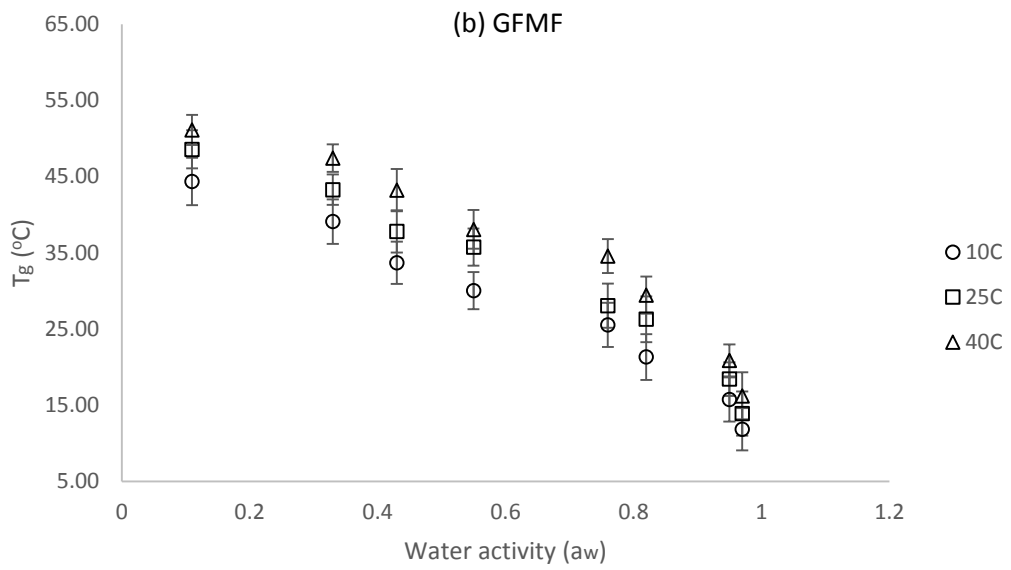
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723 **Fig. 7** Effect of water activity on glass transition temperatures of (a) NGFMF and (b)
724 GFMF

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