



SHARPENS YOUR THINKING

Modelling of Physical Ageing in starch using the TNM equation

MORRIS, Cecile, TALYLOR, Andy J., FARHATA, Imad A. and MACNAUGHTAN, William

Available from Sheffield Hallam University Research Archive (SHURA) at:

<http://shura.shu.ac.uk/4249/>

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

Published version

MORRIS, Cecile, TALYLOR, Andy J., FARHATA, Imad A. and MACNAUGHTAN, William (2011). Modelling of Physical Ageing in starch using the TNM equation. *Carbohydrate Research*, 346 (9), 1122-1128.

Repository use policy

Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Users may download and/or print one copy of any article(s) in SHURA to facilitate their private study or for non-commercial research. You may not engage in further distribution of the material or use it for any profit-making activities or any commercial gain.

1 Modelling of Physical Ageing in Starch using the TNM equation

2 Cecile Morris^{a,*}, Andy J. Taylor^a, Imad A. Farhat^a, William MacNaughtan^a

3 ^aUniversity of Nottingham, Division of Food Science, Sutton Bonington, LE12 5RD, United Kingdom

4 *Corresponding author: Tel +44 0 1159516578. Fax +44 01159516142. Cecile.Morris@nottingham.ac.uk

5 ABSTRACT

6 Gelatinised wheat starch, freeze dried and equilibrated at different RH, was aged at different
7 temperatures and for different times. The Tool-Narayanaswamy-Moynihan (TNM) model was
8 used to describe the ageing for all samples under all conditions.

9 Three TNM parameters: x , Δh^* and A were determined experimentally using respectively the
10 peak shift method (x) and the dependency of T_f' (the limiting value of T_f) on the cooling rate (Δh^*
11 and A). The non-linearity parameter x and the non exponential parameter β were also estimated
12 by optimising a fit of the experimental normalised specific heat at different ageing times and
13 temperatures to curves generated using the TNM model. The TNM model successfully described
14 the normalised experimental data.

15 It was found that the intermolecular forces were strong and the relaxation times depended more
16 strongly on the glass structure than the glass temperature. The hydration level of the starch had
17 a direct impact of the breadth of the relaxation time distribution. A dependency of the non-
18 linearity parameter x on ageing temperature (peak shift method) was observed. This suggests
19 that physical ageing is more complex than is described by TNM formalism.

20 *Keywords:* starch, physical aging, structural relaxation, TNM model

21 1. Introduction

22 Cooling from the liquid state can result in either crystallisation or glass formation. The former
23 takes place when the cooling rate is sufficiently slow to allow molecular rearrangement to form a

24 periodic crystal. Alternatively, cooling the liquid at a sufficiently rapid rate so as to avoid
25 crystallisation traps the system in the non-equilibrium glassy state. When stored below the glass
26 transition temperature, a spontaneous decrease in volume or enthalpy is observed. This is due to
27 the non-equilibrium state in which the glass was “frozen in” at the glass transition and the
28 relaxation towards liquid equilibrium (Figure 1). The enthalpy loss is regained on heating and the
29 pathway out of the glass leads to an endotherm appearing on the DSC thermogram.

30 **Figure 1 thereabout**

31 This phenomenon is known as physical ageing or structural relaxation. It has been studied as
32 early as 1931¹ when it was first noticed that, due to the non-equilibrium nature of the glass, its
33 configuration maintained at constant temperature and pressure continues to evolve after the
34 glass transition temperature has been traversed. The state of the glass and its departure from
35 equilibrium depends on the cooling rate and only an infinitely slow cooling rate from an
36 equilibrium point above the glass transition temperature would ensure that it maintained
37 equilibrium. The mechanical aspects of the relaxation have been extensively investigated² using
38 creep compliance tests which are, along with strain-stress tests, the most commonly used
39 experiment.³⁻⁴ An increase in Young’s modulus or storage modulus and a decrease in the creep
40 rate are always observed.

41 **1.1.Details of the Model**

42 One of the well known features of structural relaxation is its non-linearity. This was demonstrated
43 on the volume recovery after a temperature jump in the glassy state.⁵ After temperature jumps of
44 opposite signs, the equilibrium line is not reached symmetrically. This suggests that the transition
45 and the relaxation are governed by the instantaneous state of the glass as well as its
46 temperature. In order to account for this dependency, the fictive temperature T_f (first introduced
47 by Tool in 1931) was used to describe the structural properties of the material and thus the
48 dependency of the average relaxation time on the structure of the glass through the non-linearity
49 parameter x . This is reflected in the expression for the average relaxation time τ_0 as expressed in
50 the constitutive equation of the TNM model which takes the form of an Arrhenius type equation

51 with 2 terms accounting respectively for the effects of temperature (T) and glass structure
 52 through the fictive temperature (T_f)⁶ (Eq 1). The fictive temperature represents the temperature
 53 at which the glass in this configuration would be at equilibrium.

$$\tau_o = A \exp \left\{ \frac{x \Delta h^*}{RT} + \frac{(1-x) \Delta h^*}{RT_f} \right\} \quad \text{Eq 1}$$

54 Where R is the ideal gas constant and A is a pre-exponential factor, Δh^* the activation energy,
 55 expresses the temperature dependence of the relaxation time for the linear regime close to
 56 equilibrium. The partitioning due to x has no physical basis and its wide use is due to the good
 57 agreement with experimental data.

58 The definition of T_f in terms of enthalpy is:⁷

$$H(T_a) = H_e(T_f) - \int_T^{T_f} C_{pg} dT' \quad \text{Eq 2}$$

59 Where H_e is the theoretical equilibrium enthalpy at an ageing temperature T_a (figure 1) and C_{pg} ,
 60 the specific heat capacity in the glassy state (C_{pl} is the specific heat capacity in the liquid state).
 61 Eq 2 can be differentiated with respect to temperature and rearranged to give Eq 3 which shows
 62 that the derivative of T_f is equal to a normalised specific heat capacity which can be obtained
 63 experimentally from differential scanning calorimetry (DSC) traces.

$$\frac{dT_f}{dT} = \frac{(C_p - C_{pg})_T}{(C_{pl} - C_{pg})_{T_f}} \quad \text{Eq 3}$$

64 In practice, T_f was calculated using equations 4, 5 and 1 with a starting value obtained by
 65 assuming that in the liquid equilibrium state, the fictive temperature was equal to the actual
 66 temperature of the system (figure 1).

$$T_f(T) = T_o + \sum_i \Delta T_i [1 - \phi(t - t_i, t)] \quad \text{Eq 4}$$

67 T_0 refers to the starting temperature of the cooling-ageing-heating cycle, above the glass
68 transition temperature, in the liquid equilibrium state.

69 Another important aspect of the structural relaxation is the non-exponentiality of the process. The
70 glass transition and the structural relaxation are governed by a distribution of relaxation times.
71 This is added to the TNM equation in the form of the parameter β , where β is inversely
72 proportional to the width of relaxation time distribution (Eq 5).

$$\phi(t-t_i, t) = \exp \left[- \left(\int_{t_i}^t dt' / \tau_0 \right)^\beta \right] \quad \text{Eq 5}$$

73 The TNM model is the most widely used model to predict physical ageing and has been applied
74 to a range of polymers.⁸⁻⁹ Recently, it has also been used for the description of ageing in
75 biopolymers.¹⁰⁻¹¹ A table of the four parameters used in the TNM equation for a range of
76 synthetic polymers has been published.⁷ However, it is now recognised that the parameters can
77 depend on thermal history¹² which is not in agreement with the theory. x and β were also shown
78 to be interdependent.¹³⁻¹⁴

79 The objective of this work is to examine the extent to which the ageing at different temperatures
80 and for different times of a starch matrix at various moisture contents can be described by
81 application of the TNM model.

82 **1.2. Experimental estimation of x**

83 The non-linearity parameter can be calculated using the peak shift method.¹⁵ This method is
84 derived from the equations involving the partial derivatives of the reduced variables of the KAHR
85 (Kovacs-Aklonis-Hutchinson-Ramos) model¹⁶ which shares with the TNM model the same non-
86 linearity parameter. It was shown that the partial derivatives of the peak temperature (T_p) with
87 respect to any of the four experimental parameters (cooling rate, heating rate, ageing
88 temperature and loss enthalpy) are practically independent of the shape and breadth of the

89 retardation spectrum of the system for well stabilised glasses.¹⁷ They are therefore essentially
90 dependent only on the structure parameter x.

$$F(x) = \Delta C_p \frac{\partial T_p}{\partial \Delta H} \quad \text{Eq 6}$$

91 Where ΔH is the enthalpy lost during ageing at the annealing temperature. ΔH was determined
92 by subtracting the DSC scan of a fresh sample to that of the aged sample. Therefore, the
93 mastercurve $F(x)$ can easily be determined experimentally¹⁵ by varying the ageing time while
94 keeping the ageing temperature, cooling and heating rates constant. The slope of T_p vs. ΔH was
95 extracted from cooling-ageing-heating cycles for different ageing times and used in Eq 6. x was
96 calculated by combining Eq 6 and 7.

97 $F(x)$ was approximated as: ¹⁷

$$F(x) = \frac{1}{x} - 1 \quad \text{Eq 7}$$

98 As already stated, these equations only apply to well stabilised glasses or glasses that have
99 been annealed for a long period and show substantial non-linearity. This is not the case for
100 some of the glasses in the present work. In such cases the estimation either by the peak shift
101 method or by curve fitting is problematical. However in the Foods area short annealing times are
102 commonly encountered and complex DSC curves are observed. Therefore we have decided to
103 use both these methods in the present work despite the limitations.

104 **1.3. Experimental estimations of Δh^* and A**

105 The glassy value of the fictive temperature is denoted T_f' (figure 1). It is called the limiting value
106 of T_f and is obtained by integration of the normalised heat capacity measured during heating (Eq
107 8):

$$T_f' = T_{\max} - \int_{T_{\min}}^{T_{\max}} \left(\frac{dT_f}{dT} \right) dT \quad \text{Eq 8}$$

108 Where T_{\max} and T_{\min} are, respectively, temperatures well above and below the glass transition
109 temperature.

110 Eq 9 was derived¹⁸ for the evaluation of Δh^* from the dependency of the fictive temperature on
111 the cooling rate (q). It is based on the fact that increasing the cooling rate or equivalently the
112 average relaxation time has an identical effect on the fictive temperature. Eq 9 represents how
113 decreasing the cooling rate (or equivalently τ_0) shifts the relaxation time distribution towards
114 higher temperatures and thus affects Δh^* .¹⁹

$$\frac{d \ln |q|}{d \left(\frac{1}{T'_f} \right)} = - \frac{\Delta h^*}{R} \quad \text{Eq 9}$$

115 This relation was used to calculate the starting Δh^* value for the fitting routine (see figure 2 and
116 table 2).

117 The pre-exponential factor A can then be evaluated using Eq 10:⁷

$$\ln A = \frac{-\Delta h^*}{RT'_f} + \ln \tau(T'_f) \quad \text{Eq 10}$$

118 With $\ln[\tau(T'_f)] \approx \ln[\tau(T_g)] \approx 4.6$ as $\tau(T_g)$ can be approximated to 100s⁷

119 The aim of this study was to estimate experimentally the values of Δh^* , A and x for two
120 gelatinised and freeze-dried wheat starch systems (13.0% and 9.8% water). These values were
121 then used to generate a number of thermal histories for the two systems using the TNM model.
122 The parameters β and x were then adjusted to obtain the best fits to the experimental data.

123 2. Materials and Methods

124 2.1. Sample preparation

125 Wheat starch was gelatinised by heating in excess water (9 times the weight of starch) at 80°C
126 for 20 minutes under constant agitation. The samples were then freeze-dried and equilibrated

127 over saturated salt solutions (KCl: 84%RH and $Mg(NO_3)_2$: 53%RH) to achieve different water
128 contents. The water contents were determined in triplicates by placing the samples in an oven at
129 80°C until constant weight was achieved.

130 **2.2. Differential Scanning Calorimetry**

131 DSC experiments were carried out using a Perkin Elmer DSC7 with Pyris absolute heat capacity
132 software. The instrument was attached to an intracooler and calibrated for temperature and
133 enthalpy with indium and cyclohexane. A three trace absolute heat capacity measurement
134 method was used. The reference material used for the specific heat determination was sapphire
135 and the baseline reference was an empty pan of the same type as the one used for the sample.
136 Dry air was used as a purging gas over the head.

137 The heating and cooling rates used were 10°Cmin⁻¹.

138 Stainless steel pans were used and the ageing cycles were performed in the calorimeter without
139 removal of pans in order to completely control the thermal history. The pans were re-weighed
140 after all the thermal cycles had been carried out to check for any weight loss.

141 **3. Results**

142 **3.1. Determination of the non-linearity parameter by the peak shift method**

143 Table 1 shows the x values obtained for 2 wheat starch systems aged at different temperatures.

144 **Table 1 thereabout**

145 The non-linearity parameter x increased with ageing temperature for both wheat starch systems.
146 When pooled, the non-linearity parameters of both systems were found to decrease linearly with
147 increasing $T_g - T_a$ ($r^2 = 0.89$) (Table 1).

148 **3.2. Determination of T_f' ; the activation energy, Δh^* and pre-exponential factor A**

149 The limiting value of the fictive temperature T_f' was calculated using Eq 6 for the following cooling
150 rates: 1; 2.5; 5.5; 8; 13; 20; 30 and 45°Cmin⁻¹.

151 Figure 2 shows how the limiting T_f value (T_f').changes with cooling rate.

152 **Figure 2 thereabout**

153 **Table 2 thereabout**

154 **3.3.Generation of ageing profiles using the TNM model**

155 The values of the experimentally determined parameters Δh^* , LnA and x were used in the TNM
156 model to generate ageing profiles for a number of thermal histories. An optimisation routine for
157 the parameters x and β was then used to obtain the best fit to experimental data for each of the
158 ageing profiles. Both Δh^* and LnA were allowed to vary within 5% of the experimentally
159 determined values to take into account the error in the determination of T_f' and the slope of the
160 lines in figure 2. Figure 3 shows the Normalised Specific Heat and curves generated from the
161 TNM model for wheat starch containing 13.0% water aged at 15°C for 0, 1.5 and 6 hours. Also
162 shown on this figure is the theoretical result for annealing the glass for 168 hours.

163 **Figure 3 thereabout**

164 Figure 4 shows the Normalised Specific Heat and curves generated from the TNM model for
165 wheat starch containing 13.0% and 9.8% water aged at different temperatures for 0 and 6 hours.

166 **Figure 4 thereabout**

167 Generally, good agreement was observed between the experimental data and the TNM
168 generated curves and the model was able to describe correctly the different shapes of
169 endotherms.

170 Table 3 shows the 4 parameters used in the TNM equation to generate the normalised specific
171 heat of wheat starch at 2 different water contents, aged at different temperatures and for 0, 1.5, 3
172 and 6 hours.

173 **Table 3 thereabout**

174 Very little adjustment needed to be made on the experimental values of Δh^* (+/-0.5%) and LnA
175 (+/-0.2%) in order to obtain good fits. The x values obtained through the curve fitting method
176 depended strongly on the ageing times for all the systems and ageing times with the initial x
177 value for the “fresh” sample (no ageing) being significantly higher ($p < 0.001$) than the x values for
178 the other ageing times. No trend between x and ageing temperature was observed. There was
179 no significant difference ($p = 0.8$) between the x values of both wheat starch samples.

180 No trend between β and ageing times or ageing temperatures was observed however, the β
181 value of the wheat starch sample at 13.0% was significantly higher ($p = 0.025$) than that of the
182 sample containing 9.8% water.

183 4. Discussion

184 Despite the structural complexity of wheat starch, good agreement between the experimental
185 data and profiles generated using the TNM model was observed. The TNM values derived in this
186 study were found to be different from those reported elsewhere²⁰ for a system of 80% starch,
187 15% sorbitol and 5% water: $\Delta h^* = 95.6 \text{ kCal.mol}^{-1}$, $\text{LnA} = -143$, $\beta = 0.32$; $x = 0.48$ but were in closer
188 agreement with those reported for a system of 89% starch and 11% water: $\Delta h^* = 114.5 \text{ kCal.mol}^{-1}$,
189 $\text{LnA} = -173.5$, $\beta = 0.24$; $x = 0.37$.¹¹ In these 2 studies however, a maximum of two ageing histories
190 were fitted.

191 The ranges of x values obtained in this study by firstly the experimental peak shift method and
192 secondly through curve fitting were of the same order of magnitude and on the low side of the
193 range published for less complex carbohydrates: 0.475 for 96% maltose¹¹; 0.47 and 0.59 for an
194 anhydrous mix of trehalose (65%), sucrose (25%), glucose (5%) and lysine (10%)¹⁰; 0.43 to 0.53
195 for sucrose/aspartame mix and 0.41 – 0.50 for aspartame/trehalose²¹ and synthetic polymers:
196 0.37 for polystyrene²², 0.43 for polyvinyl acetate²³; bisphenol A polycarbonate.²⁴ Hodge (1994)
197 published a table of the TNM parameters for synthetic polymers and inorganic glasses, the x
198 values typically lie between 0.2 (PMMA) and 0.68 (LiCl).

199 The correlation between x and the glass structure was studied,²⁵ and it was concluded that for
200 organic glasses, x values were related mainly to the magnitude of the intermolecular forces, the
201 greater the intermolecular forces, the lower the x value. Therefore, the small values obtained for
202 starch based systems in this study are indicative of the structure and functional groups found in
203 starch and demonstrate strong hydrogen bonding. The values obtained indicate that while wheat
204 starches of different water contents have similar intermolecular forces, these may strengthen
205 upon ageing as x decreases from ≈ 0.4 for a fresh glass to 0.2 at 1.5 hours of ageing to remain
206 constant upon further ageing. Attributing a physical meaning to this shift could lead to over-
207 interpretation of the data as it relies only on 2 points (the fresh samples) determined by curve
208 fitting. Indeed, x has been reported to increase with ageing time.²⁶

209 It has also been pointed out that the methods for estimating x , the peak shift method and curve
210 fitting, are less sensitive for glasses not aged sufficiently to show significant non-linearity. The
211 small mid- and sub- T_g endotherms observed here rather than the overshoots at the top end of
212 the glass transition, are consistent with non-stabilised glasses. Hence the reliability of the
213 estimation of x may be limited for the glasses in the present work. Consistent with this is the
214 result for the TNM simulation of a glass aged for 168 hours (1 week) shown on figure 3. The
215 endotherm is developing into an overshoot occurring at a temperature above T_g .

216 No trend was observed between β and any of the other parameters (x , ageing time, ageing
217 temperature). However a significant difference was found between the two samples. The non-
218 exponentiality reflects the distribution breadth of relaxation times and has been shown to be
219 dependent on the cooling rate.²⁷ In this study, the cooling rate was kept constant but the
220 hydration levels of both samples were different and less available water appeared to result in a
221 wider distribution of relaxation times. Large β values were linked in polystyrenes to intersegment
222 distances larger than 0.5nm resulting in enhanced segmental mobility.²⁸ This is consistent with
223 these findings where lower β values were observed for the system with the lower water content
224 and arguably lower mobility.

225 The activation energies for amylopectin at three different water contents have been calculated.²⁹
226 It was found that Δh^* values depended greatly on the water content and decreased with
227 increasing water levels. The relationship of the Δh^* values to the structure of polystyrenes was
228 investigated:³⁰ Δh^* increased with the average molecular weight and decreased with broadening
229 molecular weight distributions. This is in agreement with the current experiments on starch where
230 increased water contents lower the Δh^* values since the introduction of water broadens the
231 molecular weight distribution as well as lowers the average molecular weight of the system. It
232 has been reported²⁴ that good fits of experimental data using the TNM model could be obtained
233 with different activation energies. This points further to the limitations of the model: despite
234 attempts to give the different parameters a physical meaning, they appear to resemble adjustable
235 parameters which overlie a deeper more fundamental theory.

236 **The Applicability of the TNM model to ageing in starch**

237 Whilst a superficial inspection of figures 3 and 4 would suggest that the TNM model describes
238 qualitatively, if not completely quantitatively, the ageing curves produced in the DSC, a more
239 careful consideration shows that there are some areas of concern. There is a decrease in the
240 experimentally determined value (peak shift method) of the x parameter as a function of the
241 difference between the glass transition temperature and the annealing temperature (Table 1). It
242 would be expected for a successful model that these parameters would be material constants
243 and so would not systematically vary with test conditions.

244 As an example of how severe the tests of the model in this work are, some of these transitions
245 are approaching a width of 70K as opposed to the more usual values of 15K observed in
246 polymers. Consequently the beta values are well below 1 and characteristic of systems with a
247 very wide spectrum of relaxation times. It is interesting to note however that even on such spread
248 transitions, the TNM model, applied assuming a single glass transition, seems to be sufficient to
249 provide at least a qualitative fit.

250 **Limitations of the TNM model**

251 Limitations in the applicability of TNM, such as the variation in the parameters x and Δh^* with
252 thermal history, have been noted previously. In particular Hutchinson *et al*²⁶ have addressed
253 problems with the interpretation of the parameter x based on the non-linear Adams Gibb
254 equation in turn derived from the original Gibbs DiMarzio description of the glass transition. This
255 still retains features of the original TNM and lends a certain familiarity to the derived expressions.
256 In this modification a maximum and minimum T_f is proposed describing slow and fast relaxation
257 processes. A new parameter x_s describes the distribution between the equilibrium and structural
258 components (slow processes) of entropy. This parameter has a fundamental meaning and a
259 formal relationship with the x parameter of the TNM model has been derived which implies in turn
260 that the parameter x can now be interpreted in more fundamental terms. A minimum value for x
261 was derived: $x_{\min} \sim 1 - T_2/T_f$. If we assume typical values for the starch T_g and the universal
262 value from the WLF equation of $T_2 = T_f (T_g) - 51.6$ then this value is about 0.15 which is
263 consistent with table 1 (obtained experimentally) and with the exception of a few values also with
264 table 3 (obtained by curve fitting). Values obtained by fitting should be less robust than those
265 obtained experimentally as the interdependence of the 4 parameters means that a small change
266 in one can lead to a change in x to compensate. However see the previous discussion on the
267 difficulty of estimating x in non-stabilised glasses.

268 Another significant point to emerge is that the expressions relating x_s and x contain the terms T ,
269 T_2 and T_f , and are such, that decreases in T_f , as in annealing, will cause x to increase. This is not
270 clear from the curve fitting results for x presented on table 3 but relatively short ageing times
271 were used in this study inducing small changes in T_f . Similarly a decrease in the annealing
272 temperature T_a will lead to a decrease in x . This is consistent with the results obtained using the
273 peak shift method (Table 1).

274 **5. Conclusion**

275 Physical ageing of two starch systems with different water contents was successfully described
276 using the TNM model. The TNM parameters obtained were in broad agreement with the limited
277 results already published on similar systems. It was found that the intermolecular forces in

278 amorphous starch were strong and the relaxation times depended more strongly on the glass
279 structure rather than the glass temperature. The hydration level of the starch had a direct impact
280 on the breadth of the relaxation time distribution. A dependency of the non-linearity parameter x
281 on the ageing temperature using the peak shift method was observed. This suggested that
282 physical ageing is more complex than described by the TNM equation. This has lead others²⁶ to
283 propose a new approach to ageing based on the non-linear Adams Gibb equation in turn derived
284 from the original Gibbs DiMarzio description of the glass transition but which retains features of
285 the original TNM. In this modification a maximum and minimum T_f is proposed describing slow
286 and fast relaxation processes. Although this approach seemed to resolve a number of
287 inconsistencies often reported in the TNM model, it has not been developed further, probably
288 because the profiles of thermal histories generated using the TNM model adequately describe
289 experimental data.

290 6. References

- 291 (1) Tool, A. Q.; Eichlin, C. G., *J. Am. Ceram. Soc.*, **1931**, *14*, 276-308.
- 292 (2) Struik, L. C. E., *Polym. Eng. Sci.*, **1978**, *18*, 799-811.
- 293 (3) Robertson, C. G.; Monat, J. E.; Wilkes, G. L., *J. Polym. Sci. Pt. B-Polym. Phys.*, **1999**, *37*, 1931-1946.
- 294 (4) Barral, L.; Cano, J.; Lopez, J.; Lopez-Bueno, I.; Nogueira, P.; Abad, M. J.; Ramirez, C., *Eur. Polym. J.*,
295 **1999**, *35*, 403-411.
- 296 (5) Kovacs, A. J., *Fortschritte der Hochpolymeren-Forschung/Advances in Polymer Science*, **1964**, *3*,
297 394-507.
- 298 (6) Bertoft, E.; Andtfolk, C.; Kulp, S. E., *J. Inst. Brew.*, **1984**, *90*, 298-302.
- 299 (7) Hodge, I. M., *Journal of Non-Crystalline Solids*, **1994**, *169*, 211-266.
- 300 (8) Han, Y. C.; D'Amore, A.; Nicolais, L., *J. Mater. Sci.*, **1999**, *34*, 1899-1904.
- 301 (9) Ague-Beghin, V.; Leclerc, E.; Daoud, M.; Douillard, R., *Journal of Colloid and Interface Science*,
302 **1999**, *214*, 143-155.
- 303 (10) Hill, S. A.; MacNaughtan, W.; Farhat, I. A.; Noel, T. R.; Parker, R.; Ring, S. G.; Whitcombe, M. J.,
304 *Journal of Agricultural and Food Chemistry*, **2005**, *53*, 10213-10218.

- 305 (11) Noel, T. R.; Parker, R.; Brownsey, G. J.; Farhat, I. A.; MacNaughtan, W.; Ring, S. G., *Journal of*
306 *Agricultural and Food Chemistry*, **2005**, *53*, 8580-8585.
- 307 (12) D'Amore, A.; Caprino, G.; Nicolais, L.; Marino, G., *Compos. Sci. Technol.*, **1999**, *59*, 1993-2003.
- 308 (13) O'Reilly, J. M., *J. Polym. Sci. Pt. B-Polym. Phys.*, **2000**, *38*, 495-499.
- 309 (14) Hodge, I. M.; Berens, A. R., *Macromolecules*, **1982**, *15*, 762-770.
- 310 (15) Godard, M. E.; Saiter, J. M.; Burel, F.; Bunel, C.; Cortes, P.; Montserrat, S.; Hutchinson, J. M.,
311 *Polym. Eng. Sci.*, **1996**, *36*, 2978-2985.
- 312 (16) Kovacs, A. J.; Hutchinson, J. M., *J. Polym. Sci. Pt. B-Polym. Phys.*, **1979**, *17*, 2031-2058.
- 313 (17) Hutchinson, J. M.; Ruddy, M., *J. Polym. Sci. Pt. B-Polym. Phys.*, **1988**, *26*, 2341-2366.
- 314 (18) Moynihan, C. T.; Easteal, A. J.; Debolt, M. A.; Tucker, J., *J. Am. Ceram. Soc.*, **1976**, *59*, 12-16.
- 315 (19) Moynihan, C. T.; Macedo, P. B.; Montrose, C. J.; Gupta, P. K.; Debolt, M. A.; Dill, J. F.; Dom, B. E.;
316 Drake, P. W.; Easteal, A. J.; Elterman, P. B.; Moeller, R. P.; Sasabe, H.; Wilder, J. A., *Ann.NY*
317 *Acad.Sci.*, **1976**, *279*, 15-35.
- 318 (20) Lourdin, D.; Colonna, P.; Brownsey, G. J.; Noel, T. R.; Ring, S. G., *Carbohydrate Research*, **2002**,
319 *337*, 827-833.
- 320 (21) Luthra, S. A.; Hodge, I. M.; Pikal, M. J., *J. Pharm. Sci.*, **2008**, *97*, 3084-3099.
- 321 (22) Li, Q. X.; Simon, S. L., *Polymer*, **2006**, *47*, 4781-4788.
- 322 (23) Svoboda, R.; Pustkova, P.; Malek, J., *Polymer*, **2008**, *49*, 3176-3185.
- 323 (24) Badrinarayanan, P.; Simon, S. L.; Lyng, R. J.; O'Reilly, J. M., *Polymer*, **2008**, *49*, 3554-3560.
- 324 (25) Saiter, J. M.; Denis, G.; Grenet, J., *Macromol. Symp.*, **1999**, *148*, 15-30.
- 325 (26) Hutchinson, J. M.; Montserrat, S.; Calventus, Y.; Cortes, P., *Macromolecules*, **2000**, *33*, 5252-5262.
- 326 (27) Hadac, J.; Slobodian, P.; Riha, P.; Saha, P.; Rychwalski, R. W.; Emri, I.; Kubat, J., *Journal of Non-*
327 *Crystalline Solids*, **2007**, *353*, 2681-2691.
- 328 (28) Jiang, W.; Zuo, C. W.; Hu, J. L.; Gu, Q.; Chen, W.; Xue, G., *Macromolecules*, **2008**, *41*, 5356-5360.
- 329 (29) Borde, B.; Bizot, H.; Vigier, G.; Buleon, A., *Carbohydrate Polymers*, **2002**, *48*, 83-96.
- 330 (30) Privalko, V. P.; Demchenko, S. S.; Lipatov, Y. S., *Macromolecules*, **1986**, *19*, 901-904.

331

332 **Figure 1** Enthalpy loss during an isothermal ageing process in the glassy state

333 **Figure 2** Determination of the activation energy from the dependency of T_f' on the cooling rate (see
334 equation 9)

335 **Figure 3** Experimental Normalised Specific Heat and TNM generated curves for wheat starch at a
336 moisture content of 13.0% and aged at 15°C (288K) for 0, 1.5 and 6 hours. Also shown is the TNM
337 generated curve for a glass annealed for 168 hours. See table 3 for the values used in the fit. The values
338 used for the 168 hour fit are identical to those for 6 hours.

339 **Figure 4** Experimental Normalised Specific Heat and and the normalised specific heat generated from the
340 TNM model for systems aged for 0 and 6 hours. A) Wheat Starch 13.0% moisture aged at 25°C (298K) B)
341 Wheat Starch 13.0% moisture aged at 40°C (313K) C) Wheat Starch 9.8% moisture aged at 40°C (313K)
342 D) Wheat Starch 9.8% moisture aged at 60°C (333K). See table 3 for the exact parameter values used in
343 the fits.

344 **Table 1** Non-linearity parameters for wheat starch equilibrated at two water contents and aged at different
345 ageing temperatures

346 **Table 2** Activation energy and pre-exponential factors for the wheat starch systems

347 **Table 3** TNM parameters used for the generation of the thermal profiles of wheat starch

348