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Modelling of Physical Ageing in Starch using the TNM equation

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ABSTRACT

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

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

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

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

1. Introduction

Cooling from the liquid state can result in either crystallisation or glass formation. The former takes place when the cooling rate is sufficiently slow to allow molecular rearrangement to form a
periodic crystal. Alternatively, cooling the liquid at a sufficiently rapid rate so as to avoid
crystallisation traps the system in the non-equilibrium glassy state. When stored below the glass
transition temperature, a spontaneous decrease in volume or enthalpy is observed. This is due to
the non-equilibrium state in which the glass was “frozen in” at the glass transition and the
relaxation towards liquid equilibrium (Figure 1). The enthalpy loss is regained on heating and the
pathway out of the glass leads to an endotherm appearing on the DSC thermogram.

Figure 1 thereabout

This phenomenon is known as physical ageing or structural relaxation. It has been studied as
early as 1931\(^1\) when it was first noticed that, due to the non-equilibrium nature of the glass, its
configuration maintained at constant temperature and pressure continues to evolve after the
glass transition temperature has been traversed. The state of the glass and its departure from
equilibrium depends on the cooling rate and only an infinitely slow cooling rate from an
equilibrium point above the glass transition temperature would ensure that it maintained
equilibrium. The mechanical aspects of the relaxation have been extensively investigated\(^2\) using
creep compliance tests which are, along with strain-stress tests, the most commonly used
experiment.\(^3\)\(^-\)\(^4\) An increase in Young’s modulus or storage modulus and a decrease in the creep
rate are always observed.

1.1. Details of the Model

One of the well known features of structural relaxation is its non-linearity. This was demonstrated
on the volume recovery after a temperature jump in the glassy state.\(^5\) After temperature jumps of
opposite signs, the equilibrium line is not reached symmetrically. This suggests that the transition
and the relaxation are governed by the instantaneous state of the glass as well as its
temperature. In order to account for this dependency, the fictive temperature \( T_f \) (first introduced
by Tool in 1931) was used to describe the structural properties of the material and thus the
dependency of the average relaxation time on the structure of the glass through the non-linearity
parameter \( x \). This is reflected in the expression for the average relaxation time \( \tau_0 \) as expressed in
the constitutive equation of the TNM model which takes the form of an Arrhenius type equation
with 2 terms accounting respectively for the effects of temperature (T) and glass structure through the fictive temperature \( T_f \) \(^6\) (Eq 1). The fictive temperature represents the temperature at which the glass in this configuration would be at equilibrium.

\[
\tau_0 = A \exp \left\{ \frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \right\} \tag{Eq 1}
\]

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

The definition of \( T_f \) in terms of enthalpy is: \(^7\)

\[
H(T_a) = H_e(T_f) - \int_T^{T_f} C_{pg} dT' \tag{Eq 2}
\]

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

\[
\frac{dT_f}{dT} = \frac{(C_p - C_{pg})_{T_f}}{(C_{pl} - C_{pg})_{T_f}} \tag{Eq 3}
\]

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

\[
T_f(T) = T_o + \sum_i \Delta T_i [1 - \phi(t-t_i,t)] \tag{Eq 4}
\]
To refers to the starting temperature of the cooling-ageing-heating cycle, above the glass transition temperature, in the liquid equilibrium state.

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

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

The TNM model is the most widely used model to predict physical ageing and has been applied to a range of polymers. Recently, it has also been used for the description of ageing in biopolymers. A table of the four parameters used in the TNM equation for a range of synthetic polymers has been published. However, it is now recognised that the parameters can depend on thermal history which is not in agreement with the theory. $x$ and $\beta$ were also shown to be interdependent.

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

1.2. Experimental estimation of $x$

The non-linearity parameter can be calculated using the peak shift method. This method is derived from the equations involving the partial derivatives of the reduced variables of the KAHR (Kovacs-Aklonis-Hutchinson-Ramos) model which shares with the TNM model the same non-linearity parameter. It was shown that the partial derivatives of the peak temperature ($T_p$) with respect to any of the four experimental parameters (cooling rate, heating rate, ageing temperature and loss enthalpy) are practically independent of the shape and breadth of the
retardation spectrum of the system for well stabilised glasses. They are therefore essentially dependent only on the structure parameter $x$.

$$F(x) = \Delta C_p \frac{\partial T_p}{\partial \Delta H}$$  \hspace{1cm} \text{Eq 6}$$

Where $\Delta H$ is the enthalpy lost during ageing at the annealing temperature. $\Delta H$ was determined by subtracting the DSC scan of a fresh sample to that of the aged sample. Therefore, the mastercurve $F(x)$ can easily be determined experimentally\textsuperscript{15} by varying the ageing time while keeping the ageing temperature, cooling and heating rates constant. The slope of $T_p$ vs. $\Delta H$ was extracted from cooling-ageing-heating cycles for different ageing times and used in Eq 6. $x$ was calculated by combining Eq 6 and 7.

$F(x)$ was approximated as:\textsuperscript{17}

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

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

1.3. Experimental estimations of $\Delta h^*$ and $A$

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

$$T_f' = T_{max} - \int_{T_{min}}^{T_{max}} \left( \frac{dT_f}{dT} \right) dT$$  \hspace{1cm} \text{Eq 8}$$
Where \( T_{\text{max}} \) and \( T_{\text{min}} \) are, respectively, temperatures well above and below the glass transition temperature.

Eq 9 was derived for the evaluation of \( \Delta h^* \) from the dependency of the fictive temperature on the cooling rate (q). It is based on the fact that increasing the cooling rate or equivalently the average relaxation time has an identical effect on the fictive temperature. Eq 9 represents how decreasing the cooling rate (or equivalently \( \tau_0 \)) shifts the relaxation time distribution towards higher temperatures and thus affects \( \Delta h^* \).

\[
\frac{d \ln[q]}{d \left( \frac{1}{T'_f} \right)} = - \frac{\Delta h^*}{R}
\]

Eq 9

This relation was used to calculate the starting \( \Delta h^* \) value for the fitting routine (see figure 2 and table 2).

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

\[
\ln A = \frac{-\Delta h^*}{RT'_f} + \ln \tau(T'_f)
\]

Eq 10

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

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

2. Materials and Methods

2.1. Sample preparation

Wheat starch was gelatinised by heating in excess water (9 times the weight of starch) at 80°C for 20 minutes under constant agitation. The samples were then freeze-dried and equilibrated.
over saturated salt solutions (KCl: 84%RH and Mg(NO₃)₂: 53%RH) to achieve different water contents. The water contents were determined in triplicates by placing the samples in an oven at 80°C until constant weight was achieved.

2.2. Differential Scanning Calorimetry

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

The heating and cooling rates used were 10°C min⁻¹. Stainless steel pans were used and the ageing cycles were performed in the calorimeter without removal of pans in order to completely control the thermal history. The pans were re-weighed after all the thermal cycles had been carried out to check for any weight loss.

3. Results

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

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

Table 1 thereabout

The non-linearity parameter x increased with ageing temperature for both wheat starch systems. When pooled, the non-linearity parameters of both systems were found to decrease linearly with increasing Tg-Ta (r² = 0.89) (Table 1).

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

The limiting value of the fictive temperature T_f' was calculated using Eq 6 for the following cooling rates: 1; 2.5; 5.5; 8; 13; 20; 30 and 45°C min⁻¹.
Figure 2 shows how the limiting $T_f$ value ($T_f'$) changes with cooling rate.

**Figure 2 thereabout**

**Table 2 thereabout**

### 3.3. Generation of ageing profiles using the TNM model

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

**Figure 3 thereabout**

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

**Figure 4 thereabout**

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

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

**Table 3 thereabout**
Very little adjustment needed to be made on the experimental values of $\Delta h^*$ (+/-0.5%) and LnA (+/-0.2%) in order to obtain good fits. The x values obtained through the curve fitting method depended strongly on the ageing times for all the systems and ageing times with the initial x value for the “fresh” sample (no ageing) being significantly higher ($p<0.001$) than the x values for the other ageing times. No trend between x and ageing temperature was observed. There was no significant difference ($p=0.8$) between the x values of both wheat starch samples.

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

4. Discussion

Despite the structural complexity of wheat starch, good agreement between the experimental data and profiles generated using the TNM model was observed. The TNM values derived in this study were found to be different from those reported elsewhere$^{20}$ for a system of 80% starch, 15% sorbitol and 5% water: $\Delta h^*=95.6$ kCal.mol$^{-1}$, LnA=-143, $\beta=0.32$; x=0.48 but were in closer agreement with those reported for a system of 89% starch and 11% water: $\Delta h^*=114.5$kCal.mol$^{-1}$, LnA=-173.5, $\beta=0.24$; x=0.37.$^{11}$ In these 2 studies however, a maximum of two ageing histories were fitted.

The ranges of x values obtained in this study by firstly the experimental peak shift method and secondly through curve fitting were of the same order of magnitude and on the low side of the range published for less complex carbohydrates: 0.475 for 96% maltose$^{11}$; 0.47 and 0.59 for an anhydrous mix of trehalose (65%), sucrose (25%), glucose (5%) and lysine (10%)$^{10}$; 0.43 to 0.53 for sucrose/aspartame mix and 0.41 – 0.50 for aspartame/trehalose$^{21}$ and synthetic polymers: 0.37 for polystyrene$^{22}$, 0.43 for polyvinyl acetate$^{23}$; bisphenol A polycarbonate.$^{24}$ Hodge (1994) published a table of the TNM parameters for synthetic polymers and inorganic glasses, the x values typically lie between 0.2 (PMMA) and 0.68 (LiCl).
The correlation between $x$ and the glass structure was studied, and it was concluded that for organic glasses, $x$ values were related mainly to the magnitude of the intermolecular forces, the greater the intermolecular forces, the lower the $x$ value. Therefore, the small values obtained for starch based systems in this study are indicative of the structure and functional groups found in starch and demonstrate strong hydrogen bonding. The values obtained indicate that while wheat starches of different water contents have similar intermolecular forces, these may strengthen upon ageing as $x$ decreases from $\approx 0.4$ for a fresh glass to 0.2 at 1.5 hours of ageing to remain constant upon further ageing. Attributing a physical meaning to this shift could lead to over-interpretation of the data as it relies only on 2 points (the fresh samples) determined by curve fitting. Indeed, $x$ has been reported to increase with ageing time.

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

No trend was observed between $\beta$ and any of the other parameters ($x$, ageing time, ageing temperature). However a significant difference was found between the two samples. The non-exponentiality reflects the distribution breadth of relaxation times and has been shown to be dependent on the cooling rate. In this study, the cooling rate was kept constant but the hydration levels of both samples were different and less available water appeared to result in a wider distribution of relaxation times. Large $\beta$ values were linked in polystyrenes to intersegment distances larger than 0.5nm resulting in enhanced segmental mobility. This is consistent with these findings where lower $\beta$ values were observed for the system with the lower water content and arguably lower mobility.
The activation energies for amylopectin at three different water contents have been calculated.\textsuperscript{29} It was found that $\Delta h^*$ values depended greatly on the water content and decreased with increasing water levels. The relationship of the $\Delta h^*$ values to the structure of polystyrenes was investigated.\textsuperscript{30} $\Delta h^*$ increased with the average molecular weight and decreased with broadening molecular weight distributions. This is in agreement with the current experiments on starch where increased water contents lower the $\Delta h^*$ values since the introduction of water broadens the molecular weight distribution as well as lowers the average molecular weight of the system. It has been reported\textsuperscript{24} that good fits of experimental data using the TNM model could be obtained with different activation energies. This points further to the limitations of the model: despite attempts to give the different parameters a physical meaning, they appear to resemble adjustable parameters which overlie a deeper more fundamental theory.

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

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

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

**Limitations of the TNM model**
Limitations in the applicability of TNM, such as the variation in the parameters $x$ and $\Delta h^*$ with thermal history, have been noted previously. In particular Hutchinson et al.\textsuperscript{26} have addressed problems with the interpretation of the parameter $x$ based on the non-linear Adams Gibb equation in turn derived from the original Gibbs DiMarzio description of the glass transition. This still retains features of the original TNM and lends a certain familiarity to the derived expressions.

In this modification a maximum and minimum $T_f$ is proposed describing slow and fast relaxation processes. A new parameter $x_s$ describes the distribution between the equilibrium and structural components (slow processes) of entropy. This parameter has a fundamental meaning and a formal relationship with the $x$ parameter of the TNM model has been derived which implies in turn that the parameter $x$ can now be interpreted in more fundamental terms. A minimum value for $x$ was derived: $x_{\min} \sim 1 - T_2/T_f$. If we assume typical values for the starch $T_g$ and the universal value from the WLF equation of $T_2 = T_f (T_g) - 51.6$ then this value is about 0.15 which is consistent with table 1 (obtained experimentally) and with the exception of a few values also with table 3 (obtained by curve fitting). Values obtained by fitting should be less robust than those obtained experimentally as the interdependence of the 4 parameters means that a small change in one can lead to a change in $x$ to compensate. However see the previous discussion on the difficulty of estimating $x$ in non-stabilised glasses.

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

5. Conclusion

Physical ageing of two starch systems with different water contents was successfully described using the TNM model. The TNM parameters obtained were in broad agreement with the limited results already published on similar systems. It was found that the intermolecular forces in
amorphous starch were strong and the relaxation times depended more strongly on the glass structure rather than the glass temperature. The hydration level of the starch had a direct impact on the breadth of the relaxation time distribution. A dependency of the non-linearity parameter $x$ on the ageing temperature using the peak shift method was observed. This suggested that physical ageing is more complex than described by the TNM equation. This has lead others to propose a new approach to ageing based on the non-linear Adams Gibb equation in turn derived from the original Gibbs DiMarzio description of the glass transition but which retains features of the original TNM. In this modification a maximum and minimum $T_f$ is proposed describing slow and fast relaxation processes. Although this approach seemed to resolve a number of inconsistencies often reported in the TNM model, it has not been developed further, probably because the profiles of thermal histories generated using the TNM model adequately describe experimental data.

6. References

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

Figure 2 Determination of the activation energy from the dependency of $T_i'$ on the cooling rate (see equation 9).

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

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

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

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

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