The Fragility of Glassy Foods

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The theory of glass transition and the glass transition temperature (T_g) have been frequently used in the food bio-polymer literature to study structure-function relationships and their broader impact on processing and product quality. While it is recognized that amorphous materials undergo dramatic changes in physical properties when transitioning from the glassy state to the liquid/rubbery state, only recently an understanding has been gained on the differences between different materials in the extent of these changes and their sensitivity to such changes near the glass transition. Theoretical models such as the Williams-Landel-Ferry (WLF) and Vogel-Fulcher-Tammann (VFT) have been used in both synthetic and bio - polymers to describe the temperature dependent variation of material properties at and above the glass transition. However, a recent development in the synthetic polymer literature (and to a very small extent in the food literature) is the concept of 'fragility' that was broadly popularized by C.A. Angell in explaining the varying tendencies of liquids to vitrify near the glass transition (Angell, 1995).

The fragility concept was introduced to differentiate fragile systems which are highly sensitive to temperature changes above T_g, from strong liquids, which are less disturbed by the passage through the glass transition. Strong liquids have stable structures of local to intermediate order, whereas the structure in fragile liquids is unstable and they show a broader range of property changes when going from the liquid or melt state to the glassy state (Angell, 1995). Fragility has been mostly determined by two differing means: 1) as the ratio of thermodynamic heat capacities in the liquid and glassy states and 2) as the steepness factor, m, determined from dynamic relaxation data (Huang and McKenna, 2001).

Angell plots (Angell, 1995) represent relaxation data as a reduced Arrhenius plot of log (a_T) vs. T_g/T, where a_T are shift factors from Time-Temperature superposition experiments. These plots reveal the extent of the non-Arrhenius behavior in the samples studied. A linear plot of log (a_T) vs. T_g/T indicates strong Arrhenius type behavior near the T_g while a non-linear plot indicates non-Arrhenius behavior with the extent determined by the curvature.

The limiting slope of this Angell plot near the T_g provides the steepness factor (or dynamic fragility) m. Fragility, obtained as a steepness factor 'm', has high values ($100 < m < 200$) for a strongly non-Arrhenius and fragile liquids whereas values as low as ~20 ($16 < m < 100$) have been observed for strong liquids (Huang and McKenna, 2001, Champion et al, 2000). Huang and McKenna (2001) pointed out that this dynamic fragility parameter m can also be derived from the WLF constants, C_1 and C_2, and the T_g of the material as

$$m = \frac{T_g C_1}{C_2}$$

Equation 1

Angell classified many common inorganic, organic and polymeric molecules into strong and fragile liquids (Angell, 1995), but there has been a lack of such studies in the food literature. A review on the glass transition in foods by Champion and coworkers (2000) provided fragility data on simple sugars such as glucose, fructose and sucrose. They concluded that these simple sugars were fragile materials and their fragility decreased (for glucose) or remained the same (for sucrose) with an increase in water content. Polysaccharides were found to behave as fragile materials also with the fragility decreasing with increasing water content. This observation for polysaccharides was confirmed by Borde and coworkers (2002) who studied the glass transition and fragility of amylopectin using DSC as a function of water activity. While such limited information is available on the fragility of polysaccharides there is very little information on polypeptides, proteins and proteinaceous foods. In a research study on the influence of the molecular weight of pullulan on its glass transition, Lazaridou and coworkers (2002) mention that poly-L-asparagine, elastin and gluten have m values of 43, 40 and 51 respectively.

In this work, fragility of a particular food bio-polymer with high protein content - soy flour, and its protein components has been determined from published and experimental relaxation data and the effect of processing and storage parameters, such as cooking temperature and water activity on fragility were assessed.

Published works from research done in this laboratory on soy proteins and soy flour were used to obtain the fragility parameter, m, from dynamic mechanical spectroscopy data. Morales-Diaz and Kokini (1998) conducted a broad study on the phase transitions and chemical complexing reactions in the 7S and 11S protein fractions in soy which constitute up to 70% of the total protein in soy (Morales-Diaz and Kokini, 1998). Pure fractions of the proteins from native defatted soy flour were extracted. DSC and mechanical spectroscopic experiments were conducted to determine glass transition temperatures of the purified fractions at various water activities. A detailed rheological study of the proteins revealed that the temperature induced changes in the proteins were of the non-Arrhenius WLF dependence. C_1 and C_2 values, which were different from the universal values, were deduced from time-temperature superposition experiments and reported at a particular moisture content (table 1). The glass transition temperature at that moisture content for both proteins was also reported (table 1).

Using equation 1 as the definition of m, the values were calculated for the 7S and 11S proteins from the data reported by Morales-Diaz and Kokini (1998) and are shown in table 1.

Table 1. Glass transition temperatures, WLF constants (Morales-Diaz and Kokini, 1998) and fragility parameter for 7S and 11S protein fractions of soy.

Sample	T_g (K)	C_1	C_2 (K)	m
7S	235	31	207	35.19
11S	265	67	482	36.56

The m values for the 7S and 11S fractions are very low and indicate a very strong behavior. They are in the range of the value reported for poly-L-asparagine, elastin and gluten (Angell, 1995; Lazaridou and Biliaderis, 2002). The values show a slight increase from 7S to 11S which is within the error reported in the T_g, C_1 and C_2 values and so cannot be considered as a significant difference. However, the 11S fraction of soy has a molecular weight that is much higher than the 7S fraction (Morales-Diaz and Kokini, 1998). In the study using pullulan of different molecular weights, Lazaridou and coworkers (2003) estimated 'm' from DMTA results. They determined m to be 80.2 and 82.9 for lower and higher molecular weight pullulans respectively with a molecular weight difference of about 200,000. While those authors did not conclude that an increase in molecular weight increases m value, the results obtained in this study are indicative of a general trend in biopolymers of similar structure and varying size.

In another study by researchers in our laboratory, Yildiz and Kokini (2001) determined the effect of water activity on the change in the WLF constants. Defatted soy flour – water doughs were prepared and equilibrated to various water activities. Glass transition temperatures were determined using mechanical spectroscopy and time-temperature superposition was utilized to determine the WLF constants (table 2).

Table 2. Glass transition temperatures and WLF constants of defatted soy flour at various water activities (Yildiz and Kokini, 2001).

Water activity of defatted soy flour - water dough	T_g (K)	C_1	C_2 (K)
0.43	320	19	126
0.57	294	17	154
0.68	277	27	116
0.75	265	16	164

Published shift factors (a_T) data for the soy flour doughs at different water activities derived from time-temperature superposition (Yildiz and Kokini, 2001) was used to construct an Angell plot (figure 1).
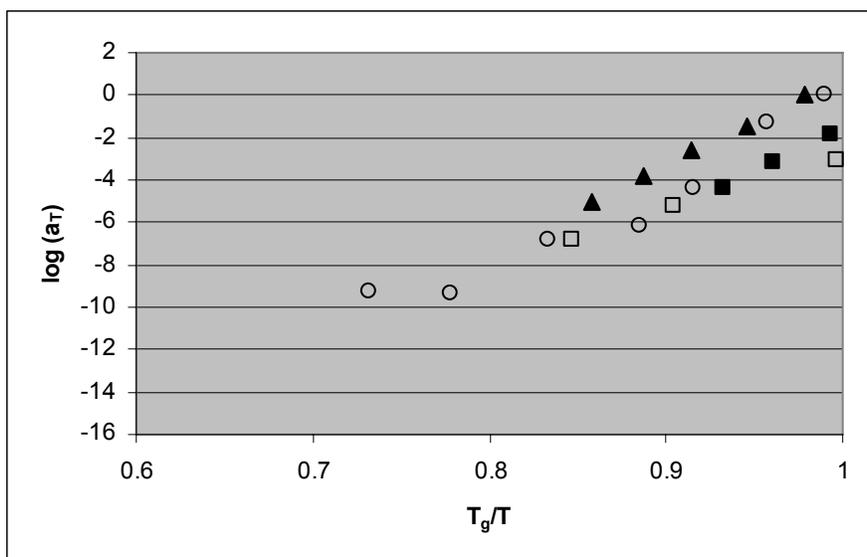
Figure 1. Angell plot of defatted soy flour – water doughs at water activity of 0.43 (■), 0.57 (○), 0.68 (▲) and 0.75 (□).

The plot reveals the strong behavior of these doughs with their strong Arrhenius-like character near T_g. The m values were also calculated using the data in table 2 and are reported in table 3.

Table 3. Dynamic fragility parameter, m, of defatted soy flour – water doughs at different water activities.

Water activity of defatted soy flour - water dough	Dynamic fragility m
0.43	48.25
0.57	32.45
0.68	64.47
0.75	25.85

The m values are close to those observed for the 7S and 11S fractions. However, the two sets of data of pure protein fractions and soy flour doughs are not comparable as they are at different water activities. The fragility values, with the exception of the value at water activity 0.68, show a decreasing trend with increasing water content. This is consistent with the observations reported for polysaccharides (Borde et al, 2002). The researchers postulated that the water in the system has a structuring role that reduces hindrance and heterogeneities associated with branched polymer systems. This structuring reduces the thermal energy

necessary for promoting the cooperative chain motions associated with the glass transition; it increases the transition steepness and decreases the fragility values.

The effect of cooking soy to different extents on its WLF constants was studied by Ashokan and Kokini (2005). Defatted soy flour (DSF) with protein content ~54%, was cooked to different extents in either a convection oven or a twin screw extruder to temperatures of 60, 95 and 145 °C to achieve different levels of crosslinking. Temperatures higher than 145 °C were not attainable due to experimental considerations and greater degree of crosslinking was achieved by using soy protein concentrate (SPC) which has up to 70% protein. Rheological studies were conducted on samples equilibrated to a water activity of 0.75 and the glass transition temperature was determined (table 4). The WLF constants, C_1 and C_2, were calculated from time-temperature superposition experiments and the dynamic fragility was estimated as values of m (table 4).

Table 4. Glass transition temperatures, WLF constants and dynamic fragility, m for soy cooked to different extents (Ashokan and Kokini, 2005).

Sample	T_g (K)	C_1	C_2 (K)	m
DSF uncooked	254	44	192	58
DSF 60	259	51	233	57
DSF 95	256	65	320	52
DSF 145	255	63	315	51
SPC 95	275	87	426	56
SPC 145	273	82	409	55

The reported values of m decreased slightly with increased networking in the soy. When the shift factors, a_T, from time-temperature superposition are plotted against T_g/T in an Angell plot (figure 2), the cooked soy also shows a strong behavior that is confirmed by the low m values.
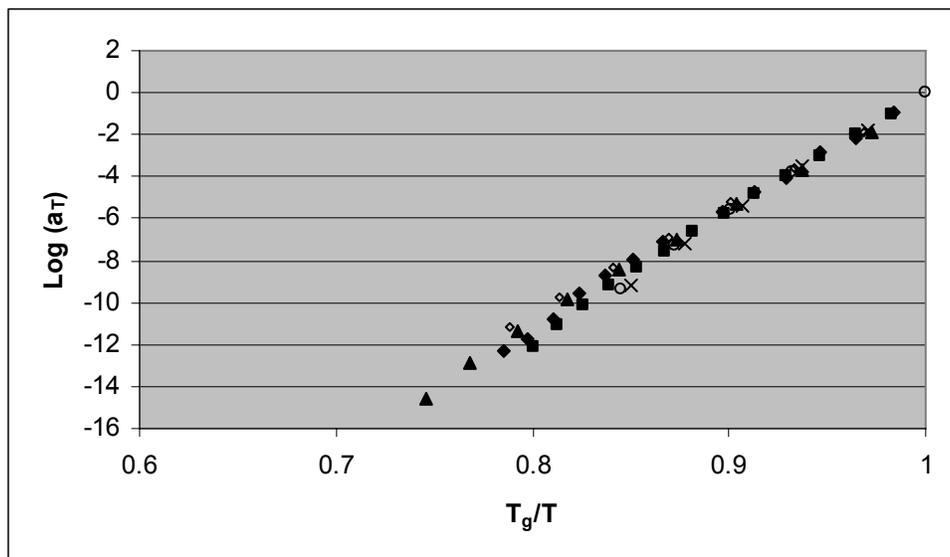
Figure 2. Angell plot of uncooked defatted soy flour (♦), defatted soy flour cooked in a convection oven at 60°C (■), defatted soy flour cooked in a twin screw extruder at 95°C (▲) and 145°C (◊) and soy protein concentrate extruded at 95°C (X) and 145°C (○).

The underlying physical mechanisms relating the fragility to changes in molecular weight or networking density in the material are still not well understood.

However, knowing the fragility of a material can provide a window into understanding the mechanism of vitrification in foods. It presents an opportunity to understand the role of intrinsic and extrinsic factors that shape the final structure of a glassy material through unique means of understanding the strength of the interactions involved. Preliminary findings for food polymers reported in this study offer a glimpse on the effects of water activity in the vitrification of defatted soy flour and further work is needed to understand the role that water activity and other factors, such as processing temperatures, play in this system.

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