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Determination of the WLF constants of cooked soy flour and their dependence on the extent of cooking

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Abstract The Williams, Landel and Ferry (WLF) equation is useful in predicting the temperature-induced changes in foods near the glass transition temperature. WLF constants have been found to be material properties rather than ‘universal values’. Adequate information on the magnitude of the WLF constants as a function of polymeric property changes, such as degree of crosslinking, during processing and storage is not available in the food polymer literature. The objective of the present study is to determine the variation of the WLF constants of cooked soy flour with the extent of

cooking (and therefore crosslinking) of the soy flour. WLF constants in this paper were determined using time–temperature superposition principles and Ferry’s reduction method. The WLF constants for soy flour were found to be different from the universal values reported for synthetic polymers and show significant differences across degree of crosslinking markers selected and the variation was correlated using available semi-quantitative methods.

Keywords WLF constants · Soy flour · Crosslinking · Variation · Prediction

Introduction

The Williams, Landel and Ferry (WLF) equation (Williams et al. 1955) has been used to describe the temperature induced changes in viscoelastic properties of polymeric materials in the rubbery state near the glass transition temperature. Ferry (1980) in his classic textbook, gives elegant examples of the applicability of the WLF equation in describing temperature – frequency dependence of viscoelastic and dielectric properties of amorphous polymers. Ngai and Plazek (1996) discuss the effectiveness of the WLF equation in terms of describing successfully the temperature dependence of viscous flow, viscoelastic response, dielectric dispersion, nuclear magnetic resonance response and dynamic light scattering of polymers and super-cooled liquids. The ability to successfully describe the temperature dependence of key physical properties near the rubbery state has been used to obtain parameters of free volume theory in order to predict diffusion of small solutes in

glassy and rubbery polymers. Such information has allowed the prediction of a number of industrially important phenomena including crystallization of sugars, collapse phenomena, (re)crystallization in frozen foods, estimation of non-enzymatic browning rates and diffusion in food polymers (Yildiz and Kokini 2001). The general form of the WLF equation is given as (Williams et al. 1955; Sperling 1986) Eq. 1:

$$\log \left[\frac{\eta(T)}{\eta(T_g)} \right] = \log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g}. \quad (1)$$

The WLF equation has been applied somewhat successfully for synthetic polymers using the ‘universal values’ of $C_1 = 17.44$ and $C_2 = 51.6$ (Ferry 1980; Aklonis and MacKnight 1983). Yet, there is considerable evidence in literature about the variation of the constants for different polymer systems and scientific prudence requires that such values be measured rather than using universal values. It has been shown experi-

mentally (Ferry 1980; Ngai and Plazek 1996; Yildiz and Kokini 2001) that the WLF constants C_1 and C_2 and the reference temperature T_0 can vary within wide ranges depending on the chemical and physical structure of the polymer at the time of experimental determination. Peleg (1992) has advised against the use of the universal values in food systems. Recent work (Yildiz and Kokini 2001; Morales-Diaz and Kokini 1998) has illustrated the effect of storage parameters, such as water activity, on the variability of WLF constants in food systems. There is no other work discussing the variation of the constants with other storage or processing parameters.

Soy is an important crop in food processing. Its high protein content (~52% in defatted flour), coupled with crosslinking upon cooking, enhances its applicability in many food products, including textured meat analogs. The properties of soy during cooking depend on the degree of crosslinking which occurs and the temperature of crosslinking. The degree and type of crosslinking in soy proteins can be semi-quantitatively measured through physico-chemical methods (Hager 1984; Prudencio-Ferreira and Areas 1993) through which the nature of crosslinking can be classified as covalent, non-covalent and a combination of both.

There is a lack of understanding of phenomenological reasons for variations in WLF constants. It has been recognized through the synthetic polymer literature that the derived nature of C_1 and C_2 can be explained by the free volume theory. C_1 is defined as the reciprocal of the fractional free volume at T_g . C_2 is defined as the ratio of the fractional free volume at T_g to the thermal expansion coefficient. More accurately C_1 and C_2 as derived in the WLF equation are given by (Aklonis and MacKnight 1983):

$$\log a_T = \frac{-(B/2.303f_g)(T - T_g)}{f_g/\alpha_f + (T - T_g)}, \quad (2)$$

where

$$C_1 = \frac{B}{2.303f_g} \quad (3)$$

$$C_2 = \frac{f_g}{\alpha_f}, \quad (4)$$

f_g is the fractional free volume f at T_g , α_f is the thermal expansion coefficient and B is an arbitrary constant usually set to unity.

As a consequence, the use of universal values for C_1 and C_2 in the WLF equation predicts that the glass transition temperature, T_g , is an iso-free volume state. This concept has been shown not to be rigorous (Ferry 1980; Aklonis and MacKnight 1983). Recent advances in the direct and accurate measurement of the free

volume using positron annihilation light spectroscopy (PALS) have also shown that the glass transition is not an iso-free volume state (Bandzuch et al. 2001).

Zhang et al. (1986) studied the effect of crosslinking on free volume with measurements of diffusion coefficients of camphorquinone in linear and crosslinked PS and found the values of the WLF constants in this system to increase with an increase in the extent of crosslinking. Singh et al. (1984) addressed the influence of changing molecular weight between crosslinks on the free volume, which was measured directly using PALS, in a family of Fluorene epoxy resins and developed an empirical equation that could predict the free volume for a given molecular weight between crosslinks. These studies have led to some understanding of the effect of crosslinking on the WLF constants. Such studies have not been extensive in synthetic polymers and there are none relating to food polymers.

The objective of the present study is to determine the variation of the WLF constants of cooked soy flour with the extent of cooking of the soy flour, to examine the effect of protein content in the soy flour on this variation and to understand the phenomenological reasons for these variations.

Materials and methods

A variation in the degree of crosslinking in soy flour was brought about by cooking soy flour at various temperatures and also by utilizing soy flour with different protein contents—defatted soy flour and soy protein concentrate. Increasing the protein content of soy flour lessens the amount of starch that is present as an impurity in the flour, thus enhancing the degree of crosslinking by providing a greater number of crosslinks. Chemical and rheological experiments were conducted to assess the degree of crosslinking and rheological experiments were performed to calculate the WLF constants.

Defatted non-roasted soy flour (NutriSoy 7B) and soy protein concentrate (Arcon F) were obtained from ADM (Decatur, IL). The protein content of the defatted soy flour (DSF) was given by the supplier to be 52% and that of the soy protein concentrate (SPC) as 69%. The moisture content of the soy flour was 7.02 and 6.9% for the defatted soy flour and soy protein concentrate respectively when measured using the AACC method # 44-19 (AACC 1984).

Cooking

In order to crosslink the soy to various extents, the defatted soy flour was cooked to 60°C in a convection oven and both the defatted soy flour and soy protein

concentrate were cooked to 95 and 145°C in an extruder.

To prepare the dough to be cooked at 60°C, defatted soy flour was mixed with deionized distilled water to bring the moisture content of the dough to ~40%. The dough was pressed between two glass plates and kept overnight in a refrigerator at 4°C. The flat sheets of dough were cut into strips suitable for torsional oscillatory rheological measurements and then cooked at 60°C in a convection oven for 1 h. A portion of the dough was left uncooked as a reference material. These reference samples will be referred to as 'uncooked samples'.

Defatted soy flour was cooked to 95 and 145°C by extrusion in a Werner Pfleiderer ZSK-30 twin-screw extruder with a screw configuration as described in Table 1. The screw speed was maintained at 250 rpm and the temperature profile across the four zones (starting from the feed end and going towards the die) was set to 25, 80 and 95°C (145°C in the second case). A slit die with dimensions of $2 \times 10 \text{ mm}^2$ was used. Soy flour was fed into the extruder using a K-Tron feeder with a feed rate set to 17.94 g/min. Water was fed into the extruder using a positive displacement pump such that the exit moisture content of the cooked soy flour was ~35–40%.

Soy protein concentrate was also cooked in the twin-screw extruder at 95 and 145°C using the same screw configuration and slit die. The screw speed, temperature profiles, feed rate and moisture content of the cooked soy flour were set to replicate the extrusion conditions of the defatted soy flour as described above.

Table 1 Screw configuration of the ZSK-30 twin-screw extruder

Element type (Pitch/length)	Number of elements
Skewed 42/42	2
Transition 42/21	1
42/42	2
42/21	1
Mild kneading (IGEL) 42	1
28/28	3
Mild kneading (IGEL) 42	1
28/28	2
Kneading block 45/5/28	1
28/14	3
Kneading block 45/5/14	1
20/20	5
Kneading block 45/5/20	1
20/10 Left Handed (LH)	1
20/10	4
Kneading block 45/5/20	1
20/10 LH	1
20/10	2
14/14	2
Kneading block 45/5/14	1
Kneading block 45/5/14 LH	1
14/14	6

We recognize that cooking in a convection oven and in an extruder are radically different processes. For the purposes of this study it was important to show that significant differences existed in soy as a function of cooking and selection of different cooking methods allowed us to demonstrate this variability.

Sample preparation and storage

Uncooked samples and cooked samples from either cooking in an oven or from the extruder were cut into strips of approximately $2 \times 10 \times 50 \text{ mm}^3$ in dimension for rheological measurements using the torsional oscillatory geometry. The cut strips were stored in dessicators and were equilibrated to a water activity of 0.753 over a saturated solution of NaCl.

Parts of the samples were also ground in a Waring blender for chemical analysis. The ground product was sieved and the fraction with particle diameter below $5.9 \times 10^{-3} \text{ m}$ was collected in Ball jars. The headspace of the Ball jars was flushed with Nitrogen gas to prevent oxidation and the samples were stored in a -20°C freezer. They were used promptly within 2–3 days to prevent staling and oxidation.

Chemical analysis

Protein was extracted from the ground and frozen samples according to the procedure described by Hager (1984). Four solvents -0.35 M phosphate buffer, 0.35 M buffer + 8 M urea, 0.35 M buffer + 0.1 M Na_2SO_3 and 0.35 M buffer + 8 M urea + 0.1 M Na_2SO_3 , were prepared for extraction. Sixty milligram of the sample was added to 30 ml of the solvent in a 50 ml centrifuge tube. The contents were homogenized in a Polytron homogenizer at low speed for 1 min and then centrifuged at 5,000g for 1 h. The supernatant was analyzed for protein content using the BIO-RAD RC-DC colorimetric assay (Bio-Rad 2000).

Rheological analysis

An Advanced Rheometrics Expansion System (ARES) from Rheometrics Inc., Piscataway, NJ, USA (now a part of TA Inc.) was used for all rheological analysis. A torsion rectangular fixture was used for rheological analyses. Strain sweeps were performed at room temperature and at a frequency of 1 Hz to determine the linear viscoelastic region.

Frequency sweeps were performed from 0.5 to 100 Hz at a strain rate of 1% to determine the extent of crosslinking in the cooked sample. The molecular weight between crosslinks (M_c) was determined using the equation (Morales-Diaz and Kokini 1998):

$$M_c = \frac{\rho RT}{G'} \quad (5)$$

where ρ is the material density (values obtained for soy flour from Morales-Diaz and Kokini 1998), R is the gas constant and T is the absolute temperature at which the frequency sweeps were conducted (room temperature ~ 298 K). G' is the plateau storage modulus of the samples taken at 80 rad/s. The results are an arithmetic average of three replicates. This method of determination of the M_c is a direct outcome of the rubber-elasticity theory and has been used in literature for the determination of M_c in wheat gluten (Muller 1969) and of M_c in the 7 S and 11 S fractions of soy (Morales-Diaz and Kokini 1998).

Temperature sweeps were performed at a heating rate of 5°C using a strain level of 0.1% and a frequency of 1 Hz between -80 and 55°C to determine the glass transition region. The maximum in the loss modulus G'' , coupled with the inflection in the G' versus temperature curve, was considered to be the glass transition. The results are an arithmetic average of three replicates.

The transient step-strain mode of the torsion rectangular geometry was used to obtain stress relaxation data of the samples at a strain rate of 0.1% and a frequency of 1 Hz for a duration of 240 s. All stress relaxation experiments were performed at temperatures increasing from T_g to $T_g + 50^\circ\text{C}$. The samples were held at the temperature of the experiment for 5 min to allow for equilibration. Relaxation modulus, $G(t)$ versus time curves were obtained for each temperature selected.

A single sample, lightly coated with vacuum grease to avoid loss of moisture, was used for one set of strain sweep, temperature sweep and stress relaxation experiment. Strain sweeps and temperature sweeps were conducted (results not shown) on samples with and without a coating of vacuum grease and it was ascertained that the vacuum grease did not influence the rheological measurements.

Time-temperature superposition was accomplished by shifting the relaxation curves using a one-dimensional minimization algorithm, developed with the Brent's method, in the ARES Orchestrator software (Press et al. 1992). The algorithm shifted the curves to make the best fit using a residuals minimization method that determined the shift factor yielding the smallest residuals. Triplicate shift factors were obtained for each sample and average shift factors were computed. The average shift factors were then plotted versus temperature in the linearized form of the WLF equation to obtain C_1 and C_2 as outlined in a standard reference on this topic (Aklonis and MacKnight 1983).

WLF constants obtained at a reference temperature (T_r) were then adjusted to the glass transition temperature (T_g) using the Eqs.

$$C_1 = \frac{C_1^r C_2^r}{C_2^r + T_g - T_r}, \quad (6)$$

$$C_2 = C_2^r + T_g - T_r. \quad (7)$$

Results

Experiments to establish the extent of crosslinking

Chemical analysis

Data obtained from chemical analysis is presented in Fig. 1. The amount of protein that dissolves in the buffer decreases from 45 to 10% as the degree of cooking increases. The amount of protein that dissolves in 8 M urea is lower at higher cooking temperatures indicating a decrease in the fraction of non-covalent linkages with increasing processing temperature. Eight molar urea disrupts non-covalent crosslinks (secondary bonds consisting of hydrogen and hydrophobic bonds) and degree of dissolution in this solvent has been used as a measure of crosslinking due to non-covalent linkages (Hager 1984). The fraction of protein that dissolves in 0.1 M Na_2SO_3 , a marker of covalent crosslinks, is almost the same for samples cooked at 95 and 145°C while the protein dissolution in a combined 8 M urea and 0.1 M Na_2SO_3 buffer solution is highest at the higher cooking temperatures of 95 and 145°C with as much as 70% of the crosslinked protein dis-

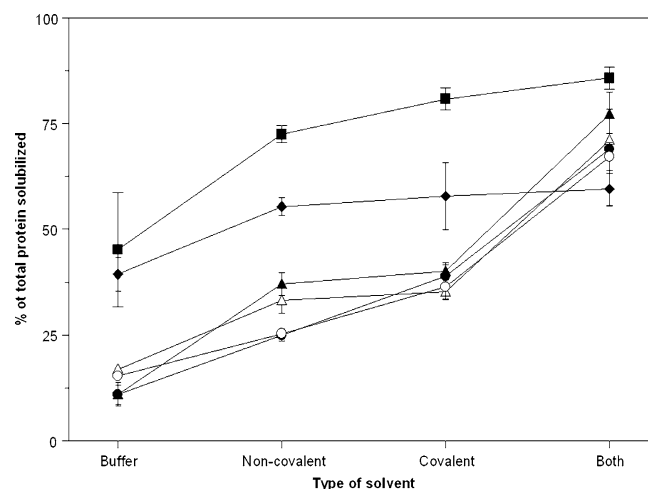


Fig. 1 Protein dissolution of DSF Uncooked (filled square), DSF 60°C (diamond), DSF 95°C (filled triangle), DSF 145°C (filled circle), SPC 95°C (open triangle) and SPC 145°C (open circle) in various solvents. The connecting lines in the plot are included as guides for the eye

solving in this solvent system. Defatted soy flour and soy protein concentrate extrudates do not show significant difference in the fraction of proteins dissolved by each solvent.

The chemical analysis reveals the nature of crosslinking in the soy flour samples. The results indicate a progressive increase in the fraction of protein that is crosslinked by covalent bonding as the cooking temperature rises. It also suggests that there is a synergistic effect between non-covalent and covalent bonds at the higher cooking temperatures of 95 and 145°C that increases with the degree of crosslinking of the protein. At 60°C the samples are not crosslinked with possibly only a few non-covalent linkages active as shown by the dissolution in urea. As the cooking temperature increases to 95°C and beyond, the crosslinking is up to 20% greater than in the 60°C sample. Further, the results show that the amount and nature of crosslinking does not change significantly going from 95 to 145°C varying by as less as 3%.

Results from literature indicate similar trends. Hager (1984) and also Prudencio-Ferreira and Areas (1993) point out that increasing the cooking temperature up to 180°C results in maximizing the covalent disulfide links in soy proteins. Such temperatures could not be realized in this study due to the difficulty in extruding samples at such temperatures while still preserving the non-porous and unexpanded state of the sample, to make them suitable for rheological studies. While the results agree well with that of Hager (1984) and Prudencio-Ferreira and Areas (1993), care has to be taken in comparing the results of this paper and that of the other studies as the materials and extrusion methods used in those studies are different.

Estimations of the amount of protein dissolved in various buffer solutions are methods which are semi-quantitative and are subject to possible error sources but they are the state-of-the-art in protein dissolution techniques leading to the quantification of covalent and non-covalent crosslinks. They were conducted to demonstrate the changing nature of the crosslinking mechanism as the processing temperature rises. The rheological experiments that follow will establish the varying extents of crosslinking as the cooking temperature and the protein content increase.

Rheological analysis

Frequency sweeps of the samples with various extents of crosslinking was conducted and are shown in Fig. 2. The results reveal that the 95 and 145°C defatted soy flour and soy protein concentrate samples were crosslinked to a greater extent, which is indicated by their higher modulus values, than the 60°C defatted soy flour sample. Furthermore, the 95 and 145°C soy protein concentrate samples have a modulus that is

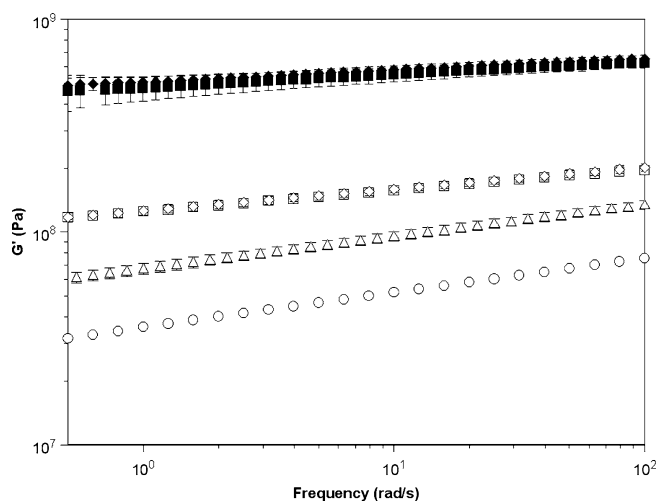


Fig. 2 Frequency sweeps of DSF Uncooked (circle), DSF 60°C (triangle), DSF 95°C (open square), DSF 145°C (diamond), SPC 95°C (filled square) and SPC 145°C (filled diamond)

almost a decade higher than those of the defatted soy flour samples indicating a much higher extent of crosslinking.

The slopes of the frequency sweeps also decrease as the cooking temperature and the protein content increase and are reported in Table 2. The uncooked sample gives the highest slope for storage modulus (G') versus frequency sweep and the lowest value for G' (Fig. 2). These two parameters are indicators of the degree of crosslinking and the uncooked sample clearly has the lowest degree of crosslinking among the four thermal treatments studied. The samples cooked at 60°C and the samples extruded at 95 and 145°C give us increasing degrees of crosslinking that are quantitatively indicated by the decreasing slope of the G' vs. frequency sweeps and also by the increasing magnitude of G' .

The molecular weights between crosslinks obtained are tabulated in Table 3. The uncooked samples have the highest molecular weight between crosslinks indicating a low degree of crosslinking. The M_c decreases progressively with increasing processing temperature and protein content, with the soy protein concentrates cooked at 95 and 145°C having the lowest M_c , indicating

Table 2 Slopes of G' versus frequency curves

Sample	Slope
DSF uncooked	17.41×10^{-2}
DSF 60°C	16.00×10^{-2}
DSF 95°C	9.83×10^{-2}
DSF 145°C	10.45×10^{-2}
SPC 95°C	5.87×10^{-2}
SPC 145°C	5.56×10^{-2}

Table 3 Molecular weight between crosslinks (M_c)

Sample	M_c (Da)
DSF uncooked	47.96
DSF 60°C	25.55
DSF 95°C	17.52
DSF 145°C	16.79
SPC 95°C	6.10
SPC 145°C	5.60

the highest degree of crosslinking achieved in this study. The presence of hydrogen bonds and hydrophilic interactions in food biopolymers in addition to the covalent bonds add to the increased crosslinked nature and can explain the relatively low values for M_c . The addition of a plasticizer such as water dilutes the effect of hydrogen bonds and hydrophilic interactions by preferring binding to water rather than intramolecular crosslinks.

These results illustrate how an increasing processing temperature when combined with greater protein content can enhance the degree of crosslinking allowing us to access more information on the influence of the degree of crosslinking on the WLF constants of soy flour.

Experiments to determine the WLF constants

T_g measurements

The glass transition temperatures of all the samples analyzed are shown in Table 4. Temperature sweeps of uncooked defatted soy flour, defatted soy flour cooked at 60°C, defatted soy flour extruded at 145°C and soy protein concentrate extruded at 145°C are shown in Fig. 3.

The glass transition temperature increased from -19°C to about -16°C as the defatted soy flour samples were cooked. The glass transition temperatures of 60, 95 and 145°C defatted soy flour samples were almost similar averaging around -16°C and were within experimental error. The T_g increased to about 0°C as the protein content in the samples increased, suggesting a greater degree of crosslinking and complementing the rheological results such as the decrease in the slope, the

Table 4 Glass transition temperatures

Sample	T_g ($^\circ\text{C}$)
DSF uncooked	-19.26 ± 0.37
DSF 60°C	-14.59 ± 1.16
DSF 95°C	-17.19 ± 1.58
DSF 145°C	-18.20 ± 0.95
SPC 95°C	1.64 ± 1.82
SPC 145°C	0.06 ± 1.75

increase in the value of the storage modulus, G' and a decrease in the M_c that established the increase in the degree of crosslinking. It is possible that the decreasing starch content in the soy protein concentrate allows for the covalent and non-covalent crosslinks in soy to increase without dilution or possible interruption on the part of starch. The glass transition temperatures observed in this study are also close to the T_g reported in similar studies (Yildiz and Kokini 2001).

Stress relaxation experiments and construction of master curves

The relaxation modulus decreased as the experimental temperature increased. This behavior is illustrated in Fig. 4. The data obtained at each temperature was overlaid and then shifted to produce master curves, Fig. 5. The average shift factors were determined as discussed previously and an Angell plot (Bohmer et al. 1993) of $\log(a_T)$ versus T_g/T is presented in Fig. 6. Such plots have been used frequently in the polymer physics literature (Bohmer et al 1993; Angell 1995; Ediger et al. 1996; Richert and Angell 1998; Martinez and Angell 2001) to demonstrate the variation of viscosities or relaxation times with temperatures that have been normalized with the glass transition temperature.

The WLF constants were computed by plotting the linearized form of the WLF equation and the values of C_1 and C_2 were then reduced to values at the samples' glass transition using Eqs. (6) and (7). The C_1 and C_2 obtained are reported in Table 5.

The dynamic fragility (or steepness factor) m (Huang and McKenna 2001) was determined as $T_g \cdot C_1/C_2$ and are reported in Table 6. The values of 'm' were ~ 55 showing a 'strong' behavior while falling within the range of values for glass forming polymers that were discussed by Huang and McKenna (2001).

The values of C_1 and C_2 show an increasing trend as the degree of crosslinking in the samples increases. The C_1 and C_2 values of uncooked soy samples, 44 and 193 K respectively, are the closest to the 'universal' WLF constants and agree well with published values in literature for uncooked soy flour at that moisture content (Yildiz and Kokini 2001). The WLF constants increase to 51 and 233 K for the 60°C sample and then to around 64 and 315 K for the 95 and 145°C defatted soy flour samples. The highest values of C_1 and C_2 are for the soy protein concentrate cooked at 95 and 145°C, which have values around 85 and 410 K.

An increase in the protein content of the soy led to an increase in the WLF constants since the degree of crosslinking increases with greater protein concentration. This would further suggest that the protein content in the soy plays a vital role in determining the degree of crosslinking. A plot of the C_1 and C_2 values versus slope of the frequency sweeps (Fig. 7) clearly illustrates the

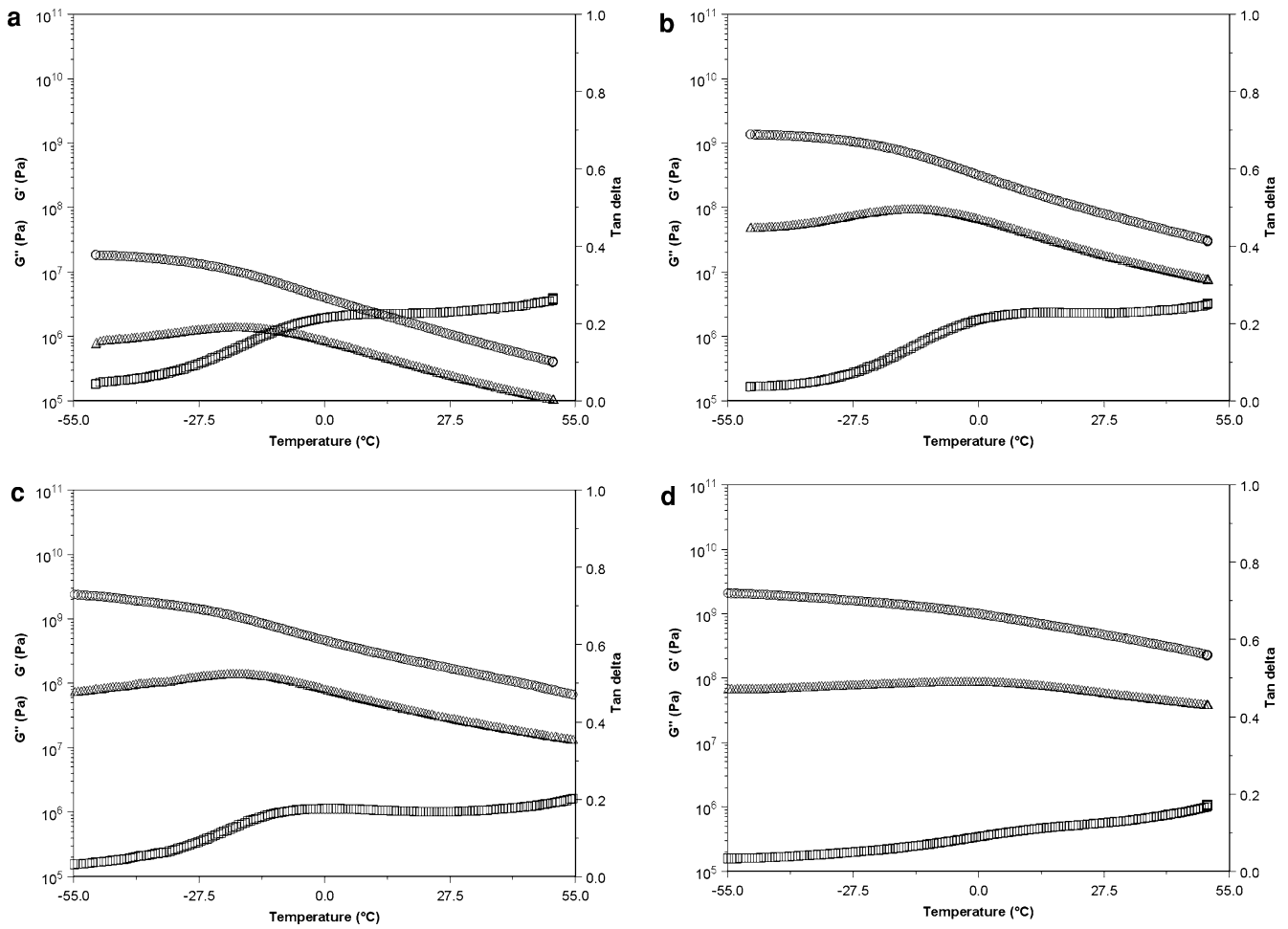


Fig. 3 Temperature sweeps showing G' (circle), G'' (triangle) and tan delta (square) of **a** DSF uncooked **b** DSF 60°C **c** DSF 145°C and **d** SPC 145°C

influence of degree of crosslinking on the WLF constants in this study. It also shows that there is not much variation within the 95 and 145°C samples of the defatted soy flour but a greater degree of crosslinking could be achieved by utilizing soy protein concentrate extrudates at 95 and 145°C with their higher protein contents.

Zhang et al. (1986) studied the effect of crosslinking on the WLF constants with measurements on the diffusion coefficient of camphorquinone in linear and crosslinked polystyrene (PS). They reported C_1 and C_2 values of 4.68 and 49.16 K for linear PS and 21.1 and 231.9 K for crosslinked PS respectively. Their study concluded that the WLF constants increased with crosslinking due to a decrease in the free volume at T_g (f_g).

In this study, the value of C_1 increased with an increase in crosslinking. Following Eq. (3), C_1 is inversely proportional to free volume and hence an increase in C_1 would suggest that the assumption of the glass transition

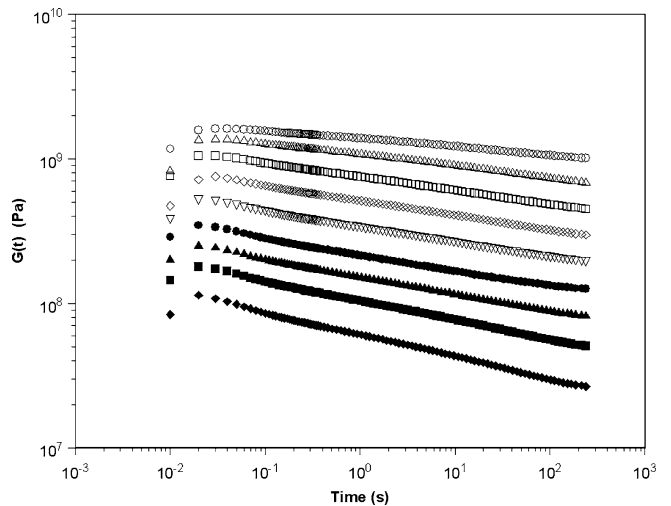


Fig. 4 Stress relaxation curves of a DSF 145°C at -30°C (open circle), -20°C (open triangle), -10°C (open square), 0°C (diamond), 10°C (open inverted triangle), 20°C (filled circle), 30°C (filled triangle), 40°C (filled square) and 50°C (filled diamond)

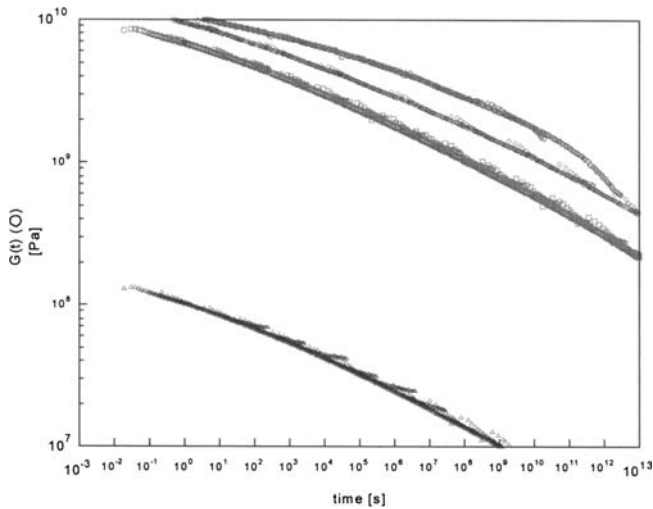


Fig. 5 Master curves of DSF uncooked (triangle), DSF 60°C (square), DSF 145°C (diamond) and SPC 145°C (+)

being an iso-free volume state is incorrect. In other words, f_g is not a constant but is decreasing as the crosslinks in the sample increases. Zhang et al. (1986) suggest that the crosslinking would breakdown bigger voids into smaller ones. This would increase the number of voids but would also decrease the total volume occupied by the voids, which would directly result in a

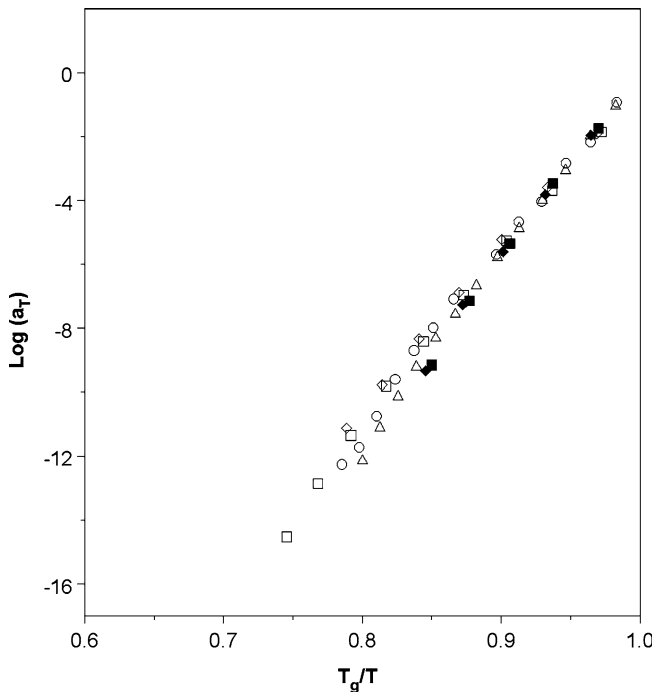


Fig. 6 Angell plot of the relaxation shift factors, $\log(a_T)$ versus T_g/T for DSF Uncooked (circle), DSF 60°C (triangle), DSF 95°C (open square), DSF 145°C (open diamond), SPC 95°C (filled square) and SPC 145°C (filled diamond)

Table 5 Williams, Landel and Ferry constants C_1 and C_2

Sample	C_1	C_2 (K)
DSF uncooked	44.03	192.78
DSF 60°C	51.10	233.31
DSF 95°C	65.70	320.74
DSF 145°C	63.49	315.90
SPC 95°C	87.72	426.97
SPC 145°C	82.64	409.07

decrease in the free volume at T_g . The value of B can also play a role in the variation of C_1 . Ferry (1980) provides data that shows the variation of B between 0.2 and 1.6 for various synthetic polymers. Bandzuch et al. (2001) use positron annihilation light spectroscopy (PALS) to directly determine the free volume in a sample at a particular temperature and demonstrates that B is not unity in many examples.

An increase in the value of C_2 would indicate either an increase in f_g or a decrease in α_f , according to Eq. (4). Using Zhang et al. (1986) argument as above, there would only be a slight decrease in the values of f_g as the crosslinking increases. One can argue that the large increases in C_2 are brought about by a decrease in the thermal expansion coefficient. It has to be noted that the crosslinking might have altered the chemical and physical nature of the soy which would also bring about a change in α_f .

Singh et al. (1984) developed a model of the form

$$V_f = AM_c^B, \quad (8)$$

where V_f is the free volume cell size, M_c is the molecular weight between crosslinks, A and B are constants for the test polymer and are expected to be independent of the degree of polymerization. This model successfully described the variation in the free volume, that was directly measured using PALS, with the variation in the molecular weight between crosslinks (M_c) in a Fluorene epoxy resins family. This model is similar in form to the Mark-Houwink (M-H) equation (Du et al. 1996),

$$[\eta] = KM_v^a \quad (9)$$

that relates the intrinsic viscosity of dilute polymer solutions, $[\eta]$ to their viscosity averaged molar mass, M_v . K and a are the M-H constant and exponent respectively.

Table 6 Dynamic fragility (steepness index), m

Sample	m ($T_g^*C_1/C_2$)
DSF uncooked	57.95
DSF 60°C	56.90
DSF 95°C	52.40
DSF 145°C	51.21
SPC 95°C	56.42
SPC 145°C	55.16

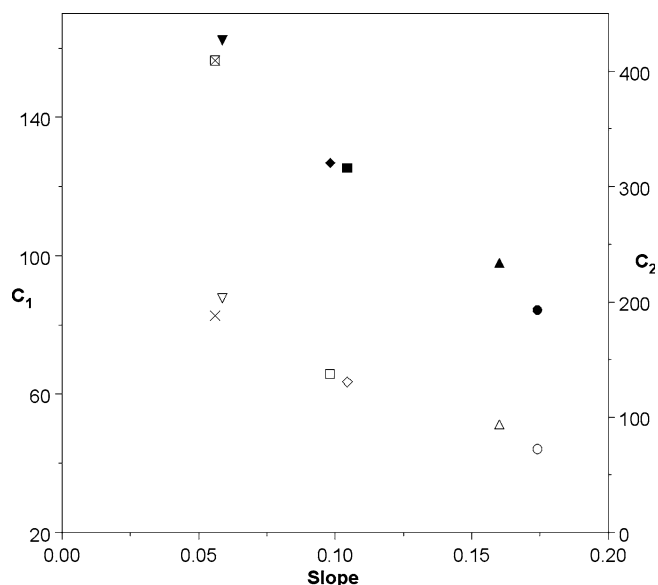


Fig. 7 C_1 (open symbols) and C_2 (shaded/closed symbols) versus slope of (G' versus frequency) sweeps for DSF Uncooked (circle), DSF 60°C (triangle), DSF 95°C (open square), DSF 145°C (open diamond), SPC 95°C (inverted triangle) and SPC 145°C (multiplication symbol)

We propose a similar formalism in which the glass transition temperature, T_g and the WLF constants C_1 and C_2 , which are directly derived from free volume arguments as discussed above and shown in Eqs. (3) and (4), can be related to the molecular weights between

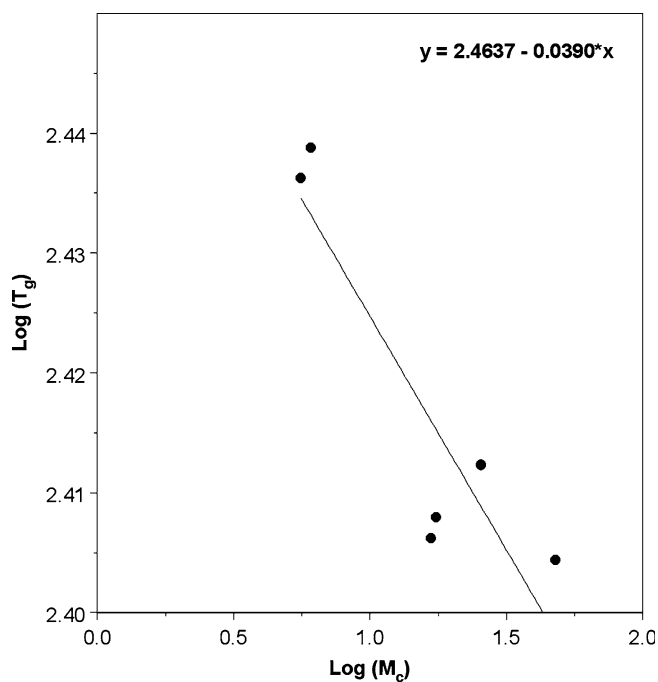


Fig. 8 Linearized Mark-Houwink type fit of T_g versus M_c with experimental data (filled circle) and linear regression fit (solid line)

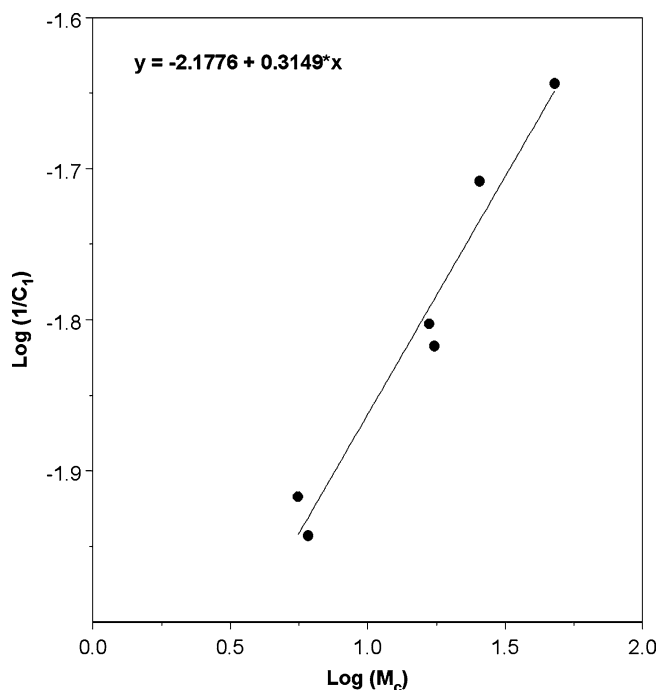


Fig. 9 Linearized Mark-Houwink type fit of $1/C_1$ versus M_c with experimental data (filled circle) and linear regression fit (solid line)

crosslinks, M_c . The glass transition temperature, T_g , the reciprocal of C_1 and C_2 , which are proportional to free volume, were plotted against the values of M_c (Figs. 8,

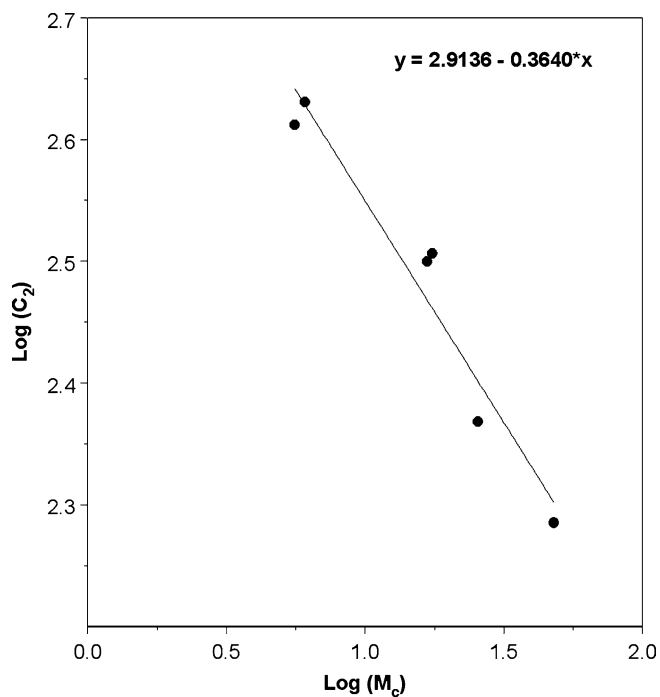


Fig. 10 Linearized Mark-Houwink type fit of C_2 versus M_c with experimental data (filled circle) and linear regression fit (solid line)

9, 10) using a linear version of a power model similar to Eq. (8) to fit the data.

A good fit ($R^2 > 94\%$) for C_1 and C_2 and an acceptable fit ($R^2 > 80\%$) for T_g were obtained and the values of A and B for each fit were as follows:

$$T_g = 290.86M_c^{-0.04}, \quad (10)$$

$$\frac{1}{C_1} = \frac{1}{151.51}M_c^{0.31}, \quad (11)$$

$$C_2 = 819.56M_c^{-0.36}. \quad (12)$$

These equations can be used to predict the WLF constants at any other degree of crosslinking in this system. The proposed relations can also be used as a basis to develop similar equations that will be useful tools in predicting the WLF constants for a given system with known values of molecular weights or molecular weights between crosslinks.

Conclusions

This work reiterates the significance of the WLF equation in foods and also shows the importance of being aware of differences in C_1 and C_2 with changes in processing parameters. It adds valuable information about the values of C_1 and C_2 for a representative food biopolymer. With the study of the chemical and physical changes underlying the cooking process in soy, an effort has been made to lay the framework for future research in this area. A better understanding of these phenomena will lead to improved knowledge in predicting the values of the WLF constants with changes in storage and processing conditions.

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