

A Model of Mechanical Changes in Biomaterials at and around Their Glass Transition[†]

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The transition of biological and food materials from a glassy to a leathery or rubbery state and the accompanying loss of stiffness, hardness, or strength are traditionally described by a relationship between the magnitudes of these parameters and the temperature, moisture, or water activity. At the transition region, the curve depicting such a relationship has a sigmoidal shape that can be described by the model, $Y(X) = Y_g / \{1 + \exp[(X - X_c)/a]\}$, where X is either temperature, moisture content, or water activity, $Y(X)$ is a mechanical parameter (e.g., modulus), Y_g is the latter's magnitude in the glassy state (assumed to be practically constant), X_c is a characteristic temperature, moisture, or a_w level of the transition, and a is a constant. This model was tested with the published data of various biomaterials (baker's yeast, casein, coffee creamer, luncheon meat, sodium caseinate, sucrose/glucose glass, wheat grains, and bread). In all cases, it gave a consistent description of the mechanical changes at and around the transition and had a very satisfactory fit.

Introduction

Many solid biological and food materials, at a certain range of moisture content and temperature, undergo drastic physical changes as a result of relatively minor changes in conditions. Notable examples are the plasticization of breakfast cereals or instant coffee agglomerates when exposed to a moist atmosphere and the hardening of plant and animal materials upon dehydration. These changes have been attributed to glass transition (Slade and Levine, 1991), a phenomenon that has been investigated thoroughly in polymers (Ferry, 1980). The transition affects not only the mechanical properties of biological materials but also, simultaneously, many other physical properties, especially those governed by internal molecular mobility (Slade and Levine, 1991).

The dependency of the rheological properties of polymers on temperature, at temperatures well above their glass transition, is most conveniently described by what is known as the WLF model, named after Williams, Landel, and Ferry (Williams et al., 1955), or

$$\log_{10} a_T = -C_1(T - T_g)/(C_2 + T - T_g) \quad (1)$$

where a_T is a shift factor expressed as the ratio between the polymer's viscosity at a given temperature T and its viscosity at a reference temperature, T_g , and C_1 and C_2 are constants. [The magnitudes of C_1 and C_2 depend on the selected reference temperature T_g , and it varies considerably among polymers (Ferry, 1980).]

The WLF model is not limited to viscosity ratios, and the shift factor a_T can represent other mechanical properties (Ferry, 1980). It has recently been applied extensively to describe physical changes in biological materials and foods in general (Slade and Levine, 1991), but sugars in particular (Roos and Karel, 1990; Ollet and Parker, 1990; Peleg, 1992). The Arrhenius model has also been applied to food systems, although to a lesser extent. It was used to estimate the viscosity of interparticle liquid

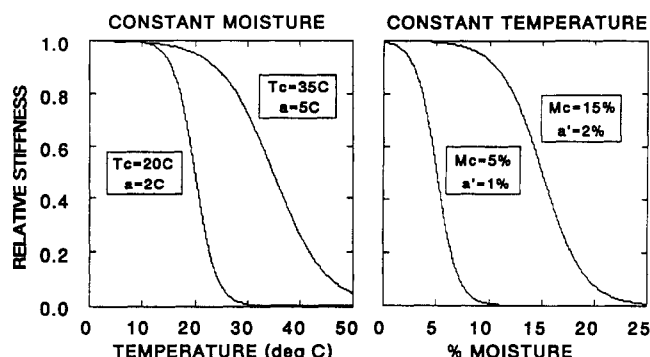


Figure 1. Simulated changes in the relative stiffness of biological materials around the glass transition produced by eqs 2 and 3 as a model. (The relative stiffness is defined as $Y(T)/Y_g$ or $Y(M)/Y_g$.) Note that, at the onset of the transition region, the relationships have downward concavity (in contrast with the upward concavity implied by the WLF and Arrhenius models). A similar phenomenon can also be observed in certain synthetic polymers (Ferry, 1980).

bridges during instant coffee powder agglomeration, for example (Wallack and King, 1988). The WLF and Arrhenius models are not interchangeable, and it was proposed that they may still be applicable in food systems, but at different temperature ranges (Slade and Levine, 1991).

It is well-known (Ferry, 1980; Slade and Levine, 1991) that, in both polymers and biomaterials, the plot of the modulus or storage modulus vs T has a change of concavity at the transition region. It is also known that the magnitude of the modulus or other stiffness or strength parameters, irrespective of how it is determined, can be fairly constant in the glassy state and that it drops considerably as a result of the transition to a rubbery state (Figure 1). Many solid foods and biological materials do not have a very sharp transition, and the drop in stiffness may occur, gradually, over an appreciable temperature range (see below). Such behavior is also known in certain synthetic polymers, e.g., poly(methyl methacrylate) and its mixtures with poly(vinyl acetate) (Ferry, 1980).

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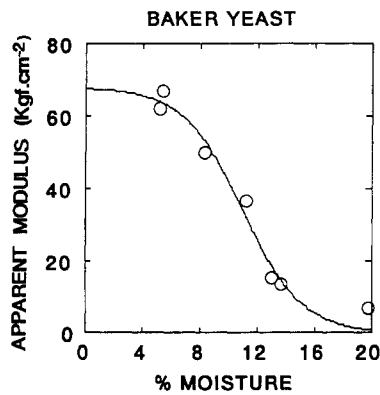


Figure 2. Glass transition of baker's yeast at ambient temperature. Circles are data from Dobbs et al. (1982); solid line is the fit of eq 3. (For the regression parameters, see Table 1.)

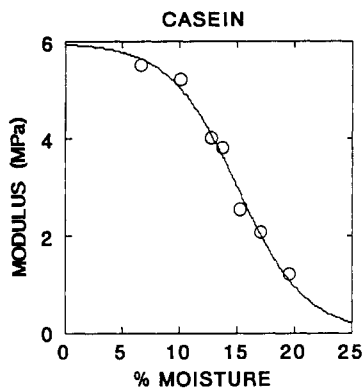


Figure 3. Glass transition of casein at ambient temperature. Circles are data from Kalichevski et al. (1993); solid line is the fit of eq 3. (For the regression parameters, see Table 1.)

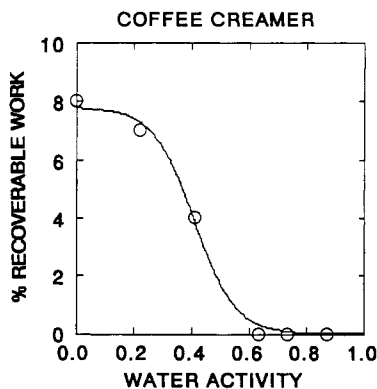


Figure 4. Glass transition of coffee creamer at ambient temperature. Circles are data from Moreyra and Peleg (1981); solid line is the fit of eq 4. (For the regression parameters, see Table 1.)

In many biological systems, the mechanical behavior at and around the transition region is of particular interest. Familiar examples are the brittleness of crunchy foods that is lost by moisture uptake and the caking of hygroscopic powders. However, diverse phenomena such as the flexibility of skin and hair or the efficacy of microencapsulation also appear to be regulated by whether the material is plasticized and to what extent.

Because the WLF and Arrhenius models imply stiffness-temperature relationships that have only upward concavity, it has recently been suggested (Peleg, 1993) that a consistent description of the mechanical behavior of biomaterials at and around their glass transition requires an alternative model. The objective of this article is to present such a model and to demonstrate its applicability with published rheological data.

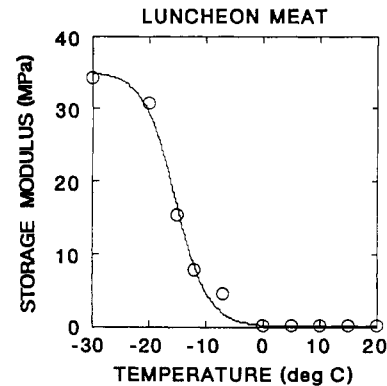


Figure 5. Glass transition of luncheon meat. Circles are data from Letort et al. (1993); solid line is the fit of eq 2. (For the regression parameters, see Table 1.)

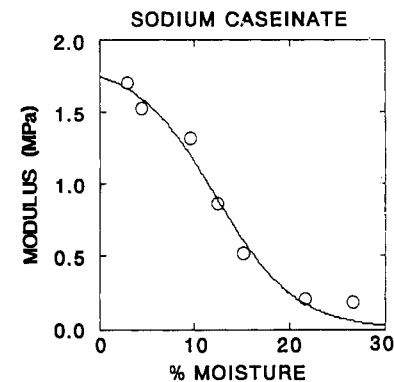


Figure 6. Glass transition of sodium caseinate at ambient temperature. Circles are data from Kalichevski et al. (1993); solid line is the fit of eq 3. (For the regression parameters, see Table 1.)

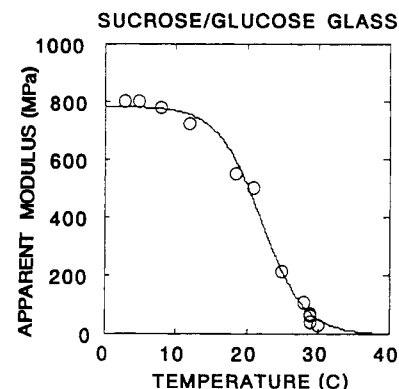


Figure 7. Glass transition of sucrose/glucose glass. Circles are data from McNulty and Flynn (1977); solid line is the fit of eq 2. (For the regression parameters, see Table 1.)

The Model

At and around the transition, the relationship between a pertinent mechanical parameter and temperature (at a constant moisture content or water activity) or that between the mechanical parameter and moisture content or water activity (at a constant temperature) has the characteristic sigmoidal shape shown in Figure 1. Relationships of this kind can be described by mathematical expressions of the same general form. Thus, the relationship between stiffness and temperature at a constant moisture or water activity (a_w) can be described by

$$Y(T) = Y_g / \{1 + \exp[(T - T_g)/a]\} \quad (2)$$

and that between stiffness and moisture content of water

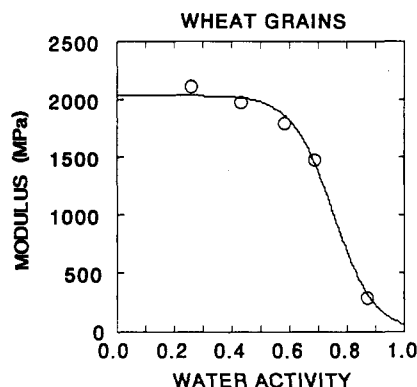


Figure 8. Glass transition of wheat grains at ambient temperature. Circles are data from Multon et al. (1981); solid line is the fit of eq 4. (For the regression parameters, see Table 1.)

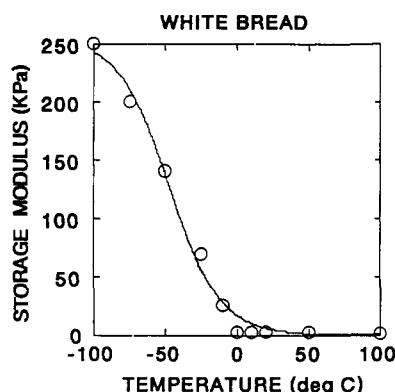


Figure 9. Glass transition of white bread. Circles are data from Hallberg and Chinachoti (1992); solid line is the fit of eq 2. (For the regression parameters, see Table 1.)

activity at a constant temperature by

$$Y(M) = Y_g / \{1 + \exp[(M - M_c)/a']\} \quad (3)$$

or

$$Y(a_w) = Y_g / \{1 + \exp[(a_w - a_{wc})/a'']\} \quad (4)$$

$Y(T)$, $Y(M)$, and $Y(a_w)$ in these equations are the magnitudes of stiffness, hardness, or any other mechanical integrity or strength parameter at the corresponding temperature, T , moisture content, M , or water activity, a_w , respectively. Y_g is the magnitude of this parameter in the unplasticized (glassy) state, and T_c , M_c , and a_{wc} are characteristic temperature, water activity, and moisture content, respectively. (Although, as already mentioned, $Y(T)$, $Y(M)$, or $Y(a_w)$ can represent different mechanical properties, they will be referred to as indicators of "stiffness" in the text for the sake of simplicity.) The a 's in eqs 2-4 are empirical constants and need not have the

same or similar magnitudes. Their units are those of the corresponding independent variable, that is, a has temperature units, a' those of moisture content, and a'' is dimensionless.

According to this model, the transition range is represented by the level of T_c , M_c , or a_{wc} whose values specify the location of the inflection point of $Y(T)$, $Y(M)$, or $Y(a_w)$ (Figure 1). The steepness of the region depicting the mechanical integrity loss is characterized by the magnitude of the constant, a , a' , or a'' (Figure 1). Thus, when the a 's $\rightarrow 0$, the shape of the curve approaches that of a step function, and when they have a relatively large value the relationship is rather flat. Or in other words, according to this model about 90% of the drop in the magnitude of $Y(T)$, $Y(M)$, or $Y(a_w)$ occurs within $T_c \pm 3a$, $M_c \pm 3a'$, or $a_{wc} \pm 3a''$, respectively. [The mathematical form of eqs 2-4 was borrowed from Fermi's distribution function (Seaborg and Loveland, 1990), although the model, of course, does not deal with any distribution.]

Demonstration of the Model's Applicability. The fit or the model expressed by eqs 2-4 to published experimental data of eight biomaterials is shown in Figure 2-9. The regression parameters are summarized in Table 1. (The nonlinear regression was performed with the Systat 5.2.1 package on a Macintosh SE/30 microcomputer.) The materials whose mechanical behavior is shown in the figures are very different as far as structure, composition, and overall stiffness are concerned. Also, their mechanical behavior during the transition was monitored by different kinds of mechanical tests, whose results are expressed in terms of different mechanical parameters (e.g., moduli and storage moduli). The same model format, however, was found to be applicable in all cases, despite the notable differences among materials and testing methods. Because the model as expressed by eqs 2-4 is phenomenological or empirical, it has no predictive capabilities. It is also doubtful that the magnitudes of its constants can be derived directly from the composition and fundamental physical properties of the material.

The model can be used, however, to characterize and compare the transition patterns of different materials. For example, as Table 1 shows, casein and sodium caseinate, despite the differences in their overall stiffness as expressed by Y_g , have a similar softening pattern at room temperature ($M_c = 15\%$ vs 18% and $a' = 3\%$ vs 2.9% , respectively), while the yeast softens at a lower moisture level and does so more steeply ($M_c = 11\%$ and $a' = 2.1\%$). One can also see that coffee creamer is plasticized at a lower water activity than wheat grains ($a_{wc} = 0.41$ vs 0.75 , respectively), although the steepness of the softening curve is about the same ($a'' = 0.07$). The obvious differences between the luncheon meat, sugar glass, and bread are expressed by their very different T_c 's (-15 , $+22$, and -47 °C, respec-

Table 1. Description of the Mechanical Changes in Solid Biomaterials at and around Their Glass Transition Using Equations 2-4 as a Model

material	mechanical parameter	equation ^a	r ²	data source
baker's yeast	apparent modulus, E (kgf cm ⁻²)	$E = 67 / \{1 + \exp[(M - 11)/2.1]\}$	0.993	Dobbs et al., 1982
casein	modulus, E (MPa)	$E = 5970 / \{1 + \exp[(M - 15)/3.0]\}$	0.998	Kalichevski et al., 1993
coffee creamer	recoverable work, W_R (%)	$W_R = 7.8 / \{1 + \exp[a_w - 0.41]/0.07]\}$	0.998	Moreyra and Peleg, 1981
luncheon meat ^b	storage modulus, G' (kPa)	$G' = 35 / \{1 + \exp[(T + 15)/2.9]\}$	0.995	Letort et al., 1993
sodium caseinate	modulus, E (MPa)	$E = 1840 / \{1 + \exp[(M - 18)/2.8]\}$	0.994	Kalichevski et al., 1993
sucrose/glucose glass	apparent modulus, E (MPa)	$E = 784 / \{1 + \exp[(T - 22)/3.0]\}$	0.997	McNulty and Flynn, 1977
wheat grains	modulus, E (MPa)	$E = 2040 / \{1 + \exp[(a_w - 0.75)/0.071]\}$	0.999	Multon et al., 1981
white bread ^b	storage modulus, G' (kPa)	$G' = 255 / \{1 + \exp[(T + 47)/17.8]\}$	0.995	Hallberg and Chinachoti, 1992

^a a_w is the water activity (dimensionless), M is the moisture content (% wet basis), and T is temperature (°C). The fit can also be seen in Figures 2-9. ^b The critical temperatures of luncheon meat and bread were -15 and -47 °C, respectively; hence the positive sign in the exponential argument.

tively), an observation that could be anticipated in light of the differences in their moisture contents.

The model can also be employed to quantify the effects of additives (especially plasticizers) and the roles of temperature, moisture, or water activity in terms of the values of Y_s , T_c , M_c , or a_{wc} and the a 's, whose meaning is intuitively clear. The main advantage of the proposed model, however, is that it accounts for the right concavity in the transition region. Therefore, it is especially attractive for describing the rheological behavior of materials just before, during, and/or soon after the transition. (For example, powders cake well before the particles are fully plasticized, and breakfast cereals lose their crunchiness well before their strength drops by several orders of magnitude, as would be predicted by the WLF model.) Also, according to the proposed model, the drop in the magnitudes of mechanical parameters is allowed to be moderate at the onset of the transition, which is in agreement with the actual behavior of at least several biological materials, as shown (Figures 2–9).

In its general form (eqs 2–4), the model has three constants, namely, Y_s , T_c , M_c , or a_{wc} and a , a' , or a'' . However, the magnitude of the stiffness parameter in the glassy state, Y_s , can and preferably should be determined experimentally. This will reduce the model to a two-parameter expression, on a par with the WLF model as far as mathematical simplicity is concerned.

The Model's Limits. The model, as shown, provides a consistent description of the mechanical behavior at and around the transition region, where $Y(T)$, $Y(M)$, or $Y(a_w)$ has downward concavity. At temperatures above the transition, $Y(T)$ has an upward concavity, of which the model also gives a proper account, at least qualitatively, as shown in Figures 1–9. However, at temperatures well above the transition range, that is, when $T \gg T_c$, eq 2 is reduced to

$$\ln[Y(T)/Y_s] = -T/a \quad (5)$$

which is a linear relationship between \ln or $\log Y(T)$ and T . Equation 5, however, is not interchangeable with the WLF model except, theoretically, when $T \gg T_s$ and $T - T_s \ll C_2$ (eq 1). Thus, the departure from the transition region and entrance into a region governed by the WLF or an alternative kinetic can be identified simply by testing the linearity of the $\log Y(T)$ vs T plot.

In principle, the same should be true for $Y(M)$ and $Y(a_w)$. However, since the upper limit of M , when expressed on a wet weight basis, is 100% and that of a_w is 1.00 by definition, any reference to $M \gg M_c$ or $a_w \gg a_{wc}$ has, in most cases, no physical significance. (A possible exception is a case where $M_c \approx 0$ or $a_{wc} \approx 0$.) Thus, whether the model is applicable to materials having very high moisture content or water activity can best be judged by statistical criteria used to determine the goodness of fit in nonlinear

regression and not by the linearity of $\log Y(M)$ vs M or $\log Y(a_w)$ vs a_w .

If the moisture content is expressed on a dry basis, then $M \gg M_c$ has, of course, a physical meaning. In such a case, however, the material is most likely to be in a liquid state, i.e., a suspension or a solution, and any reference to stiffness, hardness, or strength becomes irrelevant.

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