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On Modeling Changes in Food and Biosolids at and Around Their Glass Transition Temperature Range

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ABSTRACT: Temperature-induced mechanical and other changes in biosolids are regulated by three types of kinetics, depending on whether the material is in the glassy state, undergoing a transition, or fully plasticized. The transition itself can take place over a considerable temperature range, which in many food and biological systems happens to be the most pertinent to their functionality and stability. At the transition onset, the plot of stiffness vs. temperature has a downward concavity. It is reversed only at an advanced stage of plasticization after much of the stiffness has already been lost. Consequently, the WLF, Arrhenius, or any other model that implies a continuous upward concavity cannot account for changes in the transition region, and it is unsafe to use them to predict properties through extrapolation.

The mechanical changes in the transition region can be described by a model with the mathematical structure of Fermi's function. Its applicability has been demonstrated with published data on a variety of foods and biosolids. Because the plot of stiffness vs. moisture, or water activity, has the same general shape as that of the stiffness vs. temperature plot, it too can be described by a model with the same mathematical format.

Because moisture lowers the transition center temperature in a manner that can be described by a simple algebraic expression, the combined effects of temperature and moisture can be incorporated into a single general model. The latter can be used to create three-dimensional displays of the stiffness-temperature-moisture characteristic relationships of biosolids at and around their transition. At temperatures well above that of the transition, though, where a plot of log stiffness vs. temperature has a clear upper concavity, this model is no longer applicable, and the changes are better described by the WLF or an alternative model.

KEY WORDS: kinetics, glass transition, moisture, stability, plasticization.

I. INTRODUCTION

The concept that the kinetics of many processes — physical, biochemical, and biological — that affect the stability or functionality of solid foods and biomaterials is determined by the latter's glass transition temperature has recently become widely accepted.[1–3] The most familiar mathematical model that incorporates the idea is the one known as the *WLF equation*[4,5]

$$\log a_T(T,T_s) = -C_1(T-T_s) / (C_2+T-T_s) \quad (1)$$

where a_T is the shift factor (see below), T the temperature, T_s a reference temperature and C_1 and C_2 constants. If the glass transition temperature is selected as the reference temperature, Equation 1 becomes

$$\log a_T(T,T_g) = -C_1' (T-T_g) / (C_2'+T-T_g) \quad (2)$$

and it can be shown[4–6] that if $T_g - T_s = \Delta$ then $C_1' = C_1C_2 / (C_2 + \Delta)$ and $C_2' = C_2 + \Delta$.

Equations 1 and 2 were originally developed for describing the relationship between viscosity and temperature of polymers at temperatures well above their glass transition temperatures, in which case a_T is defined as a viscosity ratio, i.e.,

$$a_T(T,T_s) = \eta(T) / \eta(T_s) \text{ or}$$
$$a_T(T,T_g) = \eta(T) / \eta(T_g) \quad (3)$$

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where $\eta(T)$, $\eta(T_s)$ or $\eta(T_g)$ are the polymer's viscosity at temperature T, T_s, or T_g respectively. Because, according to Ferry[5], it is very difficult to make reliable viscosity measurements at temperatures around T_g, it is common in polymer research to set the reference temperature T_s within the experimental range and to use Equation 1 to calculate C_1 and C_2. These values can then be used to calculate C_1' and C_2' as described for comparison between materials with a different T_g.

The shift factor, a_T, need not, however, be expressed solely as a viscosity ratio. It can be and was defined in terms of moduli, strength, and strain in polymers[5] and in terms such as "time to crystallize"[7,8] or "a kinetic rate constant"[9] in biomaterials. Although the WLF equation is the most commonly used model, alternative models have also been used successfully to describe the relationship between a_T and T. Among the alternatives, the one most prominent in food research is the traditional Arrhenius equation or, when formulated in terms of a_T vs. T relationship,

$$\log a_T = (E / R)(1 / T - 1 / T_s) \qquad (4)$$

where E is the "energy of activation" and R the universal gas constant. It is commonly presented in a linear plot of log η (or the logarithm of another parameter) vs. 1 / T, from the slope of which the energy of activation, E, is calculated. The latter has been used extensively in lists of rheological characteristics of liquid foods and their temperature dependencies. The Arrhenius equation was also used in attempts to estimate the viscosity of liquid bridges that induce caking in instant coffee and other powders that are formed after plasticization of the particles' surface material.[10,11] It is, of course, the most commonly used model when it comes to the kinetics of chemical and biological reactions, including the destruction of microbial populations during heat treatment (see below).

Both the WLF equation and the Arrhenius model imply that the plot of a_T vs. T, irrespective of how a_T is defined, has an upward concavity down to the reference temperature, be it T_s or T_g. However, inasmuch as the two are not interchangeable, the degree of concavity of the corresponding a_T vs. T plots is usually very different.[1] This has led to the suggestion that both models are valid, but at different temperature ranges.[1,2] As long as the temperature range in which the experimental measurements of a_T are made is well above the transition temperature (30 to 50°C, for example) either model is a legitimate candidate, and, from a purely formalistic viewpoint, deciding between them can be done on the basis of the fit of the corresponding equation as judged by statistical criteria. The same applies to alternative kinetic,[3] phenomenological, or empirical models unless there is a special reason, based on mechanistic considerations, for preferring a certain type of mathematical format.

A serious difficulty may arise when either the WLF or the Arrhenius model is extended or extrapolated to the temperature range in which the transition takes place. The reason is that in this region the plot of a_T vs. T, again irrespective of how a_T is defined, has or can have a downward concavity[12–16] (see below) that cannot be accounted for by either model nor by any other model of a similar mathematical construction.

It so happens that in many foods and biological systems, the pertinent temperature range as far as stability and functionality are concerned is that in which the transition occurs. A familiar example is the loss of crunchiness in breakfast cereals and snacks[16] (see below) or the caking of hygroscopic powders.[12]

The objectives of this communication are to present a new model especially developed for the transition region, to assess its usefulness and limitations, and to demonstrate that the combined effects of temperature and moisture and probably that of other plasticizers can be described by a general form of the very same model.

II. THE DEFINITION AND DETERMINATION OF T_g

Glass transition is a phase transition that involves relatively small amounts of energy, when compared with melting, for example. The glass transition temperature, T_g, is defined as the temperature at which the relationships between the specific volume, V_s, and T and the heat capacity, C_p, and T have a characteristic discontinuity.[5,17]

Its direct determination, by means of DSC, for example, is complicated by the fact that the cooling or heating rate affects the measurement; also, the transition itself may not be sharp. So, although the T_g of a specific food or biomaterial may be a debatable issue, there is little doubt among investigators in the field that a glass transition does take place at or around this temperature. There are also indirect methods for determining T_g. The ones frequently adapted from polymer science are based on the fact that as a glassy material undergoes the transition it becomes plasticized, which is manifested in the loss of stiffness and its transformation into "viscosity". Inasmuch as the degree of stiffness is expressed in the magnitude of the storage modulus, G', and the viscosity by the loss modulus, G'', plots of G' and G'' vs. T, or the tangent of the phase angle (tan δ) vs. T can indicate, in principle, the temperature at which the transition occurs. An example is the temperature at which tan δ or G'' has a maximum.[5,17–20]. It has also been demonstrated that, at least in certain biomaterials, T_g as determined by a mechanical method closely agrees with that determined by scanning calorimetry.[18–20] Although the exact value of T_g, or the onset and termination of the transition as expressed by T_{g1} and T_{g2},[7,8] can be important for a food or biomaterial characterization, the issue will not be discussed further here. This is because, according to the proposed approach, the changes in mechanical or other properties are considered as being generally a continuous process, and consequently the transition is treated as happening over a temperature range rather than at a singular temperature. However, the existence of sharp transitions is neither excluded nor denied. It is simply treated as a borderline case where one of the model parameters approaches a zero value (see below).

III. RESISTANCE VS. TEMPERATURE AT A CONSTANT MOISTURE CONTENT

A. Mechanical Stiffness

Examples of stiffness vs. temperature relationships at and around the transition are given in Figure 1. They all clearly show the downward concavity of the relationship at the onset of the transition when the temperature is increased. The concavity is reversed at higher temperatures, when the transition is almost complete, in which case the relationship can be described by a WLF or a similar model, as mentioned previously.

At and around the transition, the stiffness vs. temperature relationship can be described by a model of the same format as Fermi's equation, which was originally developed for nuclear density.[21] When used to describe mechanical changes at and around the transition it becomes[12]

$$Y(T) = Y_s / \{1+\exp[T-T_c) / a]\} \qquad (5)$$

where Y(T) is the stiffness parameter (modulus, storage modulus, etc.), Y_s the latter's magnitude in the glassy state (assumed to be practically constant), T_c a temperature specifying the inflection point of Y(T) (also, $Y(T_c) = Y_s / 2$), and $\underline{a}$ a constant having the temperature units of T and T_c, which indicates the steepness of the decay of Y(T) in the transition region. Thus, when $\underline{a} \rightarrow 0$, Y(T) approaches the shape of a step function, indicating a sharp transition. When $\underline{a}$ has a large value it indicates that the transition takes place over a wide temperature range, as shown in Figure 2. According to Equation 5, about 90% of the drop in stiffness occurs in the range of $T_c \pm 3a$. Although T_c may coincide with T_g if the transition is sharp, this need not be the case in general.[12]

Demonstration of the fit of Equation 5 to the published experimental data is also shown in Figure 1. The reader should notice, however, that this model is best used when there are enough data points in the temperature region below that of the transition, that is, where $T \ll T_c$ and $Y(T) \simeq Y_s$. If such data are available, Y_s can be determined directly rather than calculated by nonlinear regression, leaving T_c and $\underline{a}$ as the only adjustable parameters of the model.

In case such data are difficult to obtain for technical reasons, or when materials having very different Y_s are to be compared, Y(T) can be replaced by a relative stiffness parameter, $0 < R(T) < 1$, defined as

$$R(T) = Y(T) / Y(T_s) \text{ or } Y(T) / Y_s \qquad (6)$$

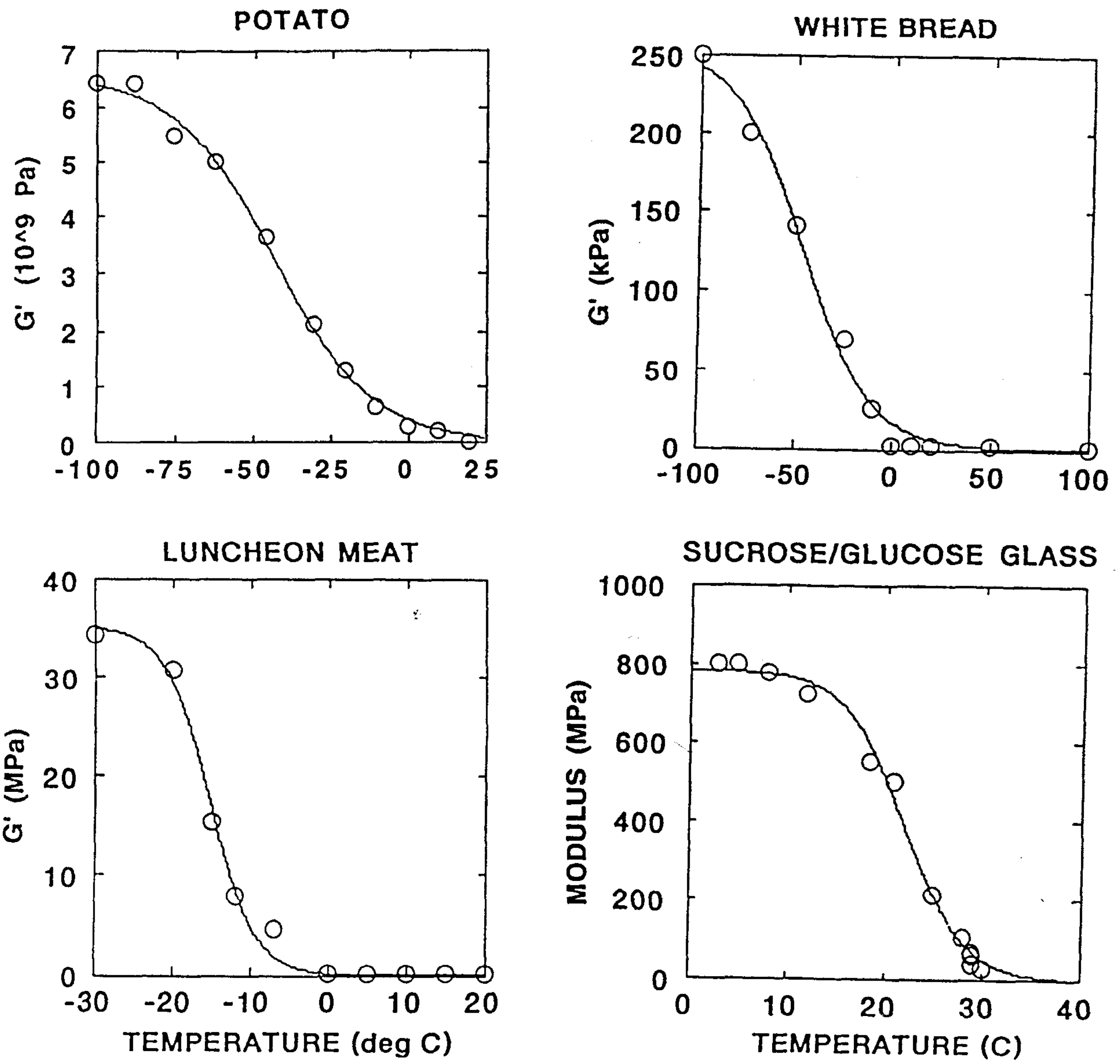

FIGURE 1. Effect of temperature on the stiffness of biosolids.[13,14] Open circles: published experimental data; solid line: the fit of Equation 5. Data for potato, bread, luncheon meat, and sugar glass from References 20, 29, 30, and 31, respectively.

where $Y(T_s)$ is the stiffness parameter at a convenient reference temperature $T_s \ll T_c$. This will transform Equation 5 into

$$R(T) = 1 / \{1+\exp[(T-T_c) / a]\} \quad (7)$$

Examples of the fit of Equation 6 to published experimental data of gliadin at various moisture contents with $T_s = -50°C$ are shown in Figure 3.

B. The Resistance of Spores to Thermal Inactivation

Traditionally, the kinetics of spores destruction by heat has been presented and quantified by the Arrhenius equation. An example of an experimental Arrhenius plot is given in Figure 4 (left). The plot is very linear in most of the temperature range, but the linearity does not hold at the high

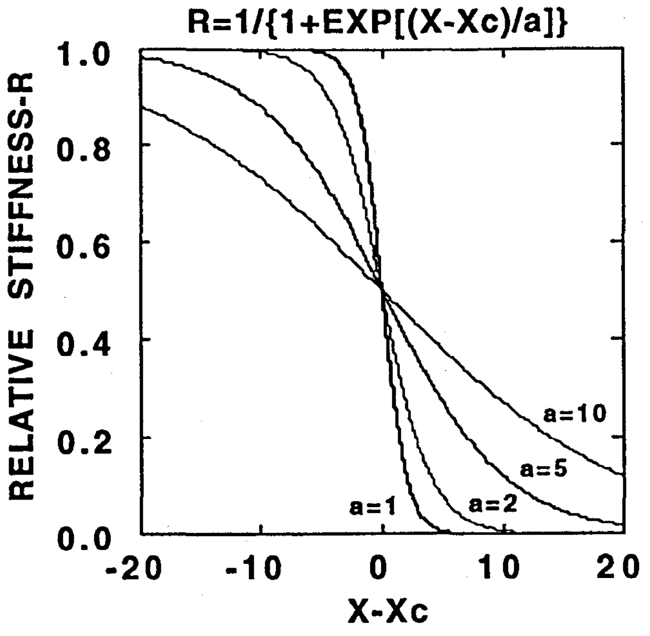

FIGURE 2. Schematic view of the properties of Fermi's function presented in the form of R(X) vs. X – X_c. Note that when X is temperature, the parameter a has the same temperature units. When X is moisture or a_w, a has moisture units or is dimensionless, respectively.

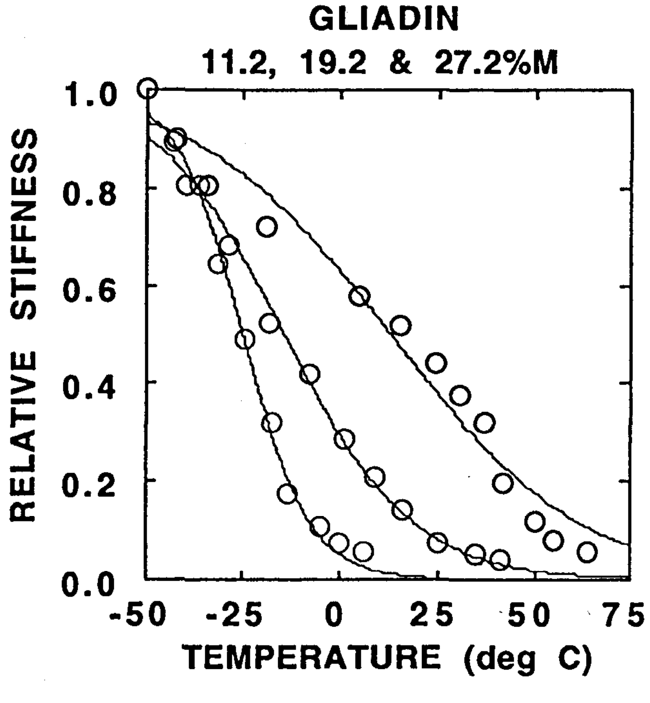

FIGURE 3. Relative stiffness vs. temperature relationships of gliadin at various moisture contents. Open circles: published experimental data; solid lines: the fit of Equation 7. The regression parameters were T_c: 13, –14, and –25°C; a: 23.9, 16.2, and 8.6°C; and r^2: 0.991, 0.995, and 0.998, respectively. (Data from Reference 18.)

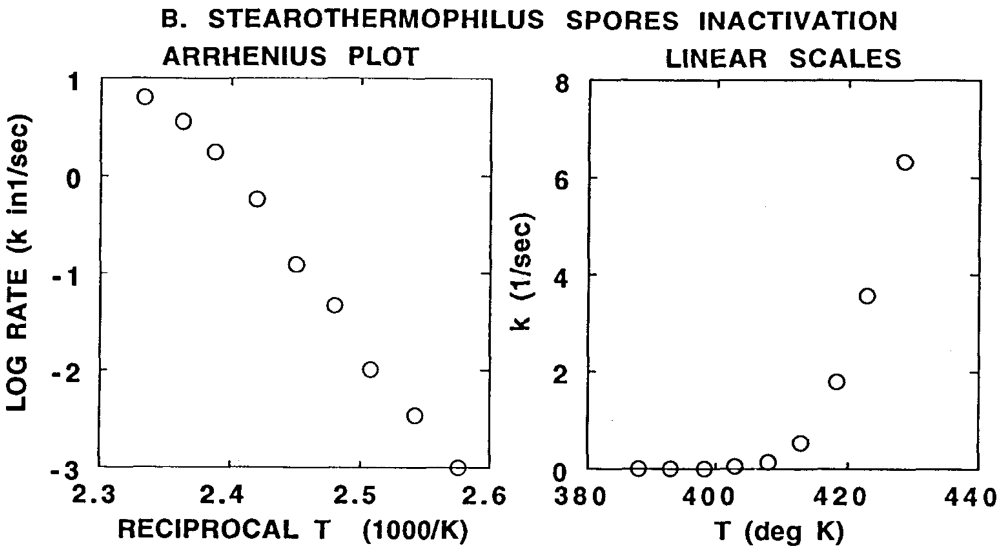

FIGURE 4. Spores inactivation rates (k) viewed in an Arrhenius plot and linear coordinates. (Data from Reference 32.)

temperature region (low 1 / T values). This has led to the suggestion that the data should be presented in the form of k vs. T (k being the reaction rate constant) as shown in Figure 4 (right), and fitted by the WLF model with its "universal constants," that is, with C_1' and C_2' fixed and T_g and k_g (k at $T = T_g$) variable. In this case, as with data from other sources, the fit was found satisfactory, and it was concluded that the thermal resistance of bacterial spores is considerably reduced when the material of which they are made is transformed from a glassy to leathery or rubbery state.[9]

The same concept, however, can be implemented in a different manner. When the observed inactivation rate is very low, the spores' resistance is obviously very high and the difference between a rate of, let's say, $10^{-2}\ s^{-1}$ and $10^{-3}\ s^{-1}$ has no or very little practical significance. Consequently, it is reasonable to define a practical index of thermal resistance or a relative thermal resistance R(T) not as the destruction rate constant k(T) itself, but as an algebraic transform of the latter. The magnitude of such an index will be about unity at low temperatures, and it will progressively approach zero as the temperature increases. Two examples of such mathematical transformations are

$$R = \exp(-k) \tag{8}$$

and

$$R = 1 / (1+k) \tag{9}$$

As can be seen in Figure 5, the plot of R(T) vs. T as defined by either Equation 8 or 9 has the same shape as that of the plot of the relative stiffness vs. T (Figures 1 to 3), and it also can be described by Equation 7. In the case of *B. thermophilus* spores inactivation, the corresponding values of T_c were 414 and 416 K, those of the constant $\underline{a}$ 2.9 and 4.9 K and the r^2 0.9999 and 0.9985, respectively. In other words, a similar picture of the spores' thermal resistance emerges irrespective of how the relative resistance index, R(T), is defined. The characteristic temperature T_c on the order of 415 K or 132°C, representing the center of the transition temperature range, is well above that of T_g calculated from the WLF model with the fixed ("universal") coefficients, which was about 90°C.[9] Or, put differently, according to Equation 7, considerable loss of heat resistance starts only at temperatures of about 130°C (see Figure 5), while according to the WLF model with the universal constants, the relative resistance drops by about three orders of magnitude already at a tempera-

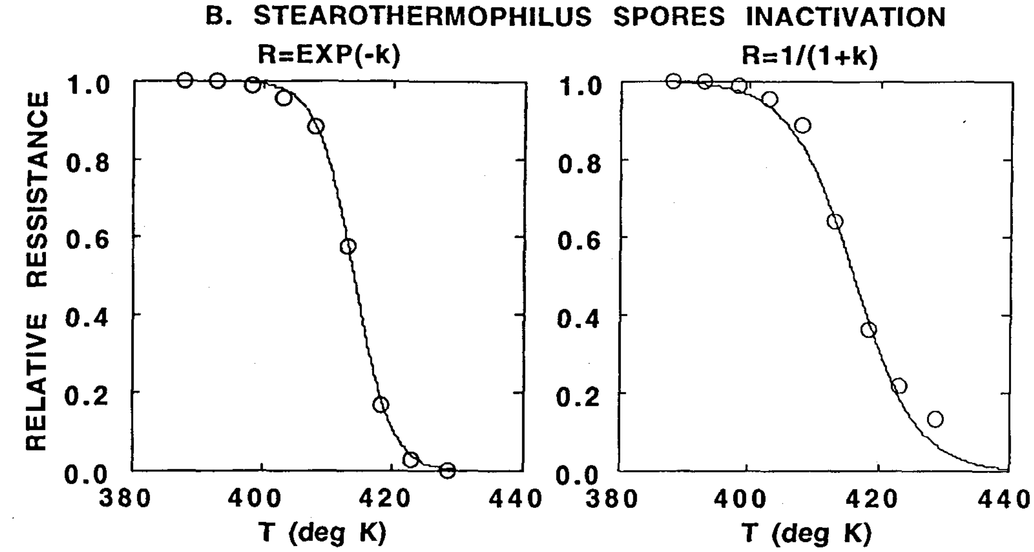

FIGURE 5. Spores relative resistance, defined in two ways, vs. temperature relationships. Open circles: published experimental data; solid lines: the fit of Equation 7. The regression parameters were T_c: 414 and 416 K, a: 2.88 and 4.86 K, and r^2: 0.9999 and 0.9985, respectively. (Data from Reference 32.)

ture not much higher than 100°C and by about five orders of magnitude at a temperature not much higher than 110°C. Whether the observation that Equation 7 can be used to describe spores destruction kinetics has a general validity is a question that can only be answered after a much larger data base is examined.

C. Comparison of Fermi's Equation and the WLF Model

Numerous investigators have reported a good fit of the WLF model to their experimental data,[3] and there is no reason to doubt the validity of their observations. (Whether it is permissible to use the model with fixed ["universal"] constants is another problem, which is discussed elsewhere.[6]) In fact, and as already stated, many log a_T vs. T relationships definitely have an upward concavity at temperatures well above the transition region for which the WLF model provides an appropriate account, but Equations 5 and 7 do not. At temperatures well above the transition region, that is, when $T \gg T_c$, these equations are reduced to

$$\log Y(T) = \log Y_s - T / a \qquad (10)$$

and

$$\log R(T) = -T / a, \qquad (11)$$

which are linear relationships. Thus, the upper limit of the validity of the model and the beginning of WLF or alternative kinetics can be established simply by testing the linearity of the plot of log Y(T) or log R(T) vs. T.

A more serious disagreement between the two models can arise when the WLF kinetics is extended or extrapolated to lower temperatures. As can be seen in Figure 6, the two models can imply a glass resistance, Y_s, that can differ by several orders of magnitude. However, a word of caution is in order here. Because Fermi's equation is an empirical phenomenological model, it only accounts for the general shape of the Y(T) or R(T) vs. T plot but cannot be used for its extrapolation. Consequently, if Y_s is to be determined or estimated reliably, the experimental data range *must* cover at least part of the region where $Y(T) \approx Y_s$. This is demonstrated in Figure 7. It shows how a set of experimental data, when fitted by Equation 5 with very different and probably unrealistic values of Y_s, can yield almost the same degree of fit, as judged by statistical criteria.

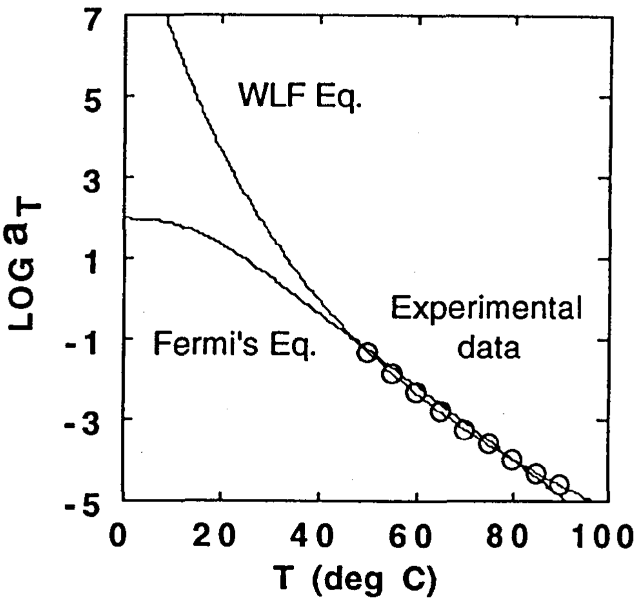

FIGURE 6. An example of how extrapolation to the transition region using the WLF model and Equation 5 can yield Y_s values that differ by several orders of magnitude (simulated data).

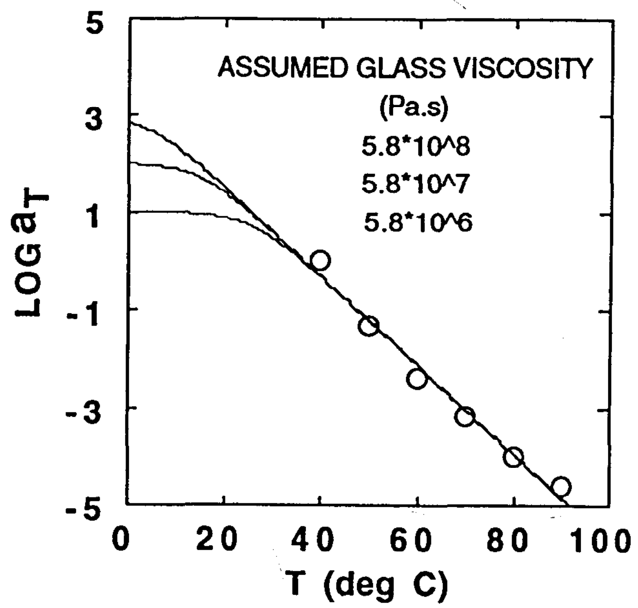

FIGURE 7. Demonstration of the insensitivity of the fit of Equation 5 to the magnitude of Y_s if data at temperatures below the transition are unavailable. Open circles: fructose viscosity data from Reference 33. Solid lines: the fit of Equation 5 with various (probably unrealistic) values of Y_s. The regression coefficient r^2 was about the same for all the curves (0.9954, 0.9953, and 0.9951, respectively).

III. RESISTANCE VS. MOISTURE OR WATER ACTIVITY AT A CONSTANT TEMPERATURE

A. Stiffness vs. Moisture or a_w

Water is an effective plasticizer, and its presence considerably lowers the glass transition temperature of sugar glasses and biopolymers.[1,2] Thus, many materials that are hard and brittle at room temperature when dry — breakfast cereals and gelatin, for example — soften considerably and lose their brittleness after moisture sorption. The loss of stiffness as a function of moisture content under isothermal conditions can be described by the same type of model that was used for the effect of temperature at constant moisture or a_w.[12–14] Thus, with moisture (M) or water activity (a_w) replacing T in Equations 5 and 7, they become:

$$Y(M) = Y_s / \{1+\exp[(M-M_c) / a']\} \quad (12)$$

or

$$Y(a_w) = Y_s / \{1+\exp[a_w-a_{wc} / a'']\} \quad (13)$$

and

$$R(M) = 1 / \{1+\exp[(M-M_c) / a']\} \quad (14)$$

or

$$R(a_w) = 1 / \{1+\exp[(a_w-a_{wc}] / a'']\} \quad (15)$$

where M_c and a_{wc} play the same role as T_c and a' and a'' that of $\underline{a}$ in Equations 5 and 7 (Figure 2). In Equations 12–15, although a' has the moisture units of M and M_c, while a'', as a_w, is dimensionless by definition.

Demonstration of the fit of Equations 12 and 13 to published experimental data is given Figure 8. It is comparable to that found in the case of Y(T), which suggests that moisture uptake has a similar effect to that of a temperature increase not only qualitatively but in a certain sense quantitatively as well.

B. Loss of Crunchiness

The phenomenon that crunchy foods lose their crunchiness after moisture sorption is well known and documented. Recently, it has been suggested that the degree of crunchiness of crunchy materials can be assessed in terms of the degree of jaggedness of their stress-strain relationship.[24,25] The degree of jaggedness in turn can be quantified in terms of the magnitude of the apparent fractal dimension or by the mean magnitude of their power spectrum.[24–26] The questions that arise are whether these parameters can also be related to the moisture content or water activity in the same manner as other mechanical parameters, that is, via Equations 12 or 13, and, if so, whether the magnitude of these equations' parameters (M_c or a_{wc} and a' or a'') is the same as those calculated for the stiffness loss. An attempt to answer these questions by simultaneous determination of stiffness and jaggedness in two crunchy foods at various levels of water activity was reported recently.[16] The results are summarized in Figures 9 and 10. They show that although there was a good agreement between the two independent stiffness parameters (average force at 10 and 20% deformation) and jaggedness parameters (apparent fractal dimension and mean magnitude of the power spectrum) the effect of a_w on them need not be the same, or, more specifically, although the critical a_w level for crunchiness loss can be about the same as for the stiffness loss (Figure 9), the two could also differ by as much as about 0.25 a_w units (Figure 10). The figures also show that after plasticization, crunchiness practically disappeared (apparent fractal dimension of about one), but there was still an appreciable stiffness left, on the order of 10 to 20% of the initial value. Thus, to account for these residual values, Equation 12 had to be modified with an added constant, that is

$$Y(a_w) = Y_1 / \{1+\exp[(a_w-a_{wc}) / a'']\} + Y_2 \quad (16)$$

where $Y_s = Y_1 + Y_2$.

That a substantial residual stiffness remains after the transition is completed may not be a unique characteristic of crunchy foods. It may have an impact on the processability of plasticized food and biological materials and therefore, at least in specific systems, is worth further investigation. It should be remembered, however, that the plasticized materials may have very different kinds of rheological properties, for example, the

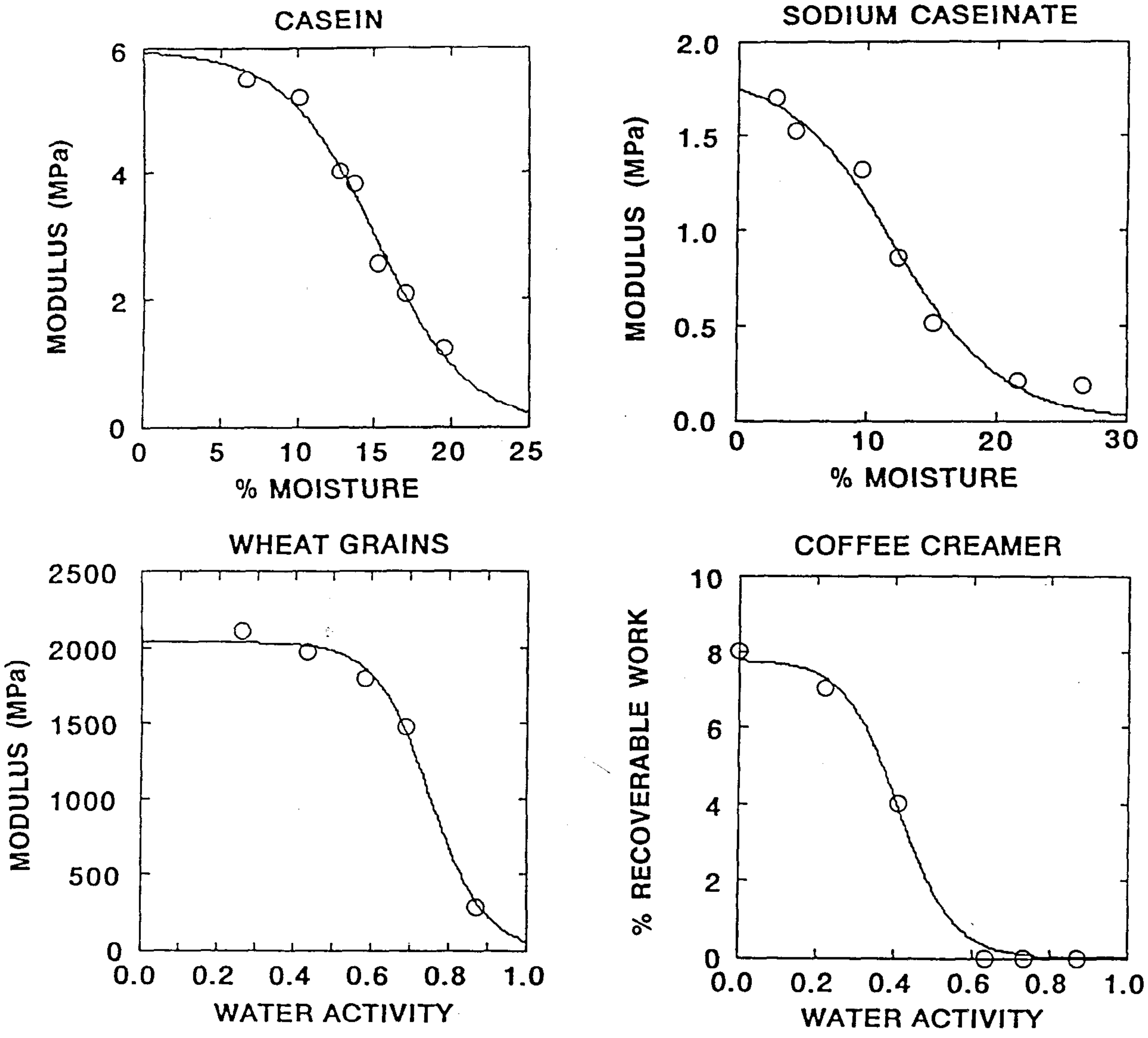

FIGURE 8. Effect of moisture or water activity on the stiffness of biomaterials and foods.[13,14] Open circles: published experimental data; solid line: the fit of Equations 12 and 13. Data for casein and sodium casein from Reference 22, for wheat grains from Reference 34, and for coffee creamer from Reference 35.

viscoelasticity of doughs, for which the use of a term like "stiffness" is probably inappropriate.

IV. THE COMBINED EFFECTS OF TEMPERATURE AND MOISTURE ON THE PLASTICIZATION OF BIOMATERIALS

A. The Gordon-Taylor Equation

Plasticizers, including water, as mentioned previously, lower the glass transition temperature.[1,2] The relationship between T_g of a plasticized material, T_{gmix}, and the plasticizer concentration expressed as a weight fraction, X, can be described successfully by the empirical Gordon-Taylor equation

$$T_{gmix} = [XT_{g1} + K(1-X)T_{g2}] / [X+K(1-X)] \qquad (17)$$

where the subscripts 1 and 2 refer to the plasticizer and host material, respectively.

The usefulness of the Gordon-Taylor equation to water-plasticized biopolymers has been demonstrated recently by several investiga-

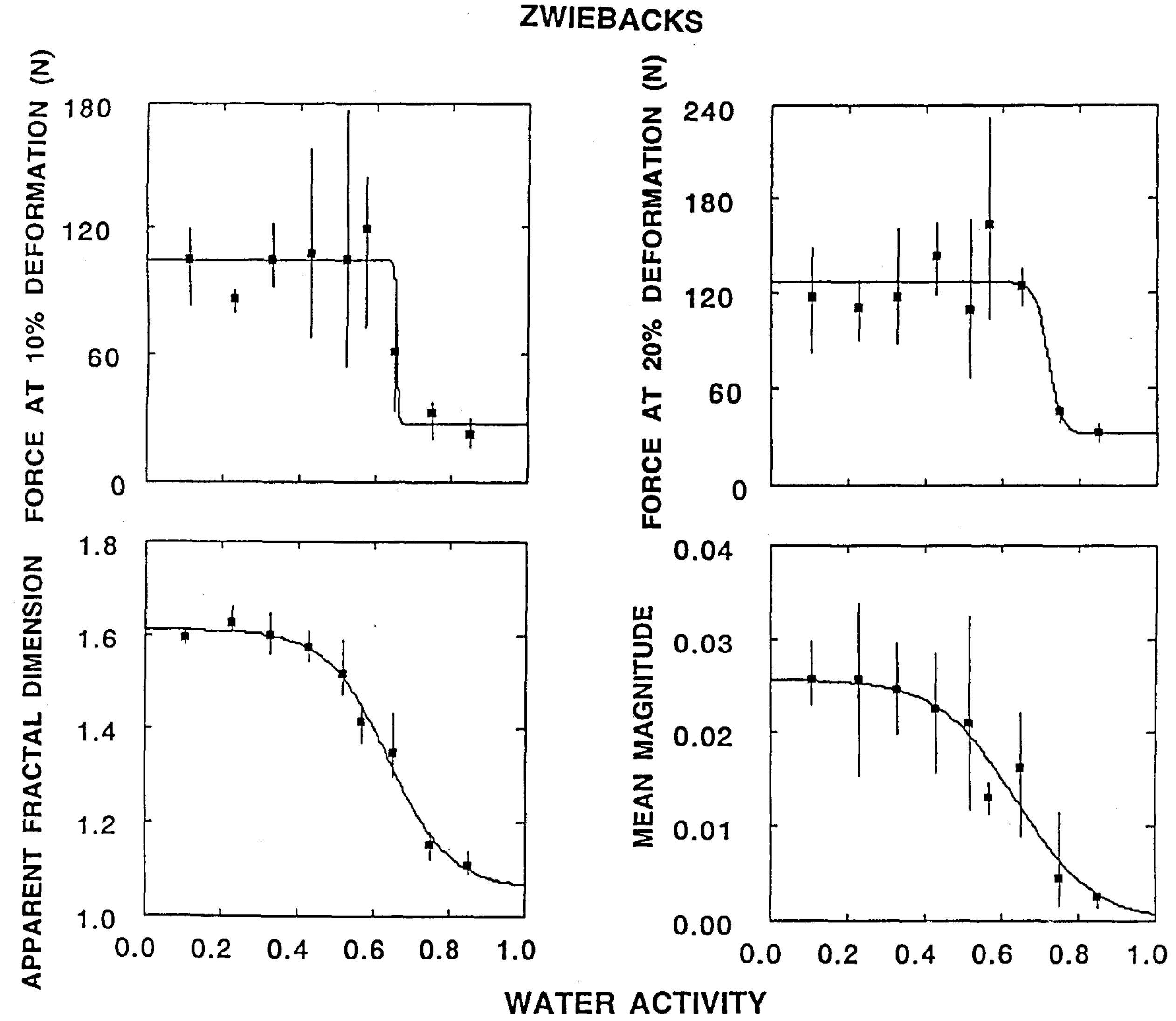

FIGURE 9. Stiffness and jaggedness parameters of Zwiebacks plotted against water activity. Vertical lines: the range of the experimental scatter; solid line: the fit of Equation 16 (r^2, 0.981 to 0.999). Note that a_{wc} for the stiffness parameters was 0.65 to 0.72, while that of the jaggedness (crunchiness) parameters was 0.64 (about the same). (Data from Reference 16.)

tors[18,22,23] with T_{gH2O} 135 or 139 K. (It can be shown, through Figure 11, that a deviation of a few degrees Kelvin in the value of T_{gH2O} has little effect on the fit of the model at moisture levels of up to about 30%, and therefore the discrepancy is of little practical significance. Reported K values of biomaterials, as defined by Equation 17, were on the order of 0.15 to 0.7. Their magnitude was treated as quantitative measure of the plasticizing effect of water for comparison between different biopolymers.[18,19] According to Equation 17, the larger the value of K, the lower is the plasticization effect. (When $K \rightarrow 0$, $T_{gmix} \rightarrow T_{g1}$ for all X values, and when $K \rightarrow \infty$, $T_{gmix} \rightarrow T_{g2}$ for all X values).

The reader will notice that although T_{g2}, the glass transition temperature of the dry biopolymer, can be calculated using Equation 17, the value so obtained is only a rough estimate. Data simulations with generated noise using Equation 17 (Table 1) show that deviation on the order of ±5 K or more in the value of T_{g2} can be expected

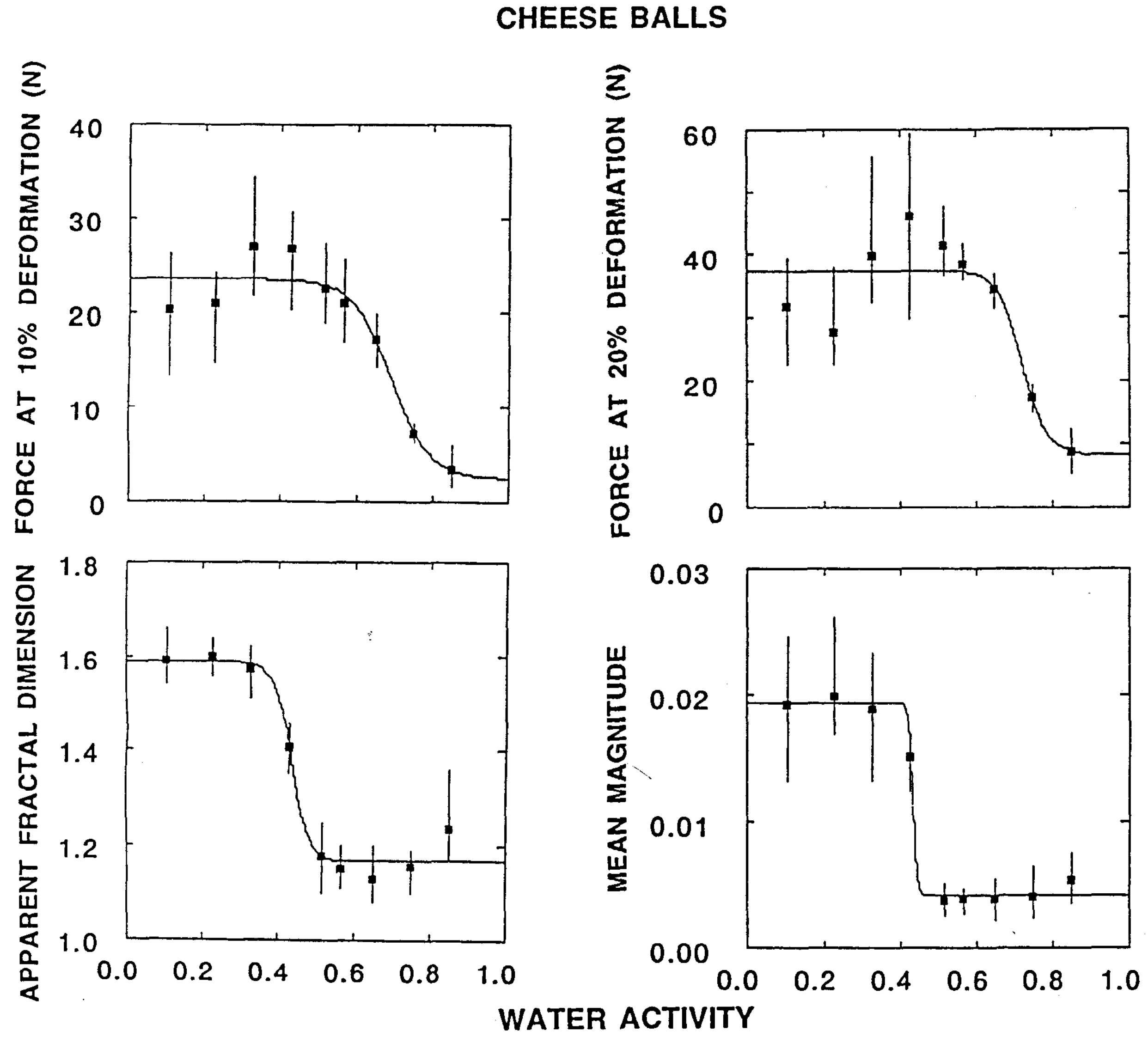

FIGURE 10. Stiffness and jaggedness parameters of cheese balls plotted against water activity. Vertical lines: the range of the experimental scatter; solid line: the fit of Equation 16 (r^2, 0.978 to 0.999). Note that a_{wc} for the stiffness parameters was 0.69 to 0.72, while that of the jaggedness (crunchiness) parameters was 0.44 to 0.43 (a difference of more than 0.25 a_w units). (Data from Reference 16.)

even with an experimental scatter as low as 2%. It is, therefore, much safer to determine T_{g2} experimentally rather than by calculation, although the results may agree despite the scatter.[18]

There are alternative empirical models to Equation 17 as well as similar models derived on the basis of thermodynamic considerations.[27] The latter, however, require knowledge of certain thermal properties of the food or biomaterial in question, which may require a separate experimental determination.

B. T_c and a vs. Moisture

Because T_c in Equations 3 and 5 need not coincide with T_g, the question arises whether it too has the same type of moisture dependency. According to various early published reports, the

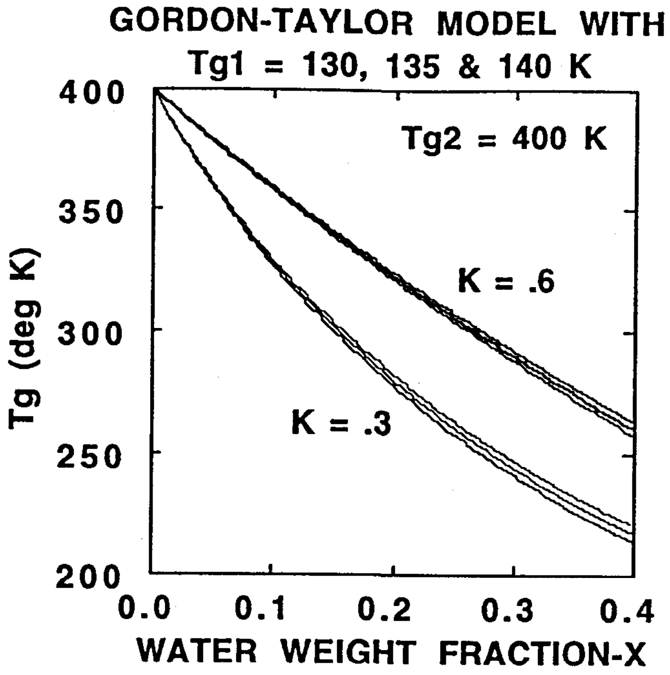

FIGURE 11. Generated T_g vs. water weight fraction using the Gordon-Taylor model with $T_{g\text{water}}$ = 130, 135, and 140 K.

dependency between the collapse temperature, T_{col}, or sticky point, T_{st}, and moisture content, M, can be described by the expression:[12,28]

$$T_{col}(M) \text{ or } T_{st}(M) = T_o \exp(-k_1 M) \quad (18)$$

where T_o is the collapse temperature or sticky point in the dry state and k_1 a constant. It was also shown that the relationship between T_g and moisture contents can be described by the same expression as well.[12] This is not surprising because, in the range of up to about 30% moisture, the Gordon-Taylor model, especially with K > ~0.3, and Equation 18 can be used interchangeably when the experimental T_g vs. M relationship has even a slight scatter (Figure 12). Therefore, it is reasonable to assume that T_c, which is also a characteristic transition temperature, has a moisture dependency that can be described by Equation 18 (or Equation 17). In the case of gliadin,[18] this kind of relationship was also established experimentally.[15]

One can also assume that at high moisture contents the transition not only occurs at a lower temperature but is also sharper. In terms of Equations 5 and 7, this translates into a smaller value of the constant $\underline{a}$. The decrease in the magnitude of $\underline{a}$ can also be assumed to obey an exponential decay function, in which case, at least as a first approximation

$$a(M) = a_o \exp-(k_2 M), \quad (19)$$

where $\underline{a}_o$ is the magnitude of $\underline{a}$ in the dry state and k_2 a constant. When tested with the gliadin data the assumption was found to be correct.[15]

C. The Combined Model

Because both T_c and the constant $\underline{a}$ in Equations 5 or 7 can be expressed as functions of moisture, the relationship between stiffness or relative stiffness, temperature, and moisture at the transition region has the general form

$$Y(T,M) = Y_s / \{1+\exp[(T-T_c(M)) / a(M)]\} \quad (20)$$

and

$$R(T,M) = 1 / \{1+\exp[(T-T_c(M)) / a(M)]\} \quad (21)$$

TABLE 1
Determination of T_{g2} and K of Equation 16 by Nonlinear Regression Using Computer-Generated Data with 2 and 5% Random Noise[a]

Original parameters		T_{g1} = 130 K			T_{g2} = 400 K	K = 0.2		T_{g1} = 130 K		T_{g2} = 400 K	K = 0.4	
Noise level		2%			5%			2%			5%	
Regression parameters[b]	T_{g2} (K)	K	r^2	T_{g2} (K)	K	r^2	T_{g2} (K)	K	r^2	T_{g2} (K)	K	r^2
No.												
1	400	0.206	0.9999	391	0.195	0.9995	400	0.392	0.9999	396	0.441	0.9994
2	400	0.203	0.9999	409	0.197	0.9993	397	0.397	0.9999	394	0.423	0.9993
3	404	0.192	0.9999	411	0.175	0.9995	402	0.388	0.9999	392	0.455	0.9993
4	395	0.209	0.9999	409	0.176	0.9996	404	0.373	0.9999	408	0.343	0.9992
5	397	0.208	0.9999	394	0.200	0.9993	395	0.426	0.9999	403	0.402	0.9997
Range	9	0.017	—	20	0.025	—	9	0.053	—	16	0.113	—

[a] The 2 and 5% random noises were produced by $T_{g2\,\text{simulated}} = T_{g2\,\text{original}}{}^{*}$ (0.98 + 0.04 URN) and $T_{g2\,\text{original}}{}^{*}$ (0.95 + 0.1 URN), respectively. (URN is a random number between 0 and 1. Both the simulations and the regressions were done with the Systat 5.2.1 package on a Macintosh SE/30 microcomputer.)

[b] Values rounded to three digits.

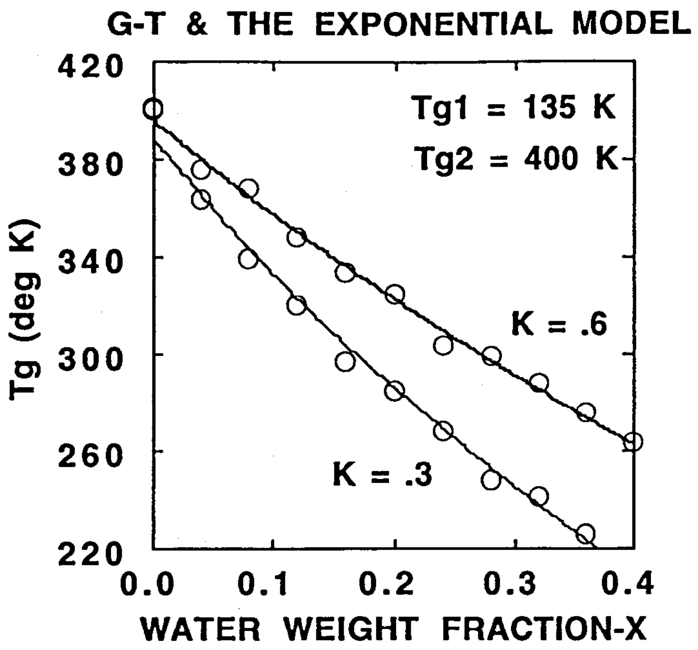

FIGURE 12. The compatibility of the Gordon-Taylor (Equation 17) and the single term exponential expression (Equation 18). Open circles: data generated with the Gordon-Taylor model (T_{g1} = 135 K and T_{g2} = 400 K) with a random scatter of 2%. Solid lines: the fit of Equation 18 ($r^2 > 0.999$).

If $T_c(M)$ and $\underline{a}(M)$ can be written in the form of Equations 18 and 19, the stiffness-temperature-moisture relationship becomes

$$Y(T,M) = Y_s / \{1+\exp[(T-T_{co}\exp(-k_1M)) / a_o\exp(-k_2M)]\} \quad (22)$$

or, in terms of a relative stiffness,

$$R(T,M) = 1 / \{1+\exp[(T-T_{co}\exp(-k_1M)) / a_o\exp(-k_2M)]\} \quad (23)$$

Thus, if T_{co}, a_o, k_1, and k_2 are known or can be reasonably estimated, one can generate three-dimensional plots of R(T,M), and, if Y_s is also known, of Y(T,M) as well.[13] Examples of R(T,M) plots generated with Equation 23 are shown in Figures 13 and 14.

They show that temperature-moisture combinations that result in either high stiffness [$R(T,M) \simeq 1$] or complete plasticization [$R(T,M) \simeq 0$], as well as intermediate stages, can be identified at a glance. Also, differences between materials, which may not always be obvious on the basis of their corresponding equations' constants, become self-evident when presented in the form of a three-dimensional plot.[13]

D. Other Plasticizers

In principle, the structure of Equations 22 and 23 is not restricted to moisture content. If one can formulate algebraically the relationships $T_c(x)$ and a(x), where x is another plasticizer concentration or weight fraction, then the same kind of plots shown in Figures 13 and 14 can be generated with x replacing M. It is also theoretically possible to find relationships such as $T_c(M,x_1,x_2,\ldots)$ and $a(M,x_1,x_2,\ldots)$, that is, for a material plasticized by moisture and one or more other plasticizers. However, because a graphical presentation is limited to three-dimensional displays, a series of such plots would be required to describe such relationships, which may render the method less attractive.

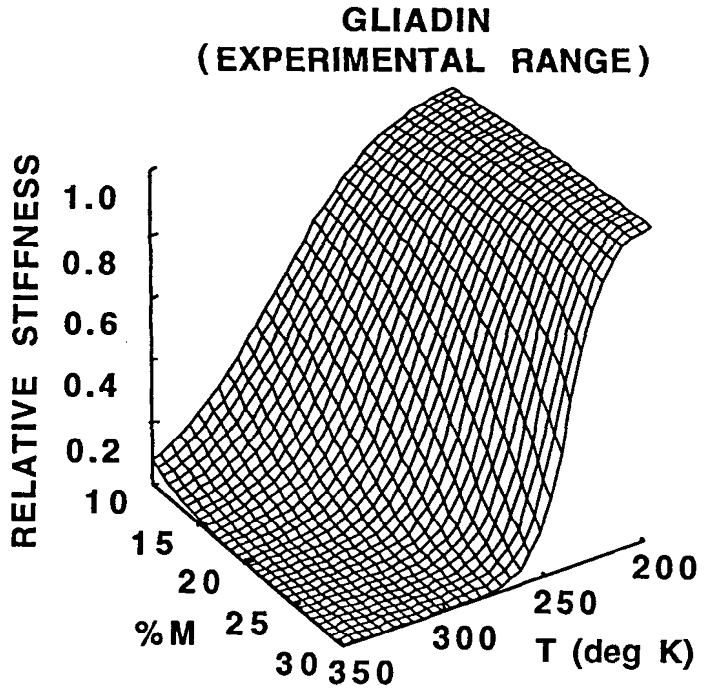
GLIADIN
(EXPERIMENTAL RANGE)

FIGURE 13. Relative stiffness-temperature-moisture relationships of Gliadin produced by Equation 23. The relative stiffness was defined as G′(T) / G′ (–50°C), T is in K and M in % weight. T_{co} = 314 K, k_1 = 0.09, a_0 = 46.7, and k_2 = 0.6 were calculated from the experimental data in Reference 18. (Data from Reference 15.)

V. CONCLUSIONS

Changes in the properties of food and biosolids are governed by different kinds of kinetics that are determined by whether the material is in a glassy state, is undergoing a transition, or is fully plasticized. Although the existence of three such states is clearly evident from the shape of the stiffness-temperature-moisture relationship, for example, the existence of borderlines between them is not. In the glassy state, changes are relatively small and consequently have not been studied as thoroughly as those occurring during and after the transition. There is ample evidence that at the transition region the stiffness (or other "relaxation" or "mobility" parameter)-temperature-moisture relationship is concave downward, irrespective of the way the stiffness or other parameter is defined. Consequently, models adopted from the polymer literature, notably the WLF equation, are inappropriate for changes that occur in this region. An alternative model that correctly accounts for the shape of the relationship appears to be consistent with the experimental relationships of a wide range of biomaterial with which it was tried. This model, discussed in this work, need not be unique; alternative models with a modified or totally different mathematical structure may prove to be just as appropriate or better. (For materials with a sharp transition, the model R(T) = (1 / π) arcctg [(T–T_c) / a], for example, can have a fit and constants comparable to those of Equation 7.)

The described model, based on Fermi's equation, entails that beyond the transition region a plot of R(T) or log a_T vs. T is a straight line, thus offering a clear criterion to establish the upper limit of its validity range. Published evidence strongly suggests that beyond the transition range, where the upward concavity of log a_T vs. T is obvious, the WLF is an appropriate and convenient model. Its use, however, is only safe within the experimental data range. If used for extrapolation into the transition region, it can lead to a considerable overestimate of the stiffness (or an

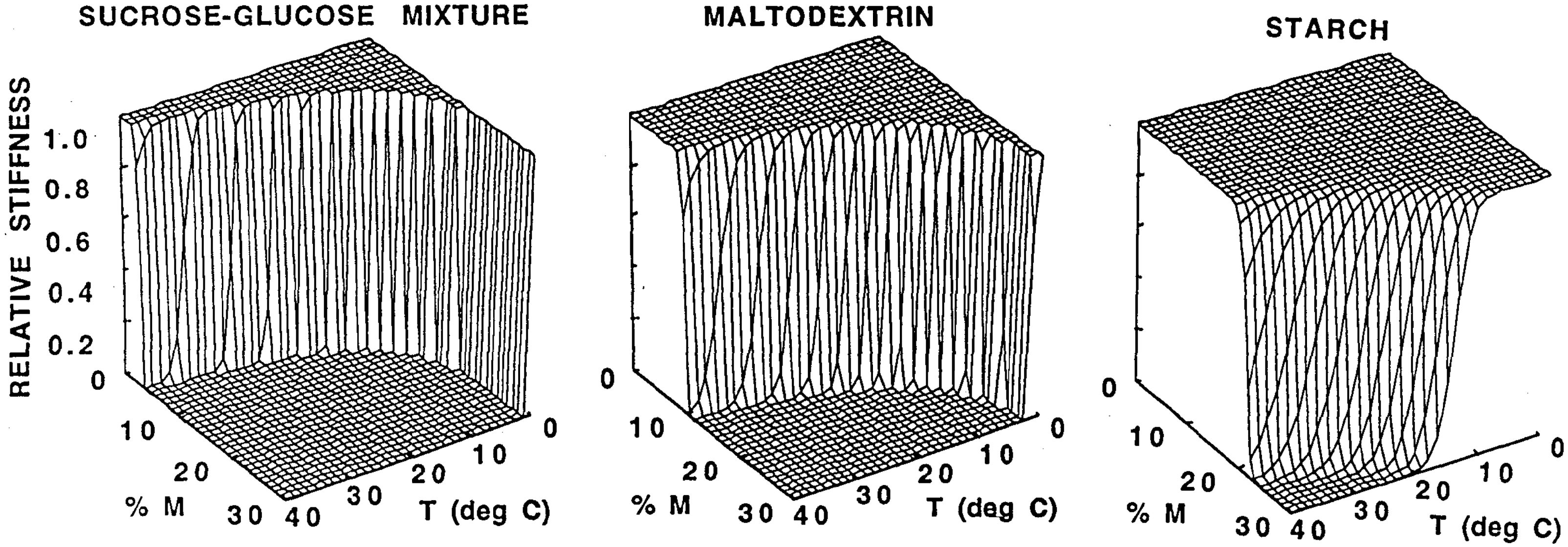

FIGURE 14. Simulated relative stiffness-temperature-moisture relationships of glucose-sucrose mixture, maltedextrin, and starch created with Equation 23. (Based on published data in References 11, 36, and 37.)

equivalent property). A possible theoretical exception is a material with an extremely sharp transition. However, the existence of biomaterials obeying the WLF equation all the way to T_g ought to be demonstrated experimentally with data recorded at temperatures *below as well as above* that at which the transition occurs.

Plasticization of biosolids is a result of the combined effects of temperature and moisture. It can be described by a single mathematical model and presented graphically in a form of a three-dimensional plot of stiffness (or any other measure of resistance), temperature, and moisture content. In principle, the same kind of model can be used to describe the effects of plasticizers other than water. However, whether this is also a practical option ought to be determined on the basis of experimental data, which are currently very scarce.

Most published reports on modeling the effect of temperature and / or moisture focus, with very few exceptions, on a single mechanical parameter, for example, modulus determined at a fixed deformation range and constant rate, or a group of related parameters (e.g., G′, G″) and tan δ determined simultaneously at a constant frequency and amplitude. Consequently, there is little evidence in the literature that a model found appropriate for a particular mechanical parameter is also valid for different mechanical parameters and other physico-chemical properties, and if valid that the model's constants, C_1 and C_2 of the WLF equation or T_c and $\underline{a}$ of the proposed model, are the same for all attributes. This issue must be resolved before any of the discussed models is used for prediction of properties other than those already determined experimentally. (For example, the question of whether it is possible to predict or at least estimate a browning reaction rate on the basis of the kinetics of stiffness loss is still unresolved.) The data on the stiffness and crunchiness loss in snack foods (Figure 10) suggest that, at least in principle, there can be properties for which this will be impossible and that only the general character of the relationship is to some extent predictable. It is therefore recommended that future research focus simultaneously on the effect of temperature and/or moisture on *unrelated* properties, in order to establish whether the mathematical expression that is used to describe the data can serve not only as a qualitative model but as a quantitative one as well.

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