

Mathematical Characterization of the Plasticizing and Antiplasticizing Effects of Fructose on Amylopectin¹

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ABSTRACT

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Published data indicate that admixture of fructose to amylopectin increases the latter's stiffness but lowers its glass transition temperature range and makes the transition sharper. It also dramatically increases the plasticizing effect of absorbed moisture. These effects are quantified in terms of the parameters of a mathematical model based on Fermi's equation, which can describe mechanical changes at and around the glass

transition of biopolymers, irrespective of whether it is sharp or broad. This model accounts for the mixture's stiffness dependency on both the fructose concentration and temperature, or moisture, with a single algebraic expression. It can also be used to create three-dimensional plots from which the combined effects of fructose and temperature, or moisture, can be viewed, and conditions of plasticization, or antiplasticization, be identified.

The transition of many food biopolymers, from a glassy to rubbery states, takes place over a relatively wide temperature range. The state of the biopolymer in this range has a profound effect on the food physical properties which influence its stability and acceptability (Levine and Slade 1992, Slade and Levine 1993). At and around the glass transition temperature (T_g), a plot of a stiffness or a rigidity parameter, E' or G' for example vs. temperature (in linear coordinates) can have a characteristic sigmoid shape of the kind shown in Figure 1, with a prominent region of downward concavity. Changes in the magnitude of E' or G' or similar mechanical parameters at this region cannot be described by extending conventional models that were developed for the behavior of polymers well above the glass transition temperature. Thus, a model such as the WLF equation, which entails upward concavity all the way, and a stiffness drop of several orders of magnitude within a few degrees C above T_g are inappropriate for the transition region. Also, while specifying a single temperature, such as T_g , may be sufficient to characterize a sharp transition, to describe a wide transition requires a model with at least two constants: one to identify the transition's temperature range, and the other its sharpness or broadness. It has recently been suggested that the stiffness or rigidity versus temperature relationship of biopolymers at the transition region can be described by a model based on Fermi's equation (Peleg, 1993, 1994a,b, 1996):

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

where $R(T)$ is the relative stiffness [e.g., $R(T) = E'(T)/E'(T_s)$]; where T_s is a reference temperature (preferably, but not necessarily); where the material is in the glassy state (i.e., $T_s \ll T_c$). T_c is the inflection point of $R(T)$, where, also $R(T_c) = 1/2$; and where a is a parameter (temperature units) that accounts for the steepness of $R(T)$ around T_c . According to this model about 90% of the drop in $R(T)$ occurs within $T_c \pm 3a$ and as $a \rightarrow 0$ the shape of $R(T)$ approaches that of a step function. Consequently this model is equally applicable to materials undergoing a sharp or broad transition.

The applicability of the model was demonstrated with a number of biopolymers and certain synthetic polymers (Peleg 1993). It was also shown that if T_c and a are expressed as functions of moisture

content, then the relative stiffness-temperature-moisture relationship can be mapped by a single equation (Peleg 1993, 1994b, 1996). In principle, the model format can be applied to plasticizers other than water, either alone, or in combination with water (Peleg 1993). The objective of this article is to provide a specific model format for the effects of plasticizers, or antiplasticizers on the properties of biopolymers, and demonstrate its applicability with published data on the stiffness of the amylopectin-fructose-water systems.

THE MODEL

For a system containing a biopolymer and a single plasticizer, or antiplasticizer, Eq. 1 can be written in the form:

$$E'(T,X) = E'_s(X)/\{1 + \exp[(T - T_c(X))/a(X)]\} \quad (2)$$

where X is the weight fraction of the plasticizer, $E'(T,X)$, the modulus at any particular T and X combination; and $E'_s(X)$ is the reference storage modulus determined either at the glassy state, or at any other temperature, T_s , provided that $T_s \ll T_c$.

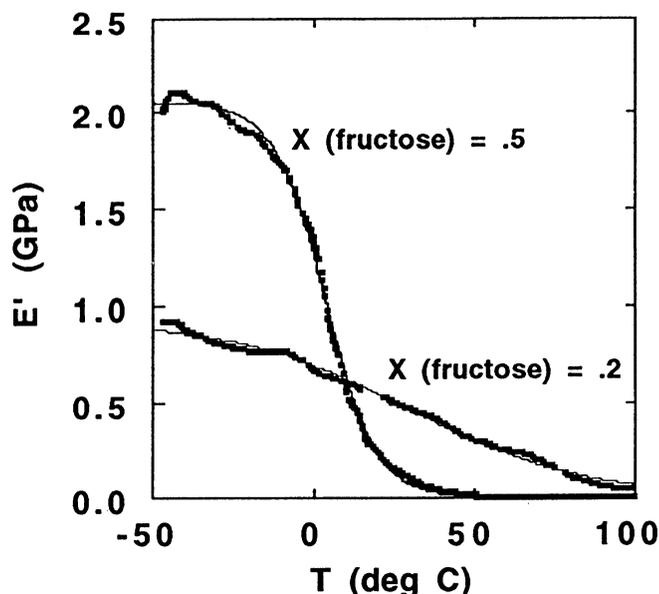


Fig. 1. Demonstration of the fit of Eq. 1 to E' vs. T relationship of amylopectin and an amylopectin-fructose mixture. Regression parameters are listed in Table I. Data from Kalichevsky et al (1993a).

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The terms $E_s'(X)$, $T_c(X)$, and $a(X)$ are determined from experimental data. "Full plasticization" is expressed by a simultaneous drop in the magnitude of all three parameters, which is an indication of an overall decrease of stiffness, lower transition temperature range, and a steeper stiffness drop at the transition region, respectively. An additive, however, depending on its chemical species, can also act as an antiplasticizer, in which case $E_s'(X)$, $T_c(X)$, and $a(X)$ are all monotonically increasing functions of X .

In principle, the introduction of an additive can also alter the polymer's structure and properties in such a way that $E_s'(X)$, $T_c(X)$, and $a(X)$ will not increase or decrease in unison. Or in other words, it is at least theoretically possible that the additive will function as a plastizer by lowering the transition temperature range, but at the same it will function as an antiplasticizer by increasing the new structure's stiffness (see below). Other sorts of mixed effects are also conceivable if and when the polymer and additive interact to produce a structure with new properties.

It was previously shown that in gliadin and glutenin plasticized by water, $T_c(X)$ and $a(X)$ can be expressed by a single exponential decay term (Peleg 1994b, 1995), but other expressions can be just as appropriate.

Eqs. 1 and 2 are phenomenological or empirical mathematical models. They have not been derived from any fundamental laws or kinetic considerations (Peleg 1993, 1994a, 1996). Consequently, they are not intended to be used for prediction of physical properties, and the magnitude of their constants is not exclusively related to any specific mechanism operating at the molecular or microstructural level. It can be argued though that mechanical properties like stiffness, which are expressed in terms such as moduli, are the overall manifestations of properties at several different levels and their interactions. The nature of the chemical and physical components can vary dramatically among materials, and its characterization requires not only different types of mechanical tests but, in addition, different types of assays: microscopy and chemical analysis, for example.

The usefulness of models like Eqs. 1 and 2 is that they enable quantitative characterization of the general patterns of change for comparison purposes and in the study of the effects of composition and environmental conditions (temperature, humidity) on the mechanical performance of model systems and products.

COMPARISON WITH PUBLISHED DATA

Amylopectin-Fructose

Published data of the $E'(T)$ relationships of various mixtures of amylopectin (a main starch component) and fructose (Kalichevsky et al 1993a) were fitted with Eq. 2 as the model. The fit is demonstrated in Figure 1, and the regression parameters are listed in Table I. They show that the model based on Fermi's equation (Eq. 1 or 2) can be used to describe the mechanical changes in amylopectin at its transition region, as was previously found in a variety of other biopolymers.

The plots of the model's parameters E_s' , T_c , and a versus the fructose weight fraction are shown in Figure 2. They had a considerable scatter, primarily because the amylopectin used was not completely dry, and its moisture contents varied somewhat (see below). Nevertheless, the dependency of E_s' , T_c , and a on the fructose weight fraction X could still be reasonably described by the empirical expressions:

$$E_s'(X) = 5.33 [1 - \exp - (1.07X)] \quad r^2 = 0.983 \quad (3)$$

$$T_c(X) = 122 \exp - (7.84X) \quad r^2 = 0.988 \quad (4)$$

$$a(X) = 31.7 \exp - (2.03X) \quad r^2 = 0.951 \quad (5)$$

at least as a rough approximation, as judged by the magnitude of the r^2 , the corresponding regression coefficients.

TABLE I
Fermi's Equation^a Fit to the Storage Modulus vs. Temperature Relationships of Amylopectin-Fructose Mixtures^b

X_{fructose} (wt/wt)	E_s' (GPa)	T_c (°C)	a (°C)	r^2
0.09	0.21	59	21	0.992
0.20	0.92	30	27	0.998
0.25	1.43	12	23	0.999
0.40	2.09	6	12	0.999
0.50	2.05	3	8	0.999

^a See Eq. 2.

^b Data from Kalichevsky et al (1993a). See also Fig. 1.

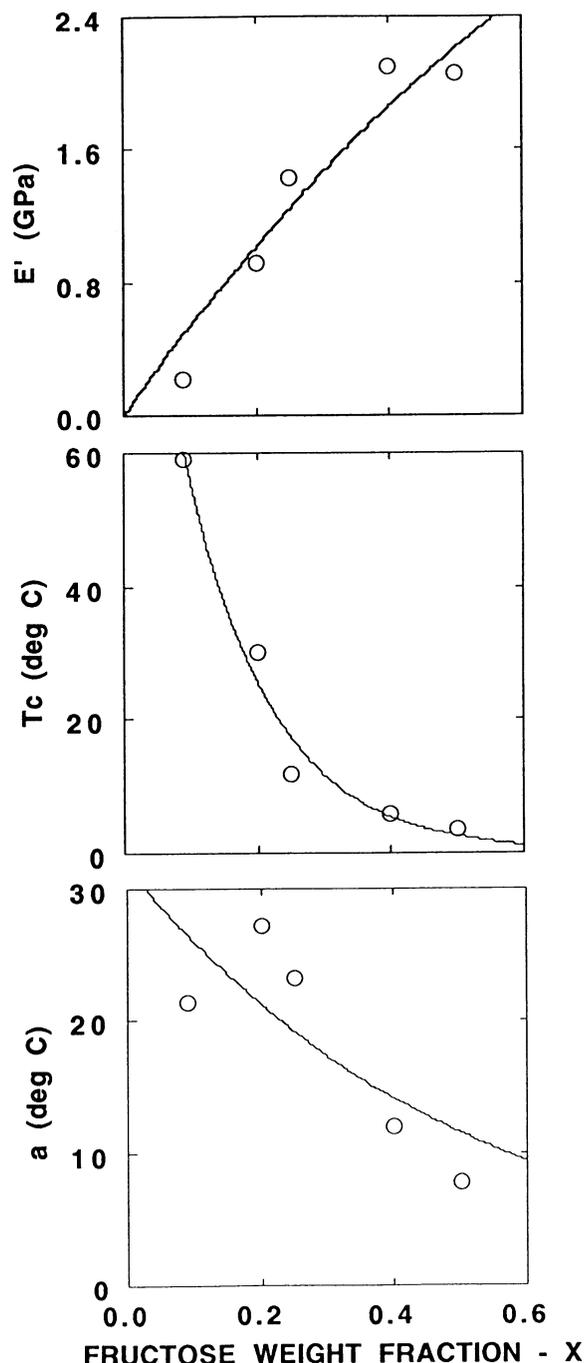


Fig. 2. Dependency of E' , T_c , and a , on the fructose weight fraction. Regression models and parameters are given in the text. Data from Kalichevsky et al (1993a).

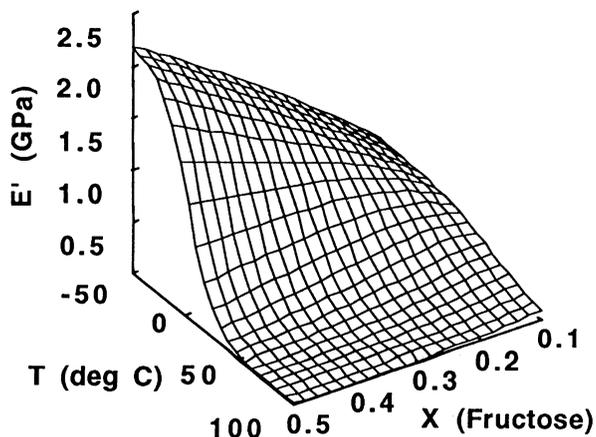


Fig. 3. Stiffness vs. temperature and fructose weight fraction relationship of amylopectin-fructose mixtures generated with Eq. 2 as a model. Data from Kalichevsky et al (1993a).

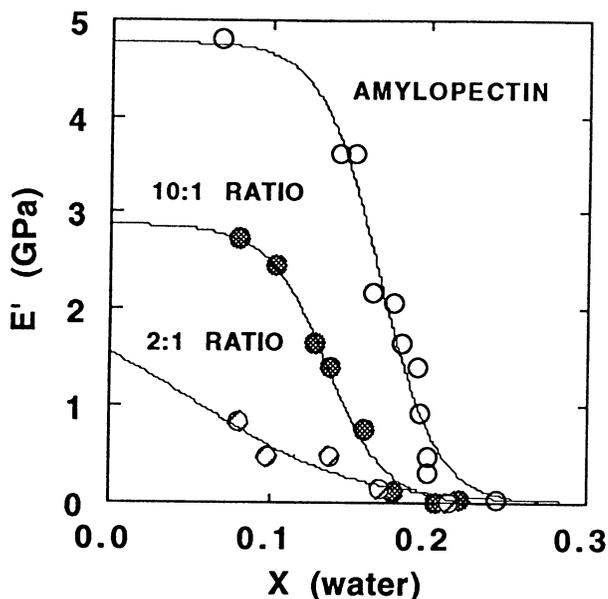


Fig. 4. Demonstration of the fit of Fermi's equation to stiffness vs. moisture relationships of amylopectin-fructose mixtures at an ambient temperature. Data from Kalichevsky et al (1993b).

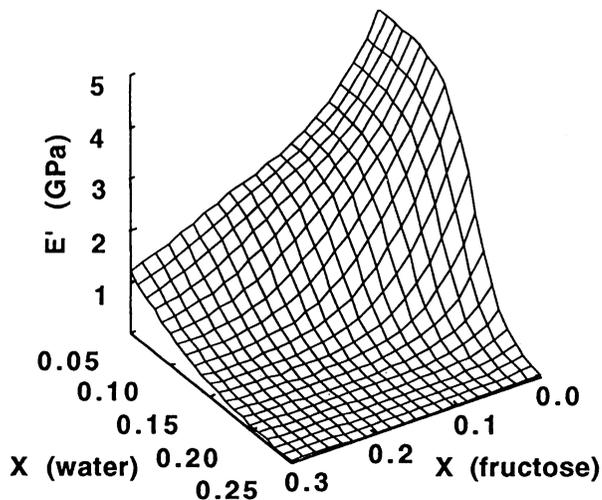


Fig. 5. Stiffness vs. moisture and fructose weight fraction relationship of amylopectin-fructose mixtures at ambient temperature generated with Eq. 6 as a model. Data from Kalichevsky et al (1993b).

Figure 2 and the equations clearly show that the presence of fructose increased the mixtures overall stiffness (i.e., the magnitude of $E'_s(X)$ increased with X). Thus, as far as stiffness is concerned, fructose acted as an antiplasticizer. But at the same time, the presence of fructose lowered the amylopectin's transition temperature range and made the transition sharper. The magnitudes of both $T_c(X)$ and $a(X)$ decreased as X increased, which is an indication that, as far as thermal properties are concerned, fructose acted as a plasticizer.

Incorporation of Eqs. 3–5 into Eq. 2 produces a model that describes the stiffness-temperature-fructose weight fraction of amylopectin in a single mathematical expression. This model can be used to map the relationship as shown in Figure 3. Such a plot can be used to visually identify the temperature-fructose concentration combinations that will produce stiff, intermediate, or fully plasticized mixtures.

Amylopectin-Fructose-Water

A limited amount of data on the stiffness of amylopectin-fructose mixtures at different moisture contents at ambient temperature were recently published by Kalichevsky et al (1993b). They were fitted by a model of the same mathematical structure as Eq. 1:

$$E'(X_{\text{water}}) = E'_s(X_{\text{fructose}}) / \{1 + \exp [X_{\text{water}} - X_c(X_{\text{fructose}}) / a(X_{\text{fructose}})]\} \quad (6)$$

The fit of Eq. 6 to the published data is shown in Figure 4. The r^2 were in the 0.955–0.996 range. The figure clearly shows that in the presence of fructose, at the concentrations reported in the original publication, the plasticizing effect of moisture increased dramatically—a phenomenon that could be expected in light of the fructose's high solubility. The presence of the fructose also alters the water sorption pattern of amylopectin and renders it more hygroscopic.

Because there were only three fructose levels reported in the original publication ($X_{\text{fructose}} = 0, 0.091$ and 0.33), and the lowest moisture content was $\approx 5\%$, there was no point in even trying to establish the exact nature of the E'_s , X_c , and a versus X_{fructose} relationships. The data were therefore fitted by the simplest possible empirical models: exponential, linear, and power law, respectively (with $r^2 = 1.000$), to produce the map shown in Figure 5. Despite the crudeness of the terms $E'_s(X_{\text{fructose}})$, $X_c(X_{\text{fructose}})$ and $a(X_{\text{fructose}})$ used for its generation with Eq. 6 as a model, the figure still enables one to see, at a glance, the combined effects of moisture and fructose on the plasticization amylopectin, at least in the concentration range where experimental data are available. Figure 5 clearly shows that in the presence of fructose, the amylopectin was almost fully plasticized at moisture contents where alone it could still maintain a considerable degree of stiffness.

CONCLUSIONS

The model based on Fermi's equation, can be used to quantify the effect of an additive on the stiffness of amylopectin and probably other biopolymers undergoing glass transition, alone or in combination with water. It enables the presentation of the relationship between stiffness and the additive's concentration, temperature and moisture content in terms of a single algebraic expression or in the form of a three-dimensional plot. The model also provides a convenient means to account, separately, for the additive influence on the material's overall stiffness, the shift in its glass transition temperature range, and the sharpness of the transition. Unlike conventional models, notably the WLF and Arrhenius, it can account for both broad and sharp transitions and for the mechanical changes at and around the glass transition region itself. When the model parameters are written in the form of functions of an additive's concentration, it can account for both plasticizing and antiplasticizing effects and, as has been demonstrated in this work, also for physical characteristics that do not change in unison, that is, when the additive acts simultaneously as a plasticizer and antiplasticizer, depending on the property. At least

in principle, the model can be used for any combination of plasticizers and antiplasticizers, provided that their effect on E_s' , T_c , and α can be expressed algebraically. (Graphical presentation, however, is limited to combination of any two only in a single plot). The model can help to identify additive concentration-moisture content-temperature combinations where the biopolymer—amylopectin in our case—is fully or partially plasticized. In the examples shown, the added fructose actually increased the amylopectin stiffness but at the same time lowered its transition temperature and made the transition sharper in the presence of moisture. The relevance of such a phenomenon to sugar-containing cereal products is obvious. Therefore, the described model, which enables the expression of different manifestations quantitatively or graphically, can be a useful tool to those who deal with it.

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