

Effect of Glass Transition on Rates of Nonenzymatic Browning in Food Systems

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The effect of glass transition on nonenzymatic browning of dehydrated vegetables and of model systems (composed of amino acids and sugars reacting in matrices with different physical characteristics) was studied. Glass transition temperature (T_g) was determined by differential scanning calorimetry. The rates of nonenzymatic browning were taken from the literature for vegetables and were determined for model systems by measuring absorbance at 280 and 420 nm. Rate constants were analyzed as a function of temperature (T) and of $(T - T_g)$. Browning below T_g was very slow. Changes in activation energy (which were affected by structural changes) could be detected near the glass transition. A complete predictive model must include the variables T , $(T - T_g)$, m , and concentration of reactants.

INTRODUCTION

The physical state of foods is one of the factors determining rates of chemical reactions. Solids in foods can exist in a crystalline state or in an amorphous metastable state, depending on composition. The state is also dependent on processing and storage conditions such as time,¹ temperature, and relative humidity. Rapidly frozen or dehydrated foods typically contain amorphous systems (White and Cakebread, 1966; Levine and Slade, 1986; Roos, 1991).

The amorphous matrix, which may be formed of food polymers and other food components, such as sugars, may exist either as a very viscous glass or as a more liquid-like rubber. The change from the glassy to the rubbery state occurs as a second-order phase transition at a specific temperature for each material, known as the glass transition temperature (T_g). T_g is strongly dependent on the concentration of water and other plasticizers (Levine and Slade, 1986).

The physical stability of amorphous foods has been related to their glass transition temperature. White and Cakebread (1966) described various physical defects in frozen and dehydrated foods with storage above T_g . In other foods and models, stickiness, collapse, crystallization, aroma retention, and oxidation of encapsulated lipids have been described as temperature-time-moisture-dependent phenomena occurring above a "collapse" temperature (T_c) (Tsourouflis, 1976; To and Flink, 1978a-c; Chirife et al., 1973). Levine and Slade (1986), Shimada et al. (1991), and Roos and Karel (1991a) related T_c to the glass transition. Acceleration of deteriorative changes is the result of the decreased viscosity and consequent increase in mobility when a system changes from the glassy (below T_g) to the rubbery (above T_g) state. The characteristic changes in mechanical relaxation processes in relation to T_g have been described by Williams et al. (1955) and further demonstrated by Soesento and Williams (1981) for viscosity. Collapse (Levine and Slade, 1986) and sugar crystallization (Roos and Karel, 1990, 1991a) in foods have also been shown to be a consequence of these changes.

Nonenzymatic browning (NEB) is a common mode of quality loss in low-moisture foods. Maximum browning

typically occurs in the water activity (a_w) range 0.5-0.75 (Labuza and Saltmarch, 1981). At lower a_w 's, the reactions proceed more slowly, and this has been attributed to diffusional limitations (Eichner and Karel, 1972). Changes in diffusion constants may in turn be related to glass transition (Karel and Saguy, 1991). Although the kinetics of NEB and related reactions have been studied as a function of many parameters [a_w , temperature (T), reactant concentration (c), pH, etc.] and even related to physical aspects such as crystallization (Vuataz, 1988; Saltmarch et al., 1981; Kim et al., 1981) and viscosity (Eichner, 1981), no relationship has been made with the glass transition temperature. This study is an initial investigation of the effect of T_g , along with other physical aspects of physical state, on NEB.

MATERIALS AND METHODS

Preparation of Samples. Model Systems. Table I shows the composition of the different systems studied. In the design of the model systems it was considered necessary to use a low concentration of reactants, in at least some of the systems, to make diffusion effects demonstrable (at high concentrations proximity of reacting molecules requires minimal diffusion for reaction). Amino acids and sugars were selected to have high reactivity, so that browning could be readily detected. Lactose in system C was at a high concentration, since it was both part of the matrix and a reactant. The model systems were also designed to have different physical characteristics during storage. Delayed crystallization of lactose was achieved in systems A-C by the addition of high molecular weight polymers such as amioca starch or (carboxymethyl)cellulose (CMC). Collapse in the present study was defined as readily visible deformation (or shrinkage) of the sample under force of gravity during the experiments. It was prevented in system B by the high concentration of CMC and the addition of trehalose, whereas in systems A and C a high degree of collapse was visually observed after storage. The two systems D, in which the matrix was poly(vinylpyrrolidone) (PVP) (of average molar weight = 10 000), were considered to be almost completely amorphous, but they had the highest degree of collapse.

Amorphous systems were prepared by freeze-drying solutions containing 20% total solids. Aliquots of 0.5 mL of each solution were distributed in 2-mL glass vials, frozen for 24 h at -30 °C, stored for 3 h over dry ice [as recommended for amorphous glass formation by Roos and Karel (1991a)], and freeze-dried (48 h, Virtis Benchtap, 3L). After freeze-drying, the model systems were equilibrated over saturated salt solutions in vacuum desiccators for 1 week to obtain the desired moisture contents.

Vegetables. The T_g for selected vegetables was determined

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Table I. Composition of Model Systems (% w/w, Dry Basis)

system	matrix	reacting sugar	amino acid
A	lactose ^a :CMC, ^b 88:10	xylose 1.0	lysine 1.0
B	lactose ^a :CMC:trehalose, 53:29:15	xylose 2.0	lysine 1.0
C	lactose:amioca, 70:20	(lactose) c	lysine 10.0
D	PVP ^d	glucose	glycine
1	99	0.5	0.5
2	95	2.5	2.5

^a Due to the high reactivity of xylose compared to lactose, only xylose was considered as reactant and lactose was considered part of the matrix. ^b CMC, (carboxymethyl)cellulose. ^c Lactose present as matrix and reactant. ^d PVP, poly(vinylpyrrolidone).

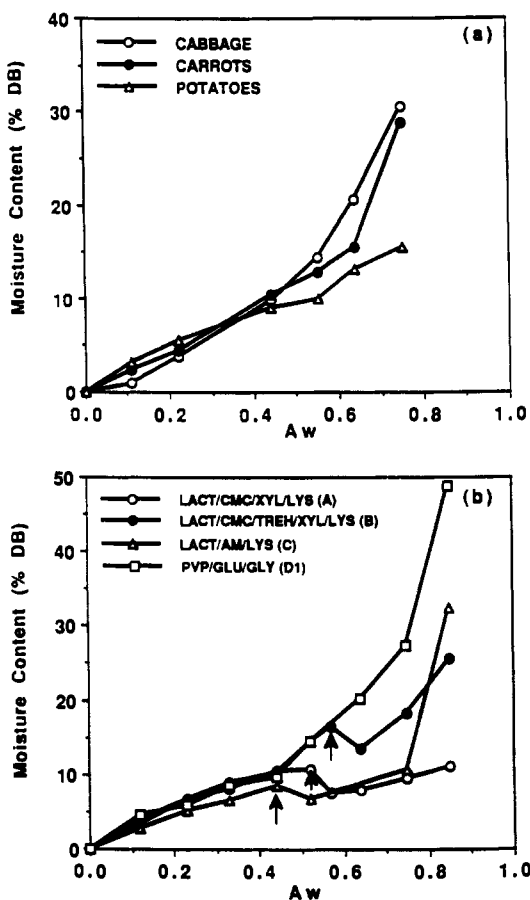


Figure 1. Moisture sorption isotherms at 20 °C for (a) vegetables and (b) model systems. The point at which a discontinuity is observed is indicated with an arrow. Each point is the average of three measurements.

at different moisture contents, obtained by equilibration of freeze-dried samples at several relative humidities. The T_g was needed to relate literature data on browning to the glass transition of these materials, since the original studies do not provide this information.

Fresh vegetables (Russet potatoes, Savoy cabbage, and California carrots) were washed and cut. Potatoes and carrots were cut in cubes (1-cm side), and cabbage was shredded in 1-cm-side slices. The cut vegetables were blanched in steam for 2 min before freeze-drying. A thin layer of these cut vegetables was frozen at -30 °C for 48 h and then put over dry ice for 3 h immediately before freeze-drying as described for model systems. The freeze-dried material was then powdered in a mortar in a dry chamber.

Sorption Isotherms. The freeze-dried materials (model

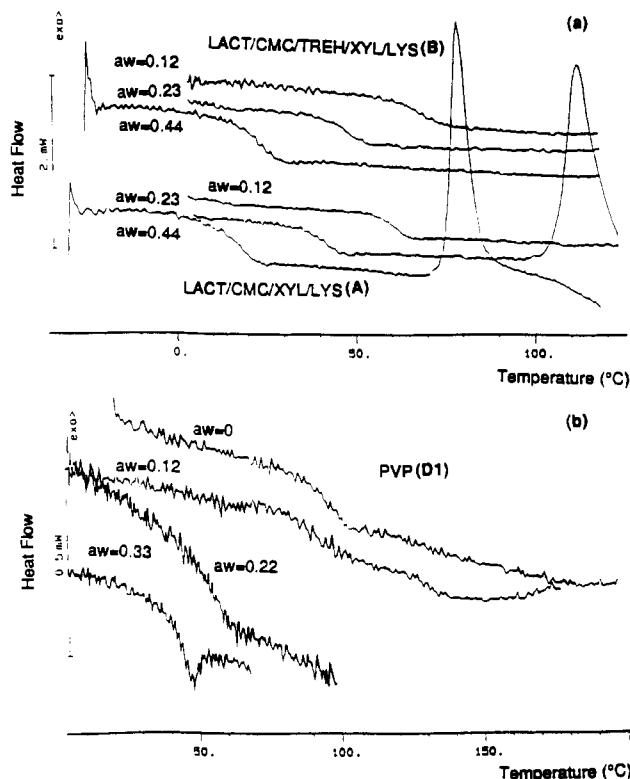


Figure 2. DSC scans for (a) lactose/CMC systems and (b) PVP systems at various water activities. The indicated a_w 's are the initial a_w 's for equilibration at room temperature.

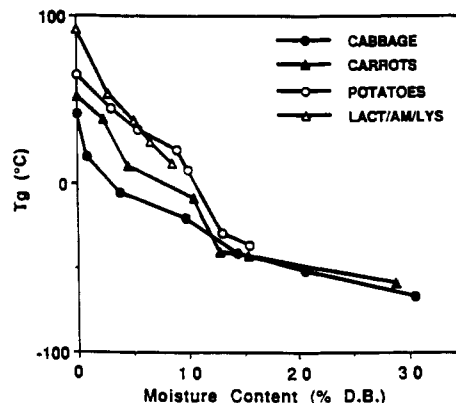


Figure 3. Glass transition temperature vs moisture content for vegetables and lactose/amioca/lysine model system. Each point is the average of three measurements.

systems and vegetables) were dehydrated to a "zero" moisture content by keeping them in vacuum desiccators over P_2O_5 for 1 week. Six aliquots, $8-15 \pm 0.03$ mg each, of powdered dried materials were transferred into six DSC pans (Mettler aluminum pans, 40- μ L volume) in a dry chamber. These pans were weighed rapidly (Mettler AE240 digital balance) and rehumidified to varying moisture contents for 1 week over saturated salt solutions in vacuum desiccators. After equilibrating, three of the pans were weighed immediately and the moisture content was calculated from the difference in weight, as an average of three determinations. The other three pans were hermetically sealed for differential scanning calorimetry (DSC).

Differential Scanning Calorimetry. Differential scanning calorimetry was used to determine the glass transition (onset of endothermal change of specific heat) of the vegetables and amorphous systems by using a Mettler TA4000 thermal analysis system with a TC11 TA processor and a DSC30S cell. The instrument was calibrated as reported by Roos and Karel (1991b). The samples were scanned over the glass transition region at 5 °C/min, and the T_g was determined as the onset temperature of the glass transition (Roos, 1987). The onset temperature of the

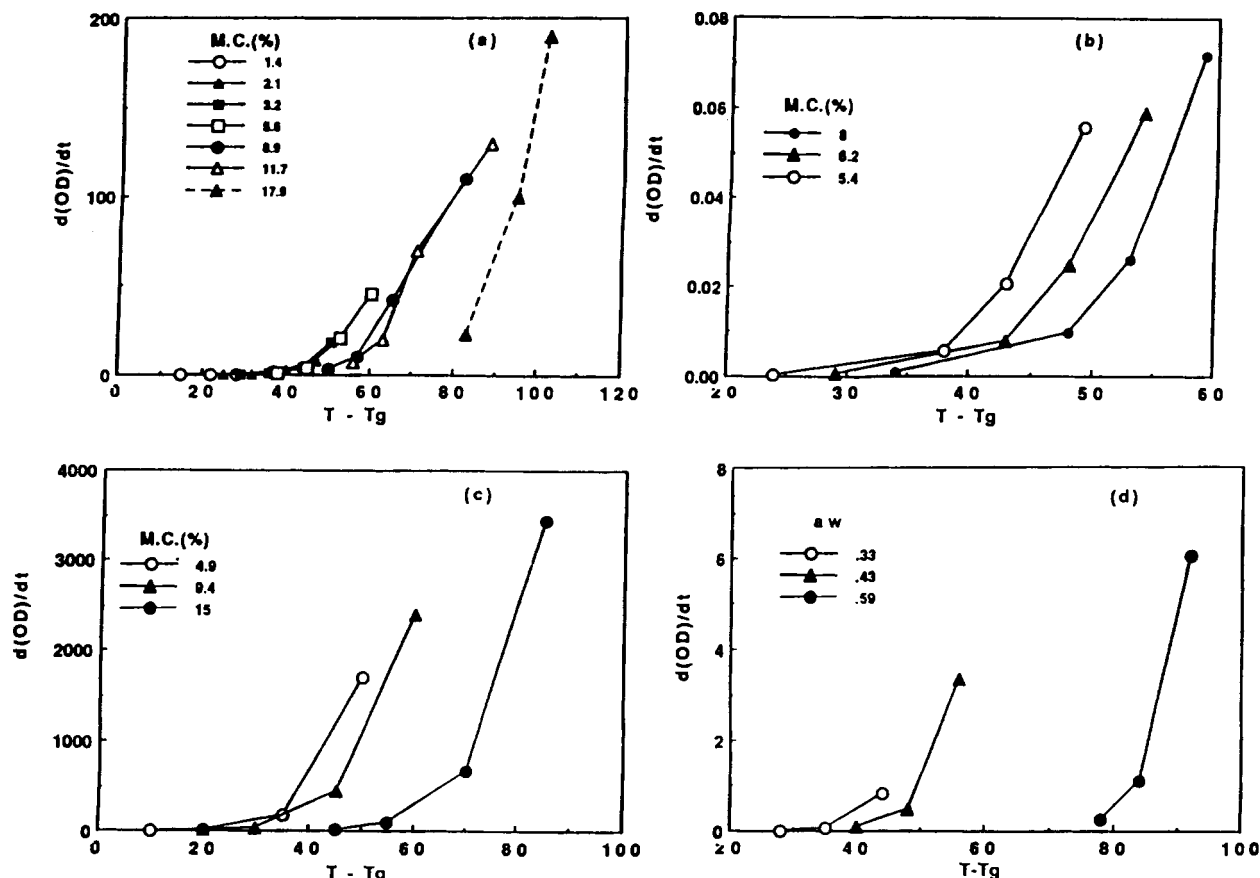


Figure 4. Rate of browning vs $T - T_g$ for vegetables: (a) cabbage [data from Mizrahi et al. (1971)]; (b) carrots [data from Legault et al. (1951)]; (c) potatoes [data from Hendel et al. (1955)]; (d) onions [data from Samaniego et al. (1991)]. a_w 's are the initial a_w 's after equilibration at room temperature.

T_g was determined by using Mettler GraphWare TA72PS.1. Results from an average of three replicate samples were used to determine the mean.

Determination of Nonenzymatic Browning Reaction Rates. After model systems were equilibrated to the desired moisture contents, vials were hermetically stoppered and placed in incubators maintained at constant temperature (from 37 to 100 °C). At suitable intervals samples were removed and kept at -18 °C until they could be analyzed for extent of browning. Systems A-C were extracted with a 50:50 ethanol/water solution, and system D (which contained PVP as matrix) was extracted with water. The extent of nonenzymatic reactions was determined by measuring absorbance at 280 nm, which has been used to detect early stages of browning (Flink, 1983) and is considered to be due to formation of furfural compounds (Hodge and Osman, 1976; Resnik and Chirife, 1979). Absorbance at 420 nm (which reflects brown pigment formation) was also monitored.

Williams-Landel-Ferry Equation. The Williams-Landel-Ferry (WLF) equation relates relaxation times of mechanical properties to a reference temperature above the T_g and was obtained empirically to describe the time and temperature dependence of amorphous materials (William et al., 1955). The temperature dependence of viscosity above T_g can be written

$$\log \frac{\eta}{\eta_g} = \frac{c_1(T - T_g)}{c_2 + (T - T_g)}$$

where η is the viscosity, η_g is the viscosity at T_g , and c_1 and c_2 are constants.

Williams et al. (1955) reported universal values for the constants to be $c_1 = -17.44$ and $c_2 = 51.6$, and these values were also applied to describe the temperature dependence of viscosity in sugar solutions (Soesento and Williams, 1981) and time to crystallization of amorphous sugars above their T_g (Roos and Karel, 1990, 1991).

RESULTS AND DISCUSSION

Figure 1 shows sorption isotherms (at 22 °C) of vegetables (Figure 1a) and model systems (Figure 1b). All

of the systems were initially amorphous. However, in systems A (Lac/CMC/Xyl/Lys), B (Lact/CMC/Treh/Xyl/Lys), and C (Lac/Am/Lys) a characteristic discontinuity in the isotherm was observed, representing the transition from amorphous to crystalline state. This also indicates the tendency for these systems to crystallize during browning experiments at higher temperatures. In the lactose systems crystallization was delayed by the presence of amioca, CMC, and/or trehalose. Crystallization occurred at the lower a_w for system A, where the matrix was mainly composed of lactose. The retardation of crystallization by the addition of high molecular weight compounds has been demonstrated by Berlin et al. (1973) for lactose and by Iglesias and Chirife (1978) for sucrose. Since systems must be in the solution or rubbery state to crystallize, an increase in the T_g promoted by the incorporation of high molecular weight compounds results in a delayed crystallization (Levine and Slade, 1989). The absence of discontinuities in isotherms for the vegetables and PVP systems indicated that they remained amorphous.

Figure 2 shows the DSC scans for selected systems at different a_w 's. Heat flow as a function of temperature is recorded when samples are heated at 5 °C/min. The endothermal baseline shift represents the glass transition, and crystallization can be observed as an exothermal peak following the glass transition for system A (Lact/CMC/Xyl/Lys) in Figure 2a. In all of the systems T_g decreased with increasing a_w and m , reflecting the plasticizing effect of water (Slade et al., 1989). It can also be observed in Figure 2a that increasing moisture content favored crystallization for system A. Crystallization temperatures decreased with increasing a_w and m . This is as expected since the decrease in T_g , and corresponding decrease in

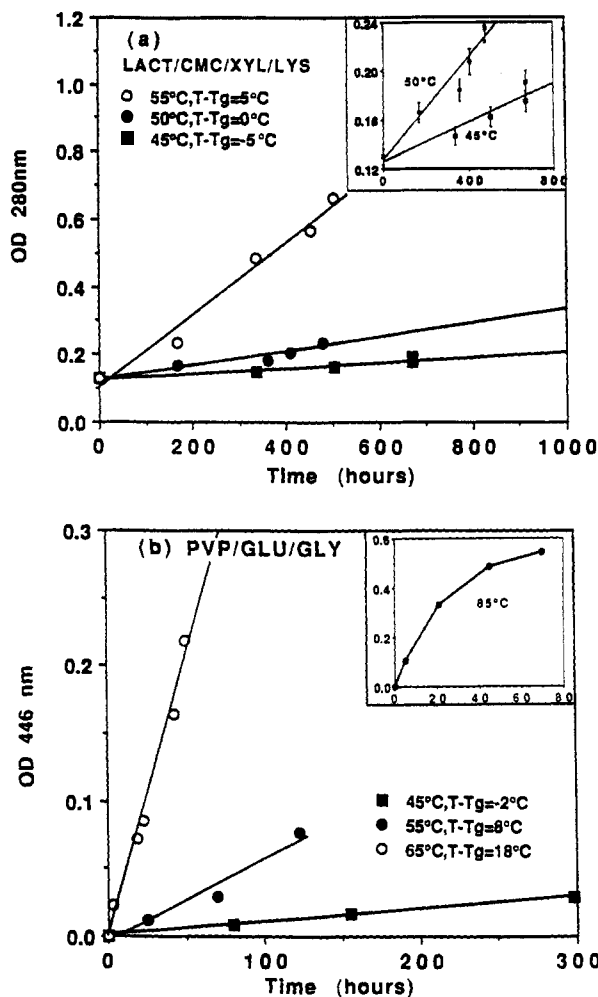


Figure 5. Absorbance vs time for model systems in the vicinity of the glass transition: (a) lactose/CMC/Xyl/Lys; the inset figure shows results below the glass transition temperature (b) PVP/Glu/Gly; (inset) results at 85 °C. Each point is the average of duplicate measurements.

viscosity, allow crystallization to take place at lower temperature (Levine and Slade, 1989; Roos and Karel, 1990). No crystallization peaks were seen during the DSC scans for system B (Lact/CMC/Treh/Xyl/Lys); however, its isotherm indicated that crystallization occurred when the system is held at room temperature for 1 week at $a_w = 0.64$. The lactose-based systems A and B have similar T_g 's, but their crystallization behaviors are different. This was observed previously in sucrose-amioca mixtures (Roos and Karel, 1990). As shown in Figure 2b, the PVP-containing samples were mostly amorphous and did not crystallize. However, some endothermic deviation from the baseline could be observed sometimes after the glass transition (Figure 2b; $a_w = 0.12$). This may be a melting endotherm, suggesting some crystallinity of the matrix.

Effects of moisture content on T_g for vegetables and the Lact/Am/Lys system (C) are shown in Figure 3. The T_g values for cabbage and carrots are close to those reported by Roos (1987) for strawberries. For potatoes the T_g 's obtained were higher and more difficult to identify, possibly due to the higher molecular weight carbohydrates present (Levine and Slade, 1989). Roos and Karel (1991a) reported that high molecular weight maltodextrins and starches have broad and less clear glass transitions, as determined by DSC. For the onions T_g was estimated on the basis of the results for cabbage and carrots.

Data on nonenzymatic browning rates for dehydrated vegetables were taken from the literature (Mizrahi et al.,

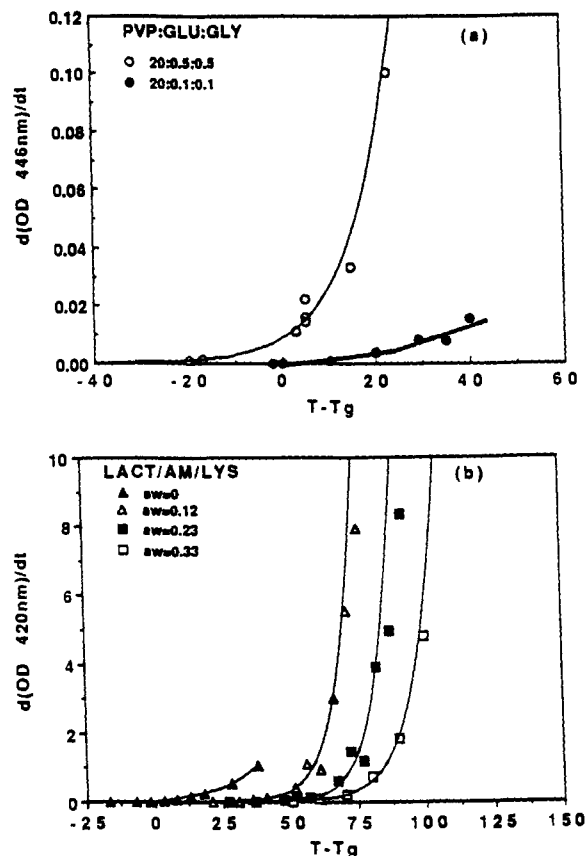


Figure 6. Rate of browning vs $T - T_g$: (a) PVP/Glu/Gly at two different concentrations at $0.22a_w$; (b) Lact/Am/Lys system at four different initial a_w 's (a_w equilibration was done at 20 °C before samples were browned).

1970; Hendel et al., 1955; Legault et al., 1951; Samaniego et al., 1991) and analyzed in relation to the experimentally determined glass transition temperature for each moisture content. The measured T_g 's served as an approximate reference point for analyzing literature browning results. All of the literature data happened to be above the glass transition temperature. Zero-order rate constants reported in these papers were plotted against the difference between storage temperature and the corresponding glass transition temperature ($T - T_g$). As shown in Figure 4, an evident effect of $T - T_g$ was observed for these vegetables on browning rate, and reaction rate constants increased noticeably above a certain temperature, mainly above $T - T_g = 40$ °C. For cabbage systems the curves for different moisture contents were closer than for the other systems, where the curves were more separated, especially at the higher $T - T_g$. Water plasticizes the systems, lowers the T_g , and increases the mobility of reactants (Levine and Slade, 1989). Beyond lowering of the T_g there seem to exist additional effects of moisture on the chemistry of the browning reaction.

For the model systems, straight lines were obtained when absorbance vs time was plotted, as Figure 5 shows. Absorbance in the UV range (at 280 nm) was parallel but at higher absolute values than absorbance in the visible range (at 420 nm). Measurement at 280 nm was particularly useful in evaluating the degree of reaction in systems when no visible browning was observed. Browning in systems A and B can be attributed to the presence of xylose, since lactose reacts much more slowly. It could also be observed (Figure 5) that browning reactions took place very slowly even below the glass transition temperature, when mobility of reactants is presumed to be very low.

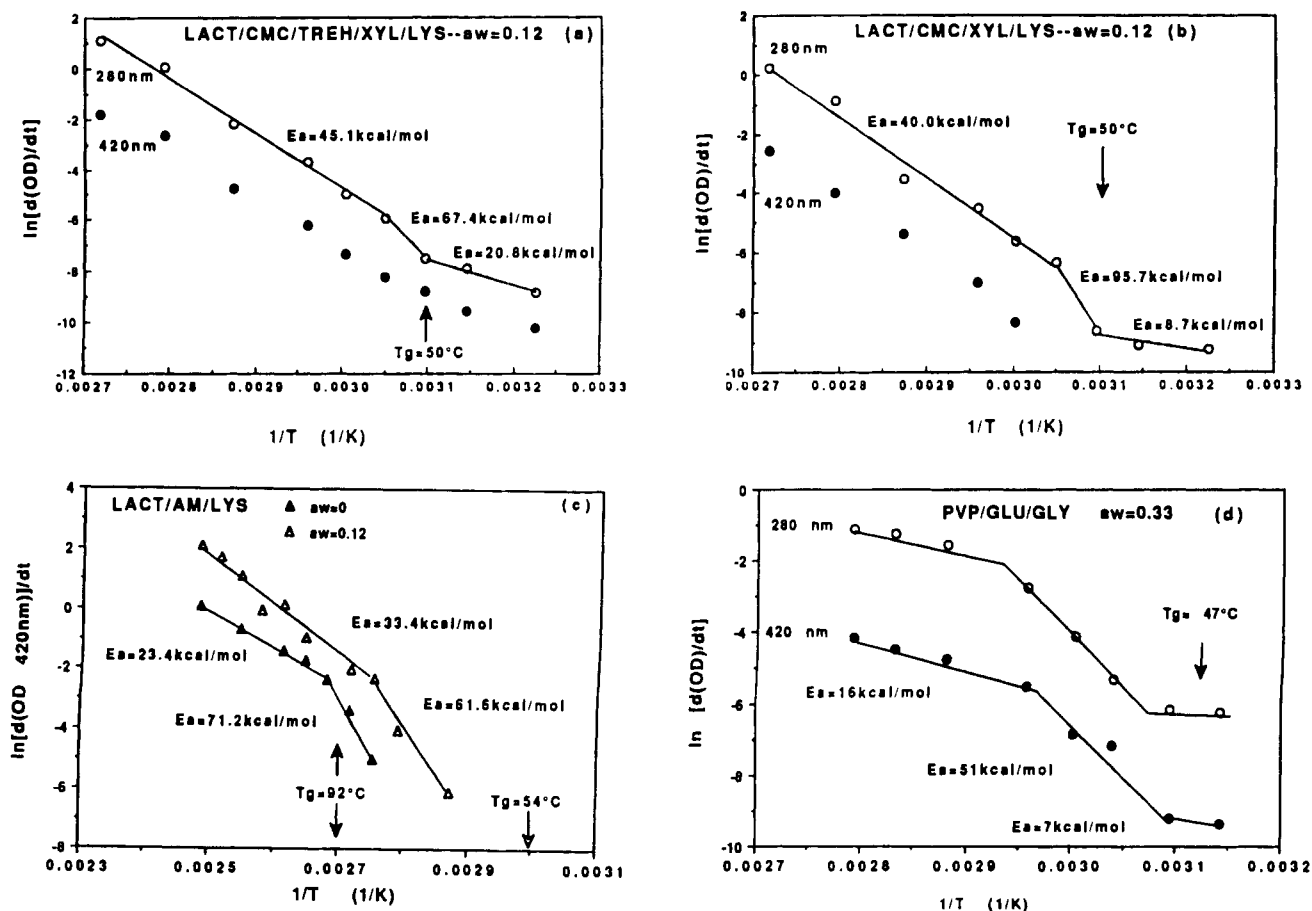


Figure 7. Arrhenius plots for model systems. The indicated a_w 's correspond to the initial a_w 's at room temperature.

In the PVP systems (D) the initial linear increase of absorbance was followed by a plateau at higher extent of reaction, achieved by high temperature or long reaction times (Figure 5b). The slopes of curves for systems A (Lact/CMC/Xyl/Lys), B (Lact/CMC/Treh/Xyl/Lys), and C (Lact/Am/Lys) and the initial slopes for systems D were used as zero-order reaction coefficients and plotted vs $T - T_g$ (Figure 6). A drastic effect of $T - T_g$ on rate constant was observed for all model systems. As in the case of vegetable systems, the reaction rate was very low in the proximity of the glass transition and increased exponentially as $T - T_g$ increased. The browning rate above T_g and its dependence on $T - T_g$ were enhanced by increasing reactant concentration (Figure 6a), and an additional effect of moisture content and/or temperature could also be observed (Figure 6b).

As Figures 4 and 6 show, there is a critical temperature above which the rates of browning start to increase noticeably. This temperature, which is system-dependent, could be related to the free volume at which, for given reactants, the diffusion coefficients increase rapidly. Free-volume theories of mobility have been discussed by Ferry (1980) and Levine and Slade (1989). Additionally, the increase may also reflect other changes in physical structure. These phenomena are related to the T_g .

The temperature dependence of rate constants in model systems was analyzed using an Arrhenius plot, as shown in Figure 7. A single line did not adequately describe the behavior of experimental points, based on the 95% confidential level (Lenz and Lund, 1980). Therefore, the data were connected with separated lines, as has been done for diffusion of probes in polymers in the vicinities of the T_g (Kovarskii et al., 1977; Hori et al., 1986). Two changes in the Arrhenius plot were observed: one close to the glass

transition temperature and another at around 10 °C above the glass transition temperature. Thus, in general three zones were observed: one below the T_g ; one intermediate, between T_g and 5–10 °C above it; and the third at higher temperatures. These changes were less drastic in system A (Lact/CMC/Treh/Xyl/Lys), in which crystallization and collapse were more effectively inhibited. System C (Lact/Am/Lys, with an intermediate degree of collapse) showed the same general trend above the T_g . Insufficient data were obtained to assess browning below the T_g . System D (PVP/Xyl/Lys, Figure 7d), in which reactants are low in concentration in a nonreactant and noncrystallizing (but showing the highest degree of collapse) matrix, had a wider intermediate zone. Activation energies were calculated for each region of these plots, as an indication of the magnitude of the changes. Estimated activation energies below the glass transition were lower than those above the glass transition. An explanation consistent with theoretical considerations is that in the vicinity of T_g and below reactions are diffusion limited. Most of the previous work on browning has been done well above the glass transition, as in the vegetable systems reported in the literature. No changes in the Arrhenius plots were observed and would not be expected (Levine and Slade, 1989). Activation energies above $T_g + 15$ °C were typical of browning reactions (Franzen et al., 1990). In this region reactions followed Arrhenius kinetics. In general, activation energies in the intermediate region were higher than typical values reported for NEB in literature (Labuza and Saltmarch, 1981). This is probably due to structural changes which occur in this region, making the browning reaction more sensitive to temperature.

These changes in activation energies are qualitatively similar to those reported for diffusion in polymers (Levine

and Slade, 1989; Ferry, 1980). It has been suggested that diffusion and reactivity changes in the temperature range above T_g may follow the WLF equation (Slade et al., 1989; Karel and Saguy, 1991). Since viscosity is ideally inversely proportional to the diffusion coefficient in solutions, it could be expected that the same type of relationship would describe reaction rates in an amorphous system undergoing browning reactions in the diffusion-limited region.

The temperature-dependence based on the WLF equation (using the universal coefficients and T_g as the reference temperature) when applied to an Arrhenius analysis predicts activation energies in the proximities of T_g of the order of 160 kcal/mol for a system with a $T_g = 50^\circ\text{C}$. The rate constant is expected to rise about 600 times from T_g to $T_g + 10^\circ\text{C}$ (Slade et al., 1989). These values are obviously higher than those observed in our systems. However, coefficients c_1 and c_2 , and also the reference temperature, could be varied to obtain a better fit (Ferry, 1980). More data in the intermediate region would be needed to obtain such parameters, since a three-variable equation would be necessary.

Browning increased simultaneously with the occurrence of physical changes (visually observed collapse). The changes in Arrhenius plots were less noticeable in the system with less degree of collapse (Figure 7). However, the exact effect of collapse on the rate of browning was unclear, and specific experiments, with quantitative determination of collapse, are needed to establish relationships.

It can be concluded that browning reactions are affected by the glass transition. These reactions occurred very slowly below the T_g in the model systems analyzed, and in this region absorbance at 280 nm proved to be a good method to follow changes. A separate effect of moisture content, other than a change in the T_g , was observed in the vegetables and in model systems. Reactant concentration affected the temperature dependence of the reaction rate. The effect of glass transition was also reflected in Arrhenius plots, where changes were observed in the region immediately above the T_g . Factors such as crystallization and collapse influenced these changes in Arrhenius plots, showing that physical structure affects reaction kinetics, as one would expect for diffusion-limited reactions.

Further experiments are necessary to decide if relationships derived from mechanical properties of polymers (i.e., WLF equation), and which have been successfully applied to physical properties of different systems (Soesento and Williams, 1981; Roos and Karel, 1990), could be also applied to relate browning rates above the T_g in diffusion-limited systems.

Phase changes in the matrix in which the reaction takes place are important factors to take into account when one is analyzing or predicting food spoilage due to browning reactions.

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