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Effect of physical changes on the rates of nonenzymic browning and related reactions

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Nonenzymic browning (NEB) due to reaction of D-xylose and L-lysine was studied in a dehydrated matrix based on poly(vinylpyrrolidone) (PVP) of different average molecular weights. Physical changes (collapse) and NEB were studied temperatures (T) and moisture contents resulting in different values of ($T - T_g$), where T_g is the glass transition temperature.

Nonenzymic browning rates at low and intermediate moisture contents in a polymeric matrix above its glass transition were shown to be closely related to ($T - T_g$). The initially porous matrices underwent a time-dependent shrinkage (collapse) above T_g and this shrinkage increased the rate of browning, presumably by minimizing diffusion paths for reactants.

When the reactants (xylose and lysine in PVP) were separated by a reactant-free layer of PVP, the reaction rate decreased as the thickness of the empty layer increased. A lag time was observed, which was directly related to the thickness of this layer.

INTRODUCTION

The physical stability of amorphous foods has been related to the change from the glassy state to a more liquid-like state occurring at the glass transition temperature (T_g). Above T_g the viscosity of the matrix may decrease to a point where it becomes too low to support its own weight, resulting in flow or deformation of the matrix (Bellows & King, 1973; Downton *et al.*, 1982; Levine & Slade, 1986; Roos & Karel, 1991*a*), which causes physical defects such as collapse (loss of shape, shrinkage), stickiness and flavor loss (Chirife *et al.*, 1973). It has also been observed that the physical state of foods is a factor affecting rates of chemical reactions (Eichner, 1981; Kim *et al.*, 1981; Vuataz, 1988; Slade & Levine, 1991; Karmas *et al.*, 1992). It has been proposed (Karel & Saguy, 1991) that the glass transitions affect diffusion-controlled chemical reactions through the increase of the diffusion coefficient (Karel & Saguy, 1991; Slade & Levine, 1991). The two most important nonenzymic deteriorative reactions, nonenzymic browning (NEB) and lipid oxidation, are often diffusion-limited. The increase of browning rate constants with moisture content of the system in the low water activity (a_w) region has been attributed to diffusional effects (Labuza & Saltmarch, 1981). Shimada *et al.* (1991) showed that exposure of unsaturated lipids entrapped in a sugar-based matrix occurs above T_g, and coincides with sugar crystallization. Labrousse *et al.* (1992) extended this study to noncrystallizing systems in which collapse of the matrix has an important effect on lipid oxidation. Previous investigations (Karmas *et al.*, 1992; Karel *et al.*, 1992; Buera & Karel, 1993) indicated that phase changes and associated physical aspects in the matrix are factors affecting the rates of nonenzymic browning reactions. In these papers the effects of glass transitions on NEB reactions were correlated using a linearized form of the Williams, Landel and Ferry (WLF) equation (Williams *et al.*, 1955), developed for relating relaxation times of mechanical properties of polymers to the glass transition. The purpose of the present work was to investigate how the combined effects of physical structure and physical changes resulting from glass transitions affect the rates of NEB in model food systems. For this purpose, NEB reactants (xylose and lysine) were made to react in an amorphous polymer matrix.

MATERIALS AND METHODS

Preparation of model systems

Model systems were designed to have low concentrations of compounds with high reactivity, dispersed in a non-

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crystallizing matrix with the T_g defined over the whole range of a_w activity values of interest. The model systems consisted of D-xylose (Fisher Scientific) and L-lysine (Alfa Division) as reactants in amorphous matrices of poly(vinylpyrrolidone) (PVP) of different average molecular weights (10000, 24000 or 40000) (Aldrich). The ratios of PVP, xylose and lysine were 98 : 1 : 1 (w/w).

Amorphous systems were prepared by freeze-drying solutions containing 20% total solids. Aliquots of 0·5 ml of each solution were placed in 2 ml glass vials, frozen for 24 h at –30°C, stored 3 h over dry ice (as recommended for amorphous glass formation by Roos & Karel 1991*a*) and freeze-dried (48 h Virtis Benchtop, 3 liter). After freeze-drying, the model systems were equilibrated over saturated salt solutions in vacuum desiccators for 1 week to obtain the desired moisture contents and water activities.

Collapse

The effects of sample collapse (or shrinkage) prior to incubation on browning reactions were investigated in some systems. Collapse was achieved in these samples in two ways: (a) by exposing them to humidified atmospheres at which $T > T_g$, and (b) by mechanical compression. In the samples exposed to high moisture levels, collapse was determined semiquantitatively by calculating sample volume from measured height and diameter of the samples. The degree of collapse was expressed as percentage collapse:

$$\frac{V_i - V_f}{V_i - V_t} 100 = \%\ \text{collapse}$$

where V_i = initial volume of the sample into the vial, V_f = volume of the sample after shrinkage occurred, V_t = volume of PVP (MW = 10000) sample after 7 days of storage at a_w = 0·85 (considered as 100% collapsed).

Collapse levels achieved by exposing the samples of PVP 24000 to a_ws of 0·33 and of 0·57 for 1 day were 50 and 90%, respectively. After the shrinkage occurred, the samples were re-equilibrated to the desired water activity.

The samples that were compressed prior to incubation were prepared in the form of pellets. Aliquots of 5 ml of each solution were freeze-dried in glass vials (2 cm diameter) as indicated above. After freeze-drying the samples were pulverized in a mortar and 1 g of each sample was pressed in an hydraulic press at a pressure of 3000 kg/cm^2. These samples had a specific bulk volume which was 25% of the volume of the uncompressed systems and corresponded to a degree of collapse of *c.* 100%.

In some of the compressed systems the reactants were separated in different layers. Solutions of PVP–xylose (99 : 0·5) and PVP–lysine (99 : 0·5) and PVP (alone) were prepared. These solutions (each at 20% total solids) were freeze-dried and pulverized separately. The pellets were formed by pressing three alternate layers: PVP–xylose, PVP, and PVP–lysine. The intermediate layer of PVP was prepared with different thickness.

Differential scanning calorimetry

Differential scanning calorimetry was used to determine the glass transition (onset of endothermal change of specific heat) of the 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 & Karel (1991*b*). 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 T_g was determined by using Mettler Graphware TA72PS.1. Results from an average of three replicate samples were used to determine the mean.

Incubation of model systems

After model systems were equilibrated to the desired relative humidities at room temperature, some of the vials were hermetically stoppered with Teflon–rubber septa and placed in a forced air circulating oven maintained at 59°C (Experiment A). The pellets and the rest of the vials were kept in open containers inside the dessiccators and incubated at constant relative humidity at different temperatures between 45 and 87°C (Experiment B). At suitable intervals samples from Experiments A and B were removed and kept refrigerated until they were analyzed for extent of browning and related reactions.

Analysis for carbon dioxide

Carbon dioxide is a product of amino acid decarboxylation through the Strecker degradation (Hodge, 1953; Osman, 1976) and was observed to be an early indicator of the degree of NEB-related reactions (Piva *et al.*, 1986; Lerici *et al.*, 1990; Min & Lee, 1990). It was determined in the present work in the headspace of the vials after incubation. Before the analysis was done, the samples were preconditioned during 30 min at 30°C in a heating block (Fisher). For the headspace analysis a Hewlett–Packard gas chromatograph model 5890A was used. It was equipped with a thermal conductivity detector and a stainless steel column (300 cm × 0·175 cm i.d.) packed with 60/80 Chromosorb Q102 (Supelco, Bellefonte, PA). The gas-chromatographic conditions were: column temperature 60°C, injector temperature 120°C; detector temperature 200°C and carrier gas (He) flow rate: 40 ml/min. The headspace volume injected was 1 ml, using a Pressure Lok Series A2 model syringe (Supelcol).

The content of carbon dioxide was expressed as the area relative to the area of the oxygen peak (%). The standard deviation of the method (estimated from eight measurements of 1 ml of a CO_2 gas standard (Supelco), was estimated to be 2%, and two separate measurements of each sample were performed, giving 95% confidence of an error smaller than 5%.

Optical density measurement

The uncompressed samples were dissolved in 2 ml of water in the same vials in which they had been stored. The pellets were placed into small Petri dishes and dissolved in 10 ml of water. The extent of nonenzymic browning reactions was determined by measuring the absorbance at 446 nm (OD 446), which reflects pigment formation and was observed to be a good index in having PVP as a matrix system (Karmas *et al.*, 1992). Two separate measurements were done for each sample. In order to compare results from both types of samples the absorbance values were normalized by dividing by the weight of the dry matter of each sample.

The slopes of the zero-order reaction constants and their standard deviations were calculated from linear regression, using the least-squares criterion. The confidence interval was estimated with a student t-test for a significance degree of 95% (α = 0·05). The F test of an ANOVA (analysis of variance) was performed when necessary to check if separated mean values were significantly different (Hogg & Ledolter, 1987). The relative errors of the rate constants were between 12 and 17%.

RESULTS AND DISCUSSION

Experiment A

Table 1 shows the characteristics of the equilibrated systems stored in the closed vials. When CO_2 and the absorbance at 446 nm were plotted versus time of storage at 59°C, straight lines were obtained, suggesting that both reactions followed pseudo-zero order kinetics. Some selected curves are shown in Fig. 1. The zero order reaction for browning development had been reported by many authors (Labuza & Saltmarch, 1981). Piva *et al.* (1986) also found a linear increase of CO_2 with storage time in samples of apricots at different moisture content. In their work, CO_2 development preceded the appearance of a visible brown color. In our work, however, the increase of absorbance in the visible range was almost parallel to the increase of CO_2 in the headspace. The samples that had collapsed during exposure to high moisture atmospheres (50 and 90% collapsed) browned faster than the samples which had not been previously collapsed. Although the rate constants for the 50% collapsed samples were not significantly different (at a level of 95%) from those 0% collapsed, the general trend can be stated since the rate constants for the 90% collapsed samples were significantly higher than the ones for the 0 and 50% collapsed samples. The rate constants for carbon dioxide formation, however, were significantly smaller in the collapsed systems (Table 2). It is likely that the CO_2 could not be fully recovered from the dense, fully collapsed matrix.

Table 1. Characteristics of the model systems stored in closed containers (experiment A)

Sat. salt soln.[a]	a_w[b]	PVP[c]	T_g[d]	m.c.[e]
P_2O_5	0	10	86	0
		24	111	0
		40	132	0
CH_3COOK	0·22	10	39	6·0
		24	51	7·3
		40	54	11·0
$MgCl_2$	0·33	10	28	8·6
		24	41	11·1
		40	46	12·5
K_2CO_3	0·44	10	15	9·9
		24	34	14·7
		40	39	15·3
$MgNO_3$	0·52	10	0·5	14·6
		24	19	17·1
		40	27	16·0
NaBr	0·57	10	-3	18·0
		24	14	20·0
		40	21	19·0
$SrCl_2$	0·65	10	-6	23·0
		24	2	23·0
NaCl	0·74	10	-18·5	27·5
		24	-13	27·0
		40	-1	27·1
KCl	0·85	24	—	35·0
		40	-20	35·4

[a] Saturated salt solutions used to equilibrate the samples.
[b] Water activity of the samples at room temperature.
[c] PVP: poly(vinylpyrrolidone) used as the matrix.
[d] Glass transition temperature (°C).
[e] Moisture content (%, dry basis).

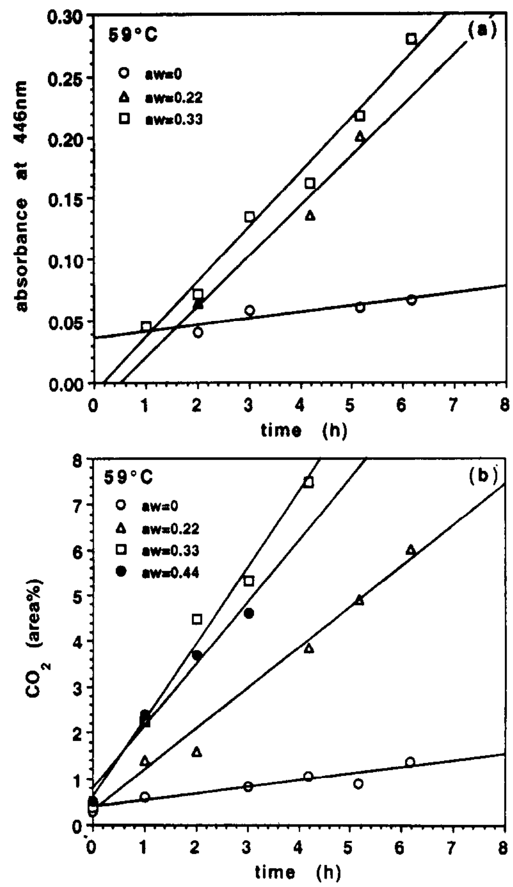

Fig. 1. Absorbance at (a) 446 nm and (b) CO_2 development vs. time of storage at 59°C for a PVP (MW = 40000) xylose–lysine (98 : 1 : 1) system.

Figure 2(a) shows zero-order reaction rate constants (OD units per h) plotted versus moisture content (m.c.), and Fig. 2(b), CO_2 relative production rate in a

Table 2. Effect of collapse on zero-order rate coefficients. Storage temperature: 59°C

	k (OD units/h)[a]			k_c (% area/h)[b]		
	0%[c]	50%[c]	90%[c]	0%[c]	50%[c]	90%[c]
$a_w = 0{\cdot}33$[d]	0·07	0·09	0·13	1·8	0·75	0·1
$a_w = 0{\cdot}42$[d]	0·04	0·06	0·08	0·6	0·70	0·2

[a] Zero-order rate coefficient for color development.
[b] Zero-order rate coefficient for CO_2 development.
[c] Degree of collapse.
[d] a_w = Water activities at which the samples were equilibrated after collapse and before storage at 59°C.

similar plot. The dependence of browning on moisture content at constant temperature is similar to that obtained by other authors (Eichner & Karel, 1973; Labuza *et al.*, 1980). The maxima of these curves were shifted towards high moisture values when the molecular weight of the matrix increased.

When the same constants were plotted as a function of (T–T_g) (Fig. 3 (a) and (b)) the curves for the three matrices showed the maximum at almost the same value of T–T_g, suggesting that the maximum rate may be related to the physical characteristics of the matrix. Furthermore, the dependence of rate constants on T–T_g followed the same curve for the three matrices over a range of moisture contents below the maximum rate, and this is the region in which the reaction may be limited by diffusion.

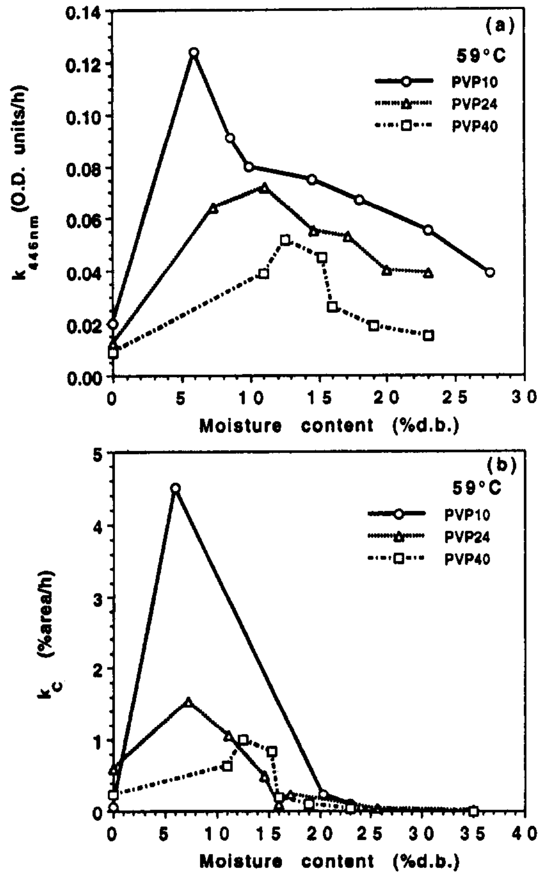

Fig. 2. Zero-order rate coefficients vs. moisture content for a xylose–lysine reaction in different matrices at 59°C: (a) rate constants for absorbance at 446 nm (OD units/h); (b) rate constants for CO_2, development (% area/h) PVP10, PVP24, PVP40 = PVP's of MW 10 000, 24 000 and 40 000, respectively.

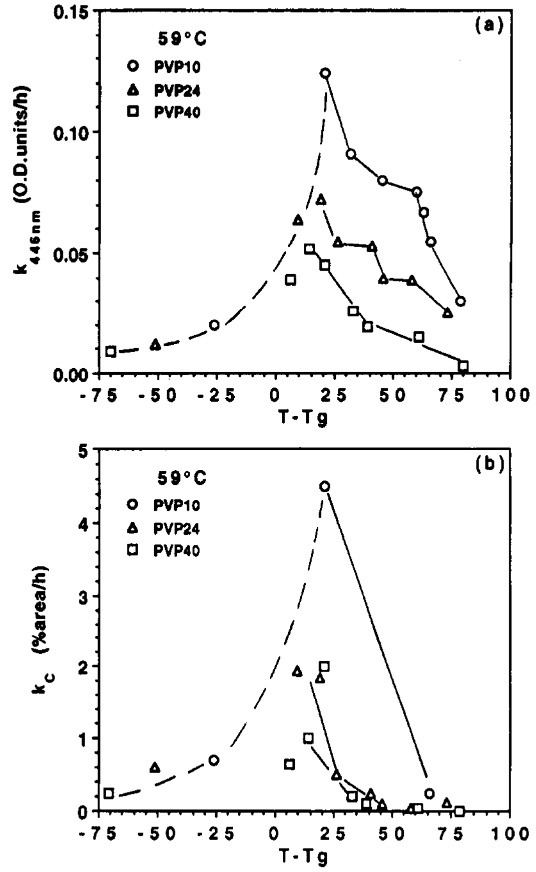

Fig. 3. Zero-order rate constants vs. (T–T_g) for xylose–lysine reaction in different matrices at 59°C: (a) rate constants (k) for absorbance at 446 nm; (b) rate constants (K_c) for CO_2 development.

One of the physical consequences of the phase transition is the collapse or shrinkage of the samples. Figure 4(a) shows how moisture content affects the degree of collapse of the samples at a fixed time of 5 h. A sigmoid-type curve was obtained for each system, and the degree of collapse decreased with increasing molecular weight of PVP. This effect, which was more evident in the low moisture content range, was to be expected, since the Tg increases with molecular weight, and the degree of collapse is inversely related to the T_g. When the degree of collapse was plotted versus T–T_g (Fig. 4(b)) the points for the different systems fell on the same curve, indicating that it is directly related to the phase transition.

Experiment B

The pelletized samples and some of the vials were stored over saturated salt solutions. Table 3 shows the characteristics of these systems. Due to the change in the equilibrium moisture content with temperature, a different T_g was observed when the storage temperature changed, as shown in Table 3. Pseudo-zero order kinetics were observed for browning development in the compressed and noncompressed systems stored at con-

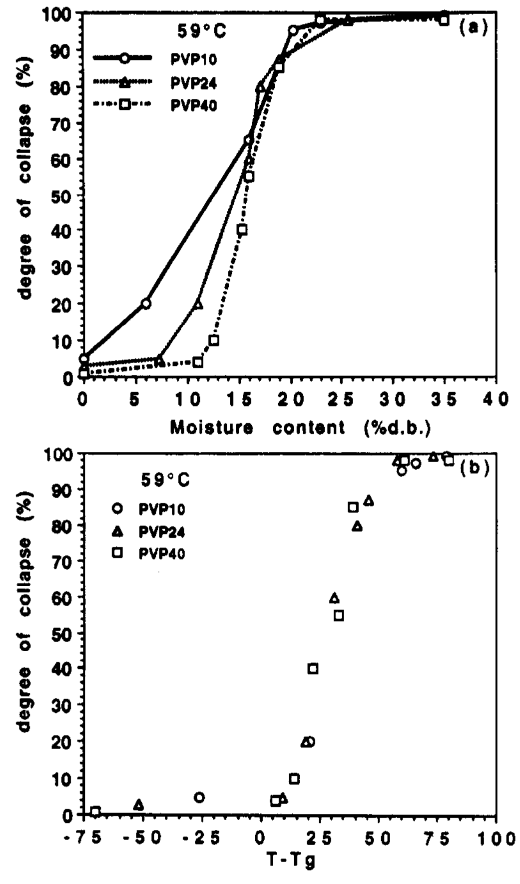

Fig. 4. Effect of moisture content on the degree of collapse after 5 h of storage at 59°C. (a) degree of collapse vs. moisture content; (b) degree of collapse vs. T–T_g; d.c.= degree of collapse, defined as $[(V_i{-}V_f)/V_i{-}V_t)]100$, where V_i = initial volume of the sample, V_f = volume of the sample after storage; V_{100} = volume of a sample collapsed completely.

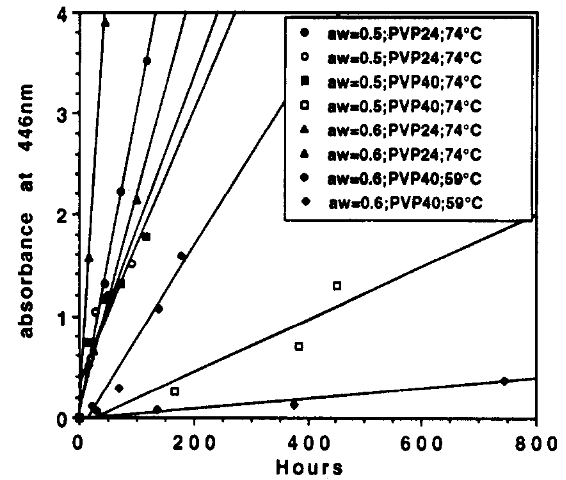

Fig. 5. Absorbance at 446 nm as a function of time for some selected systems. PVP24 and PVP40 systems in which the matrices were poly(vinylpyrrolidone) of average MW 24 000 and 40 000, respectively. Water activities and temperatures of incubation are reported in the inset. Solid symbols: compressed samples. Open symbols: noncompressed samples. a_w = 0·5 corresponds to samples stored over Co Cl_2. A_N = 0·6 corresponds to samples stored over Sr Cl_2.

stant relative humidity. The compressed samples browned faster than the samples that had not been compressed (Fig. 5). It can be assumed that the sample compression increases the proximity of reactants in the matrix. A similar trend to that obtained for the systems of Experiment A (stored in the closed vials at constant temperature) was observed for rate dependence on (T–T_g) for the pelletized and noncompressed samples described in Table 3. This dependence is shown in Fig. 6. In Experiment B, however, the storage temperature was not the same for the different samples, and the use of the (T–T_g) values allowed one to combine data from different moisture contents and different temperatures.

The ratio between the rate constants obtained for the compressed (k_p) and for uncompressed samples (k_{nc}) was plotted against T–T_g (Fig. 7). This ratio decreases when T–T_g increases. This suggests that the initial compression (i.e. collapse) of the sample is less important at the high degrees of mobility reflected by a high (T–T_g). Collapse is a time-dependent phenomenon and if the storage temperature is far above the T_g, collapse occurs rapidly and the matrix approaches a bulk density similar to that of the compressed samples. The F test showed that the last three points of this curve and the points at T–T_g = 13 and 14°C were not significantly

Table 3. Characteristics of the model systems stored in open containers (Experiment B)

PVP	Sat. salt soln.[a]	T^b	T_g^c	m.c.[d]	a_w^e
24	$CoCl_2$	59	30	9·7	0·503
24	$CoCl_2$	74	55	9·2	0·467
24	$SrCl_2$	59	45	14·0	0·640
24	$SrCl_2$	74	52	13·0	0·620
40	$SrCl_2$	87	53	11·0	0·610
40	$CoCl_2$	74	69	9·0	0·467
40	$SrCl_2$	59	50	15·0	0·640
40	$SrCl_2$	74	59	12·0	0·620
40	NaCl	59	17	29·0	0·745
40	KCl	82	20	35·0	0·788
10	$MgNO_3$	45	25	7·0	0·460

[a] Saturated salt solutions at which the samples were exposed during storage.
[b] Storage temperature (°C).
[c] Glass transition temperature (°C).
[d] Moisture content (%, dry basis).
[e] Calculated from Greenspan (1977).

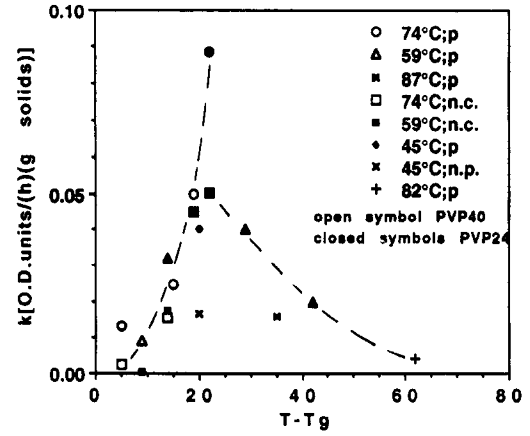

Fig. 6. Zero-order rate constants for browning (k) plotted against (T–T_g). p: compressed samples; n.c..: noncompressed samples.

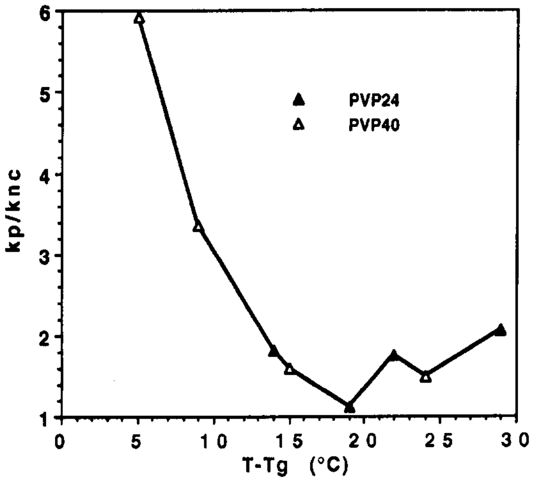

Fig. 7. Ratio of the browning rate constants for the pelletized systems (k_p) and the noncompressed systems ($k_{n.c.}$) vs. T–T_g.

different (p = 0·5) at a level of 95%, but the point at T–T_g = 19°C was significantly lower than the others. However, the general trend of this curve shows a significant decrease of the ratio $k_p/k_{n.c.}$ when T–T_g increases up to about 14°C and then this ratio remains constant at a value close to 1.

Figure 8 shows the increase in browning with time, for pellets in which a reactant-free layer of PVP was included between a layer of PVP–xylose and another of PVP–lysine. A plot for a system without this layer was also included for comparison purposes. A lag time appeared in the samples with this intermediate layer, and this lag time increased (significant at the 95% level) with increasing thickness of the intermediate layer. Except for the rate constants (defined as the slopes of the linear part of the curves) for the systems at T–T_g = 5°C with layers of 0 and 2 mm, which were not significantly different (p = 0·09), the rate of reaction was significantly lower in the systems which had the intermediate layer (Table 4). The increase of the lag times and the decrease of the slopes due to the increase of the thickness of the intermediate layer were more important at the lower (T–T_g) value. Presumably the diffusion rate of reactants in the matrix is high at higher (T–T_g) levels, thus counteracting the effect of the separation by an intermediate reactant-free layer.

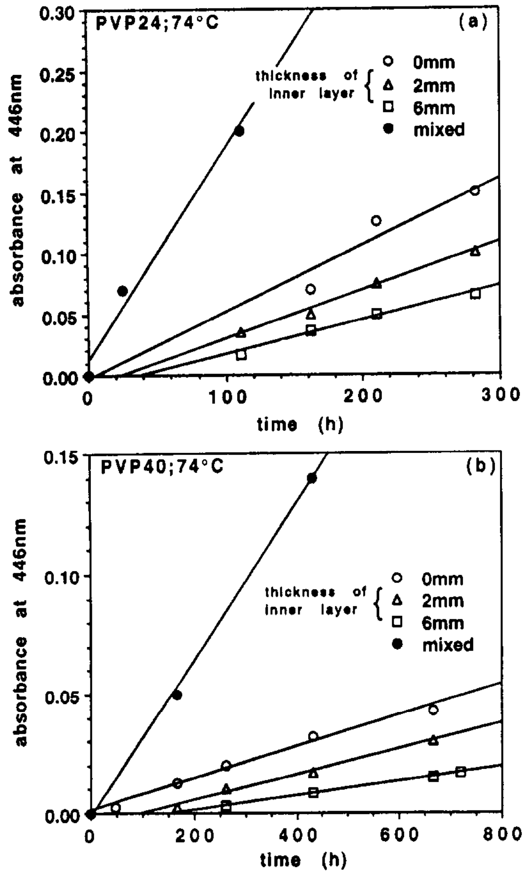

Fig. 8. Absorbance at 446 nm vs. storage time for the layered compressed systems with different thicknesses of intermediate layer (i.l.): (a) systems in a matrix of PVP 24 (T–T_g) = 19°C; (b) systems in a matrix of PVP 40 (T–T_g) = 5°C. Storage temperature: 74°C; stored at a_w = 0·47.

Table 4. Effect of the thickness of the intermediate layer (i.l.) on the lag times and zero-order rate coefficients from browning development

Thickness of i.l. (mm)	$T - T_g$ = 5°C		$T - T_g$ = 19°C	
	Lag time (h)	$k \times 10^5$	Lag time (h)	$k \times 10^5$
0	0	6·60	8	55·7
2	110	5·41	28	39·7
6	165	3·03	43	28·3

CONCLUSIONS

Nonenzymic browning rates at low and intermediate moisture contents in a polymeric matrix above its glass transition were shown to be closely related to (T–T_g). The initially porous matrices underwent a time-dependent shrinkage (collapse) above T_g and this shrinkage increased the rate of browning, presumably by minimizing diffusion paths for reactants. The rate constants for CO_2 formation were lower for the systems that had been previously collapsed. We suggest that collapse may affect CO_2 recovery from the dense collapsed matrix. The browning was accelerated by attaining collapse of the matrix prior to incubation, especially in the case of compressed samples in which the collapse was essentially complete. This effect was less important at high values of (T–T_g). Probably the rapid collapse of the samples at high (T–T_g) makes the rate of browning less dependent of the initial degree of collapse induced by compression.

When the reactants (xylose and lysine in PVP) were separated by a reactant-free layer of PVP, the reaction rate decreased as the thickness of the empty layer increased. A lag time was observed, which was directly related to the thickness of this layer. The effects of the intermediate layer were less important at high (T–T_g) values, presumably because of rapid diffusion in the separating layer.

It can be concluded that the rate of browning is affected both by the $(T-T_g)$ and by the initial degree of collapse. The effects of initial collapse and diffusional limitations (represented in this work by separation of reactants by an intermediate layer) decreased with increasing values of $(T-T_g)$.

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REFERENCES

Bellows, R. J. & King, C. J. (1973). Product collapse during freeze-drying of liquid foods. *AIChE Symp. Ser.*, **69**, 33–41.

Chirife, J., Karel, M., & Flink, J. (1973). Studies on mechanisms of retention of volatile in freeze-dried food models: The system PVP-*n*-propanol. *J. Food Sci.*, **38**, 671–4.

Downton, G. E., Flores-Luna, J. L. & King, C. J. (1982). Mechanism of stickiness in hygroscopic, amorphous powders. *Ind. Eng. Chem. Fundam.*, **21**, 447–51.

Eichner, K. (1981). Antioxidative effect of Maillard reaction intermediates. *Prog. Food Nutr. Sci.*, **5**, 441–51.

Eichner, K. & Karel, M. (1972). The influence of water content and water activity on the sugar-amino browning reaction in model systems under various conditions. *J. Agric. Food Chem.*, **20**, 218–23.

Greenspan, L. (1977). Humidity fixed points of binary saturated aqueous solutions. *J. Res. Natl. Bur. Stand. A, Phys. Chem.*, **81A**, 89–96.

Hodge, J. E. (1953). Chemistry of browning reactions in model systems. *J. Agric. Food Chem.*, **1**, 928–36.

Hodge, J. E. & Osmand, E. M. (1976). Carbohydrates. In *Principles of Food Science*; ed. O. R. Fennema. Marcel Dekker, New York, Part I, Chap. 3.

Hogg, R. V. & Ledolter, J. (1987). *Applied Statistics for Engineers and Physical Scientists*. Maxwell Macmillan International, New York, pp. 257–79.

Karel, M. & Saguy, I. (1991). Effects of water on diffusion in food systems. In *Water Relationships in Foods*, eds H. Levine & L. Slade. Plenum Press, New York, pp. 157–74.

Karmas, R., Buera, M. P. & Karel, M. (1992). Effect of glass transition on rates of nonenzymatic browning in food systems. *J. Agric. Food Chem.*, **40**, 873–9.

Kim, M. N., Saltmarch, M. & Labuza, T. P. (1981). Nonenzymatic browning of hygroscopic whey powders in open versus sealed pouches. *J. Food Process. Preserv.*, **5**, 49–57.

Labrousse, S., Roos, Y. & Karel, M. (1992). Collapse and crystallization in amorphous matrices with encapsulated compounds. *Sci. Aliments*, **12**(4), 757–69.

Labuza, T. & Saltmarch, M. (1981). The nonenzymatic browning reaction as affected by water in foods. In *Water Activity: Influence on Food Quality*. Academic Press, San Francisco, pp. 605–49.

Lerici, C. R., Barbanti, D., Manzano, M. & Cherubin, S. (1990). Early indicators on chemical changes in foods due to enzymic or non-enzymic browning reactions. 1. Study on heat treated model systems. *Lebensm. -Wiss. u.-Technol.*, **23**, 289–94.

Levine, H. & Slade, L. (1986). A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPS). *Carbohydr. Polym.*, **6**, 213–44.

Min, D. B. & Lee, S. H. (1990). Gas chromatographic determination of carbon dioxide in non-fat dry milk during non-enzymatic browning reaction. *J. Sci. Food Agric.*, **53**, 93–99.

Piva, M., Lerici, C. R. & Dalla Rosa, M. (1986). Reazioni di imbrunimento non enzimatico (NEB) durante la conservazione di derivati di frutta. *Ind. Aliment.*, **25**, 277–83.

Roos, Y. (1987). Effect of moisture on the thermal behavior of strawberries studied using differential scanning calorimetry. *J. Food Sci.*, **52**, 146–9.

Roos, Y. & Karel, M. (1991*a*). Phase transitions of mixtures of amorphous polysaccharides and sugars. *Biotechnol. Prog.* **7**, 49–53.

Roos, Y. & Karel, M. (1991*b*). Amorphous state and delayed ice formation in sucrose solutions. *Int. J. Food Sci. Technol.*, **26**, 553–66.

Saltmarch, M., Vagnini-Ferrari, M. & Labuza, T. P. (1981). Theoretical basis and application of kinetics to browning in spray-dried whey food systems. *Prog. Food Nutr. Sci.*, **5**, 331–44.

Shimada, Y., Roos, Y. & Karel, M. (1991). Oxidation of methyl linoleate encapsulated in amorphous lactose-based food models. *J. Agric. Food Chem.*, **39**, 637–41.

Slade, L. & Levine, H. (1991). Beyond water activity. Recent advances based on an alternative approach to the assessment of food quality and safety. In *Food Science and Nutrition. CRC Crit. Rev.*, **30**, p. 115.

Vuataz, G. (1988). Preservation of skim milk powders: Role of water activity and temperature in lactose crystallization and lysine loss. In *Food Preservation by Water Activity Control*, ed. C. C. Seow. Elsevier, Amsterdam, pp. 73–101.

Williams, M. L., Landel, R. F. & Ferry, J. D. (1955). The temperature dependence of relaxation mechanisms in amorphous polymers and other glass forming liquids. *J. Am. Chem. Soc.*, **77**, 3701–7.