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The kinetics of browning measured during the storage of onion and strawberry

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Summary The kinetics of non-enzymatic browning of onion and strawberry during storage at different temperature (5, 15, 25, 35, 45 °C) and equilibrium relative humidities (33%, 44%, 53%) was measured. Colour formation in onion was observed by measuring absorbance versus time in aqueous extract solutions. Experimental results of colour formation of onion as a function of time for each level of water activity were best represented by a zero order kinetics, while anthocyanin degradation in strawberry followed a second order kinetics. Rate coefficients obtained in both cases showed an increase in the rate of the reactions with both temperature and water activity. With regard to temperature dependence of rate coefficients, statistical evidence suggest that in the case of colour formation in onion, the Williams-Landel-Ferry model is a better representation than Arrhenius. In the case of strawberry it was not possible to reach such conclusion in spite of a lower summation of residuals obtained with the WLF model.

Keywords Glass transition, WLF equation.

Introduction

Moisture and temperature are two important parameters affecting rate of reaction in foods. Until the 1980s, the influence of moisture on chemical reaction, in particular the reactions important to food stability, had been described in terms of water activity (Labuza, 1975). Recently a new and alternative approach, based on glass transition theory, considers the effect of the state of the system on the reaction. The physical stability of amorphous foods has been related to the change from the glassy state to a rubbery state occurring over a temperature range known as the glass transition. A characteristic point of such a range, usually the onset temperature, is taken as the reference glass transition temperature (T_g) (Bellows & King, 1973; Levine & Slade, 1986; Roos & Karel, 1991). Above T_g the viscosity of the matrix decreases and some physical changes (such as collapse, loss of shape, shrinkage or stickiness) may occur. It is also possible that the properties of the state of the system, glassy or rubbery, may contribute to differences in chemical reaction rates in each of these states.

Some of those reactions tend to degrade foods during storage. It is thus of major importance to know the temperature dependence of the rate of such reactions in order to predict product shelf life. The most common and generally valid assumption is that temperature dependence of the rate of deterioration will follow the well-known Arrhenius relationship. It has been stated that the Arrhenius model is applicable for describing the temperature dependence of reactions within a food matrix in the glassy state and also at higher temperatures, say some 100 °C above the same glass transition temperature (Slade & Levine, 1991).

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In the range from T_g to $T_g + 100$ °C, increasing diffusion may be related to decreasing viscosity and the alternative model as proposed by Williams, Landel & Ferry (1955) might be better (Slade & Levine, 1991; Karmas *et al.*, 1992; Buera & Karel, 1993). The Williams-Landel-Ferry equation takes the following form to describe viscosity dependence with temperature:

$$\log \frac{\eta}{\eta_g} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \qquad (1)$$

where η and η_g represent the viscosities at T and T_g, and C_1, C_2 are constants.

Since the kinetic coefficient of non-enzymatic browning is directly proportional to diffusion and this is inversely proportional to the viscosity, the temperature dependence of the kinetic coefficient would be, according to the WLF model:

$$\log \frac{k_g}{k} = \frac{-C_3(T - T_g)}{C_4 + (T - T_g)} \qquad (2)$$

where k and k_g represent the browning rate constants at T and T_g, and again C_3 and C_4 are constants.

Data over a broad temperature range are required in order to differentiate between the WLF and the Arrhenius model. The WLF approach provides a physical explanation for changes in rate observed for temperature changes within rubbery systems (Nelson & Labuza, 1994).

Non-enzymatic browning is a common and highly investigated mode of quality loss in low-moisture foods. However, there are few works studying its relationship with the glass transition temperature (Karmas *et al.*, 1992; Roos & Himberg, 1994).

The objective of the present work is to investigate how the effect of the physical structure and the physical change resulting from the glass transition affect the rate of non-enzymatic browning in freeze-dried onion and strawberry. For this purpose the kinetics of non-enzymatic browning of onion and the degradation of the red pigment in strawberry were determined experimentally.

Materials and methods

Materials

Povoa Red onion (*Allium cepa*), a local cultivar with large reddish bulbs and strawberry (*Fragaria x ananassa*) of the Chandler cultivar were used in this study. The products were supplied by Agricultural Stations from the Portuguese Ministry of Agriculture, Fisheries and Food. The fresh products were washed and dried with paper cloth. Hulls and seeds were taken out and round slices of onion and strawberry, 7 mm thick, were cut, freeze-dried and stored under P_2O_5 after grinding.

Freeze-drying

Strawberry and onion were frozen at −40 °C and freeze-dried at 65 Pa in a Telabe LF10 plate freeze-dryer for over 24 hours. The dried samples were immediately packed in aluminium foil and stored in a desiccator under P_2O_5 before use.

DSC measurements

Samples of 5–30 mg of freeze-dried onion and strawberry were equilibrated over saturated salt solution ($a_w = 0.33$–0.53) during three days at room temperature. Moisture uptake was measured by successive weighing. After humidification each sample was placed in a 30 μl aluminium DSC pan, sealed and weighed. A Shimadzu DSC-50 differential scanning calorimeter fitted with a LTC-50 cooling unit was used. The instrument was calibrated for heat flow and temperature with n-hexane, distilled water and indium. Helium at a flow rate of 30 ml min^{-1} was used as carrier gas. At least five thermograms were obtained for each level of moisture content.

Browning evaluation

The freeze-dried onion powder were stored in containers at controlled temperature and relative humidity during approximately five months. Three sets of containers conditioned at 33, 44 and 53% of relative humidity were stored at 5, 15, 25, 35 and 45 °C. Storage temperatures were selected in order to have the systems in the range between T_g and ($T_g + 100$ °C). At appropriate storage time intervals, samples were taken for analysis.

Extent of browning of the freeze-dried onion was determined by the measurement of the absorbance using the official method of the ADOGA (1976). A sample of 0.3 g (moisture free basis) was extracted with 15 ml of 10% NaCl solution, for one hour. The crude extract was filtered through a Whatman 2V filter paper (Whatman International Ltd., Kent, England). After 20 min, the absorbance of the filtrate was read in 1 cm quartz cells at 420 nm with a UV/Vis Lambda 2 Spectrophotometer (Perkin Elmer, Connecticut, USA).

Red pigment loss evaluation

Likewise, freeze-dried strawberry were also stored at 33, 44 and 53% relative humidity and 15, 25, 35 and 45 °C during three months.

In the case of strawberries, since Mackinney *et al.* (1955) verified a linear relationship between the red pigment loss (anthocyanins) and the increase in browning, anthocyanin degradation was followed.

Anthocyanin content was determined by the spectrophotometric method of Swain & Hills (1959): in this method the pigment concentration is expressed in terms of the difference in absorbance at $\lambda = 528$ nm between two samples extracted with ethanol, one maintained at pH = 3.5 and the other being fully oxidized with hydrogen peroxide at pH = 1. The absorbance of the first solution was measured at 528 nm with a Spectrophotometer UV/Vis Perkin Elmer Lambda 2, using 1 cm quartz cell and the second solution as reference.

Results and discussion

Glass transition temperatures

Glass transition temperatures for onion and strawberry obtained are given in Table 1. A complete description of the method is presented by Sá & Sereno (1994a, b) and Sá (1997).

Table 1 Onset glass transition temperatures (T_g) of freeze-dried onion and strawberry for a_w = 0.33, 0.44 and 0.53

a_w	T_g (onion)	T_g (strawberry)
0.33	−11.0	−11.5
0.44	−21.1	−24.7
0.53	−26.1	−38.3

Non-enzymatic browning

The colour of freeze-dried onion powder changed during storage from a uniform cream colour to yellow brownish and then to brown. Non-enzymatic browning increased with time, temperature and humidity (Fig. 1). The values presented represent the average of three experiments. A zero-order reaction model (Equation 3) produced a good fit of the data.

$$A = A_o + kt \tag{3}$$

where A is browning concentration measured as absorbance, A_o the initial absorbance, k the reaction rate constant (time^{-1}) and t time.

A zero-order kinetic was also obtained by Samaniego-Esguerra *et al.* (1991) for a commercial dried onion flakes and the k values reported by these authors agree with the present work.

The rate constants (kinetic coefficients) calculated from the slope of the regression lines are

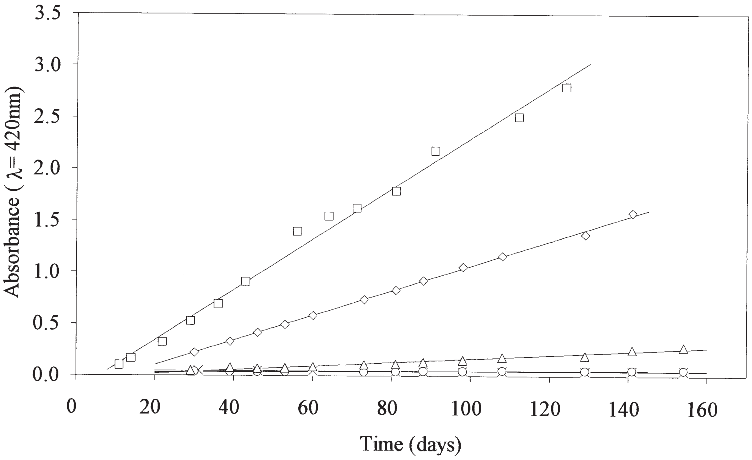

Figure 1 Non-enzymatic browning of freeze-dried onion equilibrated at 53% relative humidity, at various temperatures (×: 5 °C; ○: 15 °C; △: 25 °C; ◇: 35 °C; □: 45 °C).

Table 2 Corrected reaction rate constants for browning in freeze-dried onion and strawberry powder at various temperatures and water activities

Temperature (°C)	a_w	**k (day^{-1}) (onion)**	**k (day^{-1}) (strawberry)**
15	0.33	5.96E-6	3.54E-2
	0.44	8.90E-5	1.00E-1
	0.53	1.55E-4	1.51E-1
25	0.33	3.27E-4	1.83E-1
	0.44	9.19E-4	5.15E-1
	0.53	1.79E-3	1.03
35	0.33	2.90E-3	7.22E-1
	0.44	8.46E-3	213
	0.53	1.29E-2	3.26
45	0.33	1.39E-2	3.47
	0.44	2.20E-2	8.33
	0.53	2.84E-2	12.2

given in Table 2. Due to a very low rate of reaction, *k*-values obtained at 5 °C showed very large experimental uncertainties and were not further considered. Due to the change of the equilibrium water activity of saturated salt solutions with temperature, *k* values were corrected by linear interpolation for the same reference value of the water activity at 25 °C (0.33, 0.44, 0.53).

Red pigment loss

The colour of freeze-dried strawberry powder changed during storage from rose to reddish and then to brown. The effect of temperature on the rate of anthocyanin degradation in the case of is shown in Fig. 2.

Kertesz & Sondheimer (1948) and El-Kady & Ammar (1977) investigated the kinetics of the thermal degradation of strawberry anthocyanin pigments in strawberry preserves and juice, respectively, and found, in both cases, first order reactions. Markakis *et al.* (1957); Tinsley & Bockian (1960); Keith & Powers (1965) and Daravingas & Cain (1968) found the same order of reaction for the degradation of the commercial pigment. However, Erlandson & Wrolstad (1972), in a study of thermal degradation of anthocyanin in freeze-dried and powdered strawberry at 37 °C, humidified at various relative humidities, observed a kinetic order greater than one.

After fitting the results obtained here to both first and second order kinetics it was verified that this decolouration was better represented by a second order reaction. Table 2 presents calculated *k*-values after a_w correction, as mentioned above.

Temperature dependence of rate constants

The temperature dependence of rate constants was analyzed using the Arrhenius and the William-Landel-Ferry models. For the WLF fit the coefficients were calculated as suggested by Peleg (1992). Calculated parameters and standard deviations for the two models are presented in Table 3 and 4. Figure 3 and 4 show plots of (ln *k*) vs. (1/*T*) for both materials.

As the data at 5 °C were eliminated, the lower (T-T_g) value was 26 °C. As the more evident curvature in the WLF curve is expected for (T-Tg)

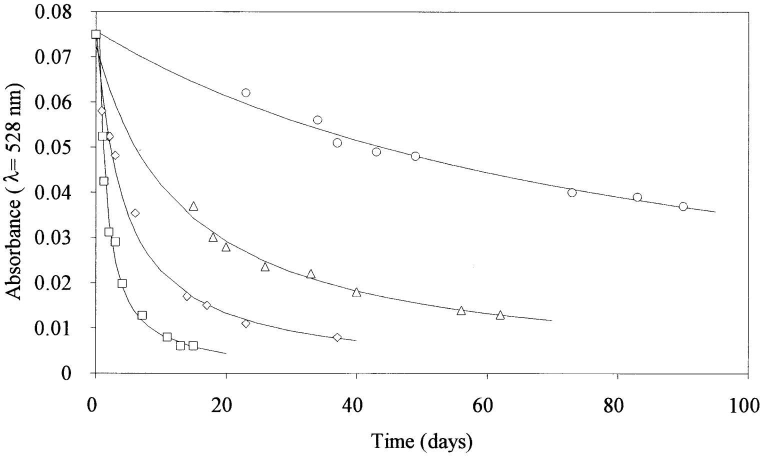

Figure 2 Degradation of anthocyanin pigment in freeze-dried strawberry at 53% relative humidity and various temperatures (○: 15 °C; △: 25 °C; ◇: 35 °C; □: 45 °C).

Table 3 Parameters for the Arrhenius model and standard deviation of freeze-dried onion and strawberry

	a_w	k_o	$-E_a$	s
Onion	0.33	8.14E25	168.8	0.50
	0.44	1.32E23	149.7	0.72
	0.53	2.97E20	133.0	0.70
Strawberry	0.33	2.77E19	115.6	0.12
	0.44	2.11E19	112.2	0.05
	0.53	1.20E19	109.8	0.29

Table 4 Parameters for the WLF model and standard deviation of freeze-dried onion and strawberry

	a_w	k_g	C_1	C_2	s
Onion	0.33	8.66E-13	15.49	28.94	0.04
	0.44	2.39E-28	29.98	10.02	0.32
	0.53	2.92E-28	30.04	10.80	0.32
Strawberry	0.33	4.82E-4	1.24E2	7.33E2	0.10
	0.44	2.11E-5	4.14E1	1.55E2	0.03
	0.53	3.70E-18	5.32E1	2.08E1	0.17

values lower than 20 °C (showed in Fig. 3 and 4 in the Arrhenius plots for $1/T > 0.0035$), the Arrhenius deviations were not very clear, and the E_a values did not differ from those obtained in systems with no diffusional limitations.

Visual analysis of the plots suggests that a better fit is obtained with WLF. An F-test analysis of variance showed that, with 90% confidence, the WLF model is better than the Arrhenius model in the case of onion browning. The same test conducted on strawberry results did not support the hypothesis of the WLF being a better fit than Arrhenius. Residual analysis conducted on both onion and strawberry browning confirmed the F-test analysis.

Conclusions

The kinetics of non-enzymatic browning of freeze-dried onion powder and the degradation of

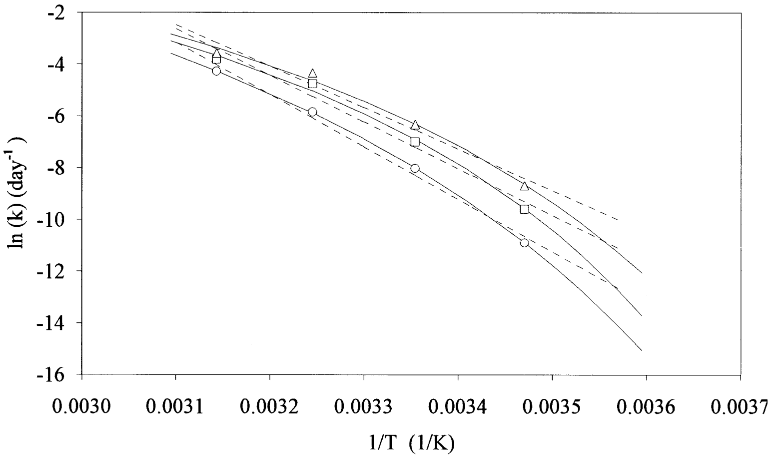

Figure 3 ln(k) vs. $1/T$ for freeze-dried onion (○: $a_w = 0.33$; □: $a_w = 0.44$; △: $a_w = 0.53$; – – – – Arrhenius model; ——— WLF model).

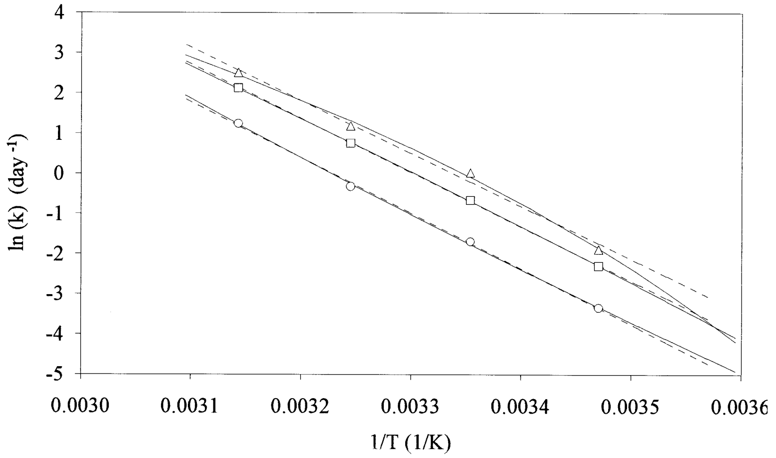

Figure 4 ln(k) vs. $1/T$ for freeze-dried strawberry (○: $a_w = 0.33$; □: $a_w = 0.44$; △: $a_w = 0.53$; – – – – Arrhenius model; ——— WLF model).

anthocyanin in strawberry were determined as a function of temperature and moisture. Analysis of results suggests a zero-order reaction for onion while a second order kinetics was found for strawberry.

Arrhenius and William-Landel-Ferry models were used to explain the dependence of kinetic coefficients with temperature. In the case of onion browning it was concluded both by visual inspection and statistical analysis that the WLF model seems to be a better model to describe such dependence under the tested conditions. For strawberry discoloration the results were not conclusive and further work is required.

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