

Water–solids interactions, matrix structural properties and the rate of non-enzymatic browning

N. Acevedo *, C. Schebor, M.P. Buera

Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria (1428), Ciudad de Buenos Aires, Argentina

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Abstract

The kinetics of non-enzymatic browning (NEB) was studied in freeze-dried model and food systems in a wide range of relative humidity (R.H.) values.

PVP, lactose, lactose–starch solutions and food (milk, cabbage, apple, potato, and chicken meat) systems were freeze-dried, equilibrated at 11–85% of R.H. and incubated at 70 °C. Thermal transitions were determined by DSC. The kinetics of NEB development was analyzed. In PVP systems the maximum rate occurred at 33% R.H., at which T_g was close to the storage temperature. Above 33% R.H. the samples presented a fluid aspect at 70 °C and the NEB rate decreased when increasing R.H. In tissues containing structuring water insoluble biopolymers and presenting an intermediate degree of collapse, the maximum rate of NEB occurred at relative humidities in a range of 50–80%, when the samples were well above T_g at the storage temperature. In the lactose systems the maximum rate occurred at R.H. close to 40%, at conditions at which lactose was highly crystalline.

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1. Introduction

The non-enzymatic browning (NEB) reaction is one of the most prevalent and studied chemical reactions that occurs in foods during heating and storage. The NEB rate is known to be affected by several physico-chemical factors, being the most studied: concentration, ratio and chemical nature of the reactants (type of amine and carbonyl groups involved); pH; relative humidity; temperature and time of heating (Labuza & Baisier, 1992).

In fluid liquid systems, NEB rate diminishes continuously as relative humidity (R.H.) increases, mainly due to the fact that water is a product of the reaction (Eichner & Karel, 1972; Labuza & Saltmarch, 1981). On the other side, in solid or quasi-solid systems, in which NEB reactants are submitted to mobility restrictions, a maximum

rate of NEB is observed at a given intermediate R.H. value. The decreasing browning rate at high water content/relative humidity has also been related to the dilution of reactants at constant reactant mass (Loncin, Jackmain, Tutundjian Provost, Lengés, & Bimbenet, 1965; White & Bell, 1999). Thus, the existence of a maximum in the plot NEB rate versus water content (or R.H.) is a consequence of the low reaction rates due to mobility limitations of reactants at low water contents (Buera & Karel, 1995; Karmas, Buera, & Karel, 1992) and inhibition by product/dilution of reactants at high water contents (Karmas & Karel, 1994; van Boekel, 2001; White & Bell, 1999). It was generally accepted that the maximum NEB rate in food systems is in the range of R.H. between 60% and 80% and that it depends on the type of food (Eichner & Karel, 1972; Labuza & Saltmarch, 1981). The kinetics of NEB has also been related to the glass transition phenomenon (Bell, Touma, White, & Chen, 1998; Bell, White, & Chen, 1998; Karmas et al., 1992). Although the formation of amorphous glassy

* Corresponding author. Tel./fax: +54 11 4576 3366.
E-mail address: nacevedo@di.fcen.uba.ar (N. Acevedo).

solids in dried foods results in a significant arrest of translational molecular motion (Franks, 1993; Koster, 1990; Levine & Slade, 1992; Slade, Levine, & Finley, 1989; Sun & Leopold, 1994), browning development occurs in glassy systems (Bell, 1996; Karmas et al., 1992; Schebor, Buera, Karel, & Chirife, 1999).

Amorphous materials undergo a structural change at the glass transition temperature (T_g), which is a function of the relative proportion of its glass-forming components and of water content. As the water content increases, the matrix is plasticized, T_g decreases, and various-time dependent changes in the physical properties of the matrix occur at temperatures above T_g , altering the rate of chemical reactions. Matrix collapse caused by storage above T_g or by mechanical compression and porosity (Buera & Karel, 1995; Burin, Jouppila, Roos, Kansikas, & Buera, 2004; White & Bell, 1999) affected browning rates, indicating that besides water content, the system structure plays a role. Crystallization during storage above T_g dramatically increased NEB rate (Burin et al., 2004; Karmas & Karel, 1994; Miao & Roos, 2005).

All cited observations indicate that there are many ways in which water influences the reaction rate and define the position of the maximum browning rate in the relative humidity scale.

The purpose of the present work was to analyze the combined effects of the several water–solids interactions and the structural properties of food matrices on the NEB rate.

2. Materials and methods

In order to analyze the effect of structural properties and water interactions on the maximum rate of non-enzymatic browning in the relative humidity scale, three groups of systems with defined structural characteristics were selected:

- (a) Water soluble, non-crystallizing and highly collapsing with low reactant concentration (PVP polymeric matrices).
- (b) Water soluble, crystallizing, showing low or intermediate structural collapse with high reactant concentration (lactose systems).
- (c) Matrices containing water insoluble biopolymers:
 - (c1) With low reactant concentration (potato, chicken muscle).
 - (c2) With high reactant concentration (cabbage, apple).

2.1. Food systems

Fresh vegetables (Granny Smith apples, Spunta white potatoes, Savoy cabbage) and boneless chicken breast meat were obtained from the local market. The meat was trimmed of any visible fat. Peeled potatoes and apples were

washed and cut in cubes (1 cm side) and cabbage was shredded in 0.5 cm side slices. The cut materials were blanched for 3 min over steam and immediately frozen at $-20\text{ }^{\circ}\text{C}$.

2.2. Model systems

The following matrices were employed: polyvinylpyrrolidone (PVP) of average molecular weight 58000 obtained from ISP Technologies, Inc. (Wayne, NJ); Lactose and a mixture 3:1 (in weight) of Lactose obtained from Mallinckrodt Chemical Works (St. Louis, USA); gelatinized wheat starch (obtained from Sigma Chemical Co., St. Louis, USA).

Wheat starch was previously gelatinized by heating an aqueous suspension for 15 min at $80\text{ }^{\circ}\text{C}$. Gelatinization was confirmed by observation under polarized light microscopy.

Samples were prepared by freeze-drying aqueous solutions of the corresponding matrices in phosphate buffer 0.175 M pH 6, containing 15% (w/w) of the matrix material and the browning reactants, glycine and glucose, both on 0.5% on solid basis. The systems containing lactose did not contain glucose. Glycine and glucose were analytical grade (obtained from Merck Darmstadt, Germany and Anedra San Fernando, Argentina; respectively). These compounds were chosen because of their high reactivity towards NEB, and they were employed at very low concentrations so that diffusional effects could be expected.

Aliquots of 1 ml of each solution were placed in 3 ml glass vials and frozen at $-20\text{ }^{\circ}\text{C}$ for 24 h.

2.3. Freeze-drying

Food and model systems were quenched with liquid nitrogen before freeze-drying. The freeze-drying process lasted 48 h. A Heto-Holten A/s, cooling trap model CT110 freeze drier (Heto Lab Equipment, Denmark) was used; it was operated at $-110\text{ }^{\circ}\text{C}$, at a chamber pressure of 4×10^{-4} mbar. After freeze-drying, food systems were powdered in a mortar in a dry chamber and distributed into 5 ml vials. Powdered foods and freeze-dried model solutions were equilibrated over saturated salt solutions (in a range of 11–84% R.H.) in vacuum desiccators for 15 days to obtain the desired water contents (Greenspan, 1977).

2.4. Water content

The water content was determined (in duplicate samples) by difference in weight before and after vacuum drying over magnesium perchlorate at $70\text{ }^{\circ}\text{C}$ for 48 h.

2.5. Reducing sugars

The glucose concentration was determined by Fehling's method (Qin, 1991).

2.6. Heat treatment

After equilibration, the vials containing the samples were hermetically sealed with a cap covered with an aluminum strap, and placed in forced air ovens operated at constant temperature (43, 55 or 70 °C ± 1 °C). At suitable intervals, samples were removed from the oven and kept at –20 °C until they were analyzed.

2.7. Thermal transitions

Glass transitions were determined by differential scanning calorimetry (DSC; onset values) using a DSC 822^c Mettler Toledo calorimeter (Schwerzenbach, Switzerland). The instrument was calibrated with indium (156.6 °C), lead (327.5 °C) and zinc (419.6 °C). All measurements were performed at a heating rate of 10 °C/min. Hermetically sealed 40 µl medium pressure pans were used, (an empty pan served as reference). Thermograms were evaluated using Mettler Star^c program. An average value of two replicates was reported.

2.8. Degree of reaction

In food systems the degree of Maillard reaction was determined by reflectance measurements of the color attribute luminosity (L) with a white background of reflectance (L_0). A handheld tristimulus reflectance spectrophotometer with integrating sphere (Minolta CM-508-d, Minolta Corp., Ramsey, NJ, USA) was employed. Two replicates were analyzed for each storage time. Color functions were calculated for illuminant C at 2° standard observer and in the CIELab uniform color space. The color function $L - L_0$ was found to be an adequate parameter to evaluate the non-enzymatic browning reactions in opaque samples (Buera & Resnik, 1989), and was calculated as follows: $L = 116 * (Y/Y_n)^{1/3} - 16$, where Y is the Y tristimulus value of the sample and Y_n the Y value for illuminant C.

The heated model systems were reconstituted with 1 ml distilled water to their original volume. Browning was determined by measuring absorbance at 445 nm at the adequate dilution and normalized for 1 g of dry solids.

The browning analysis was performed in duplicate for each sample and an average value was reported being the standard deviations about 3%.

3. Results and discussion

Based on previously reported data on the kinetics of the Maillard reaction, three important aspects of the matrices regarding their interactions with water and their possible role in affecting NEB rate were analyzed: plasticizing effect of water on the matrices and consequent physical and structural changes, water sorption monolayer value and solvent characteristics.

The plasticizing effect of water was analyzed through the T_g values of the systems at different R.H. values (summarized in Table 1). For PVP, cabbage, apple and lactose T_g values were in agreement with those previously reported (Buera, Levi, & Karel, 1992; del Valle, Cuadros, & Aguilera, 1998; Fernández, Schebor, & Chirife, 2003; Karmas et al., 1992; Roos & Karel, 1991). The glass transition temperatures obtained for potato were about 10 °C lower than those reported by Karmas et al. (1992) probably due to the different variety or maturation degree of the vegetable. The T_g values were associated to the amorphous soluble solids, which are the main components in the solid fraction of vegetables and model lactose systems. The insoluble components (such as cellulose, casein or starch) may form separate phases with low effect on the T_g values (Burin, Buera, Hough, & Chirife, 2002).

Glass transition temperatures have been reported for animal frozen tissues (Brake & Fennema, 1999; Delgado & Sun, 2002; Lo et al., 1991). However, there is a lack of information regarding T_g of dehydrated muscle tissue. In fact, the high amount of insoluble proteins and low amount of sugars made it difficult their experimental determination. Thermograms for chicken muscle had lower ΔC_p values at T_g , and the shifts of the baselines were difficult to detect and this was indicated with a question mark in Table 1.

The typical drop in T_g was observed as R.H. increased and samples adsorbed water.

Crystallization of pure lactose was observed above 33% R.H. at 20 °C, and it was manifested in the thermograms by the absence of the T_g endothermal shift (Buera, Schebor, & Elizalde, 2005) and in the sorption isotherms as a discontinuity in the amount of sorbed water. The T_g values obtained for the lactose/starch system, and for milk powder were similar to those obtained for pure lactose but they could be detected up to 43% R.H. In the lactose–starch and milk systems the discontinuities in the sorption isotherm

Table 1
Glass transition temperatures (°C) for all freeze-dried systems at various relative humidities

Relative humidity (%)	System							
	PVP	Lactose	Lactose/starch	Milk	Cabbage	Chicken ^a	Potato	Apple
11	96.4	47.6	50.0	59.3	29.3	–	32.0	9.1
22	80.8	36.9	32.0	52.7	0.9	–	29.0	–6.2
33	66.6	22.4	14.0	43.7	–3.8	20?	–7.2	–16.2
43	50.3	–	6.0	9.5	–22.3	–10?	–16.5	–25.1
52	45.9	–	–	–2.09	–29.2	–20?	–35.9	–44.0
75	3.58	–	–	–	–62.3	–60?	–62.2	–71.2

^a Difficult experimental determination due to the low ΔC_p values.

Table 2
Water sorption and water plasticizing characteristics in the studied systems

	System							
	PVP	Lactose	Lactose/starch	Milk	Cabbage	Chicken	Potato	Apple
$-K_p$ (°C) ^a	4.47	8.05	10.07	15.15	4.04	7.27	6.71	3.46
M_o ^b	11.58	6.27	4.03	4.50	8.08	5.82	7.79	8.31
I (% R.H.) ^c	60	52	52	>80	65	62	70	60

^a K_p represents the decrease in T_g per 1% increase of water mass fraction.

^b M_o is the mass fraction of water corresponding to the monolayer value.

^c I is the relative humidity at which the second inflection point of the sorption isotherm occurs.

occurred at 44% R.H., indicating that the presence of biopolymers delayed sugar crystallization. Several other studies have also indicated that the addition of a polymer to an amorphous matrix delayed the crystallization of the sugar (Biliaderis, Lazaridou, Mavropoulos, & Barbayiannis, 2002; Burin et al., 2004; Gabarra & Hartel, 1998; Mazzobre, Soto, Aguilera, & Buera, 2001; O'Brien, 1996).

Although in the vegetable tissues sugars remained at supersaturation levels in the whole range of R.H. analyzed, sugar crystallization was not manifested in the thermograms neither in the sorption behavior. The presence of insoluble (cellulose) or soluble (pectins) biopolymers and compartmentalization in cellular structures could explain this behavior.

Water sorption and water plasticizing characteristics on the studied systems were summarized in Table 2. The plasticizing effect of water (K) was calculated from the slope of the plot T_g versus mass fraction of water, which presented a linear correlation in the analyzed range. As higher is the K value, as higher is the plasticizing effect of water in the given matrix. It is interesting to note that water is a more effective plasticizer for lactose-containing systems and tissues than for the synthetic polymer PVP.

Table 2 also shows the data obtained from the analysis of the sorption isotherms of the different systems through the GAB (Tolaba, Peltzer, Enriquez, & Pollio, 2004) model. Non-crystalline, highly collapsing PVP matrices presented the highest monolayer value at 20 °C. The R.H. above which water behaves as a solvent was obtained from the second inflection point of the sorption isotherm (I). This point was calculated as the intersection of the tangent lines to the sorption isotherm at water contents higher than the monolayer value. In the systems that presented discontinuities in the sorption isotherm (lactose, lactose/starch) the second inflection point was taken in the second ascendent part of the isotherm.

In all analyzed systems NEB rate was extremely slow at temperatures below T_g and increased as increasing water content in the low R.H. range. This was attributed to the fact that NEB is diffusion-controlled and it is favored by water plasticization of the matrix where the reaction takes place. It is to be noted, however, that except the PVP matrices all the analyzed systems were more than 10 °C above the glass transition temperature at the storage temperature (Table 1). Fig. 1 shows the non-enzymatic

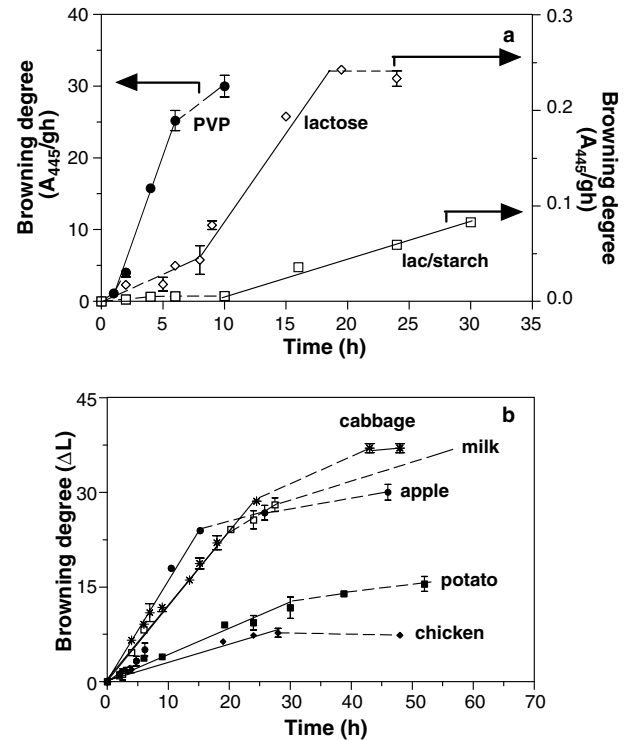


Fig. 1. Browning development as a function of time for freeze-dried model systems (a) and foods (b) both equilibrated at 52% R.H. and stored at 70 °C.

browning development for model systems (a) and foods (b) equilibrated at 52% R.H. and stored at 70 °C. The browning development both in model and foods systems showed an initially linear increase with storage time, followed by a zone in which browning rate decreased. Among the model systems, the PVP system showed the highest degree of browning (Fig. 1a). The lactose/gelatinized starch system showed much lower browning degree than that observed for lactose (Fig. 1a). This fact can be explained in part by the dilution of the reactant lactose in presence of gelatinized starch, but also by mobility restrictions promoted by the presence of the polymer. However, lactose was in a high proportion (3:1) in the mixture lactose:starch and the amorphous phase remained saturated with lactose. Burin et al. (2004) showed that the lower browning rate when maltodextrin was present in lactose-containing systems was mainly related to the delay of lactose crystallization.

Milk powder, freeze-dried cabbage and apple systems showed a higher degree of browning than potato and chicken systems, when compared at similar conditions (Fig. 1b). This fact can be attributed to the presence of high concentrations of reducing sugars in these systems: 52.4% on dry basis (d.b.) for milk, 42.8% (d.b.) for cabbage and 50.8% (d.b.) for apple tissue. The concentration of reducing sugars in potato and chicken tissues is much lower (less than 4 g reducing sugar/100 g solids for both systems). In addition, the major compounds in potato and chicken muscle are starch and proteins, respectively, which are not reactive towards Maillard reaction and provide a less mobile matrix that can diminish the rate of the diffusion limited reactions.

The rate of NEB for each system was calculated from the slope of the initial part of the curves of browning versus storage time (Fig. 1), through linear correlation analysis of data (quasi-zero-order kinetics), as reported before (Burin, Jouppila, Roos, Kansikas, & Buera, 2000; Burin et al., 2004).

Figs. 2 and 3 show the rate of NEB versus relative humidity for the different model and foods systems stored at 70 °C. Fig. 2 shows NEB rate versus R.H. for PVP system stored at 55 and 70 °C (Fig. 2a) and lactose and lactose/starch (3:1) systems incubated at 70 °C (Fig. 2b). The decreasing NEB rate can be also attributed to structural collapse of the samples, which may cause elimination of preferential sites for the reaction (White & Bell, 1999).

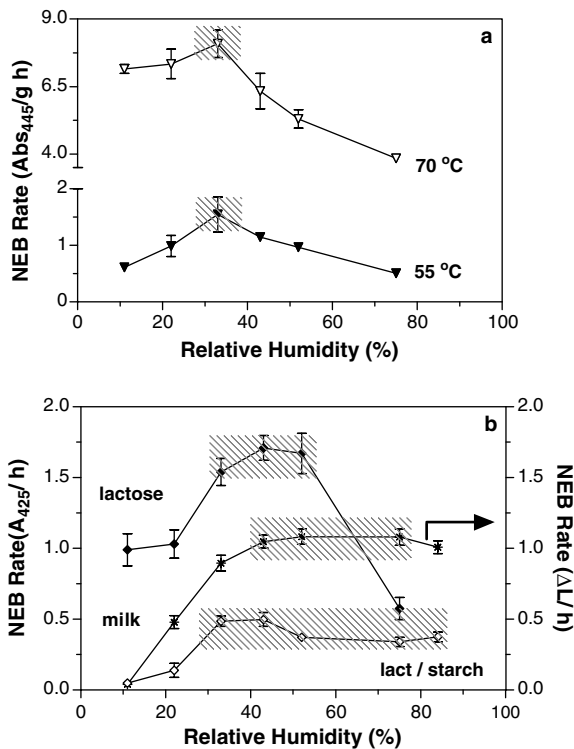


Fig. 2. NEB rate versus R.H. for collapsing PVP system stored at 55 and 70 °C (a) and crystallizing lactose systems stored at 70 °C (b).

In PVP systems the R.H. value at which NEB rate was maximum was 33%, close to the water content of the monolayer value calculated by GAB (Table 2), which was coincident with the water content at which the glass transition occurred at the storage temperature. In these systems, the NEB rate at above 33% R.H., was relatively low, and, as in the liquid systems analyzed by Eichner and Karel (1972), only the inhibitory effect of water and of sample collapse was manifested. No dilution effect was expected at these R.H. lower than the monolayer value (Table 2), since water has not solvent properties up to well above the monolayer value (Duckworth, 1981). The possible effect of dilution of reactants, besides inhibitory effects of water, could influence NEB kinetics in the PVP systems only at 75% H.R. (last point in Fig. 1a). Buera and Karel (1995) and Bell (1996) analyzed the kinetics of NEB in PVP systems, and they also observed the maximum NEB rate at 33% R.H., in the glassy state. The decreasing NEB rate can be also attributed to structural collapse of the samples, which may cause elimination of preferential sites for the reaction. White and Bell (1999) suggested that pores may be sites of reactivity and the elimination of porosity due to structural collapse may cause a decrease in reaction rates. Buera and Karel (1995) and Burin et al. (2004) found that in collapsed or mechanically compressed systems browning was accelerated in the low water content region due to the impediments of water to be released in the low R.H. range of at which water favors the development of the reaction.

It is interesting to note that for the lactose systems, the maximum rate of NEB occurred at 43% R.H. (Fig. 2b). At this R.H. value lactose crystallization had occurred at the storage temperature (70 °C) (Jouppila & Roos, 1994). Although the conversion from amorphous to crystalline lactose may lead to a decrease of lactose availability and to the loss of possible preferential sites of reaction in the porous regions, the reaction rate increased upon lactose crystallization (at 33% R.H., close to the monolayer value) probably due to the formation of a liquid phase supersaturated in lactose when water is released from the amorphous phase. At higher R.H., NEB rate decreased above the point at which the sorption isotherm reached the second ascending part, indicating also that water with manifest solvent properties inhibited the reaction. Gelatinized starch, when mixed with lactose delayed crystallization of the sugar as determined by DSC measurements.

However, the R.H. value at which crystallization started was the same as in the lactose system, and the rate of NEB decreased only slightly above 52% R.H. (Fig. 2b). Thus, the decreasing NEB rate at high R.H. was not observed in this system, although the inflection point of the isotherm (*I*) was estimated at 52% R.H. In the starch–lactose and milk systems, the matrix components could adsorb part of the water and thus, its inhibitory effect was less evident and the decrease in NEB rate is not observed.

The maximum NEB rate in milk powder was located between 43% and 75% R.H. This maximum value was maintained through the supercooled region in the zone when

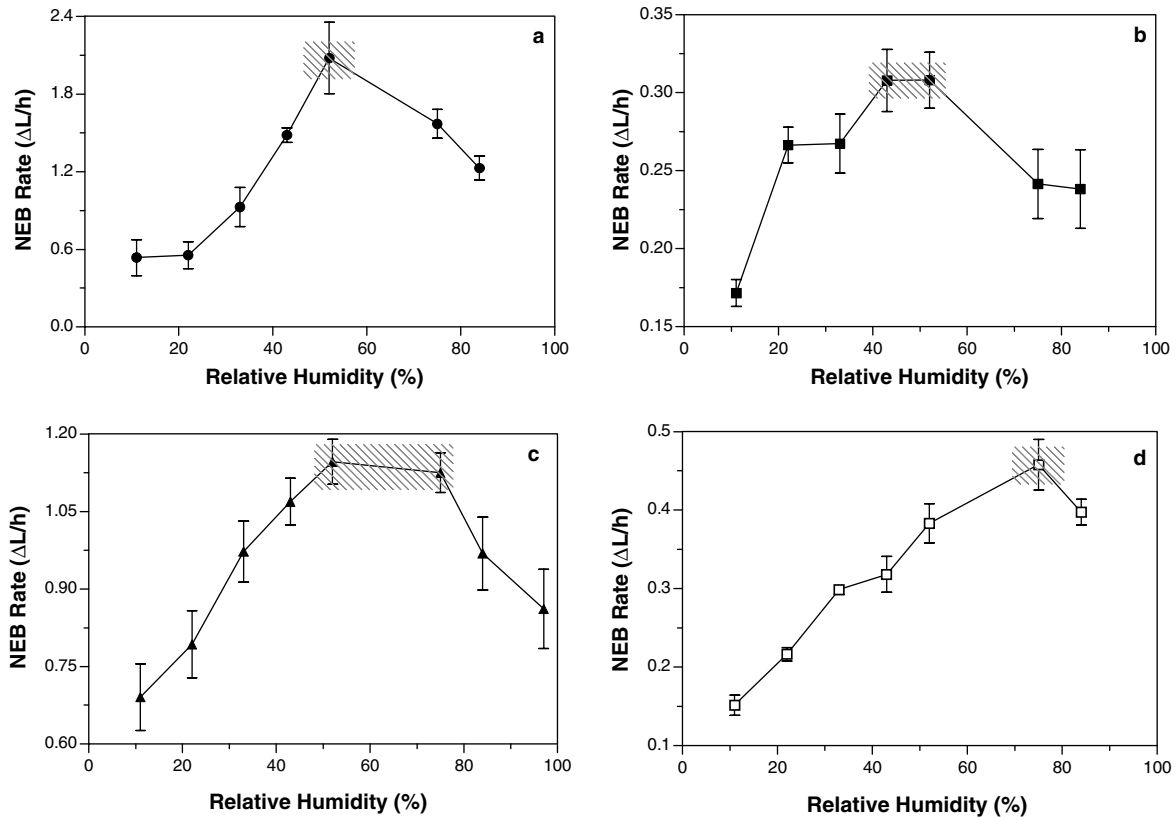


Fig. 3. NEB rate versus R.H. for apple (a), chicken (b), cabbage (c) and potato (d) stored at 70 °C.

sugar crystallization is favored (Fig. 2b). The presence of proteins can be the cause for the higher R.H. at which the maximum NEB rate is observed in milk powder compared to pure lactose systems. These results are in accord with the values of the second inflection point of the isotherm (I) for milk (shown in Table 2), at which the solvent characteristics of water are manifested, and was observed at a R.H. value higher than 80%. The NEB rate did not show any decrease below that value. Franzen, Singh, and Okos (1990) showed that the maximum NEB rate for milk powder was at 33% R.H. In Franzen's experiments, however, the humidification of the systems was performed with ice and this procedure could lead to systems with a higher degree of lactose crystallization. Roos, Jouppila, and Zielasko (1996) found that the rate of non-enzymatic browning reaction in dairy powders increased significantly when the materials were stored above 44% R.H. which was sufficient to depress T_g to below storage temperature and promote lactose crystallization.

In the tissue systems, the NEB rate presented a maximum value at R.H. levels close to the second inflection point of the sorption isotherms of the corresponding matrices. It is possible that above that point water molecules were less implicated in interactions with the solid matrices and could exert their inhibitory effect on the reaction. Due to the presence of structural components (cellulose, starch), the samples were not as sensitive to collapse as PVP or lactose systems.

The R.H. values for the maximum NEB rate (shaded bands in the plot) were: 52% for apple (3a), 43–52% for chicken (3b), 52–75% for cabbage (3c) and 75% for potato (3d). Hendel, Silveira, and Harrington (1955) studied dehydrated potato systems at temperatures in a range from 40 to 99.5 °C and reported a maximum NEB rate at 15–20% water content (dry basis), which corresponds to 70–75% R.H. (Karmas et al., 1992). Mizrahi, Labuza, and Karel (1970) analyzed dehydrated cabbage systems up to approximately 20% water content (60% R.H.) (Karmas et al., 1992), and observed that the NEB rate increased with the increase in water content, without showing a clear NEB rate maximum in a temperature range from 30 to 52 °C. Toribio, Nunez, and Lozano (1984) informed a NEB rate maximum at 55% R.H. for apple juice at 37 °C, however this was a concentrated juice and not a dehydrated system.

As observed in Figs. 2 and 3, the relative humidity values for the maximum NEB rate were located at different R.H. values, according to the water sorption and structural characteristics of the systems. Table 3 shows the $T-T_g$ values at which the maximum rate of non-enzymatic browning was observed for each system.

In non-crystallizing systems forming a liquid-like structure (PVP), and also in those capable to form a crystalline structure (lactose and milk powder) the R.H. for the maximum NEB rate was in the range 33–43%, quite lower than the intermediate R.H. range, and coincident with the structural changes promoted by thermal treatment. It is to be

Table 3
 $T-T_g$ values corresponding to the maximum browning rate in foods and model systems stored at 70 °C

System	R.H. (%) ^a	W.C. (% db) ^b	$T-T_g$ range (°C) ^c	Physical structure
PVP	25–38	12	0–5	Fully collapsed liquid-like, not crystallized
Lactose	43–52	4–7	>64	Crystallized
Lactose/starch	33–75	5–7	56–64	Partly crystallized
Milk	43–75	8–9	60–73	Partly crystallized
Apple	45–57	15–20	100–130	Caked, soft
Chicken	43–52	7–10	80–90	Caked
Cabbage	52–75	14–31	99–130	Sticky
Potato	70–80	15	140–160	Caked, tough

^a Relative humidity.

^b Water content (% dry basis).

^c T : storage temperature = 70 °C; T_g corresponds to the water content range for the maximum rate.

noted that in these systems the maximum rate of browning is very close to the systems which have a stable structure, provided by insoluble components, like vegetable tissues or those containing polymers (such as gelatinized starch), which can prevent crystallization and collapse, show the maximum NEB rate at high relative humidities (60–80%), in the supercooled (rubbery) state, at least 60 °C above the T_g of each system (Table 3). The maximum for the NEB rate is shifted in these systems towards high R.H. values due to mobility reasons caused by the presence of insoluble components and by compartmentalization.

Although the decreasing rate of browning after the maximum was attributed also to dilution of reactants in the reaction media, it is to be noted that in all the lactose-containing matrices, cabbage and apple systems the reducing sugars remained in a supercooled state, even considering that all the water molecules present are capable to act as solvent (which is not evidently the case). For the less concentrated in NEB reactants like PVP, potato and chicken muscle systems, the dilution effect may play a role in decreasing the browning rate only at R.H. above 80%.

4. Conclusions

The dependence of browning rate with R.H. was governed by solid–water interactions and by structural characteristics of the systems. The two inflection points of the sorption isotherms were reflected on the dependence of browning rate with R.H. In some systems (PVP matrix) the monolayer value seems to be a critical point above which the NEB rate decreased. It is interesting to note that in these polymeric collapsing systems the maximum NEB rate was located at temperatures close to T_g , before the collapse of the sample and may be related to the point at which the systems became fluid, with low density, and their behavior in the water content scale resembled to that observed in liquid systems (Eichner & Karel, 1972).

In some other systems (tissues) the second inflection point of the isotherm (I), which represents the point at which water has solvent properties, determined the R.H. above which NEB decreased. The presence of water insoluble components affecting structure, crystallization and collapse, modified the dependence of browning rate on

water content, making the maximum rate to shift towards high R.H.

The most complicated picture is presented in crystallizing lactose systems. Sugar crystallization occurs close to the monolayer value and promoted an increase of the browning rate, due probably to the concentration of reactants in the non-crystalline parts of the matrix. NEB rate was maintained up to the second inflection point after which it decreases, due to the excess water released during lactose crystallization.

Thus, the R.H. at which the browning reaction will be maximum is a combination of all these factors, and can be predicted on the basis of sorption, structural and thermal transition of the matrices where the reaction takes place. The knowledge of the mechanisms involved in NEB reactions can offer the opportunity to develop strategies to control the kinetics of this deteriorative reaction.

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