Color Formation in Dehydrated Modified Whey Powder Systems As Affected by Compression and T_g

Leila Burin,*[,†] Kirsi Jouppila,[‡] Yrjö Roos,[§] Jarno Kansikas,[#] and María del Pilar Buera[†,⊥]

Department of Food Technology, P.O. Box 27, University of Helsinki, Latokartanonkaari 7, FIN-00014 Helsinki, Finland; Department of Food Science and Technology, University College, Cork, Ireland; and Department of Chemistry, P.O. Box 55, University of Helsinki, FIN-00014 Helsinki, Finland

Whey powders have attracted attention for use in the food industry. The Maillard reaction is a major deteriorative factor in the storage of these and other dairy food products.The objective of the present work was to further study the Maillard reaction as related to the physical structure of the matrix, either porous or mechanically compressed, or to storage above the T_g of anhydrous whey systems. Sweet whey (W), reduced minerals whey (WRM), whey protein isolate (WPI), and whey protein concentrate (WPC) were stored in ovens at selected temperatures. Colorimetric measurements were performed with a spectrocolorimeter, thermal analyses (TGA) by means of a thermobalance, and glass transition temperature studies by DSC. The browning order in the vials and in the compressed systems followed the order W > WRM> WPC > WPI. k_{w2}, the slope of the second linear segment of the TGA curve, was related to the loss of water due to nonenzymatic browning (NEB). Browning development was in good relationship with this loss of weight. In the glassy state, the compressed systems developed higher rates of browning and weight loss (assigned to NEB reactions) than the porous systems. Reaction rates in both (porous and compressed) systems became similar as ($T - T_g$) increased.

Keywords: *Browning; whey powder; glass transition; compression*

INTRODUCTION

Dried whey powders, a major byproduct of cheese manufacturing, have attracted attention for use in the food industry due to their low price, versatility with respect to functionality, and nutritive value as a food ingredient (Kim et al., 1981). Whey proteins are well-known for their high nutritional value and versatile functional properties in food products. During recent decades, interest has grown in the nutritional efficacy of whey proteins in infant formula and in dietetic and health foods (de Wit, 1998). At the 1997 International Whey Conference, the presentations highlighted the multitude of valuable components present in whey, methods for their commercial isolation, approaches to maximizing their various functionalities, and their wide application in the food, medical, biotechnology, veterinary, chemical, and plastics industries. Particulary, the 1997 conference reflected the growing interest of the food industry in functional foods—those that promote health beyond providing basic nutrition (Smithers and Copeland, 1998). Both nutritional value and functional properties of whey proteins are governed by the composition and structure of the protein and influenced by the prevailing environmental conditions, prior treatments, and processing conditions. With increasing uses, there has arisen a practical need to predict the shelf life of whey powders.

It is well recognized that nonenzymatic browning (NEB) through the Maillard reaction is a major deteriorative factor in the storage of dehydrated dairy food products (Choi et al., 1949; Labuza and Saltmarch, 1981; Roos, 1996).

Molecular mobility in the amorphous region of the solid is important in determining its physical stability (Hancock et al., 1995), and the nature of the amorphous solid will change depending upon the difference between the temperature (T) and the glass transition temperature (T_g). In glassy systems, molecular mobility and diffusion are claimed to be virtually nonexistent (Levine and Slade, 1986; Slade, 1989). There has been consideration of the great significance of changes in physical state of the solid having an impact on the diffusion and access of water into products (Parker and Ring, 1995). The presentation of the product (pellets or powders) during storage can thus be very important from the standpoint of quality loss and could result in the acceleration of deteriorative reactions in hygroscopic whey products (Kim et al., 1981), limiting its shelf life and the food products into which they are incorporated as a principal ingredient.

The objective of the present work was to further study the Maillard reaction as related to the physical structure of the matrix, either porous or mechanically compressed, or to storage above the T_g of anhydrous whey systems.

MATERIALS AND METHODS

Preparation of Model Systems. Amorphous matrices were obtained by freeze-drying solutions containing 20% (w/

* Address correspondence to this author at the Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, (1428) Buenos Aires, Argentina [telephone (5411) 4576-3397; fax (5411) 4576-3366; e-mail leis@di.fcen.uba.ar].

† Universidad de Buenos Aires.

‡ Department of Food Technology, University of Helsinki.

§ University College, Cork.

Department of Chemistry, University of Helsinki.

⊥ Member of Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina.

10.1021/jf000240y CCC: $19.00
Published on Web 10/27/2000

Table 1. Composition of the Commercial Powder Systems

	system			
	W	RMW	WPC	WPI
lactose, %	73.7	76.5	4.0	0.8
protein, %	12.3	12.6	81.5	95.0
minerals, %	8.0	4.9	4.0	3.7

w) of each of the following powders, industrially produced by spray-drying: sweet dairy whey, TEKLAC (W); reduced minerals whey, NUTRITEK 250 (RMW); and whey protein isolate, DARITEK NBV (WPI), all from Foremost Farms, WI; whey protein concentrate, 80% protein (WPC), from Land O'Lakes, Inc., Food Ingredients Division, St. Paul, MN. The compositions of the commercial powder systems are shown in Table 1. The powders also contained 1−4% fat and 4−5% water.

Aliquots of 1 mL of each model solution were placed in 4 mL vials and immediately frozen using liquid nitrogen. A Stokes freeze-dryer model 21 (F. J. Stokes Co., Equipment Division, Pennsalt Chemical Corp., Philadelphia, PA) was used, which operated at a −40 °C condenser plate temperature and a chamber pressure of <100 μmHg during 48 h.

The compressed samples were prepared in the form of pellets prior to incubation. After freeze-drying, the samples were pulverized in a mortar and further dehydrated for 1 week over $MgClO_4$ to facilitate the compressing of the systems in order to avoid stickiness of the powders toward the lead disks during the preparation of the pellet. Approximately 0.15 mg of each sample was used in a Beckman KBr die K-13 (Beckman Instruments, Inc., Irvine, CA) and compressed at a pressure of 50 kg/cm^2 under vacuum during 5 s. The sample size was 1.3 cm diameter × 0.2 mm heigth. The freeze-dried powders in vials (porous) and the pellet systems were placed over $MgClO_4$ for "zero" moisture content, at 26 °C, during 10 days.

Heat Treatment. The model systems were stored and placed open in forced-air convection ovens at selected temperatures (between 80 and 170 °C). At suitable intervals two samples were removed for colorimetric measurements, as described below.

Color Determination. The porous or pellet systems were reconstituted with 2 or 1 mL of distilled water, respectively, and 0.6 mL of this suspension was used for color determination.

Colorimetric measurements were performed with a HunterLab 5100 Color Difference Meter (Hunter Associates Laboratory) using a 1.6-cm-diameter aperture and an illumination mode that illuminated the aperture area from the bottom of the sample. A white background was placed on the top of the sample holder. The CIE tristimulus values, *X*, *Y*, *Z*, were obtained directly from the instrument.

For the model systems color functions were calculated for illuminant *D* and a 10° observer. Browning index [BR = $100(x - 0.31)/0.172$, where $x = X/(X + Y + Z)$], was found to be an adequate measure of nonenzymatic browning reactions (Buera and Resnik, 1990). The average of five determinations was reported for each sample.

Thermal Analyses. *Thermogravimetric Analyses.* The systems were measured using a Mettler Toledo TA 8000 system equipped with a TGA850 thermobalance (TB). The instrument was calibrated with the melting point of indium and aluminum. The inert gas used was N_2. The dehydrated porous and pellet systems were placed in aluminum 100 μL open pans. The typical sample mass was ∼40 mg for the pellet samples and ∼15 mg for the porous samples. Reproducibility of the pellet sample data was achieved through the random disposition of small pieces of the pellet in the aluminum pan. Duplicate or triplicate samples were placed in the TB cell, and isothermal thermogravimetric scans at various temperatures were performed. The scan program used was as follows: 30 °C for 1 min, heating at maximum rate (220 °C/min) to several selected final temperatures (from 80 to 190 °C), and holding at this temperature for different times, according to the holding temperature. An empty aluminum pan was used as a reference in a blank curve in all experiments.

Table 2. T_g Obtained for the Model Systems Dehydrated over $MgClO_4$

system	T_g, °C	system	T_g, °C
W porous	83.1	W pellet	82.2
RMW porous	79.6	RMW pellet	85.3

Glass Transition Temperatures. Glass transition temperatures of the different model systems were determined by differential scanning calorimetry (DSC) using a Mettler TA 4000 system with TC 15 TA processor, DSC 30 measuring cell, and STAR^e thermal analysis system version 3.1 software (Mettler Toledo AG).

The instrument was calibrated using *n*-pentane (mp −129.7 °C; $\Delta H = 116.7$ J/g), *n*-hexane (mp −94.0 °C; $\Delta H = 151.8$ J/g), mercury (mp −38.8 °C; $\Delta H = 11.4$ J/g), distilled water (mp 0.0 °C; $\Delta H = 345.5$ J/g), gallium (mp 29.8 °C; $\Delta H = 80$ J/g), and indium (mp 156.6 °C; $\Delta H = 28.45$ J/g). All measurements were made at a scanning rate of 5 °C/min using hermetically sealed aluminum pans of 40 μL of inner volume. Triplicate samples in open pans were stored in vacuum desiccators over saturated salt solutions. After 10 days, the pans were hermetically sealed and scanned from at least 40 °C below the onset of the glass transition temperature to at least 40 °C above the onset of the glass transition temperature. An immediate rescan was run for each sample to verify the endothermic baseline shift associated with the glass transition. The onset temperature of the change in heat capacity was considered to be the glass transition temperature. An empty aluminum pan was used as reference.

RESULTS AND DISCUSSION

Table 2 shows the T_g values obtained for the W and RMW pellet and porous systems exposed to the desiccant agent ($MgClO_4$). The T_g values of the anhydrous W and RMW systems were between 80 and 85 °C. Jouppila and Roos (1994) and Karmas et al. (1992) reported T_g values for dehydrated skim milk and lactose-based model systems, respectively, that were almost the same as those in the present study. The T_g values of the anhydrous systems determined by DSC are similar to that of lactose, which is their main component. It can be suggested that either lactose governs the T_g values of the whey systems (Jouppila and Roos, 1994) for skim milk powders or lactose and carbohydrates may exist in different phases, as immiscible compounds, with only the carbohydrate-rich phase being detectable by DSC. Kalichevsky et al. (1993a,b) demonstrated that the addition of sugars to casein did not reduce its T_g, although the preparation and composition of the model systems are different from that performed in the present work. It is noted that porous and compressed systems had similar T_g values, thus negating any humidity uptake during the preparation of the compressed systems. Experimental difficulties were found to determine the T_g values for WPI and WPC systems, and this could be atributed to the composition of these systems, which are mainly constituted by proteins for which glass transition values could be hard to determine. Le Meste and Duckworth (1988) could not determine the T_g of caseinate. There are no T_g values of whey proteins systems in the literature, but Matveev et al. (1997) reported calculated T_g values for whey proteins of 153 °C, and their calculation, based on the additive contribution method, is in good agreement with the experimental data for some food proteins. The experimentally determined T_g values and those calculated by Matveev et al. (1997) were taken into account to select experimental conditions.

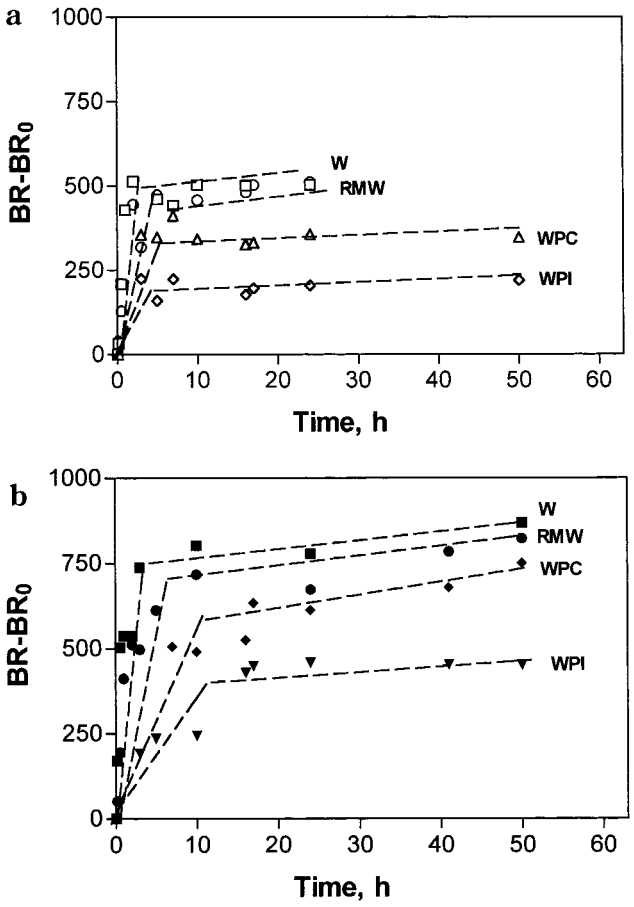

Figure 1. Browning development ($BR - BR_0$) in anhydrous samples of (a) porous and (b) pellet systems, as measured at 130 °C, as a function of time.

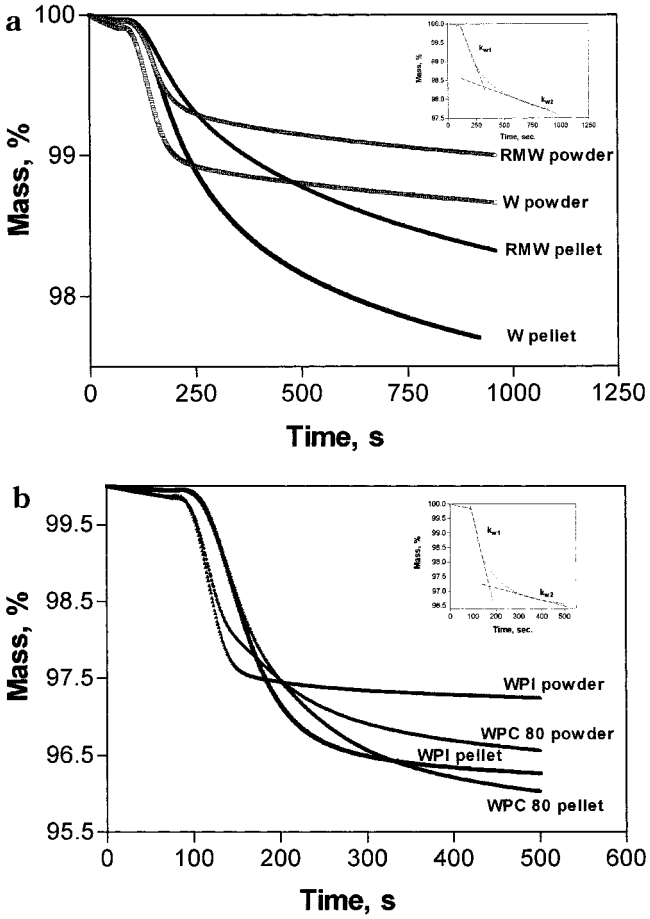

Figure 2. TGA traces recorded of the anhydrous porous and pellet systems at (a) 110 °C for W and RMW and (b) 170 °C for WPI and WPC, as holding temperatures. Insets shows k_{w1} and k_{w2}.

The color development was analyzed in porous and compressed samples at 80, 110, 130, and 170 °C. At all temperatures the initial linear increase for the browning development region leveled off at a plateau after a certain extent of reaction, as shown in Figure 1 for 130 °C. Parts a and b of Figure 1 show browning development as a function of time for the W, RMW, WPI, and WPC porous and pellet systems, respectively. Browning development was observed to be faster in the compressed systems than in the porous systems. This observation could be explained as a consequence of the closer proximity of the reactants in a compressed matrix for the NEB reactions to be developed in these anhydrous systems. It could be suggested that, as soon as browning starts, there is formation of water. This water remains entrapped, does not diffuse out very quickly, and could catalyze the reaction. Similar results have been reported by Buera and Karel (1995), who compared the color formation in compressed and uncompressed PVP samples at $a_w = 0.5$ and 0.6. k_{BR}, the slope of the initial linear segment of the curves, was calculated for all of the storage temperatures analyzed (80, 110, 130, and 170 °C). At a given storage temperature, the browning rate order in the porous and pellet systems followed the order W > RMW > WPC > WPI. This order in the rate of browning development could be related to the reducing sugar concentration present in these systems, as shown in Table 1. The lower color extent in the RMW systems, as compared to the W systems, could be due to its reduced content of minerals, mainly phosphate salts (54% less than the W systems). It is well-known that the presence of certain salts and buffers has an accelerating effect on Maillard reactions in solutions (Saunders and Jervis, 1966; Bell, 1997). The results of the present study indicated that salts may play also important effects in anhydrous systems. Although the T_g values of WPI and WPC could not be experimentally determined, they have probably higher T_g values than the W and RMW systems, as previously discussed, and their lower browning rate could be attributed to this fact. However, it is interesting to note that the W and RMW systems have similar T_g values (Table 1) but that their browning rate behaviors were different and more dependent on their reducing sugar content.

Parts a and b of Figure 2 show typical TGA traces normalized to sample size for the anhydrous porous and pellet systems of W and RMW, at 110 °C as holding temperature, and for WPI and WPC, at 170 °C as holding temperature, respectively. The first descendent part of these curves can be attributed to the loss of the remaining water in the systems. The slope of these curves is indicated as k_{w1} in the insets and represents the rate of weight loss. Although exposed to desiccant, the systems retains water, as observed by Bonelli et al. (1997) for anhydrous sugars at 100 °C. Figure 3a,b shows the k_{w1} values obtained for the different pellet and porous systems. It can be observed that the rates of weight loss for the compressed systems were lower than that of the porous systems. This is in agreement with Kalichevsky et al. (1993a,b), who showed that the rate of weight loss of heating amylopectin stored at 85%

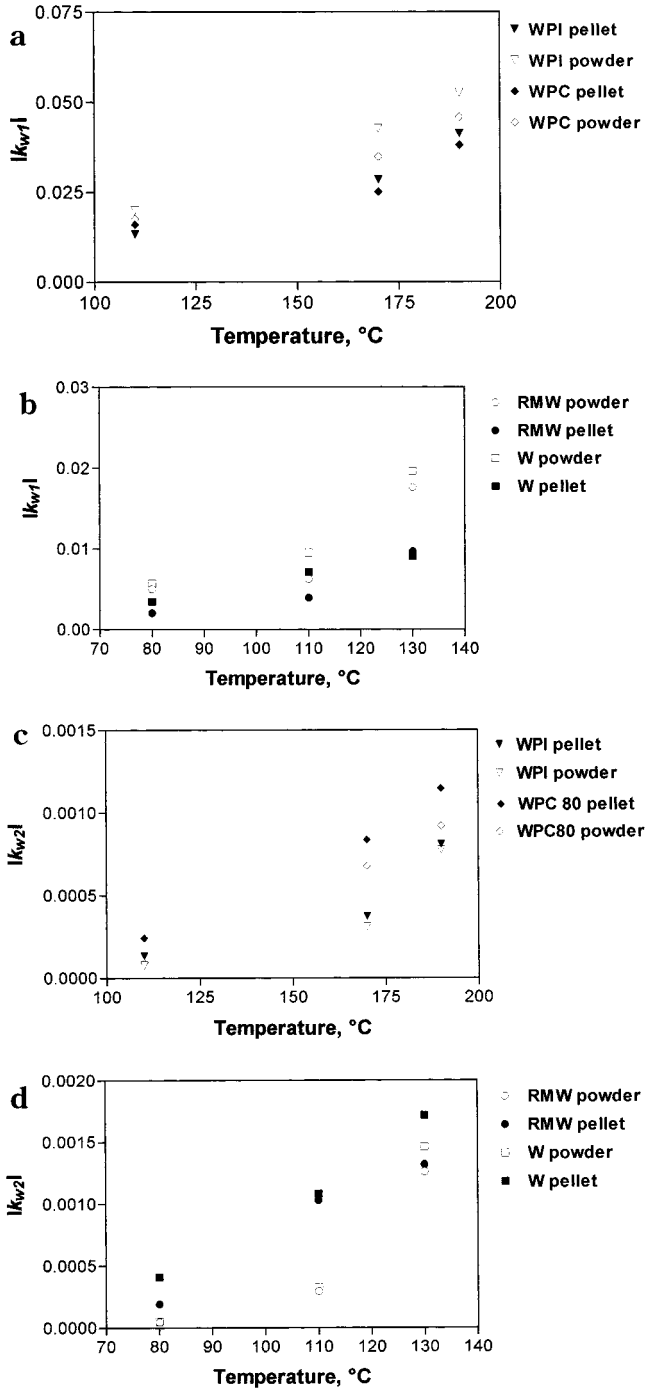

Figure 3. k_{w1} values as a function of holding temperature for (a) WPI and WPC pellet and porous systems and (b) W and RMW pellet and porous systems; k_{w2} values as a function of holding temperature for (c) WPI and WPC pellet and porous systems and (d) W and RMW pellet and porous systems.

relative humidity was faster in powder systems than in compressed form, as measured with TGA. The second part of the curves in Figure 2 can be attributed to the loss of water occurring during Maillard reactions under low moisture conditions as shown in the typical scheme developed by Hodge (1953). To have an estimation of the rate of weight loss due to Maillard reactions, the slope of the second linear segment of the TGA curve (k_{w2}, dashed line in the insets of the Figure 2) was calculated for all holding temperatures studied (80, 110, 130, 170, and 190 °C) and defined as k_{w2}. As shown in Figure 3c,d, the k_{w2} values for the compressed systems were higher than those of porous systems.

Table 3. E_a Values Obtained from the Arrhenius Plots for Browning Development and Loss of Weight (Assigned to NEB Reactions) of the Pellet and Porous Systems[a]

	E_{aBR} (kJ/mol)	E_{aw2} (kJ/mol)
WPI pellet	43	30
WPI porous	42	39
WPC pellet	24	28
WPC porous	16	43
W pellet		33
W porous	179	77
RMW pellet	148	46
RMW porous	176	75

[a] Estimated relative error for the E_a values was 20%.

Activation energies (E_a) were calculated through the Arrenhius relationship for browning development rates (k_{BR}) and for weight loss rate (k_{w2}) and are reported in Table 3. The E_a values estimated for browning development for the high protein content systems (WPI and WPC) were lower than typical values, usually ranging from 80 to 130 kJ/mol, in dairy low-moisture systems (Flink, 1974; Labuza and Saltmarch, 1981; Franzen et al., 1990; Roos and Himberg, 1994), but they were in the range of those reported by Karmas et al. (1992) for nonenzymatic browning of low-moisture lactose/CMC/trehalose and PVP systems. These lower E_{aBR} values for the WPI and WPC reflect a less sensitive variation of k_{BR} with temperature changes on these high protein content systems. The E_a value for the W pellet system was not calculated because of its low coefficient of determination ($r^2 = 0.9110$) in the Arrehnius plot.

The correlation between both rate constants (k_{w2} and k_{BR}) is shown in Figure 4. As a general trend, the rate of browning development correlated with the rate of loss of weight in the early stages of the reaction (described as a loss of water due to Maillard reactions). The pellet systems with higher content of reducing sugars (W and RMW) developed a higher rate of color formation (k_{BR}) at the higher temperature than expected from their loss of weight and the data obtained at lower temperatures. It should also be mentioned that for the higher protein content systems, the same variation on temperature was reflected in small changes in k_{BR} and greater changes in k_{w2}, and this is an indication that the loss of water (k_{w2}) could be a more sensitive determination of the degree of reaction than browning development (k_{BR}). It could be proposed that k_{w2} is an early indicator of Maillard reaction, and, if so, the lower E_{aw2} observed as compared to E_{aBR} is in agreement with this observation. This was also observed by Eichner and Ciner-Doruk (1981), who found that E_a values for the Amadori compounds in tomato powder were significantly lower and considered them to be sensitive indicators of the heat impact of low-moisture foods.

The ratio $(k_{pellet} - k_{porous})/k_{pellet}$ was considered as an index of the influence of the initial degree of compression on the rate of browning development (k_{BR}) or of weight loss (k_{w2}) and was determined as a function of $(T - T_g)$ (Figure 5). When the reaction rates of porous systems are negligible, as compared to the compressed systems, the above-mentioned ratio (ordinate in Figure 5) becomes close to 1, and this is the case of systems of $(T - T_g) < 0$. Figure 5 also suggests that the initial compression of the sample is less important at high $(T - T_g)$, because the ratio tends to 0 as the initial porous systems collapses, due to storage at temperatures far above the T_g. The bulk density was similar to that of the compressed samples, as also observed by Buera and

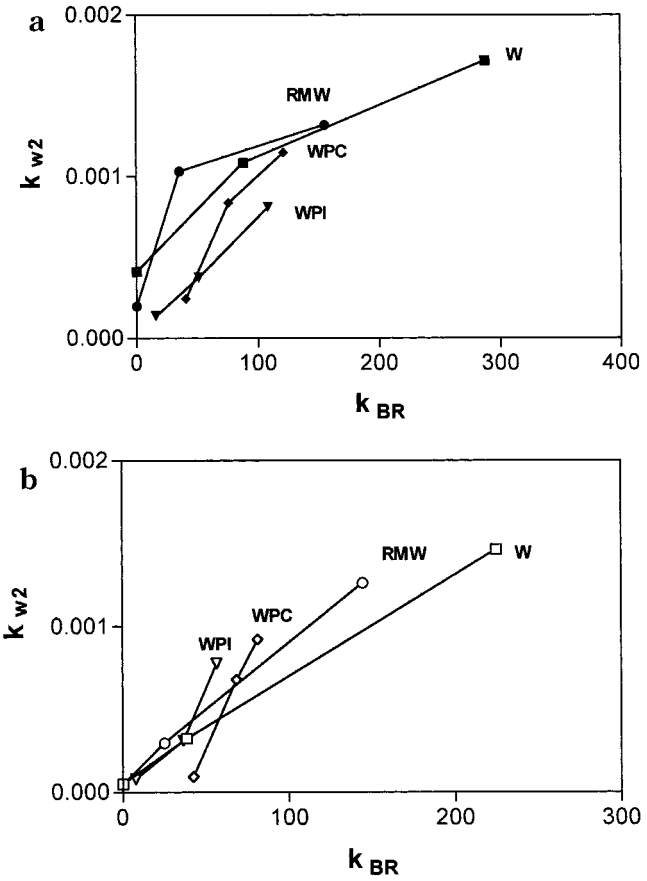

Figure 4. Relationship of the k_{BR} and k_{w2} values of (a) pellets (solid symbols) and (b) porous (open symbols) of W, RMW, WPI, and WPC systems.

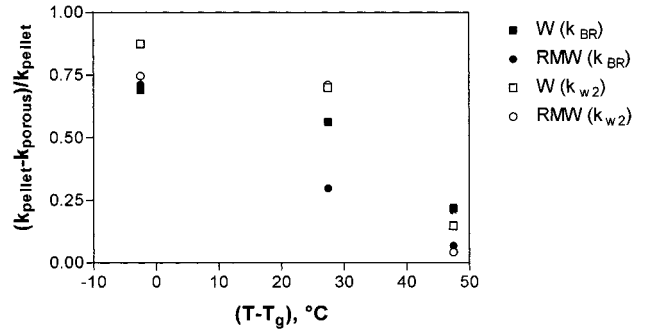

Figure 5. Ratio $(k_{pellet} - k_{porous})/k_{pellet}$ as a function of $(T - T_g)$, of the k_{BR} (solid symbols) and k_{w2} (open symbols) of the W and RMW systems.

Karel (1995), who compared color formation in compressed and uncompressed PVP samples.

In an anhydrous system, the occurrence of chemical reactions could be dependent on the restricted molecular mobility and the proximity of the reactants.

As was well established by Schebor et al. (1999), skim milk powder in the glassy state browned due to the high concentration of the reactant molecules (lactose and amino groups), facilitated by their proximity in the dehydrated systems. It was suggested that diffusion and rotational mobility in solid polymers below T_g might still occur through pre-existing holes (pores), due to the defects and porosity in the structure. Also, Kovaskii et al. (1978), Hori et al. (1986), and Roudaut et al. (1999a,b) detected relaxations below T_g, and attributed them to mobile "clusters", to "islands" of mobility, or to loosely packed regions of high entropy where localized reorientation can occur.

At the conditions of this study, below the macroscopic T_g there may be local heterogenities that allow diffusion and reaction. Therefore, if the reaction starts in local zones below the macroscopic T_g as determined by DSC, the water content around the reaction site increases, allowing further reaction to occur through further plasticization. Andronis and Zografi (1997) have shown that indomethacin in the amorphous form has a high degree of molecular mobility around its T_g as determined through dielectric measurements, and they stated that the relatively short time scales for molecular mobility in the region of T_g could explain the significant rate of crystallization of indomethacin from the amorphous state. Amorphous materials below T_g, especially immediately after their preparation, are characterized by much shorter relaxation times than simple extrapolation of the equilibrium relaxation times obtained above T_g would suggest. This behavior should be taken into account when processing and storage conditions for amorphous pharmaceuticals are selected so that their physical state and chemical stability can be optimazed (Andronis and Zografi, 1998).

The compositions of the anhydrous whey model systems, besides their physical characteristics, are important factors defining the stability toward browning development.

The rate of loss of weight at early stages of the reaction assigned to NEB reactions was a good indicator of the rate of color development over long periods of time.

In the glassy state, the compressed systems developed higher rates of browning and weight loss (assigned to NEB reactions) than the porous systems. Reaction rates in both (porous and compressed) systems became similar as $(T - T_g)$ increased. Due to collapse, the porous systems showed a behavior similar to that observed in the compressed systems.

ABBREVIATIONS USED

NEB, nonenzymatic browning; T, temperature; T_g, glass transition temperature; W, sweet dairy whey; RMW, reduced minerals whey; WPI, whey protein isolate; WPC, whey protein concentrate 80% protein; BR, browning index; TGA, thermogravimetric analyses; TB, thermobalance; DSC, differential scanning calorimetry; E_a, activation energy.

ACKNOWLEDGMENT

We are grateful to Dra. Mireille Perec for the use of the vaccum press.

LITERATURE CITED

Andronis, V.; Zografi, G. Molecular mobility of supercooled amorphous indomethacin, determinated by dynamic mechanical analysis. *Pharm. Res.* **1997**, *14* (4), 410−414.

Andronis, V.; Zografi, G. The molecular mobility of supercooled amorphous indomethacin as a function of temperature and relative humidity. *Pharm. Res.* **1998**, *15*, 835−842.

Bell, L. N. Maillard reaction as influenced by buffer type and concentration. *Food Chem.* **1997**, *59* (1), 143−147.

Bonelli, P.; Schebor, C.; Cukierman, A. L.; Buera, M. P.; Chirife, J. Residual moisture content as related to collapse of freeze-dried sugar matrices. *J. Food Sci.* **1997**, *4*, 693−695.

Buera, M. P.; Karel, M. Effect of physical changes on the rates of nonenzymic browning and related reactions. *Food Chem*. **1995**, *52*, 167−173.

Buera, M. P.; Resnik, S. L. Colorimetric measurements in a turbid medium: hydrolyzed concentrated cheese whey. *Farbe* **1990**, *35*, 268−272.

Choi, R.; Koncus, A.; O'Malley, C.; Fairbank, B. A proposed method for the determination of color of dried products of milk. *J. Dairy Sci.* **1949**, *32*, 580.

de Witt, J. N. Nutritional and functional characteristics of whey proteins in food products. *J. Dairy Sci.* **1998**, *81*, 597−608.

Eichner, K.; Ciner-Doruk, M. Early indication of the Maillard reaction by analyses of reaction intermediates and volatile decomposition products. *Prog. Educ. Nutr. Sci.* **1981**, *5*, 115−135.

Flink, J. Properties of the freeze-drying "scorch" temperature. *J. Food Sci*. **1974**, *39*, 1244−1246.

Franzen, K.; Singh, R.; Okos, M. Kinetics of nonenzymatic browning in dried skim milk. *J. Food Eng.* **1990**, *11*, 225−239.

Hancock, B.; Shamblin, S.; Zografi, G. Molecular mobility of amorphous pharmaceutical solids below their glass transition temperatures. *Pharm. Res.* **1995**, *12*, 799−805.

Hodge, J. E. Chemistry of browning reactions in model systems. *J. Agric. Food Chem*. **1953**, *1*, 928−933.

Hori, T.; Fujita, I.; Shimizu, T. Diffusion of disperse dyes into Nylon 6 above and below the glass transition temperature. J. S. D. C. **1986**, *102*, 181−185.

Jouppila, K.; Roos, Y. Glass transitions and crystallization in milk powders. *J. Dairy Sci.* **1994**, *77*, 2907−2915.

Kalichevsky, M.; Blanshard, J.; Marsh, R. D. L. Applications of mechanical spectroscopy to the study of glass biopolymers and related systems. In *The Glassy State of Foods*; Blanshard, J., Lillford, P., Eds.; Nottingham University Press: Nottingham, U.K., 1993a; pp 133−156.

Kalichevsky, M.; Blanshard, J.; Tokarczuk, P. Effect of water content and sugars on the glass transition of casein and sodium caseinate. *Int. J. Food Sci. Technol.* **1993b**, *28*, 139−151.

Karel, M.; Anglea, S.; Buera, M. P.; Karmas, R.; Levi, G.; Roos, Y. Stability-related transitions of amorphous foods. *Thermochim. Acta* **1994**, *246*, 149−269.

Karmas, R.; Buera, M. P.; Karel, M. Effect of glass transition on rates of nonenzymatic browning in food systems. *J. Agric. Food Chem*. **1992**, *40*, 873−879.

Kim, M.; Saltmarch, M.; Labuza, T. P. Non-enzymatic browning of hygroscopic whey powders in open versus sealed pouches. *J. Food Process. Preserv.* **1981**, *5*, 49−57.

Kovarskii, A.; Placek, J.; Szocs, F. Study of rotational mobility of stable nitroxide radicals in solid polymers. *Polymer* **1978**, *19*, 1137−1141.

Labuza, T.; Saltmarch, M. Kinetics of browning and protein quality loss in whey powders during steady state and nonsteady-state storage conditions. *J. Food Sci.* **1981**, *47* (1), 92−96.

Le Meste, M.; Duckworth, R. Effect of water content on the mobility of solute molecules and of protein side chains in caseinate preparations. *Int. J. Food Sci. Technol.* **1988**, *23*, 457−466.

Levine, H.; Slade, L. Polymer physicochemical approach to the study of commercial starch hydrolysis products. *Carbohydr. Polym*. **1986**, *6*, 213−244.

Matveev, Y.; Grinberg, V.; Sochava, I.; Tolstoguzov, V. Glass transition temperature of proteins. Calculation based on the additive contribution method and experimental data. *Food Hydrocolloids* **1997**, *11* (2), 125−133.

Parker, R.; Ring, S. Diffusion in maltose-water mixtures at temperatures close to the glass transition. *Carbohydr. Res.* **1995**, *273*, 147−155.

Roudaut, G.; Maglione, M.; van Dusschoten, D.; Le Meste, M. Molecular mobility in glassy bread: a multispectroscopy approach. *Cereal Chem*. **1999a**, *76* (1), 70−77.

Roudaut, G.; Maglione, M.; Le Meste, M. Relaxations below glass transition temperature in bread and its components. *Cereal Chem*. **1999b**, *76* (1), 78−81.

Roos, Y. In *Phase Transitions in Foods*; Academic Press: San Diego, CA, 1995.

Roos, Y.; Himberg, M. Nonenzymatic browning behavior, as related to glass transition, of a food model at chilling temperatures. *J. Agric. Food Chem*. **1994**, *42*, 893−898.

Roos, Y.; Jouppila, K.; Zielasko, B. Non-enzymatic browning-induced water plastification. Glass transition temperature depression and reaction kinetics determination using DSC. *J. Thermal Anal.* **1996**, *47*, 1437−1450.

Saunders, J.; Jervis, F. The role of buffer salts in non-enzymatic browning. *J. Sci. Food Agric.* **1966**, *17*, 245−251.

Schebor, C.; Buera, M. P.; Karel, M.; Chirife, J. Color formation due to non-enzymatic browning in amorphous, glassy, anhydrous, model systems. *Food Chem*. **1999**, *65*, 427−432.

Slade, L.; Levine, H.; Finley, J. Protein-water interactions: water as a plasticizer of gluten and other protein polymers. In *Protein Quality and the Effects of Processing*; Dixon Phillips, R., Finley, J., Eds.; Dekker: New York, 1989; pp 9−124.

Smithers, G.; Copeland, A. 1997 International whey conference. *Trends Food Sci. Technol.* **1998**, *9*, 119−123.

Received for review February 25, 2000. Revised manuscript received July 13, 2000. Accepted July 19, 2000. This study received financial support from the Academy of Finland (Projects 35764 and 44382) and from the Commission of the European Communities, Agriculture and Fisheries (FAIR) specific RTD program, CT96-1085, Enhancement of Quality of Food and Related Systems by Control of Molecular Mobility. The paper does not necessarily reflect the Commission's views and in no way anticipates the its future policy in this area. We also acknowledge financial support from Universidad de Buenos Aires (IX05) (Secretaría de Ciencia y Técnica), Agencia Nacional de Promoción Científica y Tecnológica, and from the International Foundation for Science (Sweden). This work is part of CYTED Project XI.13.

JF000240Y