Color Stability of Edible Coatings During Prolonged Storage

T.A. TREZZA AND J.M. KROCHTA

ABSTRACT: The yellowing rates of edible coatings were determined at 23, 40, and 55 °C at 75% relative humidity (RH). Whey protein isolate (WPI) coatings had lower yellowing rates than whey protein concentrate (WPC) and the same rates as shellac coatings. Hydroxypropyl methylcellulose (HPMC) coatings had the lowest yellowing rates. Zein coatings became less yellow during storage; however, their color was still pronounced. Activation energies and Q_{10} values for the yellowing of whey protein coatings were similar to those previously reported for the browning of whey powder. The results indicate that WPI coatings can be used in place of shellac coatings when low-color development is desired. WPC coatings can be used to tailor color development of a food.

Keywords: edible coatings, shellac, shelf-life, whey proteins, yellowing kinetics

Introduction

EDIBLE COATINGS ON PANNED CONFECTIONERY PRODUCTS add gloss, provide scuff resistance, act as oxygen, moisture or oil barriers, and prevent sticking of pieces in a package (Jordan 1992; Anonymous 1996). The most commonly used coatings consist of shellac or corn zein applied from ethanol-based solutions (Boutin 1997; Isganitis 1988). A significant problem with the use of shellac and zein coatings is that their solvent systems are composed mostly of volatile organic compounds (VOCs). VOCs have become strictly regulated because of their impact on air and water quality (Sawyer 1997). The government of the United States has mandated that confectionery manufacturers must gradually lower the amount of VOCs they emit into the atmosphere, to an ultimate goal of 0 discharge (Glesecke 1998). The regulation of VOC emissions has forced confectionery manufacturers to seek alternatives to shellac and other VOC-containing coatings (Anonymous 1998). In the pharmaceutical industry, water-based hydroxypropyl methylcellulose (HPMC) coatings have been successfully used as coatings for solid dosage forms (tablets) (Anonymous 1988; Banker and Peck 1981). Water-based whey protein coatings have the potential to replace shellac and corn zein as coatings on some panned confectionery products.

Whey protein isolate (WPI) coatings are excellent oxygen and aroma barriers (Miller and others 1998; Maté and Krochta 1996; McHugh and Krochta 1994). However, the color stability of these coatings is an issue. It is well known that milk protein powders can undergo Maillard reactions during storage, causing yellowing and loss of nutritional value of the product (Coultate 1988). Yellowing is attributed to the reaction of protein lysine groups with reducing sugars such as lactose or glucose (Coultate 1988). Labuza and Saltmarch (1981) found that the rate of brown pigment formation in whey powders increased as storage temperature and water activity (a_w) increased from 25 to 45 °C and 0.33 to 0.65, respectively. Heat curing of WPI films at 60, 70, and 80 °C for up to 48 h qualitatively increased film yellowing (Miller and others 1997). Whey protein concentrates (WPCs) have greater lipid and lactose contents than WPI. The lipid and lactose of WPC coatings might lead to a high degree color change during prolonged storage; however, lower cost of WPC make it an attractive alternative to WPI. To effectively use whey protein coatings, their color stability as compared to current commercial coatings should be known. Our objectives were to compare the yellowing rates of commercial coatings to those of experimental whey protein coatings, determine the effect of temperature on the rates of color change of these coatings, and calculate the kinetic parameters necessary for predicting color change of coatings during prolonged storage.

Materials and Methods

Coating Solution Preparation

Whey Protein Coatings. Ten percent whey protein coating solutions were made by mixing WPI (Bipro, Davisco Intl., LeSuer, Minn., U.S.A.) or WPC (AMP 800, AMPC Inc., Ames, Iowa, U.S.A.) powder in distilled water, denaturing the protein by heating the liquids for 20 min at 90 °C, and cooling in an ice bath to 25 °C with constant agitation. Solutions were then equilibrated to room temperature, at which point glycerol (USP/FCC, Fisher Scientific, Fairlawn, N.J., U.S.A.) was added as a plasticizer to a level of 1.5 g protein powder / g of glycerol, on a dry solids basis. Dry powder composition for WPI was 5.3% moisture, 93% protein, < 0.01% fat, < 0.1% lactose, and 1.6% ash; while, WPC composition was 5.5% moisture, 80% protein, 5.7% fat, 3.9% lactose, and 4.9% ash. Analyses were performed by Silliker/DFL Labs (Modesto, Calif., U.S.A.) and the UC Davis Division of Agriculture and Natural Resources (DANR) analytical laboratory. WPC formulations were opaque, pale yellow dispersions. WPI formed translucent, slightly yellow solutions.

HPMC. Five percent (wt/wt) solutions of HPMC (Methocel E5 Premium, Dow Chemical Co., Midland, Mich., U.S.A.) were prepared according to the manufacturer's instructions. The process consisted of dispersing HPMC powder into $^1/_3$ of the total required amount of water at 85 °C, followed by gentle stirring until the powder was wetted and a consistent dispersion was obtained. The remaining $^2/_3$ of water was then added and the dispersion was mixed until it became a clear solution. The solution was then removed from the heat and mixed until it equilibrated to room temperature. Finally, glycerol was added to a 5:1 (wt/wt) ratio of HPMC to glycerol, on a dry solids basis.

Shellac and Zein. Twenty percent (wt/wt) solutions of bleached, de-waxed shellac (Type R-49, MBZ Group, Attleboro, Mass., U.S.A.) or corn zein (FC 4000, Freeman Industries, Tuckahoe, N.Y., U.S.A.) were prepared by dissolving the powders in 95% ethanol. Next, glycerol was added to attain a 9:1 (wt/wt) ratio of shellac or zein to glycerol.

Casting of Coatings

Prior to casting, all coating formulations were degassed under vacuum until no evidence of bubbles remained (Shellhammer and Krochta 1997). Using a Bird-type applicator (Paul N. Gardner Co., Inc., Pompano Beach, Fla., U.S.A.), liquids were spread on 2" × 4.5" plates of matte, white acrylic (TAP Plastics, Sacramento, Calif., U.S.A.). Coatings were then dried for 22 h at ambient conditions, which ranged from 22 to 26 °C and 47 to 52% relative humidity (RH). Dry coatings were about 25 µm thick. White casting surfaces were used because the yellowness is determined as the deviation from whiteness (ASTM 1995a).

Storage Conditions and Color Measurement

Coatings were stored in desiccators (Catalog number 08-642-230, Fisher Scientific, Fairlawn, N.J., U.S.A.) which were held in ovens (IsoTemp, Fisher Scientific, Fairlawn, N.J., U.S.A.) at 40 and 55 °C. For 23 °C storage, coatings were held in desiccators in a controlled temperature room. RH was held constant at 75% inside each desiccator by the use of saturated sodium chloride (ASTM 1995b). To ensure uniform conditions at the surface of each coating, fans were placed inside each desiccator. The fans produced a minimum airflow of 152 $\mathrm{ft/min^{-1}}$ (McHugh and others 1993). An RH of 75% was chosen because, in general, the maximum rate of Maillard browning occurs when the a_w is in the range of 0.6 to 0.8 (Hall 1991). Loncin and others (1968) found that the maximum yellowing rate of dried milk powder occurred when the a_w of the powder ranged from 0.6 to 0.7.

A Hunter LabScan colorimeter (Hunterlab, Reston, Va., U.S.A.) was used to measure the color of the coatings. The instrument parameters used were a Mode of 0/45, a 2° Observer, a D65 (sodium) illuminant, a port size of 0.25 inches, and an area view of 0.25 inches. L, a, b values were averaged from 3 readings across each 2" × 4.5" coating. The yellowness index (YI) values of coatings were calculated according to ASTM method D1925 (ASTM 1995).

L, a, b measurements were taken every 3 d for 3 wk, then monthly for 11 mo at 23 °C, and every 3 d for 4.5 wk at 40 and 55 °C. The frequency of measurements was roughly determined from an equation given by Hall (1991), based on Q_{10} values published by Labuza and Saltmarch (1981). Because coatings at 23 °C yellowed slowly, less frequent measurements were possible. The measurements at 40 and 55 °C were stopped after $4^1/_2$ wk because after this point, the changes in YI were not linear with time.

Determination of Kinetic Parameters

Rate constants (YI increase/mo) were calculated from the slopes of curves of YI plotted against storage time using a 0-order kinetic model (Tinoco and others 1995). The slope of each line was determined using the general linear regression model (Ott 1988). A 0-order model gives the most conservative estimates of the yellowing rate. Activation energy was calculated according to the well-known Arrhenius model (Laidler and Meiser 1982; Labuza 1984). In this model, the rate constant of a reaction is related to the absolute temperature by the equation (Laidler and Meiser 1982):

$$k = Ae^{-Ea/RT} \qquad (1)$$

where k is the rate constant (YI/time), T is the absolute temperature (K), A is a constant characteristic of the system (YI/time), E_a is the activation energy ($\mathrm{J \cdot mol^{-1}}$), and R is the gas constant (8.314 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$). The E_a is the minimum amount of energy a molecule must possess in order for a reaction to occur (Belitz and Grosch 1987). The activation energy is found by plotting the log of the rate constant as a function of the inverse of the absolute temperature. If a straight line is found, the slope of the line yields $-E_a/R$. Next, Q_{10} values were determined from the equation (Belitz and Grosch 1987)

$$Q_{10} = \exp\,(10E_a/RT^2) \qquad (2)$$

The Q_{10} is the increase in the rate of a reaction for every 10 °C increase in temperature (Belitz and Grosch 1987). The Q_{10} value gives a relative measure of the temperature dependence of a chemical reaction.

Experimental Design

A completely randomized design was used (Ott 1988). The order of the preparation of coating solutions, casting of coatings, and color measurements were randomized. At each coating-temperature combination, 3 independent film coating formulations were prepared. From each of these formulations, duplicate coatings were cast. Coated acrylic plates were removed from storage, color was measured, and the plates returned to storage within 30 min at each sampling session. Coatings were kept in the absence of light at all times, except during the measurement and transfer periods.

Statistical analyses were performed using analysis of variance (AOV) for yellowing rate or YI. The Fisher LSD multiple comparison procedure was used to determine differences between specific means. StatView® software (Version 4.5, Abacus Concepts, Inc., Berkeley, Calif., U.S.A.), at level of significance of 1%, was used for both the AOV and the Fisher LSD procedures. A level of significance of 1% gives greater safety from finding that 2 means are different when they may not truly be different (O'Mahoney 1986). The Fisher LSD is the most powerful of the commonly used multiple comparison tests (O'Mahoney 1986).

Results and Discussion

Yellowing Rates

The yellowing rates of edible coatings at 75% RH were generally in the order HPMC < WPI = shellac < WPC (Table 1). Zein coatings became less yellow during storage; however, the initial and final yellow colors were greater than those of the other 4 coatings (Table 2). For this reason, zein coatings were not included in the AOV or Fisher LSD tests for yellowing rate. WPC coatings yellowed at a faster rate than shellac or WPI coatings ($p < 0.01$). The YI values of HPMC coatings did not change after 11.7 mo at 23 °C ($p > 0.03$); while, the same values for shellac, WPI and WPC coatings increased ($p < 0.01$). WPI and shellac coatings yellowed at the same rate at 23 and 55 °C ($p < 0.01$). Because of their higher lactose contents, WPC coatings yellowed at a faster rate than did WPI coatings at all 3 temperatures tested.

WPI, WPC and shellac coatings showed pseudo 0-order yellowing kinetics at 23, 40, and 55 °C. Figure 1 presents results for WPC kinetics; however, data for WPI and shellac were qualitatively similar. A line with a coefficient of determination (r^2) of greater than 0.7 is considered an acceptable fit (O'Mahoney 1986; Ott 1988). All r^2 values for WPI, WPC and shellac YI-versus-time plots were greater than 0.90. Other authors have found that browning in dairy systems fit a 0-order kinetic model (Bertelli and others 1996; Patel and others 1996; Labuza and Saltmarch 1981). In the current study the reaction is called pseudo-0 order because, although high r^2 values were obtained, YI values at longer periods of storage at 40 and 55 °C began to deviate from linearity. This means that the actual reaction mechanism may have been a complex order or, that the mechanism of the yellowing reaction may have changed at elevated temperatures or after

Table 1—Mean (± one standard deviation) yellowing rates (YI/month) of edible coatings stored at three temperatures.

Coating	23 °C	40 °C	55 °C
HPMC	$0.00^{a} \pm 0.00$	$0.00^{1} \pm 0.00$	$1.20^{\grave{a}} \pm 0.15$
WPI	$0.29^{b} \pm 0.022$	$1.81^{1} \pm 0.28$	$18.8^{*} \pm 1.6$
Shellac	$0.32^{b} \pm 0.026$	$5.72^{2} \pm 0.32$	$23.5^{*} \pm 1.4$
WPC	$0.98^{c} \pm 0.078$	$6.38^{2} \pm 0.90$	43.6 ± 8.9

Means are compared only within each temperature. Means with the same letter, number or symbol are not different ($p > 0.01$).

Table 2—Mean YI values of edible coatings (± 1 standard deviation) at day zero and after 11.7 m of storage at 23 °C and 75% RH.

Coating	YI at zero months	YI at 11.7 months
HPMC	$8.1^{a} \pm 0.38$	$7.3^{1} \pm 0.15$
WPI	$5.8^{a} \pm 0.75$	$8.5^{1} \pm 0.72$
Shellac	$8.1^{a} \pm 0.92$	$11.9^{2} \pm 1.15$
WPC	$12.2^{b} \pm 2.38$	$22.4^{3} \pm 3.61$
Zein	$37.0^{c} \pm 1.42$	$25.7^{3} \pm 1.23$

Means were compared only within each time point. Means with the same letter or number are not different ($p > 0.01$).

Table 3—Activation Energies (E_a), Q_{10} values, Arrhenius Pre-exponential factors (A) and coefficients of determination (r^2) values for the yellowing of edible coatings

Coating material	Q_{10}	E_a (kJ•mol^{-1})	A (YI/month)	r^2
WPI	4.2	104	4.9×10^{17}	0.976
WPC	3.7	95	5.2×10^{16}	0.991
shellac	4.5	109	7.3×10^{18}	0.989
whey powder	5.3	122	1.4×10^{18}	0.985
milk powder tablets	4.8	115	2.6×10^{14}	> 0.98

Q_{10} values were determined at 23 °C using equation 2.

the limiting reagent supply was exhausted. WPC, WPI and shellac coatings showed different, but linear rates of yellowing at 23 °C (Fig. 2). During the 1st few months of storage at 23 °C, the yellowness indexes of WPC, WPI and shellac coatings did not change significantly. Upon further storage, YI values increased at a linear rate. Zein coating YI data could not be fitted to a 0-, 1st- or 2nd-order kinetic model at any of the temperatures tested.

Initial and Final Yellow Index

During storage at 23 °C for almost 1 y, HPMC coatings did not yellow at the temperatures tested (Table 2). HPMC, WPI, and shellac coatings initially had the same YI ($p > 0.01$). After 12 mo of storage at 23 °C, shellac YI values were greater than those of WPI but lower than those of WPC ($p < 0.01$) (Table 2). The initial YI of WPC coatings was greater than those of WPI, HPMC, or shellac coatings ($p < 0.01$). A portion of the yellow color of WPC was due to the yellowness of its milkfat. A typical anhydrous milkfat (Level Valley Dairy Company, West Bend, Wis., U.S.A.) had a YI of 51.

Kinetic Parameters

The Q_{10} and activation energy values of whey protein coatings were found to be similar to those determined for milk powders (Table 3). In Table 3, values for WPI, WPC and shellac coatings were from storage at 75% RH. Whey powder values were calculated from data given by Labuza and Saltmarch (1981) for storage at 65% RH. The milk powder tablet Q_{10} value was calculated from N'soukpoe'-Kossi and others (1988) with no specified storage RH. The E_a value found for the WPI coatings suggested that Maillard browning was responsible for color change in these coatings. In general, activation energies for nonenzymatic (Maillard) browning reactions are in the range of 105 to 126 kJ·mol^{-1} (Hall 1991). Other common degradation reactions in foods, such as lipid oxidation and enzymatic hydrolysis have much lower activation energies of about 42 and 84 kJ·mol^{-1}, respectively (Taokis and Labuza 1996). The somewhat lower E_a of WPC indicates that the yellowing of WPC coatings may have been partially due to the oxidation of the milkfat in the coatings. Also, from at 23 and 40 °C, the relative change in yellowing rates for WPI and WPC coatings was constant. However, the relative yellowing rates of these same

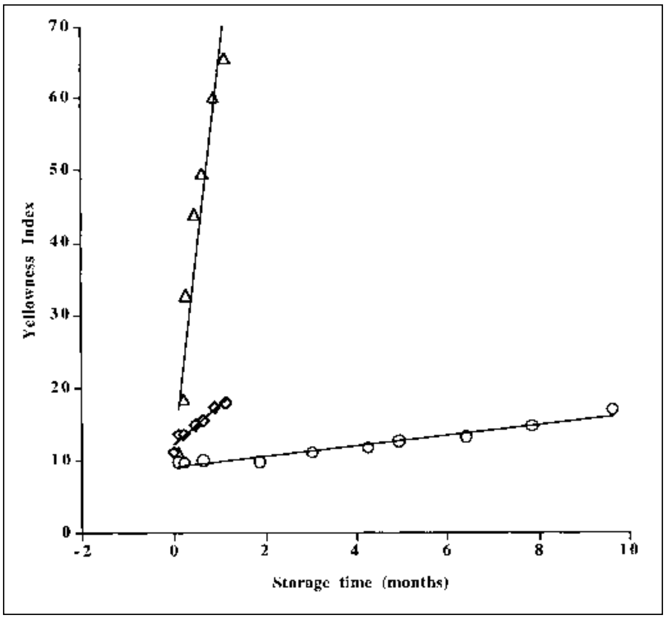

Figure 1—Yellowness Index versus storage time curves for a typical WPC coating showing linear regression lines obtained at 23 °C (○, r^2 = 0.955), 40 °C (◇, r^2 = 0.924) and 55 °C (△, r^2 = 0.923).

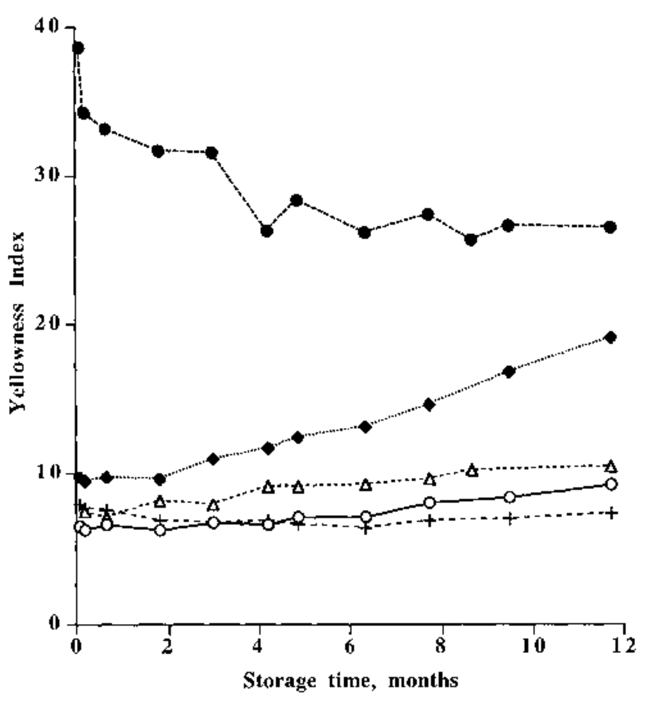

Figure 2—Typical Yellowness Index vs time curves for edible coatings stored at 23 °C. Key: + = HPMC, ○ = WPI, △ = shellac, ◆ = WPC, ● = zein

coatings were different as the temperature increased from 40 to 55 °C. This is probably due to a changing of the mechanism of the yellowing at 55 °C and is another source of variability of the E_a and A values found for WPI and WPC coatings in this study. Since shellac does not contain appreciable amounts of reducing sugars or protein, its yellowing was not due to Maillard browning. The yellowing of shellac was probably due to self-polymerization reactions (Bose and others 1963). This paper is the 1st known report of the kinetic parameters of yellowing for shellac coatings.

The decrease in yellowing of the zein coatings was probably due to the degradation of xanthophyll pigments due to combinations of oxygen, light and temperature (von Elbe and Schwartz 1996). Zeaxanthin is a xanthophyll pigment found in corn (Belitz and Grosch 1987). Lastly, decolorized zein with a much less pronounced yellow color is now commercially available; however, it is not yet widely employed as a food coating agent.

Conclusions

WHEN STORED AT 23 °C, WPI COATINGS HAVE COLOR STABILITY equal to HPMC coatings and better than shellac coatings. Due to their lactose content, WPC coatings yellowed more quickly than WPI coatings. The milk fat content of WPC also contributes to its yellow color. Zein coatings had a greater yellow color than HPMC, WPC, shellac, or WPI coatings. WPI coatings can be used as an alternate coating to shellac or HPMC when low color change is desired. WPC coatings have potential applications when color development is desired.

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Author Trezza was with the Dept. of Food Science and Technology, Univ. of California, Davis and is currently affilitated with Frito Lay, Inc. Plano TX 75024. Author Krochta is with the Dept. of Food Science and Technology, Univ. of California, Davis 95616. Direct inquiries to author Krochta (E-mail: jmkrochta@ucdavis.edu).