Physicochemical Properties and Storage Stability of Lutein Microcapsules Prepared with Maltodextrins and Sucrose by Spray Drying

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Abstract: The purpose of this study was to determine the physicochemical properties of lutein microcapsules. Nine types of lutein microcapsules were prepared in order to determine their encapsulation efficiency and yield. Results show that lutein microcapsules with maltodextrin M040 and sucrose at the weight ratio of 3:1 (designated as M040:1) had the highest encapsulation efficiency (90.1%) among the lutein microcapsules, as well as a higher encapsulation yield (90.4%). The onset glass transition temperatures (T_{gi}) and the surface dents of the lutein microcapsules decreased as the dextrose equivalent value of maltodextrin and the weight ratio of sucrose increased. Enthalpy relaxation experiments were conducted for the lutein microcapsules M040:1 at (T_{gi} − 5) , (T_{gi} − 10), and (T_{gi} − 15) °C, and the obtained data were fitted to the Kohlrausch–Williams–Watts model. Results show that the mean relaxation time (τ) (316 h) of M040:1 lutein microcapsules aged at (T_{gi} − 15) °C was greater than the τ (161 h) at (T_{gi} − 10) °C and τ (60.5 h) at (T_{gi} − 5) °C. Effects of temperature and oxygen transmission rates for package film on the storage stability of M040: 1 lutein microcapsules were also investigated. Findings show that rates of lutein degradation and color change increased by an order of magnitude as storage temperature (4 to 97 °C) and oxygen transmission rate of the package film (0.018 to 62.8 cc/m² day) increased. These results suggest that lutein is highly unstable and susceptible to thermal and oxidative degradations. However, microencapsulation with appropriate wall materials of higher relaxation time and high oxygen barrier packaging can increase the storage life.

Keywords: DSC, enthalpy relaxation, glass transition, KWW, oxygen transmission

Practical Application: Enthalpy relaxation, as determined by differential scanning calorimetry, can characterize the molecular mobility of amorphous carbohydrates. Microencapsulation, with appropriate wall materials of low molecular mobility and high oxygen barrier packaging, can increase the shelf-life of lutein.

Introduction

Carotenoids are an important class of natural pigments that are common in many fruits and vegetables (Lessin and others 1997; Sass-Kiss and others 2005). Carotenoids in the human diet can act as antioxidants through a free radical mechanism by quenching singlet oxygen and other oxidizing species (Li and others 2010; Skibsted 2012). This results in the termination of free radical chain reactions and the prevention of cellular oxidative damage (Rodriguez-Amaya 2010; Li and others 2013). Lutein, as a natural asymmetric dihydroxy-carotenoid (xanthophyll), can be esterified with fatty acids in plant cells because of the hydroxyl group at each ionone ring to produce mono- and diacylated derivatives. Therefore, lutein is found either in its free form in microalgae, or esterified as a monoester or diester in plants (Piccaglia and others

1998; Breithaupt and others 2002; Li and others 2002). Like other carotenoids, lutein cannot be synthesized by humans, and must be absorbed from diets and supplements. However, humans are capable of modifying some of carotenoids to certain degree (Semba and Dagnelie 2003). Foods rich in lutein include dark green vegetables, fruits, egg yolk, maize, and lutein extracts from marigold flower petals (Piccaglia and others 1998; Sommerburg and others 1998; Handelman and others 1999).

Although lutein has no pro-vitamin A activity, it displays some biological activities that have attracted attention in terms of human health. Several epidemiological studies show that adequate intake and high serum levels of lutein are associated with a lower risk of degenerative diseases, such as age-related macular degeneration (AMD; Granado and others 2003; Krinsky and others 2003; Carpentier and others 2009), cataracts (Arnal and others 2009), lung cancer (Voorrips and others 2002), breast cancer (Park and others 1998), and cardiovascular disease (Granado and others 2003). Lutein also has been shown to protect against light-induced skin damage, especially from ultraviolet light (Roberts and others 2009). In the human eye, lutein filters high-energy wavelengths of visible light and acts as an antioxidant to protect against the formation of reactive oxygen species and subsequent free radicals (Krinsky and others 2003; Roberts and others 2009). Because of these human health benefits, lutein is often added to foods as a colorant and nutrient.

The long chain of conjugated carbon–carbon double bonds within lutein's structure is susceptible to oxygen, heat, and light degradation reactions. Temperature, oxygen, and light during processing and storage can affect degradation of lutein (Tang and Chen 2000; Lin and Chen 2005). Therefore, stability is an important factor when considering lutein as a colorant, antioxidant and bioactive ingredient in foods and pharmaceutical products; hence, products containing lutein should be protected from physical and chemical damages.

Lutein's stability can be significantly improved with microencapsulation technology. Qv and others (2011) prepared lutein microcapsules by complex coacervation and found that encapsulated lutein improved storage stability by reducing the effects of light, humidity, and heat. Wang and others (2012) produced lutein microcapsules with a porous starch and gelatin mixture as the wall materials by spray drying. Results show that this greatly improved the stability of the lutein microcapsule against heat, pH, light, and oxygen.

Microencapsulation is an attractive technique for converting liquid food ingredients to stable, free-flowing powders, which are easier to handle and incorporate into food systems (Madene and others 2006; Xiao and others 2011; Gharsallaoui and others 2012). Microencapsulated powders prepared by spray drying usually exist in an amorphous state. Rates of physicochemical degradation reactions in amorphous powders can be dependent on molecular mobility and relaxation time (Byrn and others 2001; Yoshioka and Aso 2007; Luthra and others 2008). Few studies have investigated the effects of molecular mobility and physicochemical changes on amorphous food systems.

The objectives of this research were to (1) characterize the physicochemical properties of spray-dried lutein microcapsules with maltodextrin or the mixture of maltodextrin and sucrose, (2) determine enthalpy relaxation kinetics of spray-dried lutein microcapsules, and (3) correlate the rates of lutein degradation with enthalpy relaxation data under low or high storage temperatures and oxygen barriers.

Materials and Methods

Materials and reagents

Maltodextrins with different dextrose equivalent (DE) values (M040, DE 6.1; M100, DE 11.0; and M180, DE 17.0) were supplied by the Grain Processing Corp. (Muscatine, Iowa, U.S.A.). Food grade sucrose was purchased from Fisher Scientific (Pittsburgh, Pa., U.S.A.). Lutein crystals with a purity of 90% were purchased from Xi An Rong Sheng Biotechnology Co., Ltd. (Xi'an, China). Food grade soybean phospholipid (85% of phosphatidylcholine) was gifted by American Lecithin Company Inc. (Oxford, Conn., U.S.A.). All other chemicals and reagents used in this study were of analytical grade.

Lutein microcapsules preparation by spray drying

Maltodextrins (M040, DE 6.1; M100, DE 11.0; and M180, DE 17.0) and sucrose were weighed at different weight ratios (3:0, 3:1, and 3:3), mixed, and then dissolved into distilled water with mechanical stirring to prepare 9 different aqueous solutions (1 L), with 20% solids concentration at 23 °C. Lutein crystals (5.72 g) were dissolved into pure ethanol by controlling the concentration of lutein at about 0.2 g/mL, and emulsified with 2.6 g soybean phospholipid in each aqueous solution to prepare a coarse emulsion during mechanical stirring at 300 rpm. Then, the obtained 9 coarse emulsions were individually homogenized for 15 min at 5000 rpm with a Model 17105 Omni-Mixer Homogenizer (Omni International, Kennesaw, GA, U.S.A.) at 23 °C.

Spray drying of the obtained emulsions was carried out using a pilot scale spray dryer (Model LAB-S1, Anhydro, Denmark). The obtained emulsions were fed into the spray dryer with a peristaltic pump in the following conditions: inlet air temperature, 185 ± 1 °C; outlet air temperature, 85 ± 1 °C; average feeding rate, 33.50 mL/min; rotating speed of the centrifugal atomizer, 50,000 rpm. Spray-dried lutein microcapsules were collected in the bottle at the bottom of the cyclone separator. Finally, 9 lutein microcapsules were labeled as M040:0, M040:1, and M040:3 for Maltodextrin M040 and sucrose at the weight ratio of 3:0, 3:1, and 3:3; M100:0, M100:1, and M100:3 for Maltodextrin M100 and sucrose at the weight ratio of 3:0, 3:1, and 3:3; and M180:0, M180:1, and M180:3 for Maltodextrin M180 and sucrose at the weight ratio of 3:0, 3:1, and 3:3. The lutein microcapsules were kept in zippered bags and placed in glass bottles wrapped with aluminum foil. They were then stored in a freezer at −20 °C until further analysis.

Quantification of lutein

Surface lutein was quantified by washing 20 g of lutein microcapsules with 150 mL of hexane for 3 times (Loksuwan 2007). After mechanical stirred at 100 rpm for 5 min, the mixture solution was filtered with No. 4 filtration paper under a vacuum. Next, the collected solid phase was dried in an oven at 35 °C under a vacuum for 12 h. After removing the surface lutein, the lutein in the core of the microcapsule was determined by the method detailed later.

Next, 20 mg of lutein microcapsule was dissolved into 1 mL of distilled water kept in an ultrasound bath, and mixed with 9 mL of pure ethanol (Loksuwan 2007; Wang and others 2012). After the mixture was filtered with a filtration membrane (0.45 μm, EMD Millipore, Billerica, MA, U.S.A.), the absorbance value of the obtained clear solution was determined with a Model Ultrospec 4000 UV/Vis spectrophotometer (Pharmacia Biotech, Buckinghamshire, England) at a wavelength of 445 nm with 90% ethanol aqueous solution as the blank. Finally, the lutein content of the samples was calculated and all lutein content analysis was performed in triplicate.

The encapsulation efficiency (EE) of the lutein microcapsules was the ratio of the mass of lutein encapsulated (in the core) into the microcapsule (W_{Inner}) to the total mass of lutein distributed inside and at the surface of the microcapsule (W_{Total}):

$$EE\ (\%) = \frac{W_{Inner}}{W_{Total}} \times 100\% \qquad (1)$$

Encapsulation yields (EY) of the microcapsules were the mass ratio of the total solids in microcapsule (W_a) to the initial solids in the emulsion (W_b):

$$EY\ (\%) = \frac{W_a}{W_b} \times 100\% \qquad (2)$$

Physicochemical properties of lutein microcapsules

The water activities (a_w) of the lutein microcapsules were measured at 25 °C with a Model CX-2 vapor sorption analyzer (Aqua Lab, Decagon Devices, Pullman, Wash., U.S.A.). The water contents of the lutein microcapsules prepared using spray drying were measured with a Model HB43-S halogen moisture analyzer

(Mettler Toledo, Switzerland). An environmental scanning electronic microscope (ESEM; Quanta 200 ESEM, FEI Co., Hillsboro, Oreg., U.S.A.) was used to obtain micrographs of lutein microcapsules. Before ESEM analysis, the lutein microcapsules were sprinkled on one side of 2-sided adhesive tape for the measurement of their morphology and the estimation of particle size. The lutein microcapsules were measured under a low vacuum mode of 130 Pa and a voltage of 20 kV in the ESEM system. Particle size distribution analysis of the lutein microcapsules was carried out using a particle size analyzer (HELOS KR, Sympatec GmbH, Clausthal-Zellerfeld, Germany; Syamaladevi and others 2010). The median particle size (X_{50}) was calculated as the equivalent particle size corresponding to 50% of the cumulative distribution function of the lutein microcapsule. The color of the lutein microcapsules was determined by using a portable Minolta colorimeter (Minolta Camera, Japan). The color was expressed as the values of L^*, a^*, and b^*. All of the measurements were performed in triplicate.

Experiments on glass transition temperatures (onset T_{gi}, midpoint T_{gm}, and endpoint T_{ge}) determination and enthalpy relaxation were performed with a model Q2000 modulated differential scanning calorimeter (MDSC; TA Instruments, U.S.A.). For glass transition temperature measurements, lutein microcapsules (10–15 mg) were scanned from 25 to 150 °C at a rate of 5 °C/min. Three temperatures of 5, 10, and 15 °C below T_{gi} were selected for the physical aging/enthalpy relaxation experiments (Syamaladevi and others 2010; Syamaladevi and others 2012). All determinations were performed in triplicate.

Kinetics of enthalpy relaxation

The Kohlrausch–Williams–Watts (KWW) equation is the most extensively used equation for describing the kinetics of enthalpy relaxation in glassy materials during physical aging (Syamaladevi and others 2010; Syamaladevi and others 2012). The KWW equation is as follows:

$$\varphi_t = \exp\left(\frac{-t}{\tau}\right)^{\beta} \qquad (3)$$

where φ_t is the extent of enthalpy relaxation during time t. φ_t is the estimation method for the amount of unreleased enthalpy at the specific aging temperature. The τ value obtained from the KWW equation is the mean molecular relaxation time of the whole amorphous system, and β is the nonexponential parameter. A large τ value indicates a slow molecular mobility and a small free volume increase in the amorphous glassy materials system. The β value, which ranges between 0 and 1, is inversely related to the width of enthalpy relaxation time distribution. The smaller the value of β, the greater the distribution of enthalpy relaxation with aging time. The extent of enthalpy relaxation (φ_t) during aging time t is also expressed as follows:

$$\varphi_t = 1 - \frac{\Delta H_{relax}}{\Delta H_{\infty}} = \exp\left(\frac{-t}{\tau}\right)^{\beta} \qquad (4)$$

$$\Delta H_{\infty} = \Delta C_p(T_g - T_a) \qquad (5)$$

where ΔH_{∞} is the total enthalpy available for relaxation and ΔH_{relax} is the enthalpy relaxation during the aging time (t). ΔC_p is the heat capacity changing at the glass transition temperature (T_g) and aging temperature (T_a). The value of ΔH_{relax} is determined by calculating the enthalpy relaxation peak area by drawing a linear

baseline to the enthalpy endotherm in the nonreversible heat flow curve of the MDSC thermogram. After the aging experiment, the enthalpy relaxation data of the selected lutein microcapsule M040:1 was fitted with the KWW equation to obtain the values of τ and β using STATISTICA^{TM} version 5.0 Computer Program.

Storage stability

For stability experiments, the microcapsules with surface lutein removed were used as the surface lutein will directly be exposed to oxygen and will degrade quickly irrespective particle matrix conditions. Each 5 g of the lutein microcapsule was vacuum-packed (0.1 bar) within 3 different types of multilayer polymeric pouches: 91319 (Shields Bag & Printing Co., Yakima, Wash., U.S.A.), N#15 (Kuraray America Inc., Houston, Tex., U.S.A.) and laminated with aluminum foil (AFL, Printpack Inc., Atlanta, Ga., U.S.A.). The AFL pouches of high oxygen barrier were used as a control packaging in storage stability experiments. The 91319 multilayer films consisted of nylon and polyethylene, the N#15 films were based on bi-axially oriented polyamide film, and the AFL pouches were made with polyester, aluminum foil, nylon, and polypropylene. The thicknesses of the 91319, N#15, and AFL films were 110, 100, and 130 μm, respectively. Oxygen transmission rates (OTR) of the 91319, N#15, and AFL multiple layer pouches were determined with an Ox-Tran 2/21 instrument (Mocon Co., Minneapolis, Minn., U.S.A.) at 23 °C and 50% relative humidity (RH), according to the ASTM standard method D3985 (Sablani and others 2009), and the OTRs were 62.8, 0.034 and 0.018 cc/m^2 day, respectively. The length and width of these pouches were 10 and 8 cm, respectively. The temperatures 4, 23, 37, (T_{gi} − 15), (T_{gi} − 5), (T_{gi} + 5), and (T_{gi} + 15) °C were selected for storage stability experiments. During the storage, microcapsules were analyzed for changes in color and lutein content. Lutein retention (LR$_s$) of the sample during storage was calculated according to the equation mentioned as follows:

$$\text{LR}_s\ (\%) = \frac{C_a}{C_b} \times 100\% \qquad (6)$$

where C_b and C_a, respectively, represent the lutein content of the sample before and after storage.

Results and Discussion

Physicochemical properties of lutein microcapsules

The water activity (a_w) and water content of the spray-dried lutein microcapsules ranged from 0.057 to 0.126 and 2.13 to 2.99 g/100 g powder, respectively (Table 1). The a_w of microcapsules increased as the weight ratio of sucrose increased. For lutein microcapsules prepared with M040 and M100, the water content of the microcapsules decreased as the weight ratio of sucrose increased. The water content of microcapsules depended on their water activity, the weight fraction of sucrose in the microcapsules, and the water sorption behavior of sucrose and maltodextrin.

EE varied from 69.1% to 90.1% among the lutein microcapsules. The microcapsules M040:1 prepared with maltodextrin M040 and sucrose at a weight ratio of 3:1 had the highest EE. The EY decreased as the DE value of maltodextrin and the fraction ratio of sucrose increased. Microcapsules M040:0 prepared with maltodextrin M040 had the highest EY of 92.9%. As DE increased, the molecular weight of maltodextrin decreased, resulting in a lower glass transition and stickiness temperatures. The sticky point of materials occurs normally 10 to 20 °C above onset of glass transition temperature (Roos and Karel 1991). An increasing weight

Table 1–Physical properties of lutein microcapsules prepared using spray drying.

Microcapsules	EE (%)	EY (%)	Water content (g H_2O/100 g powder)	a_w	X_{50} (μm)
M040:0	87.7 ± 0.37[a]	92.9 ± 0.26	2.99 ± 0.07[a]	0.088 ± 0.002[e]	18.7 ± 0.17[a]
M040:1	90.7 ± 1.16[a]	90.3 ± 1.07	2.32 ± 0.10[c]	0.102 ± 0.002[c]	17.9 ± 0.16[c]
M040:3	87.3 ± 1.67[a]	85.3 ± 0.95	2.13 ± 0.06[e]	0.106 ± 0.002[b]	18.3 ± 0.13[b]
M100:0	77.4 ± 3.30[cd]	92.0 ± 0.69	2.99 ± 0.06[a]	0.087 ± 0.002[e]	18.5 ± 0.03[b]
M100:1	74.6 ± 2.12[d]	90.0 ± 0.37	2.53 ± 0.03[b]	0.096 ± 0.002[d]	18.3 ± 0.11[b]
M100:3	74.1 ± 0.78[d]	81.2 ± 1.29	2.17 ± 0.06[e]	0.100 ± 0.002[cd]	17.9 ± 0.10[c]
M180:0	82.3 ± 1.86[b]	88.1 ± 1.03	2.20 ± 0.06[de]	0.057 ± 0.002[g]	16.4 ± 0.14[d]
M180:1	79.8 ± 3.80[bc]	88.1 ± 0.91	2.15 ± 0.08[e]	0.068 ± 0.003[f]	16.3 ± 0.09[d]
M180:3	87.2 ± 2.36[a]	73.8 ± 1.35	2.30 ± 0.03[dc]	0.126 ± 0.003[a]	16.0 ± 0.13[e]

The values followed by different superscript letters within each column were significantly different ($P < 0.05$). EE, encapsulation efficiency; EY, encapsulation yield; a_w, water activity; X_{50}, median particle size.

fraction of sucrose in microcapsules also lowered the stickiness temperature. Therefore, the EY of the lutein microcapsules decreased due to its adherence to the surface of the spray dryer, as both the DE value of maltodextrin and the weight fraction of sucrose increased.

Wang and others (2012) reported that EE and EY ranged from 62.0% to 92.6% and from 76.0% to 92.6%, respectively, for lutein microcapsules encapsulated with a porous starch and gelatin mixture. Shu and others (2006) reported that the EE and EY of the lycopene microcapsules prepared with a wall system consisting of gelatin and sucrose ranged from 12.1% to 82.2% and 69.1% to 91.5%, respectively. Kha and others (2010) reported that the EE of the total carotenoids microcapsules encapsulated with maltodextrin (DE 12) varied from 55.6% to 85.0%.

Lutein microcapsules exhibited an outer topography, characterized by spherical shapes with some degree of surface dents. They also showed a high degree of integrity, with no observable cracks or pores on the outer surface (Figure 1). The surface dents of the lutein microcapsule decreased as the DE value of maltodextrin and the mass fraction of sucrose into the wall materials increased.
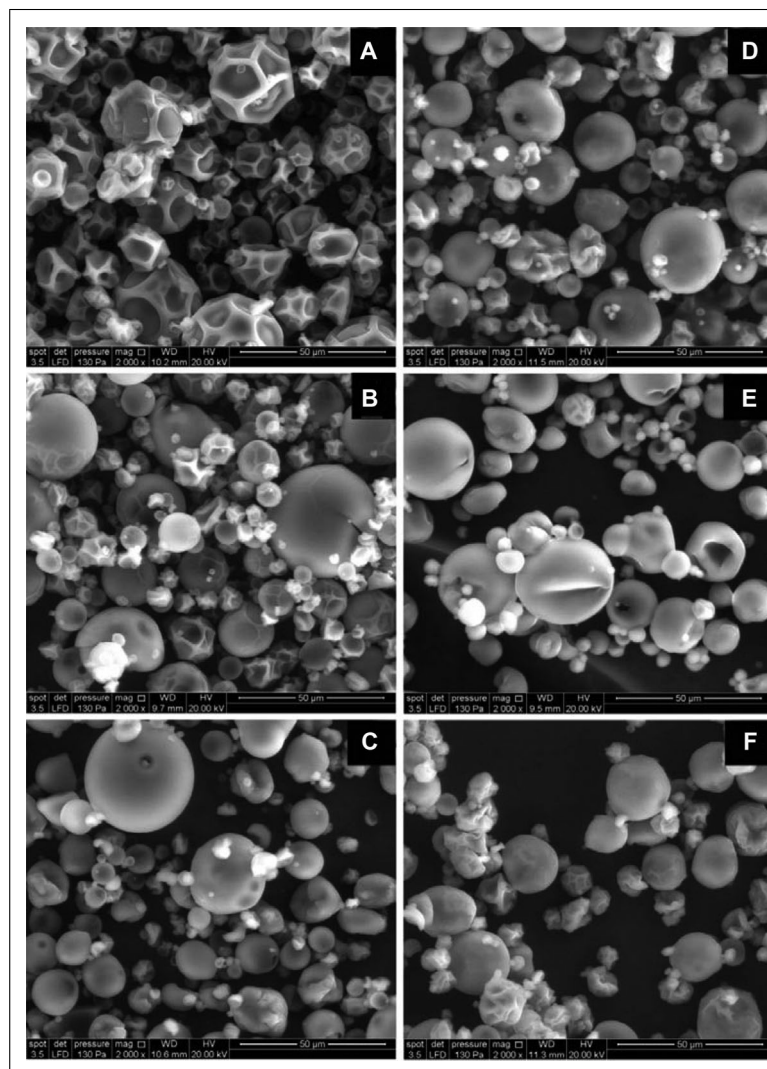

Figure 1–Environmental scanning electron microscopy micrographs of selected lutein microcapsules (A) M040:0, (B) M100:0, (C) M180:0, (D) M040:1, (E) M040:3, and (F) M040:1 (washed with hexane to remove the surface lutein).

Table 2–Onset glass transition temperature, transition width, and color parameters of the lutein microcapsules.

Microcapsules	T_{gi} (°C)	$(T_{ge} - T_{gi})$ (°C)	L^*	a^*	b^*
M040:0	NA	NA	64.9 ± 0.89[a]	−2.16 ± 0.11[d]	29.8 ± 0.51[f]
M040:1	82.4 ± 0.36[b]	23.0 ± 1.69[bc]	60.6 ± 0.36[def]	−1.42 ± 0.01[a]	36.6 ± 0.17[cd]
M040:3	65.1 ± 0.16[d]	20.3 ± 2.66[cd]	62.0 ± 0.95[cd]	−1.36 ± 0.10[a]	40.0 ± 0.56[b]
M100:0	NA	NA	64.2 ± 0.59[ab]	−2.28 ± 0.06[d]	32.1 ± 0.25[e]
M100:1	76.1 ± 2.00[c]	25.9 ± 1.45[b]	60.0 ± 0.48[ef]	−2.80 ± 0.08[e]	31.8 ± 0.23[e]
M100:3	59.2 ± 0.28[e]	18.6 ± 0.29[cd]	64.1 ± 0.89[ab]	−1.99 ± 0.04[c]	37.4 ± 0.50[c]
M180:0	106.1 ± 1.70[a]	18.4 ± 3.39[cd]	62.6 ± 1.71[bc]	−2.21 ± 0.09[d]	36.2 ± 0.86[d]
M180:1	73.5 ± 2.96[c]	32.4 ± 3.59[a]	59.3 ± 1.70[f]	−1.40 ± 0.06[a]	41.1 ± 1.08[a]
M180:3	56.7 ± 0.28[e]	17.3 ± 0.93[d]	61.3 ± 0.90[cde]	−1.78 ± 0.01[b]	39.0 ± 0.56[b]

Values represented the mean ± standard deviation, and values that were followed by different letters within each column were significantly different ($P < 0.05$). T_{gi}, onset glass transition temperature; $(T_{ge} - T_{gi})$, glass transition temperature width; NA, not available.

Higher DE values of maltodextrin and a higher the mass fraction of sucrose resulted in higher sphericity and smoother outer surface. Micrographs show that the removal of surface lutein (lutein microcapsule M040:1WH) created no substantial differences in particle morphology (Figure 1D and F).

Particle size distribution analysis of the microcapsules indicates that the particle size distribution curves were unimodal, and the particles were homogeneous, without caking or aggregation. The median particle size (X_{50}, Table 1) of the lutein microcapsules varied from 16.0 to 18.7 μm, because the viscosities of the emulsions prepared with maltodextrin and sucrose decreased as the DE value of maltodextrin and the mass fraction of sucrose increased. The particle size cumulative distribution curves of the lutein microcapsules M040:1 and M040:1WH (washed with hexane) were found to be similar. The values of X_{10}, X_{50}, X_{90}, and X_{99} were also close to each other (Figure 2). Particle analysis also indicated that the hexane wash of surface lutein did not affect the particle size distribution.

The glass transition temperatures of the lutein microcapsules decreased as the DE value of maltodextrin and the mass fraction of sucrose increased. The molecular weight distribution of the

wall materials could be changed by adjusting the DE value of maltodextrin and the mass fraction of sucrose. The glass transition temperatures of the lutein microcapsules highly correlated with the molecular weight distribution of the wall materials (Table 2). The increasing DE value of maltodextrin and the mass fraction of sucrose showed an increasing trend in color parameter b^*, but did not show a definite trend in L^* and a^* of microcapsules (Table 2).

Enthalpy relaxation kinetics

Because of higher encapsulation efficiency and yield, the microcapsules M040:1 was selected for the enthalpy relaxation and storage stability experiments. The T_{gi} value of the lutein microcapsules M040:1 aged at different temperatures and times increased by about 2 to 8 °C. However, no significant difference was observed between the glass transition temperature width ($T_{ge} - T_{gi}$) of the un-aged and aged M040:1 lutein microcapsules (Table 3).

During aging, the conformation changes of glassy polymer decreased the free volume and molecular mobility, resulting in a higher glass transition temperature (Chung and Lim 2003a). The T_g value of aged glassy polymer may decrease with increasing the aging temperature because of the greater structural and molecular

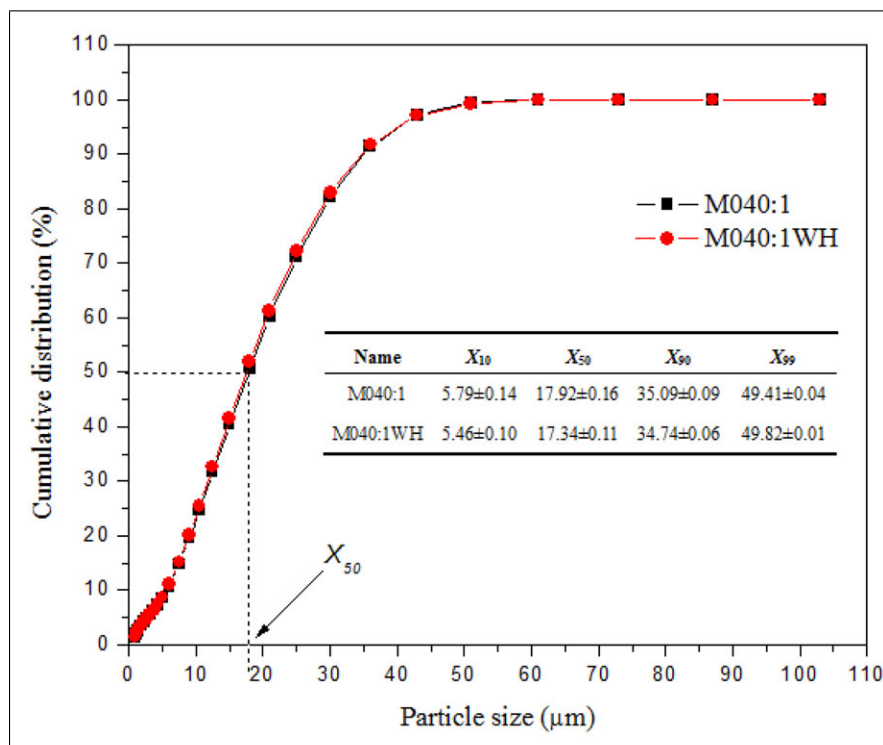<div style="writing-mode: vertical-rl">E: Food Engineering & Materials Science</div>

Figure 2–Particle size cumulative distribution of the lutein microcapsules before (M040:1) and after (M040:1WH) washing with hexane to remove the surface lutein.

Name	X_{10}	X_{50}	X_{90}	X_{99}
M040:1	5.79±0.14	17.92±0.16	35.09±0.09	49.41±0.04
M040:1WH	5.46±0.10	17.34±0.11	34.74±0.06	49.82±0.01

Table 3–Onset glass transition temperature (T_{gi}) and transition width of the M040:1 lutein microcapsules aged at different temperatures and times.

	(T_{gi} − 5)		(T_{gi} − 10)		(T_{gi} − 15)	
Time (h)	T_{gi} (°C)	($T_{ge} - T_{gi}$) (°C)	T_{gi} (°C)	($T_{ge} - T_{gi}$) (°C)	T_{gi} (°C)	($T_{ge} - T_{gi}$) (°C)
6	84.4 ± 1.31[b]	22.9 ± 2.02[b]	84.9 ± 0.07[ab]	22.7 ± 4.91[ab]	86.0 ± 1.75[ab]	24.1 ± 0.76[a]
12	86.4 ± 0.75[ab]	21.8 ± 1.20[b]	84.5 ± 0.40[b]	22.8 ± 0.02[ab]	85.4 ± 4.45[ab]	23.8 ± 5.70[a]
24	88.7 ± 3.10[a]	21.7 ± 0.91[b]	85.6 ± 0.43[ab]	25.7 ± 2.76[a]	85.6 ± 2.02[ab]	21.9 ± 0.05[a]
36	84.4 ± 0.02[b]	26.4 ± 1.35[a]	87.4 ± 3.52[ab]	21.2 ± 2.11[ab]	84.9 ± 0.30[b]	24.8 ± 0.47[a]
48	87.1 ± 0.81[ab]	21.8 ± 0.36[b]	89.0 ± 2.02[a]	18.2 ± 0.86[b]	89.2 ± 1.53[ab]	22.0 ± 2.07[a]
60	89.0 ± 0.49[a]	20.1 ± 0.12[b]	88.8 ± 0.59[a]	19.8 ± 1.10[ab]	90.4 ± 2.57[a]	19.6 ± 0.74[a]

Values represented the mean ± standard deviation, and values that were followed by different letters within each column were significantly different ($P < 0.05$).

rearrangement at higher aging temperature and as the aging temperature approaches the T_g, the relaxation from a nonequilibrium state to an equilibrium state is faster due to higher molecular mobility (Syamaladevi and others 2010).

Chung and Lim (2003a, 2003b) reported a small increase (1 to 3 °C) in T_g values with aging time, and a small decrease (1 to 3 °C) in T_g values with aging temperature when normal and waxy starches were aged at the temperatures slightly below their respective glass transition temperatures. However, we found no statistically significant difference in the T_{gi} and ($T_{ge} - T_{gi}$) values of the M040:1 lutein microcapsules with increased aging temperature (Table 3). Syamaladevi and others (2010) reported no statistically significant difference in T_g values of encapsulated raspberry powder aged with increasing aging temperature and time, and Craig and others (2000) reported no significant difference in T_g values of lactose with increasing aging time.

During aging, the relaxation enthalpy of the M040:1 lutein microcapsules increased nonlinearly and nonexponentially as aging time increased (Figure 3). The major ingredients of the M040:1 lutein microcapsules were maltodextrin and sucrose, but the relaxation enthalpy of the M040:1 lutein microcapsules were much smaller than that of sucrose (Liu and others 2007). For instance, the relaxation enthalpy of the M040:1 lutein microcapsules ranged from 0.066 to 0.848 J/g for aging times of 6 to 60 h at the aging temperatures of (T_{gi} − 5), (T_{gi} − 10), and (T_{gi} − 15) °C (Figure 3).

Table 4–Experimental values of ΔH_∞, τ, β, $\tau_{\varphi(t)=50\%}$, and $\tau_{\varphi(t)=1\%}$ calculated for the M040:1 lutein microcapsules.

	KWW equation and other relaxation parameters				
$T_{gi} - T_a$ (°C)	ΔH_∞ (J/g)	τ (h)	β	$\tau_{\varphi(t)=50\%}$ (h)	$\tau_{\varphi(t)=1\%}$ (h)
5	1.31	60.5	0.81	38.5	399
10	2.00	161	0.76	99.3	1200
15	3.93	316	0.95	215	1578

The relaxation enthalpy of sucrose ranged from 1.5 to 5.5 J/g for the aging times of 2 to 17 h at the aging temperatures of (T_{gi} − 7.5), (T_{gi} − 12.5), and (T_{gi} − 17.5) °C (Liu and others 2007). Noel and others (2005) reported that the relaxation enthalpy of maltodextrin (DE 29) with 11% water content ranged from 0.25 to 0.75 J/g for aging times of 40 to 160 min and an aging temperature of (T_{gi} − 12) °C. Enthalpy relaxation of molecules with large molecular weights, such as starch and maltodextrin, are much smaller than for molecules with small molecular weights, such as sucrose and water.

Free volume increases by increasing water content in the material facilitating the relaxation. This results in a proportional increase of relaxation enthalpy in starch (Chung and Lim 2003a). According to this rule, the enthalpy relaxation of maltodextrin (DE 6.1) with 2.32% water content should be much smaller than
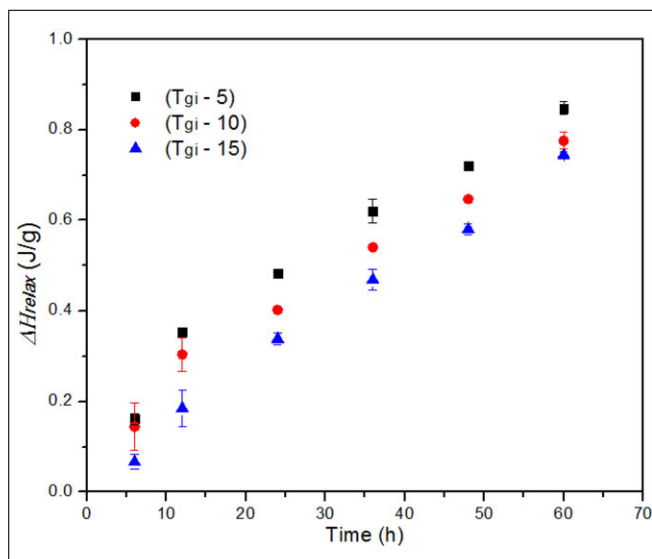

Figure 3–Relaxation enthalpy (ΔH_{relax}) of the M040:1 lutein microcapsules aged at (T_{gi} − 5), (T_{gi} − 10), and (T_{gi} − 15) °C for different aging times.

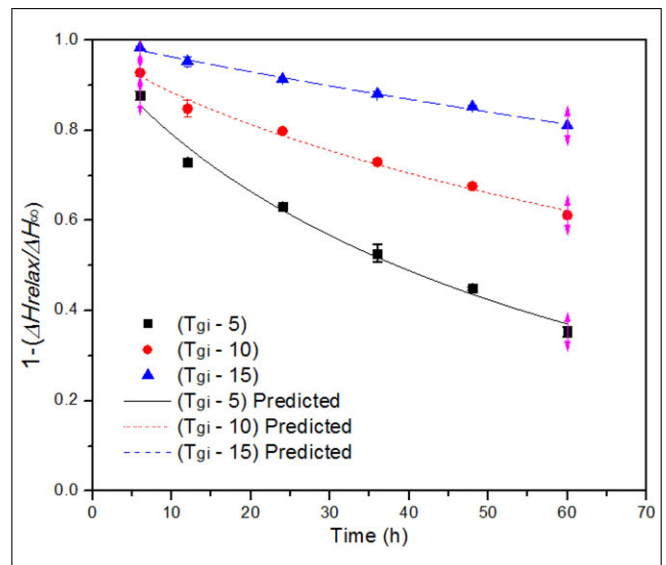Figure 4–Variations of 1 − ($\Delta H_{relax}/\Delta H_\infty$) for the M040:1 lutein microcapsules aged at (T_{gi} − 5), (T_{gi} − 10), and (T_{gi} − 15) °C for the different aging times.

that of maltodextrin (DE 29) with 11% water content, whereas the relaxation enthalpy of the lutein microcapsules M040:1 may be higher than that of maltodextrin (DE 6.1) with 2.32% water content. The relaxation enthalpy of the M040:1 lutein microcapsules between the values of maltodextrin (DE 6.1) and sucrose may be attributed to interactive molecular forces between maltodextrin and sucrose and the complex physical structures

and states (amorphous vs. crystalline) obtained by spray drying. At the same aging time, the relaxation enthalpy values of the lutein microcapsule M040:1 aged at higher temperatures were always greater than that obtained at lower temperatures, and relaxation enthalpy value would be close to the total enthalpy available for relaxation (ΔH_∞) when the aging temperature approached T_{gi}.
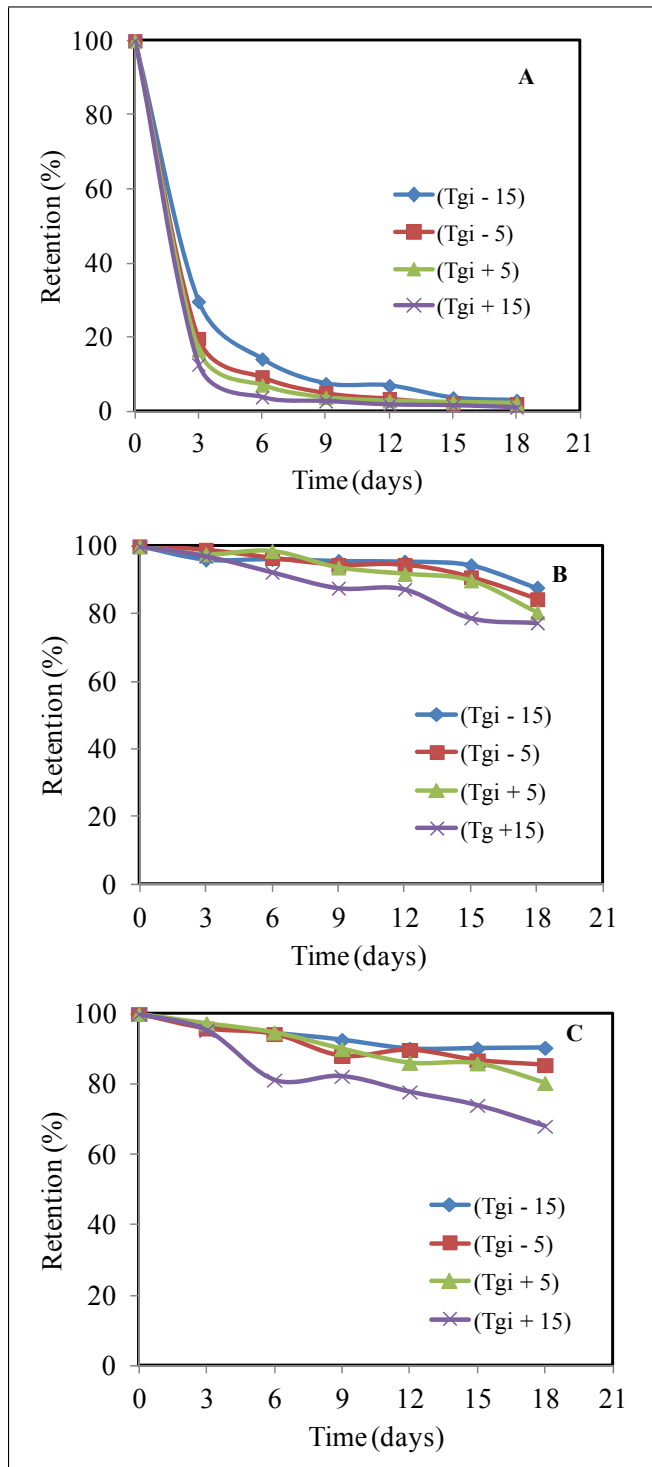
Figure 5–Lutein retention of the M040:1 lutein microcapsules vacuum-packed in 91319 (A), N#15 (B), and AFL (C) multilayer films as a function of storage time and temperature.
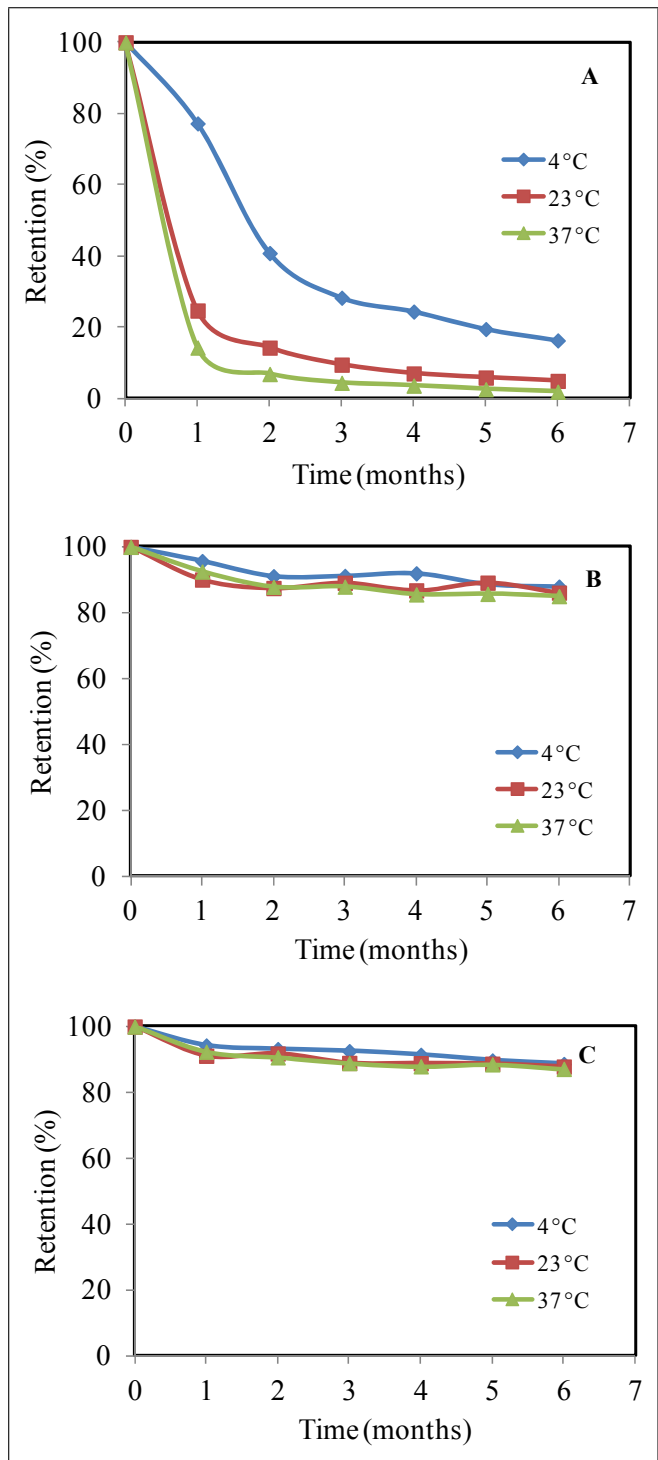
Figure 6–Lutein retention of the M040:1 lutein microcapsules vacuum-packed in 91319 (A), N#15 (B), and AFL (C) multilayer films as a function of storage time and temperature (4, 23, and 37 °C).

Therefore, the appropriate storage temperatures for foods products with low water content, such as M040:1 lutein microcapsules, should be lower than their T_{gi}. In addition, lower the storage temperatures below their T_{gi}, the smaller the enthalpy relaxation and molecular mobility. This results in better prevention against undesirable changes. Hancock and others (1995) reported when the pharmaceutical products are stored at least 50 °C below their T_{gi}, the enthalpy relaxation and molecular mobility is insignificant over normal shelf life.

The nonlinear and nonexponential behavior of enthalpy relaxation is shown in Figure 4 by plotting the extent of enthalpy relaxation (φ_t) against the aging time. The KWW equation was used to fit the enthalpy relaxation variations of the M040:1 lutein microcapsule during aging. In the KWW equation, the τ and β values were adjustable parameters obtained from fitting relaxation enthalpy data of the luein microcapsule M040:1 against aging time.

After nonlinear optimization of the experimental data, the parameter τ and β values in the KWW equation were calculated

(Table 4). The nonlinear fitting coefficients were more than 0.988. The τ value of the lutein microcapsule M040:1 aged at ($T_{gi} - 15$) °C was 316 h, which was much greater than the τ value (161 h) of the M040:1 lutein microcapsules aged at ($T_{gi} - 10$) °C and the τ value (60.5 h) of the M040:1 lutein microcapsules aged at ($T_{gi} - 5$) °C. The remarkable increase in the τ value indicates a significant reduction in molecular mobility in the M040:1 lutein microcapsules aged at temperature far below its T_{gi} compared with the one aged at a temperature near its T_{gi}. The τ values (3.59, 12.0, and 78.1 h, respectively) of sucrose aged at ($T_{gi} - 7.5$), ($T_{gi} - 12.5$), and ($T_{gi} - 17.5$) °C were much smaller than that of the lutein microcapsules M040:1 aged at ($T_{gi} - 5$), ($T_{gi} - 10$), and ($T_{gi} - 15$) °C (Liu and others 2007).

Syamaladevi and others (2010) reported a decrease in the β values as the aging temperature decreased. Chung and Lim (2003b) reported that the β values decreased with decreasing aging temperature and increasing water content. However, we did not find a similar decreasing trend of the β values as the aging temperature decreasing. The β values of the lutein microcapsules M040:1 aged at ($T_{gi} - 5$), ($T_{gi} - 10$), and ($T_{gi} - 15$) °C were 0.81, 0.76, and 0.95, respectively.

The major ingredients of the lutein microcapsule M040:1 were maltodextrin M040 and sucrose at the weight ratio of 3:1. Generally, smaller molecules have greater β values than polymers. However, the β values of sucrose aged at ($T_{gi} - 7.5$), ($T_{gi} - 12.5$), ($T_{gi} - 17.5$), and ($T_{gi} - 27.5$) °C were between 0.53 and 0.66, which was smaller than the β values of the M040:1 lutein microcapsules (Kawai and others 2005; Liu and others 2007). These larger β values of the M040:1 lutein microcapsules compared with sucrose could be attributed to the complex interaction of microcapsule components. The complex interaction could result from the formation of hydrogen bonds between sucrose and maltodextrin, the major ingredients of the M040:1 lutein microcapsules.

$\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ are the time required for 50% and 99% of the maximum enthalpy relaxation at a specific aging temperature, respectively (Liu and others 2007; Syamaladevi and others 2010). The calculated $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ values are listed in Table 4. The values of $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ for the lutein microcapsule M040:1 were much greater than that of sucrose due to the complex interactions among maltodextrin and sucrose, the major ingredients of the M040:1 lutein microcapsules (Liu and others 2007). In comparing the obtained $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ values at different aging temperature, we observed that $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ values of the M040:1 lutein microcapsules significantly increased with a small decrease in aging temperature. For instance, when the aging temperature decreased from ($T_{gi} - 5$) to ($T_{gi} - 15$) °C, the value of $\tau_{\varphi(t)=50\%}$ increased from 38.5 to 215 h, and the value of $\tau_{\varphi(t)=1\%}$ increased from 399 to 1578 h, respectively. This increase in the values of $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ indicates that the aging of the M040:1 lutein microcapsules dramatically slowed down at the aging temperature far below T_{gi} due to the high restriction of molecular mobility. Therefore, the values of $\tau_{\varphi(t)=50\%}$ and $\tau_{\varphi(t)=1\%}$ obtained in our study can be used to select the long-term storage temperatures for M040:1 lutein microcapsules, foods and pharmaceutical products containing amorphous glassy maltodextrin and sucrose.

Physical aging may change some physicochemical properties of the lutein microcapsules, resulting in unfavorable changes in functional and nutritional properties. The obtained kinetic parameters of enthalpy relaxation for the lutein microcapsules M040:1 can be related to the variations of some physicochemical properties of the M040:1 lutein microcapsules during amorphous glassy state
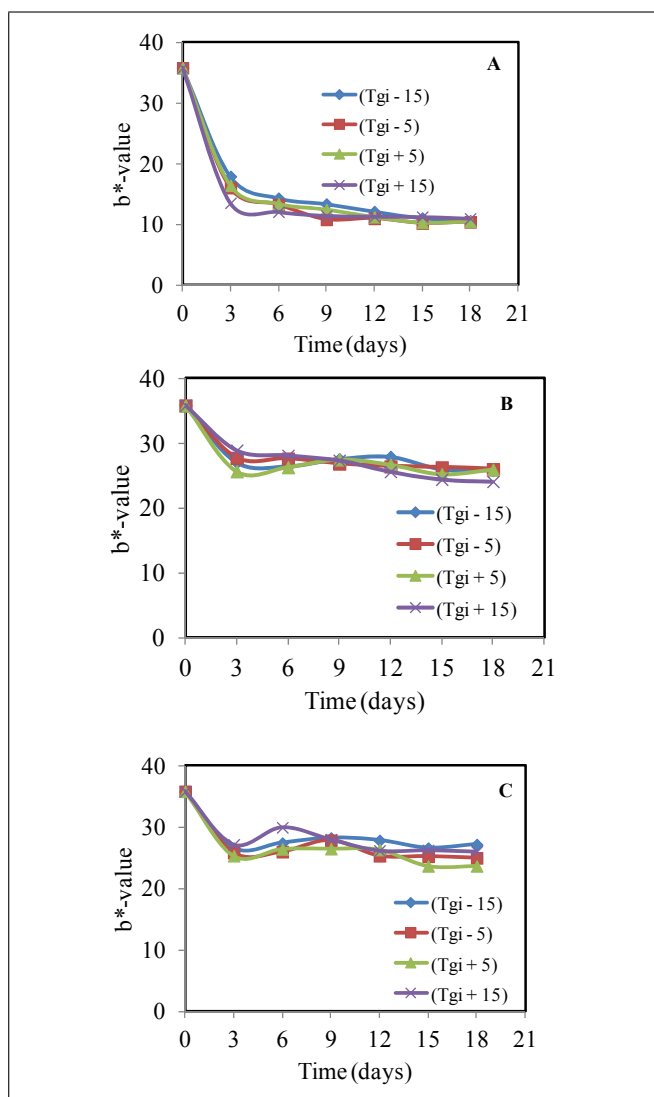

Figure 7–Influence of storage temperature on the color change (*b* value, yellowness) of the M040:1 lutein microcapsules vacuum-packed in 91319 (A), N#15 (B), and AFL (C) multilayer films.

storage. Further study on the time dependence of the enthalpy relaxation and temperature dependence of molecular mobility and relaxation time will be useful for predicting suitable storage temperatures and times for foods and pharmaceutical products.

Storage stability

Our results show that, at higher storage temperatures (67 to 97 °C), the lutein content in microcapsules decreased with increasing temperature and time (Figure 5). The lutein retention of the microcapsule stored for 18 d in low oxygen barrier film 91319 decreased to 1% to 3%, depending upon the temperature. Although the lutein retention was still higher than 68% after 18 d of storage at these temperatures for the microcapsule packaged with high oxygen barrier pouches N#15 and AFL, the lutein content continuously decreased at slower rates with time at these temperatures. At lower storage temperatures (4 to 37 °C), the lutein content also decreased with increasing temperature and time, but at slower rates (Figure 6). Depending upon the temperature, the lutein content of microcapsules was reduced to 2% to 16%

after storage of 6 months in low oxygen barrier pouches 91319. Although the lutein retention in microcapsules packaged in high oxygen barrier pouches N#15 and AFL was higher than 85% after storage of 6 mo, the lutein content continuously decreased with the increasing temperature and time. The OTR of 91319 multiple layer pouches was 62.8 cc/m² day, which is much higher than that of N#15 (0.034 cc/m² day) and the AFL multiple layer pouches (0.018 cc/m² day).

These results indicate that lutein is highly unstable and susceptible to thermal and oxidative degradations. However, microencapsulation and high oxygen barrier packaging can effectively decrease the chemical degradation of lutein. The effects of storage temperature and the OTR of packaging on the color change
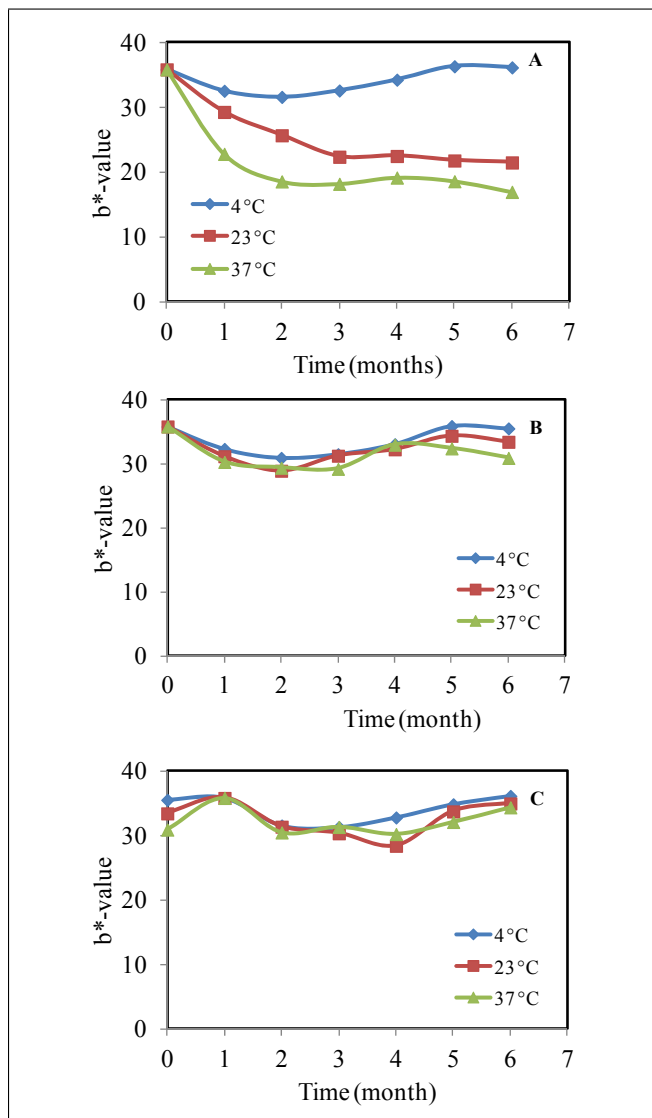
Figure 8–Influence of storage temperatures (4, 23, and 37 °C) on the color change (*b∗* value, yellowness) of the MO40:1 lutein microcapsules vacuum-packed in 91319 (A), N#15 (B), and AFL (C) multilayer films.
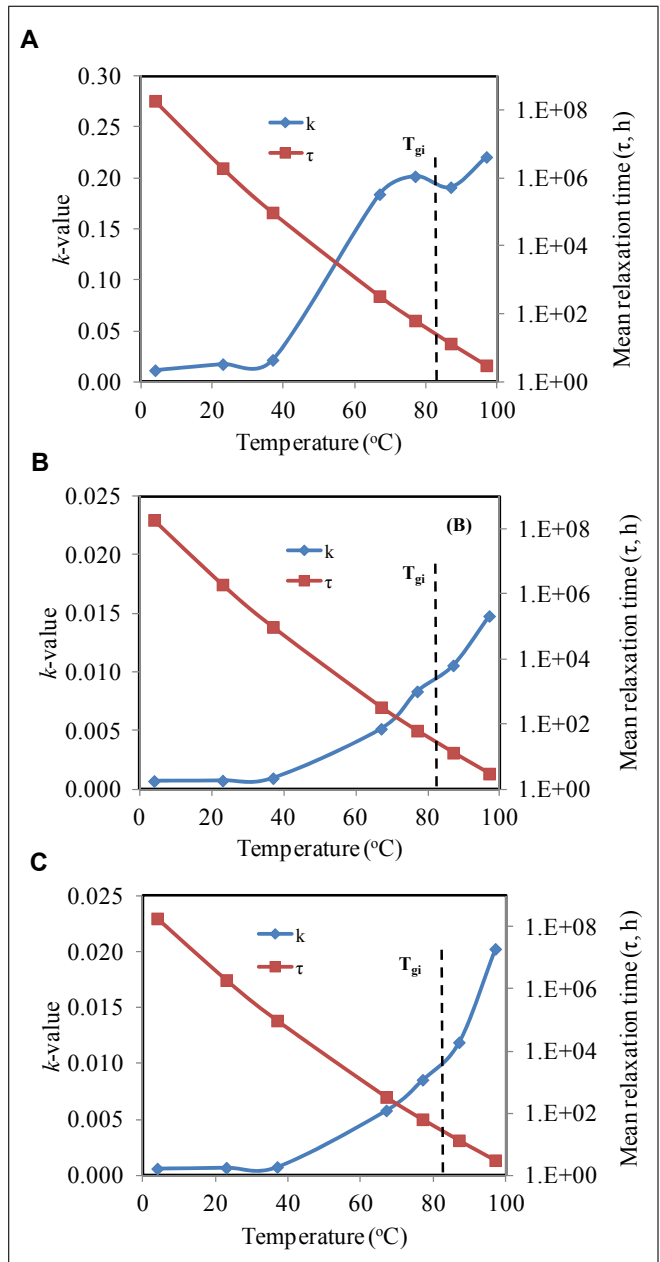

Figure 9–Lutein degradation reaction rate constant (*k* value) and mean molecular relaxation time (*τ* value) of the MO40:1 lutein microcapsules vacuum-packed in 91319 (A), N#15 (B), and AFL (C) multilayer films as a function of storage temperature.

of the lutein microcapsule followed similar trends as lutein retention (Figure 7 and 8). In general, the change in $L*$ and $a*$ of the lutein microcapsule was not significant ($P > 0.05$; data not shown), but $b*$ decreased significantly ($P < 0.05$) with increasing storage temperature and time.

Lutein retention data were described with the 1st-order reaction equation, and lutein degradation rate constants (k) for various storage temperatures were calculated. The lutein degradation rate constant decreased significantly when the storage temperature decreased from ($T_{gi} + 15$) to ($T_{gi} - 15$) °C due to change in the physical state of the microcapsules. They change from the rubbery state to the amorphous glassy state, resulting in a dramatic reduction in molecular mobility. The k-values decreased with decreasing temperature and reduced to negligible value (that is, close to zero) at 50 °C below T_{gi} (Figure 9). The Kauzmann temperature, at approximately 50 °C below glass transition temperature, is the critical temperature limit at which molecular mobility of the amorphous glass is negligible over extended experimental time scales. Thus, the τ value approaches infinity (Liu and others 2007; Syamaladevi and others 2010).

Although k values reach to negligible at storage temperatures 50 °C below T_{gi}, the k values also depended on the oxygen barrier properties of packaging. The k values in low oxygen barrier pouches were higher by an order of magnitude compared to rates constants obtained with high oxygen barrier pouches (Figure 9). These results suggest that, in addition to the physical state of microcapsules, high oxygen barrier packaging is also important to reduce chemical degradation of lutein.

Boiero and others (2014) prepared riboflavin microcapsules with gum Arabic as a wall material and incorporated the riboflavin microcapsules into whole milk, and then they found the photo-induced degradation of riboflavin was effectively decreased. Wegmuller and others (2006) prepared iodine, vitamin A, and iron microcapsules with hydrogenated palm fat by spray cooling and added the obtained microcapsules into local salt. Garg and others (2006) suggested incorporation of microencapsulated long chain n-3 polyunsaturated fatty acids in breads, biscuits, and milk powders is an important strategy for the prevention of chronic illnesses. The lutein microcapsules prepared in this study can be also incorporated into low water content food systems including milk powders and wheat flours.

Conclusions

Lutein can effectively be encapsulated using a suitable ratio of maltodextrin and sucrose as wall materials. Lutein microcapsules sampled were spherical in shape, with different degrees of dents on the surface due to shrinkage from water evaporation during spray drying. Glass transition temperatures of the microcapsules increased as DE values of maltodextrin and the weight fraction of sucrose decreased. Lutein microcapsules M040:1 was selected for storage experiments due to its higher EE and EY. At equivalent physical aging conditions, enthalpy relaxation of the lutein microcapsules M040:1 was significantly smaller than that of sucrose. The mean relaxation times of lutein microcapsules decreased as temperature of physical aging decreased. Both rates of color and lutein degradation increased as storage temperature and the oxygen transmission rate of package film increased. In addition to storage temperature, OTR of the package film was also found to be critical to the chemical degradation of lutein during long-term storage. Therefore, besides storing under temperatures far below T_g to restrict molecular mobility and relaxation, foods and

pharmaceutical products rich in lutein should be packed with high oxygen-barrier packaging.

Author Contributions

Pengqun Kuang and Shyam S. Sablani designed the study, interpreted the experimental results, and wrote the manuscript. Pengqun Kuang, Hongchao Zhang, and Poonam R. Bajaj conducted the experiments. Qipeng Yuan, Juming Tang, and Shulin Chen participated in the design of the experiments and interpreting the results.

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