Stabilization of Oils by Microencapsulation with Heated Protein-Glucose Syrup Mixtures

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ABSTRACT: The use of proteins [whey protein isolate (WPI) or soy protein isolate (SPI)] in combination with dried glucose syrup (DGS) for stabilization of microencapsulated spray-dried emulsions containing tuna oil, palm stearin, or a tuna oil–palm stearin blend was investigated. Pre-emulsions containing heated (100°C/30 min) protein–DGS mixtures and oils at oil/protein ratios of 0.75:1 to 4.5:1 were homogenized at two passes (35+10 or 18+8 MPa) and spray-dried to produce 20–60% oil powders. Microencapsulation efficiency decreased at lower homogenization pressure and as the oil load in the powder was increased beyond 50% but was independent of the type of oil encapsulated and the total solids (TS) content of the emulsions (24–33% TS) prior to drying. Oxidative stabilities of the powders, as indicated by headspace propanal values and PV after 4 wk of storage at 23°C, generally decreased with increasing oil content and homogenization pressure but increased with increasing TS of the emulsion prior to drying. Powder containing palm stearin was more stable to oxidation than powders containing a 1:1 ratio of palm stearin and tuna oil or only tuna oil. Heated WPI-DGS formulations were superior to corresponding formulations stabilized by heated SPI-DGS, producing spray-dried powders with higher microencapsulation efficiency and superior oxidative stability.

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The conversion of emulsions into powders by spray-drying enables fats and oils to be delivered in a convenient form for handling and storage. The stability of spray-dried powder during storage depends on the type and content of fat, wall materials, and the processes used for stabilization of emulsions and drying conditions (1,2). Solid fats are more amenable to conversion into high-fat powders than liquid oils and fats with intermediate m.p. (1,3). The production of powders containing as much as 75–83% oil is feasible, although higher fat contents generally result in lower microencapsulation efficiency (MEE) (4,5).

The selection of materials for stabilizing oil-in-water emulsions significantly affects the MEE and stabilities of the powders obtained by spray-drying of these emulsions. Because the formation of a fine stable emulsion is one of the main requirements for production of fat powders with low levels of unencapsulated fat, it is essential that surface-active components be present in the emulsion mixture. Protein, sugar, gum, starch, and cellulose have been used for encapsulating oils and fats (2,4–8). Milk proteins, alone or in combination with carbohydrates, have been used to encapsulate fats (5,6,9). Young *et al.* (6) showed improved MEE of anhydrous milk fat microcapsules when stabilized by a blend of whey protein and carbohydrate compared with whey protein alone. In using electron spectroscopy for chemical analysis (ESCA), the surface fat content of soybean oil powders stabilized by sodium caseinate was found to be lower than corresponding powders stabilized by whey protein (10).These authors, however, found that adding lactose improved the encapsulation properties of sodium caseinate-based soybean oil powders but not those stabilized with whey proteins. Kagami *et al.* (4) showed that incorporating dextrin into whey protein- or sodium caseinate-stabilized fish oil microcapsules significantly improved their oxidative stability.

Because many fats are prone to oxidation, an encapsulant composition that contributes to improved encapsulation efficiency as well as to enhanced oxidative stability of fat powders is desirable. Protein-carbohydrate conjugates formed by the Maillard reaction reportedly have good emulsifying and antioxidant properties (11,12). These inherent properties make them suitable materials for encapsulating fats and particularly useful for imparting stability to polyunsaturated fats. The use of Maillard reaction products (MRP) formed by heating various protein-carbohydrate mixtures to stabilize fish oil in encapsulated powders has been demonstrated (13,14). Increasing the temperature-time treatment of the protein-carbohydrate mixtures improved stability of the microencapsulated powder. In that work, the development of brown colors in casein-sugar mixtures during heating under similar conditions resulted in a reduction in sugar, confirming that the Maillard reaction had occurred (13,14).

In the present work, heated protein-sugar mixtures were used to stabilize oil-in-water emulsions that were subsequently dried to form microencapsulated oil powders. The influences of protein type [whey protein isolate (WPI) or soy protein isolate (SPI)], oil type (tuna oil, palm stearin, or tuna oil–palm stearin blend), oil load (20–60% w/w), total solids

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(TS) of emulsions (24–33% TS), and homogenization pressure (18+8 or 35+10 MPa) on the physical properties of emulsions and spray-dried powders were assessed. The viscosity and particle size distribution of emulsions were measured. MEE was estimated from the amount of solvent-extractable fat in powder. The stability of the fat powders to oxidation during storage was evaluated by measurement of the PV and headspace propanal. These indicators have been previously used to assess the oxidative stability of protein-stabilized oil-in-water emulsions (15). Our objective was to understand the factors that influence the efficiency of encapsulation and oxidative stability of the microencapsulated oils stabilized by heated protein-sugar mixtures.

EXPERIMENTAL PROCEDURES

Materials. WPI (Alacen™ 895) was purchased from New Zealand Milk Products (Melbourne, Australia). SPI (Supro® 670 IP Non-GM) was supplied by Solae (New South Wales, Australia). Dried glucose syrup [DGS: Maltostar 30 with a dextrose equivalent (DE) of 28–30] was from Weston Bioproducts (Melbourne, Australia). Tuna oil (HiDHA® 25N Food) was purchased from Nu-Mega Ingredients (Brisbane, Australia), and palm stearin was provided by Goodman Fielder (Melbourne, Australia). All chemical reagents used were of analytical grade and were obtained from Sigma-Aldrich (Sydney, Australia).

Experimental design. All emulsions were stabilized by heated protein-glucose syrup mixtures containing WPI or SPI. Emulsions were prepared with a constant protein/carbohydrate ratio (1:2), but with varying oil/protein ratios of 0.75:1 to 4.5:1, for production of powders containing 20 to 60% w/w oil. The effects of oil type (tuna oil, palm stearin, or 1:1 blend of tuna oil and palm stearin), homogenization pressure (35+10 or 18+8 MPa) and TS of emulsions (26.1 or 33.3%) were examined using emulsions with a 3:1 oil/protein ratio. The formulations of the emulsions are given in Table 1. All emulsions were prepared in duplicate.

Emulsion preparation. Protein powders were initially dispersed in warm (60–65°C) distilled water using an overhead stirrer. DGS was added, and the pH of the resulting protein-sugar solution was adjusted to pH 7.5 with a 1 M NaOH solution. The aqueous protein-sugar mixtures were heated in 3.3-L cans at 100°C for 30 min in a retort to promote formation of MRP. $L^* a^* b^*$ values were measured using a Minolta color analyzer as an indicator of the formation of MRP. The heated aqueous phase was cooled and stored overnight at 20°C.

The oil phase, as formulated in Table 1, was heated to 65°C in a water bath prior to dispersion into the aqueous phase using a Silverson laboratory high shear mixer-emulsifier at maximum speed for 2 min. The pre-emulsion was subjected to two-stage homogenization (18+8 or 35+10 MPa) using a laboratory homogenizer.

Spray drying of emulsions. The homogenized emulsions were spray-dried at a 60°C feed temperature, using a Drytec Compact Laboratory Spray Dryer with a twin fluid nozzle at 2.0 bar atomizing pressure. Drying was carried out in a co-current mode, with inlet and outlet temperatures of 180 and 80°C, respectively.

Emulsion size. The particle size distribution of the emulsion droplets was measured by using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, England). The emulsion was diluted in circulating water in the Hydro SM measuring cell, until >10% of the incident light was absorbed. A relative refractive index $\eta_{oil}/\eta_{water} = 1.095$ ($\eta_{oil} = 1.465$ and $\eta_{water} = 1.330$) was used for the calculation of particle size distribution, assuming that all droplets were spherical in shape. A polydisperse model was used to analyze the data, and the volume median diameter [$D(v,0.5)$] was taken as an indication of particle size.

Emulsion viscosity. The viscosities of homogenized emulsions were determined at 25°C by using a Brookfield Synchrolectric viscometer model LVT fitted with UL adaptor.

MEE. The total fat content of the powder was determined based on the acid extraction method specified in Australian Standard Methods of Chemical and Physical Testing for the

TABLE 1
Formulations and Processing Conditions for the Preparation of Emulsions and Powders[a]

				Emulsion				
Formulation	Core	Homogenization pressure (MPa)	Oil in powder (% w/w)	Protein ingredient (% w/w)	DGS (% w/w)	Oil (% w/w)	Oil/protein	Total solids (% w/w)
1	Tuna oil	35+10	20	6.38	12.67	4.76	0.75:1	24
2	Tuna oil	35+10	40	5.91	11.74	11.74	2:1	29
3a	Tuna oil	35+10	50	5.58	11.08	16.67	3:1	33
3b	Tuna oil	35+10	50	4.35	8.70	13.04	3:1	26
3c	Tuna oil	18+8	50	5.58	11.08	16.67	3:1	33
3d	Tuna oil	18+8	50	4.35	8.70	13.04	3:1	26
3e	Tuna oil/palm stearin[b]	35+10	50	5.58	11.08	16.67	3:1	33
3f	Palm stearin	35+10	50	5.58	11.08	16.67	3:1	33
4a	Tuna oil	35+10	60	5.15	10.23	23.08	4.5:1	38
4b	Tuna oil	35+10	60	4.10	8.14	18.36	4.5:1	30

[a]Protein/dried glucose syrup (DGS) ratio was 1:2.
[b]Tuna oil/palm stearin ratio was 1:1.

Dairying Industry AS 2300.1.3 (16). Total fat content was expressed as g of oil per 100 g of powder. The solvent-extractable fat of the powder was determined by using a method modified from Pisecky (17). Petroleum ether (50 mL) was added to 10 g of powder, and the extraction was performed by gently shaking the flask using an SF1 flask shaker (Speed 2.5) for 15 min (Stuart Scientific Co. Ltd., Redhill, Surrey, United Kingdom). The mixture was filtered, rotary-evaporated, and the solvent-free fat extract dried in the oven at 102°C for 1 h. The amount of extracted fat was determined gravimetrically, and MEE was calculated as follows:

$$\text{MEE} = \frac{(\text{total fat content} - \text{solvent extractable fat})}{\text{total fat content}} \times 100 \quad [1]$$

Powder storage. Fifteen grams of powder was placed in 125-mL loosely capped brown glass bottle. The samples were stored at 23°C for 4 wk in the dark. The extent of lipid oxidation in the powder was monitored by measuring PV and headspace propanal.

PV. The spectrophotometric method described by Shantha and Decker (18) was used with some modifications. The powder was dissolved in water to obtain an oil-in-water emulsion (5% w/w oil), and the emulsion was vortexed for 2.5 min at 2,200 rpm and allowed to settle at room temperature (~23°C) for 1 h. Then 300 μL of this mixture was mixed with 1.5 mL of isooctane/2-propanol (3:1, vol/vol), and the mixture was vortexed for 30 s and centrifuged for 2 min at 2,000 × *g*. Next, 200 μL of the organic phase was added to 2.8 mL methanol/1-butanol (2:1, vol/vol) mixture, followed by 15 μL each of ammonium thiocyanate and Fe^{2+} solutions. The absorbance of the sample at 500 nm was determined after 5 min incubation at room temperature (~23°C).

Headspace propanal. A PerkinElmer Model Autosystem XL capillary gas chromatograph (GC) fitted with a BP1 fused-silica capillary column (25 m × 0.32 mm, 5 μm film thickness; Agilent Technologies, Forest Hill, Victoria, Australia) and an FID was used for propanal headspace analysis. One gram of the powder sample was weighed and sealed in a 20-mL headspace vial before being equilibrated at 60°C for 15 min in an HS-40 autosampler (Perkin Elmer). Approximately 0.6 mL of the headspace vapor was injected into the column. The column temperature was increased initially from 60 to 75°C at the rate of 3°C/min, then to 90°C at the rate of 5°C/min and finally to 230°C at the rate of 25°C/min, where it was held for 20 min. The detector temperature was 240°C. Headspace propanal content was reported as absolute GC area.

Statistical analysis. All results reported were the mean of two replicates ± SD. Duplicate measurements were obtained for each replicate. Statistical differences between means were calculated using a one-way ANOVA followed by Tukey's test ($P < 0.05$) using Minitab Version 14 (State College, PA).

RESULTS AND DISCUSSION

Colors of aqueous protein-DGS mixtures. Heating an aqueous mixture (15% TS) containing a 1:2 ratio (w/w) of SPI-DGS decreased L^* values from 67.0 to 64.8, and increased a^* values from –1.3 to –1.1 and b^* values from 4.1 to 4.6. Similar trends in L^* a^* b^* values were obtained with 20%TS SPI-DGS mixtures. These trends in L^* a^* b^* values were consistent with increased formation of MAP (13,14). In the case of the WPI-DGS mixtures (15 and 20% TS), the trends in L^* a^* b^* values were less obvious, with negligible changes in L^* and a^* values. There were slight increases in b^* values, however, indicating an increased yellowness of the mixture. These increased from –3.9 to –3.6 for 15% TS systems and from –4 to –3.4 for 20% TS systems.

Properties of emulsions prior to drying. Emulsions with various oil/protein ratios (0.75:1 to 4.5:1), stabilized by heated protein-glucose syrup mixtures containing WPI or SPI, intended for manufacture of tuna oil powders with different oil loadings (20–60% w/w dry basis), were examined. Typical particle size distributions of the emulsions are shown in Figure 1.

All tuna oil emulsions stabilized by heated WPI-DGS mixtures had unimodal particle size distributions. Increasing the oil/protein ratios of emulsions from 0.75:1 up to 4.5:1 did not affect the particle size of emulsions stabilized by heated WPI-DGS mixtures (Table 2). Sufficient protein was present to cover the oil droplets in these systems, as indicated by the similarities in the volume median diameters of all these emulsions [$D(v,0.5)$ of 0.27–0.28 μm]. This was consistent with the observation of Hogan *et al.* (9) who reported that increasing oil/protein ratio of WPC-75 emulsions from 0.75:1 to 3:1 did not affect the droplet size but decreased the protein load.

Tuna oil emulsions stabilized by heated SPI-DGS mixtures displayed a shoulder or bimodal distributions at oil/protein ratios of 3:1 and 4.5:1 indicating that oil droplets coalesced. This was due to an insufficient quantity of surface-active material in

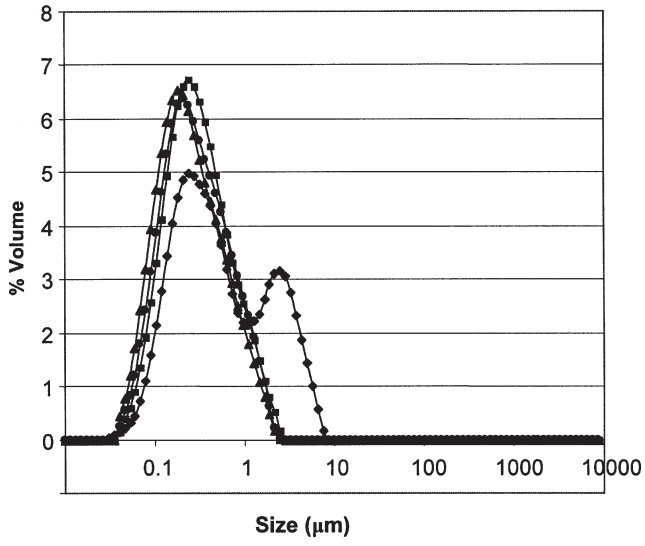

FIG. 1. Particle size distribution of emulsions stabilized by heated soy protein isolate (SPI)–dried glucose syrup (DGS) (▲ and ◆) or whey protein isolate (WPI)–DGS (● and ■) mixtures, with oil/protein ratios of 0.75:1 and 4.5:1, respectively. The protein:DGS ratio was 1:2.

TABLE 2
The Effect of Oil/Protein Ratio and Oil Type on the Viscosity and Particle Size of Heated Whey Protein Isolate (WPI)-DGS- and Soy Protein Isolate (SPI)-DGS-Based Emulsions[a,b]

Formulation	Total solids (%)	Oil/protein	Oil type	*D*(*v*,0.5) (μm) WPI-DGS	*D*(*v*,0.5) (μm) SPI-DGS	Viscosity WPI-DGS	Viscosity SPI-DGS
1	24	0.75:1	Tuna oil	$0.28^{a,*}$	$0.25^{a,*}$	$7.5^{a,*}$	$8.5^{a,*}$
2	29	2:1	Tuna oil	$0.28^{a,*}$	$0.27^{a,*}$	$17^{a,b,*}$	$23^{a,*}$
3a	33	3:1	Tuna oil	$0.28^{a,*}$	$0.32^{b,*}$	$35^{c,*}$	$735^{b,**}$
3e	33	3:1	Tuna oil/palm stearin	$0.31^{b,*}$	$0.33^{b,*}$	$44^{c,*}$	$990^{c,**}$
3f	33	3:1	Palm stearin	$0.32^{b,*}$	$0.33^{b,*}$	$48^{c,*}$	$>1900^{d,**}$
4a[c]	38	4.5:1	Tuna oil	N/A	N/A	N/A	N/A
4b	30	4.5:1	Tuna oil	$0.28^{a,*}$	$0.44^{c,**}$	$30^{b,c,*}$	$1200^{c,**}$

[a]Further details of formulations are given in Table 1. Protein/DGS ratio was 1:2; Tuna oil/ palm stearin ratio was 1:1; particle size distribution of all emulsions with SPI-DGS mixtures except those with oil/protein ratio of 3:1 had a shoulder or was bimodal. For other abbreviation see Table 1.
[b]Means within the same column with different alphabet superscripts (a–d) are significantly different ($P < 0.05$); Means within the same row with different symbol superscripts (* and **) are significantly different ($P < 0.05$).
[c]N/A, Not available, because the emulsion could not be processed through the homogenizer due to excessive thickening.

the SPI-DGS formulations available to emulsify the oil. The results demonstrated the inferior emulsifying properties of heated SPI-DGS mixtures compared with those of heated WPI-DGS mixtures. This in part may be attributed to the lower solubility of SPI compared with WPI, as sediment was visually observed during the preparation of SPI dispersions. Webb *et al.* (19) previously reported that the solubility of SPI was significantly lower than WPI, 60.7 and 96.3%, respectively. The reduced solubility of SPI would result in a lower concentration of protein that is available to interact with DGS to form MRP. In addition, proteins need to move to the interface and unfold before they can efficiently stabilize an interface. The solubility of a protein is therefore an important determinant of its emulsifying action along with such factors as the balance of hydrophobic and hydrophilic groups. Hu *et al.* (20) demonstrated that oil-in-water emulsions with the same oil/protein ratio had smaller particle sizes when stabilized by WPI compared with corresponding emulsions stabilized by SPI, suggesting that WPI was the superior emulsifying agent for oils. Others, however, have found that SPI was a better encapsulant for spray-dried orange oil emulsions compared with WPI (21). These differences could be due to the source of the proteins used and the different cores being encapsulated.

Increasing the oil/protein ratios from 0.75:1 to 3:1 increased viscosities of all tuna oil emulsions (Table 2). This increase in viscosity was attributable to the increase in TS of the corresponding emulsions, from 24 to 33% TS. Where oil/protein ratios of heated SPI-DGS-stabilized emulsions were higher than 2:1, significant increases in viscosity were observed, indicating aggregation of fat globules in the concentrated emulsions. Furthermore, increasing TS to 38% at an oil/protein ratio of 4.5:1 resulted in emulsions containing SPI that were too thick to process through the homogenizer. This emulsion was reformulated to contain 30% TS to enable processing. Despite the lower TS, the viscosity of the 30% TS tuna oil emulsion (oil/protein ratio of 4.5:1) containing SPI was significantly higher than that of 33% TS tuna oil emulsion (oil/protein ratio 3:1), possibly because of the larger particle size and coalescence in the former emulsion (Table 2, Fig. 1). Where there was no evidence of aggregation, as was the case in emulsions stabilized by WPI, the lower viscosities of emulsions with the oil/protein ratio of 4.5:1 (30%TS) as compared with those with lower ratio of 3:1 (33%TS) were simply a consequence of the reduced TS of the emulsion.

Where the same oil/protein ratio (3:1) was used, decreasing the TS of tuna oil emulsions did not significantly affect particle size (Table 3). Under these conditions, homogenization pressure markedly affected emulsion droplet size. Increasing homogenization pressure from 18+8 to 35+10 MPa significantly decreased the particle size of all emulsions (Table 3), an effect

TABLE 3
The Effect of Homogenization Pressure and Total Solids on the Viscosity and Particle Size of Heated WPI–DGS- and SPI–DGS-Based Tuna Oil Emulsions[a,b]

Formulation	Total solids (%)	Homogenization pressure (MPa)	*D*(*v*,0.5) (μm) WPI-DGS	*D*(*v*,0.5) (μm) SPI-DGS	Viscosity (cP) WPI-DGS	Viscosity (cP) SPI-DGS
3c	33	18 ± 8	$0.48^{b,*}$	$0.45^{b,*}$	$21^{b,*}$	$62^{b,**}$
3a	33	35 ± 10	$0.28^{a,*}$	$0.32^{a,**}$	$35^{c,*}$	$735^{c,**}$
3d	26	18 ± 8	$0.51^{b,**}$	$0.45^{b,*}$	$7.5^{a,*}$	$9^{a,*}$
3b	26	35 ± 10	$0.30^{a,*}$	$0.32^{a,*}$	$9.5^{a,*}$	$16^{a,**}$

[a]Further details of formulations are given in Table 1. Oil/protein ratio was 3:1; protein/DGS ratio was 1:2; particle size distribution of all emulsions with SPI-DGS mixtures had a shoulder or was bimodal. For abbreviations see Table 1.
[b]Means within the same column with different alphabet superscripts (a–d) are significantly different ($P < 0.05$); means within the same row with different symbol superscripts (* and **) are significantly different ($P < 0.05$).

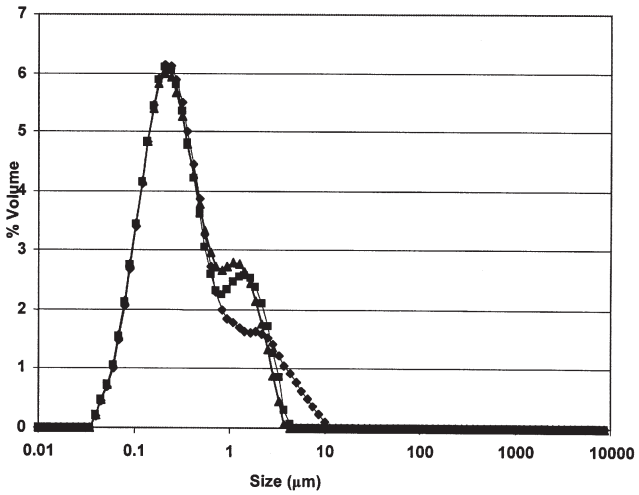

FIG. 2. Particle size distribution of tuna oil (◆), palm stearin (■), or 1:1 tuna oil/palm stearin (▲) emulsions stabilized by heated SPI–DGS mixtures. The oil/protein ratio of the emulsions was 3:1 and the protein/DGS ratio was 1:2. For abbreviations see Figure 1.

that has been previously observed (9). Increased emulsion viscosity was observed with increased homogenization pressure at higher TS. Higher shear and increased volume fraction of the dispersed phase leads to increased viscosity (22).

Tuna oil, palm stearin, and a 1:1 tuna oil/palm stearin blend were used to investigate the effect of oil types on properties of emulsions having an oil/protein ratio of 3:1. When the higher-melting fat palm stearin was used alone or as a blend with liquid tuna oil, unimodal distributions were still obtained in emulsions stabilized by heated WPI-DGS mixtures. In emulsions stabilized by heated SPI-DGS mixtures, however, there was a shoulder in addition to the main peak, suggesting that there was either partial coalescence or clustering of the protein-coated oil droplets (Fig. 2). The viscosities of emulsions increased when the palm stearin content was increased, although this was only significant in the case of emulsions stabilized by SPI-DGS mixtures (Table 2). Palm stearin is a semisolid fat whereas tuna oil is liquid at room temperature. Previous studies demonstrated that adding low concentrations of crystals (0.1–5%) to water-in-soybean oil emulsions increased initial flocculation and coalescence due to wetting of the fat crystals (23).

MEE. MEE values obtained with the various formulations are shown in Tables 4 and 5. The heated WPI-DGS mixtures performed better as encapsulants than corresponding formulations containing SPI. This was evidenced by the higher MEE of powders containing WPI compared with those containing SPI (i) where there was an equivalent oil loading in powders (20–60% w/w oil, Table 4), (ii) in powders (50% w/w oil) prepared from corresponding WPI- and SPI-based formulations (26 or 33%TS) that were homogenized at the same pressures (Table 5), and (iii) in powders containing different oil types (Table 4).

The properties of the film surrounding the oil droplets affect the MEE. Whey proteins are able to form stable, thick viscoelastic films owing to their ability to form covalent sulfur-sulfur links at the oil-water interface (24) although other types of bonds also contribute to the film strength. This may account for the higher MEE of heated WPI-DGS mixtures, as the films formed around droplets were more robust than those from heated SPI-DGS mixtures. Increasing the oil loading in powder (20 to 50% oil, w/w dry basis) by increasing the oil/protein ratio from 0.75:1 to 3:1 resulted in minor changes in MEE, but MEE of these tuna oil powders remained >90% (Table 4). At higher oil loading (60% w/w oil in powder; oil/protein 4.5:1), however, MEE decreased markedly, to 81–86%. This decrease in MEE was attributed to insufficient protein available to form films around the oil droplets beyond an oil/protein ratio of 3:1. MEE reflects not only the encapsulated oil present on the microcapsule surface but also the proportion of microencapsulated fat extracted from near the surface of the capsule. In our work, consistently higher MEE values were obtained compared with those of Hogan *et al.* (9), who re-

TABLE 4
The Effect Of Oil Loading and Oil Type on Microencapsulation Efficiency (MEE) and Oxidative Stability (headspace propanal and PV) of Heated WPI-DGS- and SPI-DGS-Based Oil Microcapsules[ab]

Formulation	Total solids (%)	Oil/protein ratio	Oil load in powder (%)	Oil type	MEE (%)		Oxidative stability[c] PV (mequiv/kg oil)		Headspace propanal (GC area)	
					WPI-DGS	SPI-DGS	WPI-DGS	SPI-DGS	WPI-DGS	SPI-DGS
1	24	0.75:1	20	Tuna oil	$96.8^{b,*}$	$93.1^{a,**}$	$0.34^{c,d,*}$	$0.47^{c,**}$	$7{,}000^{a,b,*}$	$9{,}750^{b,**}$
2	29	2:1	40	Tuna oil	$97.8^{a,*}$	$92.0^{a,b,**}$	$0.31^{c,*}$	$0.62^{d,**}$	$8{,}600^{b,*}$	$14{,}000^{c,**}$
3a	33	3:1	50	Tuna oil	$96.1^{c,*}$	$91.7^{b,**}$	$0.36^{d,*}$	$0.65^{d,**}$	$10{,}500^{c,*}$	$15{,}500^{d,**}$
3e	33	3:1	50	Tuna oil/palm stearin	$95.1^{d,*}$	$89.0^{c,**}$	$0.22^{b,*}$	$0.38^{b,**}$	$5{,}600^{a,*}$	$9{,}100^{b,**}$
3f	33	3:1	50	Palm stearin	$95.8^{c,*}$	$91.1^{b,c,**}$	$0.17^{a,*}$	$0.24^{a,**}$	$4{,}550^{a,*}$	$3{,}750^{a,*}$
4a[d]	38	4.5:1	60	Tuna oil	N/A	N/A	N/A	N/A	N/A	N/A
4b	30	4.5:1	60	Tuna oil	$85.9^{e,*}$	$80.7^{d,**}$	$0.44^{e,*}$	$0.75^{e,**}$	$12{,}500^{c,*}$	$17{,}200^{d,**}$

[a]Further details of formulations are given in Table 1. Protein/DGS ratio was 1:2; tuna oil/palm stearin ratio was 1:1.
[b]Means within the same column with different alphabet superscripts (a–d) are significantly different ($P < 0.05$); means within the same row with different symbol superscripts (* and **) are significantly different ($P < 0.05$).
[c]PV and headspace propanal of microcapsules were measured after 4 wk of storage at ~23°C.
[d]N/A, not available, as the emulsion could not be processed through the homogenizer due to excessive thickening, For abbreviations see Table 1.

TABLE 5
The Effect of Homogenization Pressure and Emulsion Total Solids on the MEE and Oxidative Stability (headspace propanal and PV) of Heated WPI-DGS- and SPI-DGS-Based Tuna Oil Microcapsules[a,b]

					Oxidative stability[c]			
					PV (mequiv/kg oil)		Headspace propanal (GC area)	
Formulation	Total solids (%)	Homogenization pressure (MPa)	MEE (%) WPI-DGS	MEE (%) SPI-DGS	WPI-DGS	SPI-DGS	WPI-DGS	SPI-DGS
3c	33	18 ± 8	91.2^{b,*}	79.6^{c,**}	0.35^{a,*}	0.36^{a,*}	7,250^{a,*}	8,450^{a,**}
3a	33	35 ± 10	94.3^{a,*}	87.8^{a,**}	0.34^{a,*}	0.60^{c,**}	9,650^{b,c,*}	14,000^{c,**}
3d	26	18 ± 8	90.4^{b,*}	82.8^{b,**}	0.32 ^{a,*}	0.42^{b,**}	8,600^{a,c,*}	10,650^{b,**}
3b	26	35 ± 10	94.4^{a,*}	89.2^{a,**}	0.47^{b,*}	0.65^{d,**}	15,300^{d,*}	18,850^{d,**}

[a]Further details of formulations are given in Table 1. Oil/protein ratio was 3:1; protein/DGS ratio was 1:2
[b]Means within the same column with different alphabet superscripts (a–d) are significantly different ($P < 0.05$); Means within the same row with different symbol superscripts (* and **) are significantly different ($P < 0.05$).
[c]PV and headspace propanal of microcapsules were measured after 4 wk storage at ~23°C. For abbreviations see Tables 1 and 4.

ported that MEE values of WPC (whey protein concentrate) 75-stabilized powders were reduced from 59 to 4% as the oil/protein ratio was increased from 0.25:1 to 2:1. A number of factors could have contributed to the differences including (i) the differences in the solubility and degree of aggregation of WPC 75 and WPI, which are influenced by the history and manufacturing conditions of these ingredients, (ii) the higher homogenization pressure, and (iii) the higher outlet temperature of the dryer used by Hogan *et al.* (9).

Destabilization of emulsions prior to drying and during the drying process may contribute to a decrease in MEE of oil powders. In the case of emulsions stabilized by heated SPI-DGS mixtures, the significant increase in droplet size of emulsions for producing powders containing >50% w/w oil indicated the reduced stability of emulsions prior to drying, contributing to the lower MEE. That the decrease in MEE of powders containing WPI as the oil content was increased beyond 50% w/w cannot be related to a lack of emulsion stability prior to drying, as all emulsions had the same particle size (Table 2). Hence, factors other than emulsion size likely affected the properties of the powders after drying. As water is removed during drying, destabilization of emulsions due to conformational changes in the protein can occur, resulting in changes to the structural characteristics of the film around the oil droplets. Previous studies on spray-dried whey protein-lactose-soybean oil emulsions suggest that there can be a loss of internal structure and coalescence of oil droplets during drying (10).

Generally, the MEE of powders (50% w/w oil) were not affected by decreasing TS of emulsions from 33 to 26% (Table 5). This result agreed with the findings of Hogan *et al.* (25), who found that MEE was not affected by increasing TS (10–40%) of emulsions stabilized by a blend of sodium caseinate and corn syrup solids (DE of 28). Our results, however, did not concur with the findings of Young *et al.* (6), who found significant increases in MEE of WPI-based powders (50% w/w oil) as TS was varied from 18 to 33%. Differences in MEE may be obtained when a change in the TS of the dispersed phase alters the state of aggregation of proteins. This will have an effect on the emulsifying properties of the protein and the droplet interface.

Regardless of emulsion TS (26 or 33%) and type of encapsulant used for production of powder microcapsules containing 50% oil, MEE was superior when higher homogenization pressures were used for emulsion preparation (Table 5). Others have also indicated that an increase in homogenization pressure from 10 to 40 MPa resulted in a progressive increase in MEE of WPC 75-stabilized powders (9). The increase in MEE with increasing homogenization pressure might be due to several factors. Rampon *et al.* (26) showed that globular proteins can be structurally modified to different extents when different homogenization conditions are used to prepare emulsions. It was therefore possible that different homogenization pressures used in this study contributed to the different structures of proteins adsorbed to the oil-water interface, thereby affecting MEE. It has been suggested that smaller emulsion droplets associated with the use of higher homogenization pressure are desirable for spray-drying (27). If smaller droplets are formed during atomization, the larger surface area exposed hastens the drying process and influences MEE. The incidence of dents and fissures in the powder particle may be greater if there is early solidification. The prevalence of dents will also depend on the viscoelastic properties of the film at the time of drying. Provided that the matrix around the oil droplet is robust, however, it is possible that the structure of the interface may be maintained, leading to efficient encapsulation. It was not possible to discriminate between the relative influence of each of these factors on powder properties as powder structure and properties of the interface during drying were not examined in this work.

MEE of oil powders (50% w/w oil) was slightly influenced by the oil type (Table 4). This may be due to coalescence occurring in palm stearin emulsions stabilized by heated SPI-DGS mixtures. These results contrasted with those of Fäldt and Bergenstahl (3), who reported that fats with intermediate m.p. were poorly encapsulated compared with fully crystalline fats or liquid oils, as determined by ESCA. The different results may have arisen from differences in encapsulation formulation, processing conditions used, and methods used for measuring efficiency of encapsulation.

Oxidative stability. The oxidative stabilities of oil powders

stabilized by heated WPI-DGS mixtures were generally superior to corresponding powders containing SPI (Tables 4 and 5), as indicated by the lower PV and headspace propanal of powders stabilized by WPI-based systems. In emulsion systems, proteins at the interface and in the bulk phase can affect the oxidative stability of the oil (28). Factors such as the interfacial film thickness and robustness, their metal chelating power, and their ability to scavenge oxygen and free radicals are all expected to play roles in oxidative stability. In our powders, MRP from heated WPI-DGS or SPI-DGS mixtures and the remaining unreacted proteins are both expected to contribute to the antioxidative action, whether they are at the interface or in the continuous matrix of the powder. WPI has been reported to have antioxidant properties (29), and it is possible that the excess WPI in the continuous matrix of the powder contributed to the better oxidative stability of the oil.

As expected, the oxidative stabilities of the powders decreased as the oil load in powder increased from 20 to 60% (Table 4). At higher oil load, the increase in oil/protein ratio results in thinner encapsulating films around the oil droplets. Thinner encapsulating film results in a reduced barrier to diffusion of oxygen and free radicals and an increased susceptibility of the encapsulated oil to oxidation (28). Another potential contributory factor is the effect of matrix components in the bulk phase, as already discussed. It is known that MRP possess antioxidant activity (12,30). The increasing content of MRP in powders as oil load is decreased would have provided additional protection to the oil, in low oil-loading powders. Previous research has shown that addition of MRP to full-cream milk during milk powder manufacture increased the resistance of milk powder to oxidation (12).

Increasing the emulsion TS prior to drying generally improved the oxidative stability of microcapsules containing 50% tuna oil (Table 5), despite its lack of influence on particle size (Table 3) and MEE (Table 5). Spray-drying of emulsions with higher TS is expected to increase the bulk density and reduce the occluded air in powders.

Although powders made from emulsions prepared using higher homogenization pressures had higher MEE and hence a higher level of encapsulated fat, they were more susceptible to oxidation (Table 5). Fat that is not encapsulated by the matrix is more prone to oxidation (31). Our results, however, suggest that factors other than the amount of unencapsulated fat have the overriding influence on the oxidative stability of oil in the powder. In our systems, there were smaller oil droplets when higher homogenization pressures were used (Table 3), which will result in a larger surface area covering the oil droplets and possibly a thinner encapsulating film around the oil droplets at higher homogenization pressures. Both factors contribute to the increased oxidation state.

Decreasing the tuna oil/palm stearin ratio resulted in increased oxidative stabilities of the powders as observed from the lower PV and headspace propanal values (Table 4). This was expected due to the higher level of saturated fat in palm stearin.

This work has shown that heated protein-glucose syrup mixtures can be used as effective emulsifying and encapsulating materials for the production of spray-dried microencapsulated fats. Heated WPI-DGS mixtures were superior to corresponding formulations containing SPI as evidenced by the improved encapsulation efficiency and oxidative stability. Both the formulation and processing conditions used in the preparation of the emulsion prior to drying influence the properties of the final powder. Further work to elucidate properties of the interface prior to and during drying changes occurring during the drying of the emulsions and the microstructure of the powder is fundamental to understanding the changes in powder properties.

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