Invited Review: Spray-Dried Dairy and Dairy-Like Emulsions—Compositional Considerations

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ABSTRACT

Milk constituents [caseins, whey proteins (WP), lactose, and anhydrous milk fat] are used widely in the manufacture of dehydrated dairy and dairy-like emulsions. When sodium caseinate- (NaCas) and WP-stabilized emulsions with an oil-to-protein ratio ranging from 0.25 to 5 are dehydrated, NaCas is a more effective encapsulant than WP because of its superior emulsifying properties and resistance to heat denaturation. Denaturation degree of WP during drying has been associated with increased powder surface fat and larger droplet size after reconstitution. Encapsulation of NaCas-stabilized emulsions improves in the presence of lactose; powder surface fat was reduced from 30 to <5% when lactose was added at a 1:1 ratio to NaCas in an emulsion containing 30% (wt/wt) oil. This has been related to the ability of lactose to form solid-like (or glassy) capsules during sudden dehydration. Encapsulation of WP-stabilized emulsions is not improved by addition of lactose, although there are conflicting reports in the literature. Storage stability of dehydrated dairy-like emulsions is strongly linked to lactose crystallization as release of encapsulated material occurs during storage at high relative humidities (e.g., 75%). The use of alternative carbohydrates as “matrix-forming” materials (such as maltodextrins or gum arabic) improves storage stability but compromises the emulsion droplet size after reconstitution. The composition of the powder surface has been recognized as a key parameter in dehydrated emulsion quality. It is the chemical composition of the powder surface that dictates the behavior of the bulk in terms of wettability, flowability, and stability. Analyses, using electron spectroscopy for chemical analysis of the surface of industrial milk powders and dehydrated emulsions that mimicked the composition of milk, showed that powder surface is covered mainly by fat, even when the fat content is very low (18 and 99% surface fat coverage for skim milk and whole milk powders, respectively). The func-

tional properties of milk constituents during emulsion dehydration are far from being thoroughly understood; future research needs include a) the encapsulation properties of pure micellar casein; b) a deeper understanding of colloidal phenomena (such as changes in the oil-water and air-oil interfaces) that occur before, during, and after dehydration, which ultimately define emulsion stability after drying; and c) reconciliation of the current different views on powder surface composition.

Key words: spray drying, emulsion, surface fat

INTRODUCTION

Emulsion stability is a relative, kinetic concept. A stable emulsion is one with no discernible change in the size distribution of droplets, their state of aggregation, or their spatial arrangement within the sample vessel over the time-scale of observation, which may vary from hours to months depending on the material (Dickinson, 1994). As such, emulsions have been subjected to more than exhaustive research. The state of aggregation of droplets depends on the interactions between adsorbed emulsifier-protein layers, which, in turn, depend on factors such as emulsifier-protein surface coverage, layer thickness, surface charge density, and aqueous conditions (especially pH, ionic strength, and calcium content). The most obvious manifestation of emulsion instability is creaming, which eventually leads to macroscopic phase separation into 2 discernible regions of cream and serum that renders the system unacceptable (Robins et al., 2002).

An alternative and convenient means of increasing the shelf-life of perishable (but not necessarily unstable) emulsions is to transform them into dry powders, which is primarily done by spray drying. Dehydrated (or solid state) emulsions are prepared by drying liquid oil-in-water emulsions containing one or more dissolved substances in the aqueous phase, which turn into a continuous solid matrix that encapsulates the fat component in the emulsion. Such encapsulation provides several advantages in further handling of the dry material: stickiness of the powder is reduced, oxidation of the fat is minimized, and ideally, the original emulsion structure (i.e., droplet size distribution) is preserved

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(Millqvist-Fureby, 2003). The drying process also minimizes the packaging and storage requirements and reduces shipping and storage weight and costs (Landsstrom et al., 2000).

The scope of the present review is limited to the discussion and consolidation of the vast knowledge already available on the area of dehydrated food emulsions, particularly those involving dairy proteins and milk fat. Intentionally, most of the literature available on the topic of characterization of whole or skim milk and cream powders has been omitted. That area is quite broad and deserves a separate compilation. Furthermore, the aim of this paper is not to discuss the intrinsic aspects of emulsion stability per se, but to focus on the effects of spray drying and subsequent storage on the ultimate properties of reconstituted emulsions. Excellent reviews on emulsion stability can be found elsewhere (Dickinson, 1997; Rousseau, 2000; Robbins et al., 2002; van Aken et al., 2003). Finally, a model of our visualization of the topography of spray-dried emulsions, under different scenarios in terms of protein and carbohydrate types and concentrations, is proposed as a means to reconcile the different current views on the subject.

SPRAY DRYING

Spray drying is one of the many encapsulation techniques available today. It is used in the manufacture of a wide range of products including foods, pharmaceuticals, cosmetics, clays, and pigments. In the context of foods, products such as milk, eggs, cheese, coffee creamers, caseinates, whey, and ice cream mixes can be processed using this technique (Fäldt, 1995; Vega et al., 2005a). Spray drying involves atomization of a liquid feed into a drying medium, resulting in an extremely rapid evaporation of solvent (e.g., water). Drying proceeds until the desired level of water content in the product is achieved (generally between 3 and 1%). The process is controlled by means of the product feed and air flow (flow and temperature). The advantages of spray drying include the following: a) the powder specifications remain constant throughout the dryer when drying conditions are held constant; b) it is a continuous and easy drying operation that is adaptable to full automatic control; and c) a wide range of dryer designs are available to suit a variety of applications, especially for dehydration of heat-sensitive materials (Vega-Mercado et al., 2001).

Atomization results from the dispersion of a liquid feed once pumped through either a nozzle at a very high pressure or through a rotary atomizer, which spins at a very high speed. The feed travels through the dryer according to the relative positions of the nozzle/atom-

izer and air inlet, and depending on this configuration, the flow can be co-current, counter-current, or mixed. The versatility of the spray-drying operation is demonstrated, for example, by the different ways by which the bulk density of the final powder can be increased: a) increasing the feed rate; b) increasing the powder temperature; c) increasing the solids content of the feed; d) atomization through a rotary atomizer; and e) use of counter-current configuration (Vega-Mercado et al., 2001).

Throughout this paper, the term encapsulation will be understood as the act of enclosing, protecting, or coating a core material. When relatively small capsules (<200 μm) are produced, microencapsulation becomes a more suitable descriptor. Similarly, dehydrated (microencapsulated) emulsions are understood to be comprised of 3 elements: a core material (to be encapsulated), an emulsifier (to create and stabilize the emulsion), and an encapsulant [to provide the solid (and glassy) matrix necessary for encapsulation].

PHYSICOCHEMICAL PROPERTIES OF DEHYDRATED EMULSIONS

The physicochemical, flow, and reconstitution properties of dairy powders and related systems (such as lactose) have been subjected to extensive research (Buma, 1971b; Freudig et al., 1999; Kim et al., 2002; Ozcan et al., 2002; Bronlund and Paterson, 2004; Fitzpatrick et al., 2004; Foster et al., 2005; Vega et al., 2005b). These studies dealt with the properties of mainstream powders available for the food industry as well as model systems composed of lactose and milk proteins to analyze more fundamental aspects of powder stability during storage. This section focuses on some of the most important physicochemical properties of spray-dried emulsions (at least those with the highest industrial relevance), with emphasis on powder surface composition and the techniques utilized to estimate it.

Surface Composition

The composition of the external surface of the capsules formed during spray drying dictates the behavior of the bulk in terms of wettability, flowability, and stability to caking or oxidative rancidity. Assuming appropriate storage conditions (relative humidity and temperature), it is the "free-fat" content that can be directly associated to how well a powder flows, wets, and remains stable (particularly against lipid oxidation). Nonetheless, free fat is still a very broad concept, as it is generally taken as the amount of fat that can be extracted from a powder after contact with an organic solvent. Such a definition does not specify the solvent,

Table 1. Summary of different methods to assess the amount of free or surface fat in spray-dried emulsions

Test (reference)	Method type ¹	Solvent	Solvent-to-powder ratio	Shaking time and temperature	Reported as
Microencapsulation efficiency (ME) (Young et al., 1993)	G	PE ²	25:1	15 min/25°C	$[(\text{total oil} - \text{extractable oil}) / \text{total oil}] \times 100$
Extractable fat (Onwulata et al., 1994)	GC	CCl ₄	5:1	15 min/22°C at 200 rpm	% (g of fat/g of powder)
Retained fat (efficiency of encapsulation) (Onwulata et al., 1996)	G	CCl ₄	5:1	15 min/22°C at 200 rpm	$[(\text{Total oil} - \text{extractable oil}) / \text{total oil}] \times 100$
Surface oil (Kim and Morr, 1996)	GC	Pentane HPLC	20:1 to 12.5:1	14 h in soxhlet extractor	mg of oil/100 g of powder
ME (Hogan et al., 2001)	G	PE	40:1	15 min/25°C	$[(\text{total oil} - \text{extractable oil}) / \text{total oil}] \times 100$
Extraction of fat (Kim et al., 2002)	G	PE	40:1	10 min, 24 and 48 h/22°C	g of extractable fat/g of powder
Encapsulation efficiency (Danviriyakul et al., 2002)	G	Hexane	6:1	2 min vortex + 20 min at 2,720 × g	% (g of extractable fat/g of total fat)
Free fat extraction (Millqvist-Fureby, 2003)	G	PE	6:1	2 min/22°C	% (g of fat/g of powder)
Surface free-fat (Kim et al., 2005)	G	PE	5:1 × 4	No	g of surface free fat/g of powder
Inner fat (Kim et al., 2005)	G	PE	40:1	48 h	g of inner fat/g of powder
Surface oil (Soottitantawat et al., 2005)	GC	Hexane	20:1	30 s/22°C	% of surface oil (not specified if from total powder or total fat load)
Free fat extraction (Vega et al., 2005a)	G	PE	40:1	10 min/22°C	g of extractable fat/g of powder

¹G = gravimetric; GC = gas chromatography.²PE = Petroleum ether.

contact time, quiescent or dynamic contact (i.e., shaking), or even temperature. There are some official methods, but these are not always followed (Niro Atomizer, 1978). Table 1 offers a thorough compilation of the variety of methods that have been reported to quantify the amount of free or surface fat of spray-dried emulsions. It is known that solvent extraction also accounts for some fat coming from the interior of the particles (Buma, 1971c; Buchheim, 1982; Fäldt et al., 1993). The solvent can reach the interior through cracks and pores, especially in agglomerated powders. It has also been shown that surface fat does not necessarily correlate to solvent-extractable free fat because the latter also includes some near-surface fat (Buma, 1971a). Surface fat and not free fat by solvent extraction was shown to be related to the oxidative stability of cholesterol in fat powders (Granelli et al., 1996). In 1971, Buma (1971c) proposed a model (Figure 1) to describe where the extractable free fat originates: f_s = surface fat, f_l = outer layer fat from fat globules in the surface layer of the particle, f_c = capillary fat constituted by fat globules that can be reached by the solvent through capillary forces, and f_d = dissolution fat consisting of fat reached by solvent through holes left by already extracted fat.

The pioneering work of Fäldt et al. (1993) made quantitative measurement of the different chemical species on the surface of food powders possible. This group adapted a technique, electron spectroscopy for chemical analysis (**ESCA**), for the direct determination of surface fat on food powders (as well as protein and carbohydrate). Using this method, samples are placed under very high vacuum (10^{-7} Torr) in an AXIS HS photoelectron spectrometer, where they are irradiated with x-ray photons of a well-defined energy. This procedure causes a complete transfer of the photon's energy to an atomic or molecular orbital electron. Where the electron binding energy is lower than the photon energy, electrons are emitted from the atom with a kinetic energy equal to the difference between the photon energy and the binding energy minus the spectrometer work function. Because the total binding energy is characteristic for each element and orbital, an analysis of the emitted photoelectrons allows an identification of elements in the near surface region (10 nm depth; Fäldt et al., 1993). This technique has been now used by several researchers to study the surface topography of a wide range of dehydrated emulsions (Pedersen et al., 1998; Kim et

Figure 1. Proposed model for the location of the different fractions of solvent-extractable fat. f_s = surface fat, f_l = outer layer fat from fat globules in the surface layer of the particle, f_c = capillary fat constituted by fat globules that can be reached by the solvent through capillary forces, and f_d = dissolution fat consisting of fat reached by solvent through holes left by already extracted fat. (Data from Neth. Milk Dairy J. 25:88. Reproduced with permission from Elsevier.)

al., 2002; Christensen et al., 2002; Millqvist-Fureby, 2003; Vega et al., 2005b).

Surface analysis by ESCA generates a typical 3-component diagram (fat, protein, and carbohydrate) in which the composition of the original emulsion (on a dry basis) and the composition of the powder after spray drying are plotted. In some cases, the surface composition after humid storage is also plotted (Figure 2). Here, the surface coverage of spray-dried emulsions containing 3 different fats immediately after drying and after humid storage was plotted. It could be observed that encapsulation was very efficient, as the surface fat content was <10% for all treatments. After storage under humid conditions, lactose crystallization caused leakage of fat to the surface in all powders studied to a level up to 75%.

Although the use of ESCA offers a new approach to the characterization of dehydrated emulsions, there are still some reconciliations to make. When measuring the surface composition of whole milk powder [(in weight percentage) fat = 30%, protein = 30%, and lactose = 40%], Fäldt and Sjöholm (1996) reported a surface composition of 55% fat, 30% protein, and 15% lactose, and Kim et al. (2002) reported a 99% fat surface coverage. Differences are difficult to attribute to differences in the bulk composition of powders, as the feed was practically the same. However, Fäldt and Sjöholm (1996) also reported the surface composition of whole milk powder

Figure 2. Triangular phase diagram showing the surface chemical composition of powder particles by electron spectroscopy for chemical analysis. Total composition of the spray-dried powder, assuming even distribution of all ingredients throughout the powder (●); spray-dried powder (■); and humid-stored, spray-dried powder (□). Powders contained hardened rapeseed oil (a), soybean oil (b), or hardened coconut oil (c). (Data from Int. J. Pharm. 171:257. Reproduced with permission from Elsevier.)

obtained at different stages of the drying process and found that the powders collected after the fluid bed and Cyclone Number 1 had almost identical surface composition, but powders collected after Cyclone 2 had a fat surface content around 90%. Those researchers attributed this difference to excessive mechanical stress that exposed fat to the surface of the powder. It is probable that the powders used by Kim et al. (2002) might have been mechanically stressed or that the drying conditions, especially the atomizer disc speed, were drastically different.

Another issue not yet addressed by this technique is the fact that surface fat quantified by this method does not account for the depth of the fat layer being scanned, which can only underestimate the real amount of fat present on the surface of the powder. No correlation was found between the fat surface calculated by ESCA and the free fat obtained by nonpolar solvent extraction (Fäldt et al., 1993; Millqvist-Fureby, 2003). A probable explanation for this is the fact that fat extraction involved an extremely long contact time (2 min) between the powder and the solvent, notwithstanding the shaking applied. This certainly extracted fat situated between cracks and pores of the powder particles.

A more systematic analysis of surface-fat distribution has been proposed (Kim et al., 2005). These researchers

categorized fat after a step-wise extraction method into the following: surface-free fat = the portion of fat extracted after rapidly washing 1 g of powder with 4×5 mL of hexane; inner free-fat = fat extracted by exposing the residue from the prior step to 40 mL of hexane for 48 h; and encapsulated fat = the fat extracted after dissolving the residue from the previous step into warm water and mixing it with a hexane-isopropanol blend (3:1, vol/vol). The most interesting outcome of the study was that there were compositional differences between the free fat and the encapsulated fat coming from either whole milk or cream powders. The free fat fraction (surface and inner fat) had slightly higher concentrations of high melting triglycerides than the encapsulated fat.

Reconstitution

A major property of dehydrated emulsions manufactured for consumer use is their ease of reconstitution. However, it is more important that they reconstitute to the same droplet size distribution of the parent emulsions. The reconstitution process in water can be divided in 4 steps: wetting, submersion, dispersion, and dissolving (Freudig et al., 1999). Among these steps, wetting of the particles is very often the reconstitution-rate controlling step. Wettability is understood as the ability of a bulk powder to imbibe a liquid under the influence of capillary forces. Generally, it depends on powder particle size, density, porosity, surface charge, surface area, the presence of amphipathic substances, and the surface activity of the particles. Surface coverage with hygroscopic components (e.g., lactose) yields good wetting properties because of the small contact angle (Fäldt and Bergenståhl, 1996b; Kim et al., 2002). Fast wetting is also favored by large particles of high porosity; this is why agglomeration of particles to larger units and addition of natural surfactants (e.g., soy lecithin) to powders are commonly used to enhance the wettability of milk powders (Schubert, 1993). The surface composition of powders is expected to play an important role in the wetting process. Whole milk powder and cream powder (1 g/100 mL of water) could not be wetted within a reasonable time frame (15 min). After a very quick wash with petroleum ether, wetting time was reduced to 35 s for whole milk powder and was reduced to 100 s for cream powder, suggesting that the surface of the powders was heavily loaded with fat (Kim et al., 2002). Even greater differences in wetting times after surface fat extraction were found for spray-dried ice cream mixes (Vega et al., 2005b). Bulk materials being wetted slowly can change during wetting. If particles dissolve in the liquid, in most cases, larger pores result, which permit faster wetting. At the same time, however, the viscosity of the liquid that surrounds the

powder might increase as a result of the dissolving of particles, to an extent that the effect caused by larger pores is canceled or it may result in a slower wetting rate. Swelling of the particles always results in a slower rate of wetting, which might approach even zero, as in the case of whey protein concentrate (WPC; Kim et al., 2002).

Storage Stability

As stated earlier, spray drying is a fast process that produces dry solids that often exist in an amorphous state. This gives thermoplastic and hygroscopic properties to the product being dried, and as a result, a) it tends to stick on the walls of the drier during processing, and b) it shows great sensitivity to moisture and temperature fluctuations during storage. This is particularly true for systems containing high levels of low molecular weight carbohydrates (Bhandari et al., 1997a; Bhandari and Howes, 1999). The susceptibility to deterioration during storage at high temperatures and/or relative humidities for sugar-containing products has been related to their glass transition temperature (T_g) (Aguilera et al., 1995; Christensen et al., 2002; Vega et al., 2005a). Liquids in the amorphous state have a very high viscosity ($>10^{12}$ Pa·s), which makes them appear as solids. As the temperature rises, the viscosity of these glasses decreases to a critical value of around 10^7 Pa·s, where they become sticky. The temperature associated with this critical viscosity decreases with increasing water content. Roos and Karel (1991) correlated the T_g to critical viscosity and found that the critical viscosity was reached at a temperature 10 to 20°C above the T_g . Based on this, it can be established that any combination of temperature and relative humidity and water activity will promote deteriorative processes (such as sugar crystallization) in food powders containing high proportions of sugars as shown by Roos (1995) and Jouppila and Roos (1994).

Cohesion, defined as inter-particle stickiness, is intrinsically linked to powder composition and storage conditions. In the context of powdered emulsions, it becomes a more complicated issue, as powders comprise a mixture of components. Sugars (i.e., lactose), fat, and proteins all contribute to cohesion. It has been reported that the fat component of whole milk powder contributes to a 2-fold increase in powder cohesion compared with skim milk powder when the temperature is increased from 30 to 65°C. If lactose and the necessary water content are present with this, increase is at least 3-fold. Water content, even without lactose plasticization, also affects cohesion, especially at values $>6\%$ wt/wt (corresponding to 50 to 70% relative humidity). This can result in the formation of liquid bridges (amorphous

lactose and water) or in plasticization of the powder because of soluble components dissolving in excess water, resulting in a greater contact area and surface stickiness (Rennie et al., 1999).

Cohesion determines flowability and, broadly speaking, powder flowability is all about powder dynamics. It is the packed state, where the particles are not suspended in a fluid and are in close contact with each other, where there is significant friction and cohesive forces resisting flow. Particle size also has a major influence on powder flowability. A powder may be considered as having a particle size of $<200\text{ }\mu\text{m}$, and as the size is reduced below this value, flowability is progressively impaired. This reduction in flowability is due to the increased surface area per unit mass of powder. More surface is available for cohesive forces, in particular, frictional forces to resist flow (Teonou and Fitzpatrick, 1999; Vega et al., 2005b).

Caking is another deleterious phenomenon affecting dairy powder stability. It involves transformation of a low-moisture, free-flowing powder into lumps, then into an agglomerated solid, and ultimately into a sticky material because of exposure to high humidity and high temperature atmospheres. This results in the loss of functionality and reduced quality. Caking can also occur as a result of crystallization, either after melting or after solubilization of crystal surfaces (including fat); surface wetting followed by water equilibration or cooling; or electrostatic attraction between particles (Teonou and Fitzpatrick, 1999). Free fat on the surface of the powder can also contribute to caking (Foster et al., 2005; Vega et al., 2005b). Further complications appear if the type and melting properties of fats being encapsulated are considered. It was found that fats that are liquid, semi-crystalline, or crystalline at room temperature rendered powders with different encapsulation efficiencies, fat surface coverage, and reconstitution properties (wettability and final particle size distribution), and fats with intermediate melting ranges (such as milk fat) showed the highest surface fat values (Fäldt and Bergenståhl, 1995b; Pedersen et al., 1998). It is expected that systems with a low-fat encapsulation efficiency will show the highest susceptibility to caking.

Having introduced the main techniques (and their variants) used to characterize spray-dried emulsions, the following sections will discuss in detail how different carbohydrates (of low and high molecular weights) as well as the 2 types of milk proteins act as (co)encapsulants during emulsion dehydration.

ENCAPSULANTS

Effective microencapsulation requires capsules of high physical integrity, i.e., the core material should

be completely surrounded and protected by the encapsulant (or wall system). An ideal wall material used for microencapsulation should have bland flavor, high solubility, and possess the necessary emulsification, film-forming, and drying properties. In addition, its concentrated solution should have low viscosity to facilitate the spraying step (Rosenberg and Young, 1993). The resulting ideal encapsulant should be a hybrid between (or a combination of) a protein and a carbohydrate.

Encapsulants used in emulsion dehydration are substances that have fat-encapsulating (but not necessarily fat-emulsifying) properties during the spray-drying process. They improve product stability by being transformed into amorphous materials (or glasses) as a result of a high dehydration rate in the spray-drying tower (Roos et al., 1996; Bhandari and Howes, 1999). An amorphous food is formed at nonequilibrium conditions either by removing the dispersing medium or solvent (in this case, water) or from the melt by cooling or rapid super-cooling. Such material is not in thermodynamic equilibrium; therefore, it is unstable relative to its crystalline form. In other words, the amorphous state is metastable, and it will tend to convert to the crystalline state with a rate depending on temperature and water content, which are both important factors for the stability of the powder during storage. The T_g is a critical and specific property of an amorphous material (i.e., food) used to map powder shelf stability using water and temperature as coordinates (Roos, 1995). Generally speaking, a particular food system could remain indefinitely stable as long as it is kept below its T_g .

Carbohydrates

Lactose. Lactose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is a disaccharide found only in milk. It is perhaps the continuous matrix forming material most widely used for spray-drying purposes. It is also one of the most extensively utilized pharmaceutical excipients, commonly used as filler in tablets and capsules and as a carrier for dry powder inhalation. Lactose shows many characteristics of the ideal encapsulant (not emulsifier), as it has a relatively bland flavor and sufficient solubility and its concentrated solution has low viscosity. Lactose products are often made by spray drying of previously concentrated and precrystallized lactose solutions. Precrystallization is necessary to avoid caking problems during drying and storage associated with the hygroscopicity and plasticization of amorphous lactose (Schuck and Dolivet, 2002). During the production of milk powders or solid-state dairy emulsions with no precrystallization step, evaporation of water during spray drying is so rapid that, despite saturation, lactose cannot crystallize, but remains in the powder as an amorphous, solid

constituent. It is this lactose glass that has been recognized as the main encapsulant of milk fat in whole milk powder and spray-dried, dairy-like emulsions made with WPC and whey protein isolates (**WPI**; Buma, 1971b; Young et al., 1993a,b).

Amorphous materials are stable only at temperatures below their T_g , which, in the case of pure lactose, is 107°C (Miao and Roos, 2004). However, the T_g is severely depressed to values below room temperature by the presence of even negligible amounts of water, which accelerates the rate of deteriorative processes in foods, including crystallization of sugars (associated with caking), fat oxidation, and the Maillard reaction (Roos and Karel, 1991; Roos, 1993; Jouppila and Roos, 1994; Roos et al., 1996; Vega et al., 2005a).

Depending on lactose concentration, the T_g of milk powders (i.e., skim or whole milk and whey powders) and/or dehydrated dairy emulsions containing lactose have been found to be very similar to that of pure lactose (Jouppila and Roos, 1994; Vega et al., 2005a). This has direct repercussions on stickiness and fouling during spray drying. As products are being dried, they become thermoplastic and hygroscopic; as a result, they tend to stick on the walls of the drier during processing (Bhandari et al., 1997b; Bhandari and Howes, 1999; Schuck et al., 2005). Stickiness of sugar-containing products has been associated with their low T_g (Roos, 1987; Roos and Karel, 1991; Vega et al., 2005a). During spray drying, the glass transition of the atomized product increases as the water content is reduced toward the end of the drying operation, and particles may reach a temperature close to the outlet air temperature. If $T > T_g + 10^\circ\text{C}$, stickiness will certainly occur. Interestingly, with the exception of work by Vega et al. (2005a), the criteria for choosing drying conditions (i.e., inlet and outlet temperatures) are not discussed in literature dealing with the manufacturing of solid-state emulsions. Consequently, little can be built around the importance of these process parameters. To further stress the importance of T_g in the postdrying stability of the newly formed dehydrated emulsion, it is important to note that such stability will continue to be governed by the relationship between humidity and temperature and its influence on product caking, lumping, flowability, and wettability (Jouppila and Roos, 1994).

When soybean oil emulsions made with sodium caseinate (**NaCas**; emulsifier) and lactose (encapsulant) were spray-dried and subsequently exposed to a 75% relative humidity, the surface fat content was low in powders with a low mass fraction of lactose and very high in those with a high lactose mass fraction. This was attributed to depressed T_g and subsequent lactose crystallization (Fäldt and Bergenstahl, 1995a). Similar results have been reported elsewhere (Moreau and Ro-

senberg, 1993; Fäldt and Bergenstahl, 1995b; Rennie et al., 1999).

Lactose is rarely used as encapsulating material on its own. It is most often used in combination with milk proteins, as earlier works aimed to mimic the composition of milk as a model emulsion system. For this reason, the properties of lactose as an encapsulant will be thoroughly discussed in the sections dealing with the use of milk proteins in dehydrated emulsion preparations.

Sucrose. Sucrose is a disaccharide with a low T_g (66°C) compared with that of lactose (Christensen et al., 2002). It is for this reason that sucrose is rarely used as encapsulant, as its T_g could be easily surpassed at most conventional outlet drying temperatures. When used, it has been in the presence of lactose (Vega et al., 2005a) or high molecular weight carbohydrates such as maltodextrins (**MDx**) and native or modified starches (Onwulata et al., 1994, 1996; Christensen et al., 2002). Vega et al. (2005a) found that the marginal feasibility of spray drying ice cream mixes with sucrose concentrations of up to 42% (dry basis) was strongly dependent on the T_g of the mix and the selected drier outlet temperature. Mixes that contained lactose in a 1:2 lactose-to-sucrose ratio showed a T_g of 77°C and behaved very similarly to a model solution with exactly the same sugar composition ($T_g = 79^\circ\text{C}$). The outlet temperature used in this study was 70°C. The water content of the powder was around 2%, which was considered enough to depress the T_g to $<70^\circ\text{C}$, which made the powder sticky; for this reason, recovery after drying was marginally successful (i.e., 50%). Onwulata et al. (1994, 1996) prepared emulsions of milk fat using sucrose and 2 types of starches as encapsulants. The fat load was between 400 and 600 g of fat/kg of dried emulsion, and the encapsulants represented between 52 and 33% of the dry weight. Milk fat was distributed in the walls of the powder particles when modified starch was the encapsulant; but powders with all-purpose flour as the encapsulant showed loose matrices enclosing large fat droplets, demonstrating structural weakness, which was attributed to the formation of a viscous pasty emulsion after homogenization that was difficult to atomize. Fat droplets were enclosed without central voids within the capsules when sucrose was the encapsulant, which was the best encapsulant with <6 g/100 g of extractable fat. Interestingly, powders made with sucrose showed no internal voids, which suggested structural stability and better fat encapsulation properties to the matrix. Researchers did not discuss the effect of sucrose concentration on yield after drying.

In a separate study, the T_g and storage stability of spray-dried sucrose-hydroxypropylmethylcellulose (**HPMC**) mixtures, relative to those of amorphous sucrose alone, were investigated (Christensen et al.,

2002). The stability of the dry emulsions was investigated in a conventional stability study. Results showed that during storage at 75% relative humidity, the water content of the dry emulsions was increased from 2.0 to 2.4% at ambient temperature and to 6.0% at 40°C. Crystallization of amorphous sucrose was initiated after 5 mo of storage at ambient temperature and after 2 mo at 40°C. At the end of the storage period, the degree of crystallization was <1 and 25%, respectively. Reconstitution properties of the dry emulsions were not affected by the crystallization of amorphous sucrose. The dry emulsions could be reconstituted into emulsions with identical properties to the original emulsions after 6 mo of storage in 75% relative humidity at ambient temperature and 40°C. The outer structure of the dehydrated emulsions was not changed after storage in 75% relative humidity at 40°C for 6 mo. The dry emulsions still consisted of well-separated spherical particles with shallow dents.

For dehydrated emulsions containing 40% HPMC, 30% fractionated coconut oil, and 30% sucrose, the T_g was increased by 12°C relative to the T_g of amorphous sucrose. At higher HPMC concentrations, deviations from the Gordon-Taylor equation were observed. This indicated non-ideal mixing above 30% HPMC. Crystallization was inhibited despite an apparent lack of anti-plasticizing (i.e., T_g -elevating) effects (Shamblin et al., 1996), and consequently, the effect of the polymer was not linked directly to T_g , and other factors were claimed to be involved. It was concluded that the dehydrated emulsions were physically stable with respect to the lifetime of a pharmaceutical product when stored under dry conditions and at temperatures up to 28°C.

MDx. Maltodextrins are the hydrolysis products of starch with a dextrose equivalent (DE) <20 (Chronakis, 1998). They represent a mixture of oligosaccharides with a broad molecular weight distribution, which are mainly commercialized as powders. Unlike starch, MDx are readily soluble in water. Very low DE MDx are used as fat replacers in products such as ice cream and low-calorie spreads, as some of their functional properties include bulking, gelling, crystallization prevention, cryo-protectants, dispersing, and binding agents (Chronakis, 1998).

Maltodextrins reduce the rate of Maillard reactions when used in the microencapsulation of food components such as fats and oils, vitamins, minerals, and colorants. Their surface active properties and the low viscosity of their solutions do not offer emulsification of oily or fatty materials. Regardless of this, relatively important disadvantage, MDx are frequently used as coencapsulating agents in emulsion spray drying (McNamee et al., 1998; Pedersen et al., 1998; Hogan et al., 2001; Christensen et al., 2001a; Watanabe et al.,

2002; Sliwinski et al., 2003). It was reported that the use of MDx (DE = 12.6) at 10 to 30% (wt/wt of liquid emulsion)—using NaCas as emulsifier—rendered stable and spray-dryable emulsions that reconstituted into their original-like emulsions as long as the ratio between MDx + NaCas (total solids) and the dispersed phase (fractionated coconut oil) was >1.35 (Dollo et al., 2003). Hogan et al. (2001) analyzed the effect of MDx DE on emulsion stability, drying, and reconstitution of soybean oil emulsions stabilized by NaCas. Results showed that increasing DE of the carbohydrates used as encapsulants reduced emulsion viscosity, reflecting the decrease in average molecular weight and improved solubility of higher DE carbohydrates. The lower viscosity of MDx solutions is advantageous in encapsulation by spray drying, as it allows a higher total solids concentration in the feed emulsion (Kenyon, 1995). The microencapsulation efficiency (ME) {defined as [(total oil – extractable oil)/total oil] × 100 after extraction with a non-polar solvent} increased from 0 to 88.4% with increasing DE from 0 to 28. The positive relationship between ME and DE was attributed to the smaller oligosaccharides in high DE powders forming less porous, more uniform matrices on drying, which were more impervious to the solvent than those formed by low DE preparations. The results suggested that the ME was optimized using carbohydrates with average molecular weight <1,000 Da (i.e., DE > 18.5). Scanning electron micrographs of powders containing NaCas and MDx with DE 5.5 appeared agglomerated (caked), possibly because of the presence of fat on the surface (i.e., low ME efficiency). In contrast, powders composed of DE 28 MDx were characterized by discrete smooth or wrinkled particles (Figure 3). There was no evidence of agglomeration for powders containing carbohydrates with a DE >5.5. Similarly, the average droplet size of spray-dried emulsions redispersed in water decreased from 15.4 to 1.3 μm when the DE was increased from 0 to 14.

Gum Arabic. Historically, gum arabic has been the most commonly used “natural” matrix material for food encapsulation. Its solubility and low viscosity in water and emulsification characteristics make it very versatile for most encapsulation applications (Kenyon, 1995). Gum arabic is composed of molecules with a highly branched arrangement of simple sugars (galactose, arabinose, rhamnose, and glucuronic acid units; Anderson and Stoddart, 1966). It also contains protein (2%, wt/wt) covalently bound within its molecular arrangement (Anderson et al., 1985). It dissolves readily in water, and because of its small hydrodynamic volume, it renders viscous solutions only at very high concentrations. A 30% solution of gum arabic is less viscous than a 1% solution of xanthan gum or carboxymethylcellulose at low shear rates with the extra benefit of showing New-

Figure 3. Scanning electron micrograph of spray-dried soy oil emulsions stabilized by wall materials combining sodium caseinate and carbohydrates prepared at a ratio of 1:4 and a core-to-wall ratio of 1.0. Carbohydrates had a dextrose equivalent of 5.5 (left) and 28 (right). (Data from *Int. Dairy J.* 11:137. Reproduced with permission from Elsevier.)

tonian flow. Probably the most interesting property of gum arabic, one that brings it close to being the “ideal” encapsulant for emulsion spray drying, is that it can act also as an emulsifier. It is known that its protein-rich high molecular mass fraction adsorbs mainly onto the surface of oil droplets. The protein component is relatively small, and the concentration of gum arabic needed to obtain long-term emulsion stability is rather high (12% for a 20% orange oil emulsion; Williams and Phillips, 2000).

McNamee et al. (1998) analyzed in detail the emulsification and encapsulation properties of gum arabic. Emulsions of gum arabic and soybean oil at an oil-to-

gum ratio of 0.25 to 5.0 were prepared to produce spray-dried powders with an oil content ranging from 20 to 82% (wt/wt). The droplet size distribution curves were unimodal, and no significant variation in the $D_{4,3}$ (the volume-surface weighted diameter) value ($0.57\ \mu\text{m}$) of the emulsions was observed when the oil-to-gum ratio was increased from 0.25 to 1.0. However, as the oil content of the emulsion was increased further, $D_{4,3}$ increased linearly ($R^2 = 0.995$) up to a maximum of $2.02\ \mu\text{m}$. These results suggested that at an oil-to-gum ratio between 1.0 and 2.0, the quantity of gum arabic available to act as an emulsifier became limiting, resulting in the formation of larger oil droplets and thus reducing the specific fat surface area, requiring stabilization (Figure 4). The $D_{4,3}$ value of emulsions prepared with an oil-to-gum ratio <2.0 was $<1\ \mu\text{m}$, which was in accordance with the diameter quoted elsewhere (Thevenet, 1995) as being sufficient to produce stable gum arabic, stabilized emulsions. Similar results were found by other groups after encapsulating D-limonene at the same oil-to-gum ratio (0.25 to 1; Sootitawatwat et al., 2005).

Microencapsulation efficiency decreased from 100 to 48% when the oil-to-gum ratio was increased from 0.25 to 5.0, respectively (McNamee et al., 1998). These results showed similar trends as those reported by others (King et al., 1976), although the latter group reported an encapsulation efficiency of about 29%. McNamee et al. (1998) attributed the difference to the fat extraction method used and to a different dispersed phase (orange flavor oil).

In terms of redispersability, McNamee et al. (1998) also found that droplet size distributions were similar

Figure 4. Effect of the soy oil-to-gum arabic ratio (0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, and 5.0) on the lipid globule size distribution of gum arabic-stabilized emulsions. (Data from *J. Agric. Food Chem.* 46:4551. Reproduced with permission.)

Figure 5. Particle size distribution of gum arabic-stabilized emulsion (solid line), a spray-dried emulsion (heavy, solid line), and a redispersed spray-dried emulsion (dashed line) prepared at an oil-to-gum ratio of 3.0 (75% oil dry wt). (Data from J. Agric. Food Chem. 46:4551. Reproduced with permission.)

to that of the original emulsion in redispersed systems with an oil-to-gum ratio of 0.25 (Figure 5), whereas for an emulsion with an oil-to-gum ratio of 3.0 (75% oil), the size distribution for the redispersed emulsion showed a bimodal distribution. The second peak was attributed to particles that did not dissolve (even after 24 h of constant stirring). To note, this was a 0.3% (wt/wt) redispersed emulsion; it seems more plausible to think that the presence of a bimodal distribution after reconstitution was due to either larger fat droplets created by coalescence during drying or to bridging flocculation caused by insufficient gum for complete emulsification. This is consistent with the lower ME values reported for this treatment.

Gum arabic was found to be the least effective encapsulating material for orange oil emulsions when compared with WPI, NaCas, or soy protein isolate (Kim and Morr, 1996). Gum arabic showed similar encapsulation efficiency and surface oil coverage, but was found to have the highest release of volatile compounds as a function of time and temperature and the highest limonene oxidation rate.

HPMC. Cellulose ethers, especially HPMC, are frequently used as the basis for sustained-release hydrophilic matrix tablets. Most studies have been performed on 4 non-ionic methylated derivatives of cellulose ethers. These have different substitution levels (16.5 to 30% of methoxy and 4.0 to 32.0% of hydroxypropoxy groups) and are methylcellulose, HPMC E type (HPMC 2910), HPMC F type (HPMC 2906), and HPMC K type (HPMC 2208). They are available in a wide range of molecular weights and are classified on the basis of the

viscosities of their 2% (wt/wt) aqueous solutions (Ford, 1999; Ishikawa et al., 2000).

Dehydrated emulsions have been prepared by spray drying liquid oil-in-water emulsions containing fractionated coconut oil dispersed in aqueous solutions of HPMC. These dry emulsions were found to be cohesive powders with poor flow properties (Christensen et al., 2001b). Addition of sucrose eliminated the cohesiveness of the dry system. As discussed previously, HPMC has been successfully used as coencapsulant with sucrose to encapsulate emulsions with up to 30% fractionated coconut oil as the dispersed phase. Of interest, was the ability of HPMC to inhibit sucrose crystallization during storage at high relative humidities and temperatures (75% relative humidity; 40°C) and also the fact that no emulsifier was used to stabilize the emulsions. This certainly represents an area where further research is needed, including: a) the minimum amount of HPMC necessary to avoid crystallization, b) the ability of HPMC to inhibit the crystallization of more humidity-sensitive sugars (i.e. lactose), and c) how emulsions were stabilized by the sole presence of the carbohydrates.

A pertinent observation on the use of HPMC during spray drying is that at high concentrations, blockage of the atomizer may arise, as aqueous solutions of HPMC exhibit thermoreversible gelation (Sarkar, 1995; Ford, 1999). To solve this issue, at least on the laboratory scale, the temperature of the atomizer has been reduced by water cooling (Christensen et al., 2001a).

Although the aforementioned materials have many of the properties of an ideal encapsulating agent, most lack the interfacial functionality of emulsifying compounds, which is vital in the initial step of emulsion formation. Proteins of different origins (in particular dairy proteins) have been the materials of choice for microencapsulation purposes. The high cost of milk proteins in comparison with carbohydrates is, however, disadvantageous. A mixture of relatively low-cost carbohydrates with casein or whey proteins (**WP**) as surfactants may offer potential as cost-effective, functional, fat-encapsulating materials.

Milk Proteins as Encapsulants

Milk proteins in soluble or dispersed forms are widely valued as food ingredients with outstanding surface-active and colloid-stabilizing characteristics (Dickinson, 1997). During homogenization, the various protein molecules and aggregates adsorb rapidly to the newly formed oil-water interface. The resulting steric-stabilizing layer immediately protects the oil droplets against coalescence and provides physical stability to the emulsion during processing and storage.

The 2 main classes of milk proteins are caseins and WP. Bovine casein consists of 4 types of protein with substantially different properties: α_{s1} -, α_{s2} -, β -, and κ -CN, representing approximately 38, 10, 36, and 12% of the whole casein, respectively (Robson and Dalgleish, 1987; Fox, 2001). All caseins, especially β -CN, contain a high level of proline, which prevents the formation of secondary structures (α -helices, β -sheets, and β -turns) and renders the caseins stable to denaturing agents, e.g., heat or urea, or processing conditions (homogenization and pasteurization), and contributes to their high surface activity, which gives them good foaming and emulsifying properties (Fox, 2001). Conversely, WP are those proteins that remain soluble after coagulation of the caseins at pH 4.6 at 20°C. The WP fraction of bovine milk contains 4 main proteins: β -LG (50%), α -LA (20%), BSA (10%), and Ig (10%) (Morr and Ha, 1993; Fox, 2001). Native WP, mainly because of their compact, globular conformation, remain soluble at or near their isoelectric points (pH 4.2 to 5) and are completely denatured by heating at 90°C for 10 min (Fox, 2001).

WP. Whey proteins were first proposed as encapsulants in the early 1990s (Moreau and Rosenberg, 1993; Rosenberg and Young, 1993; Young et al., 1993a,b). Since then, several research groups have studied the encapsulating behavior of different WPC and WPI, either alone, or in combination with NaCas or lactose (Fäldt and Bergenstahl, 1996a,b; Keogh and O'Kennedy, 1999; Landstrom et al., 2000; Millqvist-Fureby et al., 2001; Sliwinski et al., 2003). Perhaps the main disadvantage relative to the use of WP as encapsulants is their susceptibility to heat denaturation and the effects on emulsion particle size before spray drying and after reconstitution (Sliwinski et al., 2003). Heating of WP-stabilized emulsions at 80°C results in aggregation of particles and a reduction in the kinetic stability of the emulsion (Damodaran and Anand, 1997; Demetriades et al., 1997). An increase in the concentration of WP accelerates the rate and degree of aggregation, suggesting that the main mechanism is the denaturation and aggregation of unadsorbed protein (Euston et al., 2000).

Young et al. (1993a), who used different WP products (WPI, WPC75, and WPC50) to assess their ME, found that, regardless of the fat load (25, 50, or 75%, wt/wt; anhydrous milk fat) and the total solids of the emulsion prior to spray drying, WPC50 showed the best ME (ranging from 98 to 70%). Young et al. (1993a) also partially replaced WPI with lactose and showed that this gradually improved ME; at a 1:1 mass ratio, ME was 95%. The superior ME of WPC50 was attributed to its high lactose content (37%). Such results implied that the ME of WP is indeed low. Lactose was essential to improve encapsulation efficiency. Young et al.

(1993b) also analyzed the ME of WP when combined with different high molecular weight carbohydrates (such as MDx and modified starches, with or without surface-active properties). Results showed that the ME of WPI by itself was low (i.e., 37%) and did not differ much from that of the individual carbohydrates tested. Interestingly, once combined in a 1:1 ratio, ME values increased close to 90%.

Fäldt and Bergenstahl (1996a,b) also investigated the encapsulating ability of WP and found that their ability to encapsulate soybean oil was low compared with that of NaCas, based on the amount of fat covering the powder surface after spray drying. The fat coverage varied from 45 to 60% as the concentration of WP increased. This was consistent with the results of earlier investigations made on other proteins such as NaCas and BSA (Landstrom et al., 2000).

The source of WP has been found to be particularly important for controlling the initial fat globule diameter and subsequent aggregation of fat globules. Whey protein isolate-stabilized emulsions with a 5:4:4 fat:WPI:lactose ratio showed very little time-dependent aggregation at low levels of added salt (sodium and calcium salts), especially after 4 homogenization passes (Keogh and O'Kennedy, 1999). However, if WPI was replaced by WPC-35 as emulsifier, the fat globules showed significant aggregation after 2 homogenization passes. This behavior paralleled that of WPI at the higher levels of added salts. Thus, WPI (without added salts) appears to be preferable to WPC as an emulsifier. Free fat in the powders appeared to increase with fat and WP levels and decreased with lactose content. Higher lactose-to-protein ratios also reduced aggregation of fat globules in the emulsion during drying, which resulted in less free fat in the powder and lower $D(v, 0.9)$ values in reconstituted emulsions. The use of a combination of WPI and lactose largely avoids the inclusion of salts present in WPC, but WPI is a commercially significant cost factor. Increasing the level of lactose and the lactose-to-WP ratio reduced free fat significantly, but reduced surface fat only marginally. The only significant composition factor affecting surface fat, and thereby the level of oxidation, was the fat content of the emulsion (Keogh and O'Kennedy, 1999).

Whey proteins have also been combined with NaCas at different ratios for encapsulation purposes (Sliwinski et al., 2003). Use of 50% NaCas with WP was shown to have hardly any influence on the physicochemical properties of soybean oil-water emulsions after spray drying. Spray drying resulted in a) an increase of the adsorbed amount of WP of emulsions containing WP fractions of $\geq 60\%$ and 2) an increase of droplet size distribution in emulsions containing WP fractions of $\geq 70\%$, which was attributed to aggregation during

Figure 6. Percentages of adsorbed sodium caseinate after emulsion preparation (◆) and after spray drying and reconstitution (▲) and adsorbed whey protein after emulsion preparation (■) and after spray drying and reconstitution (●) for milk protein-stabilized oil-in-water emulsions with constant protein content and varying ratios of sodium caseinate to whey protein. (Data from Colloid Surface B 31:219. Reproduced with permission from Elsevier.)

spray drying. After emulsion formation, NaCas adsorbed preferentially at the oil-water interface (when NaCas and WP were present at equal amounts); almost 90% of the adsorbed layer was NaCas. Interestingly, after spray drying and reconstitution, a part of the adsorbed NaCas was displaced by WP. Sliwinski et al. (2003) concluded that during spray drying (and probably after reconstitution), WP were capable of replacing adsorbed casein proteins from the surface (Figure 6). The change in protein composition of the adsorbed layer was probably the result of heat denaturation and aggregation of WP by the formation of disulfide bonds. Of the 2 WP, the amount of adsorbed β -LG increased to the greatest extent.

Heat denaturation of WP during spray drying has received limited attention. Heating a series of WP-stabilized emulsions under a wide range of conditions (enough to cause 0 to 65% denaturation) increased the droplet size before spray drying with increasing heat treatment (Millqvist-Fureby et al., 2001). The droplet size was broader in redispersed emulsions for all heat treatments, and the most severely denatured samples showed bimodal distributions. Millqvist-Fureby et al. (2001) did not elaborate on the significant change on droplet size distribution in the nonheated sample (prior to homogenization and drying) after reconstitution. This change in droplet size was a clear indication of the degree of denaturation undergone by WP during drying. This fact should not have been overlooked (Figure 7).

Figure 7. Emulsion droplet size distribution in fresh (A) and reconstituted (B) emulsions stabilized with whey proteins and subjected to different heat treatments. (Data from Colloid Surface B 21:47. Reproduced with permission from Elsevier.)

In separate studies, Fäldt and Bergenstål (1996a,b) found that, in systems with similar composition and no protein denaturation prior drying, 45% of the powder surface was covered by fat. This suggests that WP denaturation prior to spray drying might have a less significant influence on encapsulation than previously thought.

The surface composition (see previous section) of spray-dried emulsions made with WP showed that fat was poorly encapsulated (surface fat coverage was 55 to 65%); protein was the second major surface component (23 to 32%). The variation in surface fat was rather small over the range of protein denaturation studied; however, it was greater than the standard deviation. Poor encapsulation was attributed to less flexible proteins that diffuse at slower rates after denaturation, creating a less stable emulsion that allowed leakage of fat to the surface. It should be noted that the original composition of the emulsions represented that of milk,

i.e., 40% lactose, 30% fat, and 30% protein. If we consider that a) there were more than enough WP available for liquid emulsion stabilization (provided that no denaturation occurred) and that b) WP undergo denaturation during drying, poor encapsulation is more likely to be caused by protein aggregation and subsequent fat coalescence. The hypothesis of Millqvist-Fureby et al. (2001) was that WP resided on the surface of the powder (not only the fat globule) to allow effective encapsulation. Contrary to their view, it is our opinion that the primary function of the protein is to emulsify the system rather than encapsulate it. The presence of protein on the surface of the powder responds to 2 factors: a) excess protein in solution and b) their superior surface-active properties compared with lactose that cause them to reside at the air-water interface during drying. Further research on this area is obviously necessary.

Caseins and Caseinates. There is a vast amount of knowledge on the use of NaCas as an encapsulant. In previous sections, we have presented already some data concerning several carbohydrates as encapsulants in the presence of NaCas as emulsifier. In the context of microencapsulation, casein and caseinates lack the heat sensitivity of WP and also show superior surface-active properties. These surfactant properties make casein a primary emulsifying agent for a variety of applications, including spray drying (Pedersen et al., 1998; Hogan et al., 2001; Sliwinski et al., 2003; Dollo et al., 2003). Fäldt and Bergensthåll (1996a,b) reported on the ME of WP, NaCas, and mixtures thereof with lactose at different mass ratios of lactose and fat loads. Based on fat surface coverage (see previous section), systems containing NaCas and lactose showed the most effective ME (<10% surface fat), followed by NaCas (up to 30%); WP with lactose (up to 55%), and WP alone (up to 55%) (Figure 8). These results are in agreement with those reported elsewhere (Rosenberg and Young, 1993; Young et al., 1993a,b).

Hogan et al. (2001) studied the encapsulating properties of NaCas on its own having soybean oil as the dispersed phase. They analyzed a vast array of formulations where the oil-to-protein ratio was varied from 0.25 to 3.0 (wt/wt), total oil load ranged from 20 to 75% (dry basis), and homogenization pressure ranged from 10 to 50 MPa with 4 passes. Volume average diameter decreased with homogenization pressure up to 20 MPa; higher pressures did not reduce particle size significantly even at the highest oil-to-protein ratios, which indicated that there was a limiting amount of NaCas to stabilize the liquid emulsion. Protein coverage of fat globules before drying and ME after dehydration decreased with increasing oil-to-protein ratio from 3.1 to 2.04 mg/m² and from 89 to 19% respectively. Hogan et al. (2001) did not report the protein coverage after

Figure 8. Spray-dried emulsions with different soybean oil content with and without lactose. Surface fat coverage as a function of soybean oil concentration (wt/wt, dry basis): emulsions with whey protein only (■), whey protein and lactose at a 2:3 ratio (wt/wt, dry basis; ●), sodium caseinate only (▲), and sodium caseinate and lactose at a 2:3 ratio (★). (Data from Food Hydrocoll. 10:421. Reproduced with permission from Elsevier.)

powder reconstitution; however, they have been the only group associating fat globule protein load to ME. Particle size after reconstitution in water and in a 1% Tween 20 solution showed larger emulsion droplet size than fresh emulsions, which was indicative of fat coalescence during drying (especially for high oil-to-protein ratios). The same researchers concluded that as emulsion droplet size was not dependent on oil-to-protein ratio within the range examined, NaCas needed to be in excess to play a matrix-forming role rather than a surfactant one. Questions arising from this conclusion could be a) If lactose or any other carbohydrate was added as a matrix former, will the concentration of NaCas be the same as to obtain stable emulsions before and after dehydration? And b) What is the minimum concentration of NaCas required to stabilize an emulsion in its liquid and dried/reconstituted state? Such questions are currently being addressed in our laboratory. The results of a study comparing the encapsulation properties of sodium and calcium caseinates in terms of powder surface composition and surface tension of their corresponding solutions was recently published (Millqvist-Fureby et al., 1999). At rapeseed oil loads of 30% (wt/wt), the surface fat coverage for powders made with NaCas fluctuated from 35% at pH 3 to <10% at neutrality. Conversely, calcium caseinate showed a more complex behavior with a maximum fat coverage of 45% at pH 3, a sudden minimum at pH 5.5 of <5% and finally, a surface fat content of around 25% at pH 7. Millqvist-Fureby et al. (1999) attributed this to the pH-dependent aggregation of calcium caseinate;

at intermediate pH, calcium caseinate aggregates and precipitates, and these larger structures are far more efficient at encapsulating fat. This was supported by the fact that fat was replaced by protein on the surface of the powder (i.e., even though lactose content was 40% on a dry basis, its concentration on the powder surface did not increase).

To the best of our knowledge, with the exception of the work of Keogh et al. (2001) and work in progress by the current authors, no studies are available on the direct comparison of the encapsulation properties of casein of different molecular arrays (i.e., micellar vs. nonmicellar). Keogh et al. (2001) studied the stability to oxidation of spray-dried fish oil encapsulated in sodium or calcium caseinates or skim milk powder (**SMP**). The working hypothesis was that vacuole volume (as an indirect measure of the amount of air trapped within a powder particle) is smaller as the level of protein aggregation increases ($\text{SMP} > \text{calcium caseinate} > \text{Na-Cas}$), hence the lower degree of oxidation of encapsulated oil. Emulsions contained a 1:1:1 fish oil:casein:lactose on a dry basis. Fat globule size, vacuole volume, percentage of free fat (as g of fat/g of powder) and surface fat (by ESCA) were the main parameters measured. It was found that, at increasing homogenization pressure (20 to 50 MPa) and number of passes (1 to 5), the 3 casein types showed smaller emulsion droplet sizes, as expected. There was a significant interaction between the effects of homogenization pressure $\times$ number of passes and vacuole volume on the level of free fat. At low vacuole volume (**SMP**), free fat decreased from 24.5 to 2 g of fat/100 g of fat as homogenization pressure and recirculation passes increased, whereas at high vacuole volume (**NaCas**), free fat was practically unaffected (7.6 and 4.8 g of fat/100 g of fat, respectively). Surface fat (determined by ESCA) was unaffected by either homogenization pressure or number of passes when **SMP** was used (around 60% surface fat). Powders made with **NaCas** showed the lowest surface fat coverage regardless of the homogenization conditions used. Similar results were reported elsewhere (Vega et al., 2005b). Interestingly, the best shelf-life (measured on an arbitrary scale) was achieved with **SMP**, and this was attributed to its lower vacuole volume.

THE NATURE OF THE DISPERSED PHASE

Encapsulation efficiency is influenced by emulsion droplet size; fine emulsions were better encapsulated than coarse emulsions. It has become common research practice to homogenize emulsions several times before spray drying in order to achieve the smallest and most stable/uniform particle size. Different protocols exist, from high pressure at 100 MPa with 8 passes (Fäldt and

Bergenståhl, 1996a), to 50 MPa with 4 passes (Keogh et al., 2001), to 23 MPa with only 1 pass (Vega et al., 2005a). All of these studies showed that those pressures rendered sufficiently small droplet sizes to allow successful encapsulation (when the appropriate encapsulant was selected) and suggest that relatively high pressures are not necessarily a prerequisite to achieve successful encapsulation. Similarly, it has been reported that encapsulation is influenced by the melting properties and crystal habit of the dispersed fat phase in combination with different homogenization pressures. Emulsions mimicking the dry composition of milk were spray-dried using different fat phases: fully hardened rapeseed oil (β -stable) and fully hardened palm oil (β' -stable; Millqvist-Fureby, 2003). The solid fats were used alone or in mixtures with rapeseed oil to provide fat phases with different properties; it is unknown if any of these mixtures actually represented the melting behavior of anhydrous milk fat. Emulsions prepared at low homogenization pressure (8 MPa) invariably showed a higher level of surface fat than the corresponding emulsions prepared at high pressure (65 MPa). The surface coverage of fat was related to the ratio of solid to liquid fat in the emulsion and to the pretreatment of the emulsion. Fat encapsulation was more efficient for emulsions with only liquid or solid fat than their mixtures (Figure 9). Similar results were found elsewhere (Fäldt and Bergenståhl, 1995b). For emulsions prepared at low pressure, the preheated emulsions were better encapsulated than the precrystallized emulsions. Emulsions prepared at different homogenization pressures showed, as expected, different median sizes. Emulsions prepared at 8 MPa were bimodal after reconstitution.

Another important consideration regarding the dispersed phase during spray drying is its susceptibility to loss of volatiles and its propensity to oxidation. These 2 topics are quite extensive on their own and deserve to be covered separately. For further information on this topic, the reader is referred elsewhere (Risch and Reineccius, 1995; Granelli et al., 1996; Kim and Morr, 1996; Keogh et al., 2001).

A MODEL FOR THE SURFACE COMPOSITION OF DEHYDRATED EMULSIONS

Views on what comprises the powder surface of dehydrated emulsions (regardless of the method used) and its dependence of emulsion bulk composition vary tremendously. Therefore, we propose a model that aims to include these different views and that highlights the importance of colloidal aspects related to emulsion bulk composition on the final powder surface composition.

Figure 9. Surface coverage of fat as a function of the fraction of liquid oil in the fat phase: a) hardened rapeseed oil/rapeseed oil and b) hardened palm oil/rapeseed oil. ○ = Low homogenization pressures, preheated; □ = low homogenization pressure, precrystallized; ● = high homogenization pressure, preheated; and ■ = high homogenization pressure, precrystallized. (Data from Colloid Surface B 31:65. Reproduced with permission from Elsevier.)

Figure 10 shows the 4 main scenarios on which an emulsion enters the dehydration process. Case A represents an emulsion with limiting emulsifier content (i.e., NaCas or WP) in which bridging flocculation of oil droplets is evident (clusters); similarly, relatively large fat globules are also present because of the insufficient emulsifier content. The gray background in all cases refers to the carbohydrates present in solution. Case B depicts an emulsion in which excess emulsifier is present; it is also most likely to have limited amounts of carbohydrate. Fat globule protein coverage is well above the monolayer value, emulsion droplet sizes can be extremely small (purely dependent on homogeniza-

tion pressure), and emulsions are at risk of depletion flocculation because of excess emulsifier in solution (Dickinson and Golding, 1997). Scenario C shows an emulsion in which emulsifier concentration is within the range to stabilize the emulsion without the risk of either bridging or depletion flocculation. The ratio between the protein and the dispersed phase will vary depending on the type of protein used, and this will determine the carbohydrate load in the emulsion, which, in any case, will represent at least 50% of the dry bulk composition. Lastly, the emulsion depicted in case D represents the particular case of an emulsion stabilized by pure micellar casein. Under identical fat load and homogenization conditions, the amount of micellar casein needed to stabilize an emulsion comprised of anhydrous milk fat (with similar droplet size distribution or specific surface area) is approximately 300% higher than NaCas (Euston and Hirst, 1999). This is probably due to the inability of micellar casein to stretch or unfold around the fat globule surface, which creates a rather thick protein layer around the fat globule. Conversely, we hypothesize that this layer might provide extra physical integrity to the emulsion against coalescence during spray drying, increasing the probability of maintaining the droplet size distribution almost unchanged after reconstitution.

Figure 11 shows the transverse section of a powder particle. Each of the 4 sections represents the powder surface and internal composition that correspond to the 4 bulk-liquid emulsion compositions depicted in Figure 10. Section A shows that relatively large fat globules have formed after spray drying because of coalescence of smaller, poorly emulsified, fat globules. Small globules are still present, but creaming will be observed after powder reconstitution. The surface-fat coverage is very high, i.e., >80%, and is the highest among all of the cases described in the model. The grayish background represents the high proportion of low molecular weight carbohydrates present. High surface protein coverage is obtained in systems with excess emulsifier as depicted in section B. Emulsion droplets are intact after drying and will reconstitute to their parent emulsion. In this case, the darker gray background represents the high protein load of the bulk system. Fat coverage is the lowest among the scenarios represented in the model. Nonetheless, depletion flocculation is likely to occur before and/or after reconstitution. Scenario C shows a system that is more or less balanced in powder surface composition. Here, the droplet size is also maintained, as the globules are fully covered by emulsifier. The presence of carbohydrate on the surface is expected as it represents >50% (wt/wt) of the bulk. Lastly, section D shows that emulsions prepared using micellar casein as emulsifier are stable to the drying

Figure 10. Composition and colloidal state of model emulsions after homogenization and before spray drying. A) Emulsion with limited emulsifier content (as milk protein), where bridging flocculation and relatively large fat globules are common. B) Emulsion with excess emulsifier and limited carbohydrate content (<30%); fat globule coverage is above the monolayer, and the risk of depletion flocculation exists. C) Emulsion with protein concentration just for monolayer coverage, where there are no stability issues in liquid state emulsion; carbohydrate content is >50% (wt/wt, dry basis). D) Micellar casein-stabilized emulsion.

process. The thick protein coverage offered by the bulky casein micelles is hypothesized to protect the system against coalescence of fat droplets during drying. Nonetheless, fat surface coverage is likely to be high (approximately 50%), which could be associated to a slower diffusion rate to the air-water interface of the micelle compared with that of NaCas. This particular case might represent the behavior of whole milk- or milk protein concentrate-stabilized emulsions.

CONCLUSIONS AND FUTURE RESEARCH NEEDS

Milk constituents are highly functional ingredients. They have proved to be valuable in the design and manufacture of valued-added products, such as dairy and dairy-like dehydrated emulsions. In-depth knowledge of surface and colloidal chemistry is, nonetheless, necessary to achieve high quality products. Lactose, as only one of the various carbohydrates available as encapsulants, is indispensable to provide a structural matrix in emulsion dehydration, especially when combined with NaCas. Storage conditions should be monitored carefully to avoid lactose crystallization and subsequent release of encapsulated material. Sodium ca-

seinate is preferred over WP as film-forming material because of superior emulsifying properties and lack of heat sensitivity. The effect of parent emulsion composition on emulsion instability should be understood thoroughly before drying. This is of utmost importance to isolate the influence of the spray-drying process in emulsion stability and powder surface composition, which ultimately governs the wettability, flowability, cohesion, and caking behavior of the dried system.

Emulsion dehydration, with focus on dairy and dairy-like emulsions, has been the subject of a considerable amount of research. A comprehensive understanding of such systems, however, has not been attained. Several aspects related of emulsion dehydration have received limited attention to date, such as the microencapsulation properties of micellar casein (as opposed to NaCas); the colloidal phenomena (such as changes in the oil-water and air-oil interfaces) occurring before, during, and after dehydration; how crystallization of sugars other than lactose (i.e., trehalose or sucrose) relates to surface fat coverage; and finally, the behavior of dehydrated emulsions containing anhydrous milk fat stabilized with non-milk proteins and modified starches.

Figure 11. Transverse section of a powder particle. A) Relatively large fat globules have formed after spray drying because of coalescence of smaller, poorly emulsified, fat; surface fat coverage is very high (>80%). The grayish background represents the high proportion of low molecular weight (MW) carbohydrates present (reduced surface fat coverage is expected in the case of high MW compounds, such as maltodextrins). B) High surface protein coverage in systems with excess emulsifier. Emulsion droplets are intact after drying and will reconstitute to their parent emulsion. The dark gray background represents the high protein load of the bulk system. Surface fat coverage is around 15%. C) Powder balanced in powder surface composition. Droplet size is maintained after drying. Presence of carbohydrate on the surface is expected, as it represents >50% (wt/wt) of the bulk. D) Dehydrated micellar, casein-stabilized emulsion, which is stable to the drying process. Fat surface coverage is high (approximately 50%) because of the slower diffusion rate of the micelle compared with that of sodium caseinate.

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