

THERMAL PROPERTIES AND MOISTURE SORPTION ISOTHERMS OF SPRAY-DRIED ENCAPSULATED MILKFAT

C.I. ONWULATA and V.H. HOLSINGER¹

*U.S. Department of Agriculture², ARS, Eastern Regional Research Center
600 East Mermaid Lane, Philadelphia PA 19118*

Accepted for Publication July 27, 1994

ABSTRACT

Stable emulsions containing 40 or 60% anhydrous butter oil and carbohydrate encapsulants (sucrose, modified starch or all-purpose flour) were spray dried to produce free-flowing shelf-stable powders, according to a 2 × 3 factorial design, replicated three times. Differential scanning calorimetry profiles showed well-defined melting ranges that were related to encapsulant used. Butter oil was almost completely encapsulated when fat content was 40% and sucrose was used as the wall material. Moisture sorption isotherms of powders with sucrose showed characteristic breaks caused by sugar crystallization followed by moisture desorption, whereas powders with modified starch or all-purpose flour continuously absorbed moisture with increasing relative humidity. The solvent-extractable fat fraction increased with increasing relative humidity in all cases. Scanning electron microscopy showed that sucrose-containing powder particles partially dissolved and fused together as a result of moisture uptake, whereas powders with modified starch or all-purpose flour maintained particle identity, even at 80% relative humidity.

INTRODUCTION

Spray drying of milkfat with functional encapsulants, such as starch or other carbohydrates, to form free-flowing powders can reduce storage costs and enhance stability by forming microcapsules to protect the milkfat from oxidative deterioration during storage (Young *et al.* 1993; Imagi *et al.* 1992; Gejl-Hansen

¹Address correspondence to: Dr. Virginia H. Holsinger, (215) 233-6703.

²Mention of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

and Flink 1977). Onwulata *et al.* (1994a,b) have demonstrated that anhydrous butter oil or cream may be successfully encapsulated in carbohydrate matrices (sucrose, all-purpose flour or modified starch); however, the physical and structural properties varied with the source of milkfat and the type of encapsulant used. Evaluation of some thermal properties of the encapsulated materials is also needed, since they may differ from those of the individual constituents.

Milkfat is considered to be a quality-enhancing ingredient in foods, with the melting characteristics being very significant. Proper and timely melting of milkfat is necessary in developing flavor and enhancing texture. The melting pattern of milkfat has been well-studied in the range of -10 to 40°C (Taylor *et al.* 1978; van Beresteyn and Schaap 1971; Patel and Frede 1991). Milkfat oxidizes and decomposes during prolonged heating at high temperatures. Some decomposition products of butter oil have been reported (Tangel *et al.* 1977; Chang *et al.* 1978; Keogh 1989). Encapsulation may modify the melting range of butter oil and reduce the rate and extent of decomposition.

Starch retrogrades upon heating, with gelatinization being influenced by the presence of sugars and emulsifiers. Differential scanning calorimetry has been used to monitor changes in chemical properties of starches as a function of temperature by detecting changes in heat capacity associated with such processes (Kim and Walker 1992; Wootton and Bamunua-Rachchi 1980; Buck and Walker 1988). Processing also may alter the physical state of disaccharides, changing them either to an amorphous or crystalline form. Altering the physical state of carbohydrates in foods affects their properties during processing and storage (Niediek 1988).

The physical state of the encapsulation matrix and its moisture absorption pattern is critical in stopping oxidation and rancidity development during storage (Shimada *et al.* 1991). The effect of imbibed water on the structure of the microcapsule determines its stability when blended into a dry food mix. An amorphous glass entraps flavor compounds and protects encapsulated materials from oxidation due to slow diffusion of, for example, encapsulated oil from the interior to the surface of the capsule and that of oxygen to the interior when the carbohydrate is in the glassy form; however, encapsulant crystallization results in higher diffusion rates or causes complete release of encapsulated compounds through capsule rupture (Roos and Karel 1991; Labrousse *et al.* 1992). In the crystalline state, sugars imbibe little water at low relative humidity. At high water activity ($A_w = 0.8-0.85$), sugars such as sucrose begin to dissolve. Amorphous sugars absorb substantial amounts of water at low relative humidity, leading to crystallization and sudden moisture desorption (Riganakos *et al.* 1992). An excellent example of such behavior is that of the milk sugar, lactose, in milk or whey powder which, if present in the amorphous state, absorbs water and crystallizes to form the alpha monohydrate, resulting in caking (Mistry *et al.* 1992; Saltmarch and Labuza 1980; Bushill *et al.* 1965).

The objectives of this study were to investigate the thermal behavior of anhydrous butter oil encapsulated in a variety of carbohydrate matrices and to examine the effect of water imbibition on the structural integrity of the spray dried microcapsules when exposed to high humidity at ambient temperatures.

MATERIALS AND METHODS

Anhydrous butter oil was purchased from a commercial distributor (Land-O-Lakes, Minneapolis, MN). Encapsulants chosen were sucrose (Domino's, Domino Sugar Corp, New York, NY), modified starch (M-starch) Capsul™ (National Starch and Chemical Co., Bridgewater, NJ) and all-purpose flour (N-starch) (ADM Milling Co., Kansas City, MO). An emulsifying agent (mono- and diglycerides) (American Ingredients Co., Kansas City, MO) was also used. The protein source was nonfat dry milk (Maryland and Virginia Milk Producers Association, Inc., Laurel, MD).

Encapsulated powders were formulated to have 40 or 60% milkfat, 5% emulsifier, 5% nonfat dry milk and the remainder disaccharide. Sample preparation was done as follows: The encapsulant was blended with nonfat dry milk solids, dissolved in water, then mixed with a warmed (23.9C) emulsion of anhydrous butter oil and emulsifier, and heated at 23.9C for 5 min with stirring. The constantly stirred slurry (40% total solids) was slowly brought to the final temperature (62.8C), and homogenized at 17.2 MPa with a Manton-Gaulin Model 100 DJF3 855X Triplex homogenizer (APV Gaulin, Inc., Everett, MA). The homogenized emulsion was spray dried in a compact dryer (APV Crepaco Inc., Attleboro Falls, MA). Spray dryer inlet temperature was 180–190C, and an outlet temperature of 80–110C was maintained. The powders were produced in batches, removed from the dryer after 30 min and stored at 4C. A 2 × 3 factorial design was completed, replicated 3 times. Milk protein content was about 2% in the finished powders. When all-purpose flour was used as the encapsulant, it was necessary to homogenize at a lower pressure and temperature (10.3 MPa and 54.4C) to accommodate pasting properties.

A Perkin-Elmer differential scanning calorimeter, Model DSC-7, equipped with an Intracooler II refrigeration unit was used to measure thermal characteristics (Perkin Elmer Corp., Norwalk, CT). The purge gas was nitrogen, at 20 ml/min. High purity indium was used to calibrate the instrument. A 10 mg (\pm 1 mg) portion of sample was weighed into aluminum pans (Perkin-Elmer) and hermetically sealed. An empty sample pan was used as a reference. Heating was from –25 to 350C at 20C/min after initial cooling to –30 at 20 C/min. The heat of melting, in joules per gram of sample, was determined by dividing the area under the curve by the sample weight. Samples were analyzed in duplicate.

^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS) spectra were obtained on a Bruker MSL-300 spectrometer (Bruker, USA, Billerica, MA) operating at 75.5 MHz, using a Doty Scientific, Inc. (Doty Scientific, Inc., Columbia, SC) CPMAS NMR probe. The CPMAS spectra were obtained using a 1 ms contact time and 1.5 s recycle time. The sweep width was 25,000 Hz; 1024 data points were collected. 4096 transients were collected for each spectrum. The high resolution experiments were conducted using magic angle spinning nuclear magnetic resonance (MAS). The spectra were obtained using high powered gated decoupling. The ^{13}C pulse width was 7 μs pulse with a 5 s recycle time. The sweep width was 25,000 Hz and 2048 data points were collected. 512 transients were collected for each spectrum.

Moisture sorption isotherms were obtained at 25C by equilibrating 10-g powder samples with known water vapor pressures provided by the following saturated salt solutions: CaSO_4 , LiBr, LiCl, K_2CO_3 , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, KI, and $(\text{NH}_4)_2\text{SO}_4$ (Rockland and Nishi 1980) for 72 h. Moisture uptake by encapsulated powders was determined after equilibrating for 200 h over anhydrous K_2CO_3 . The weight change was determined after drying under vacuum for 4 h at 102C (AOAC 1984).

Extractable fat (YF) was determined by dispersing 10 g powder in 50 ml carbon tetrachloride and shaking for 15 min (Anon. 1978). (Warning: carbon tetrachloride is a known carcinogen and appropriate safety precautions must be taken for its use.) After decanting and filtering the supernatant, the filtrate was evaporated, leaving the extracted milkfat. The extractable fat fraction was expressed as the fat weight recovered from the powder, divided by the original weight (Anon. 1978).

Surface structures of encapsulated powders after equilibration at 20 or 80 % relative humidity were evaluated with a scanning electron microscope (JEOL Model 840A, JEOL, Peabody, MA) in the secondary electron imaging mode. Samples of powders were sprinkled on aluminum specimen stubs coated with Spot-O-Glue labels (Avery, Azusa, CA). Excess, nonadherent particles were removed from the surfaces of the sample stubs with a jet of pressurized air. Specimen stubs were coated with a thin layer of gold in a DC cold sputtering module in an E306A vacuum evaporator (Edwards High Vacuum, Inc., Grand Island, NY).

RESULTS AND DISCUSSION

The transition points of the components used for the encapsulation of milkfat are presented in Table 1. The DSC thermogram for butter oil had a melting pattern with numerous peaks from -40 to 40C. Continued heating

TABLE 1.

MELTING PROPERTIES OF MATERIALS USED FOR ENCAPSULATION

Product	Peak (C)	Melting range (C)	ΔH (J/g)
Butter oil	*	-40 - 40	**
Sucrose	190	180 - 196	122.2
M-Starch	99	60 - 150	85.4
N-Starch	118	60 - 201	250.4
Emulsifier	46	37 - 165**	27.6

* Numerous peaks within the melting range

** More than one peak

M-starch = modified starch; N-starch = all-purpose flour; emulsifier = mono- and di-glycerides

above this region led to gradual thermal decomposition, without the appearance of additional peaks. Thermal decomposition of butter oil beyond this melting region has been reported (Taylor *et al.* 1978). The melting range for the emulsifier (mono- and diglycerides) used was from 37–165C with peaks at 46 and 150C. The M-starch matrix had melting peaks around 99C, N-starch at 118C, and sucrose at 190C. Identification of the melting peaks of the various components was essential in identifying shifts and complex patterns in the thermograms of the encapsulated powders.

DSC thermograms of the spray dried powders containing 40 or 60% anhydrous butter oil encapsulated in three different carbohydrate matrices are shown in Fig. 1, 2 and 3; the heat of melting and peak temperatures are reported in Table 2. The thermal profiles show two major melting zones for each product containing 40 or 60% encapsulated fat, indicating the melting of the surface or unencapsulated fat and fusion of the wall material. Thermograms of butter oil encapsulated within the N-starch matrix (Fig. 1A and B) show melting of the butter oil from 0 to 40C. The butter oil peaks were more defined for thermograms of powders with 60% fat. The heat of melting of the milkfat was much greater at 60% fat, indicating the presence of more butter oil. Thermograms for the M-Starch/butter oil capsules show one main peak and a curve from 53 to 175C (Fig. 2C and D). Heat of melting again varied with the amount of fat in the M-starch-encapsulated powder. In contrast to the other samples, capsules with sucrose as the encapsulating agent (Fig. 3E and F) had

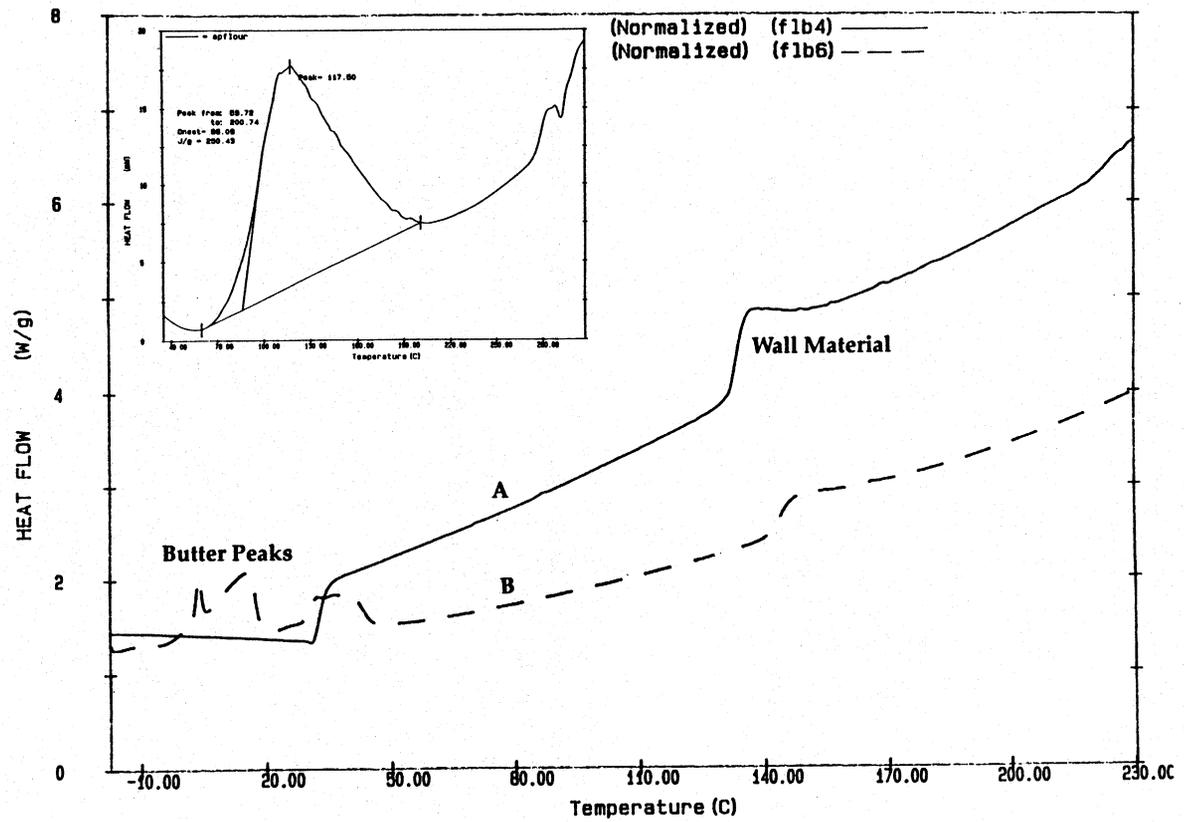


FIG. 1. DSC THERMOGRAMS OF BUTTER OIL ENCAPSULATED IN ALL-PURPOSE FLOUR (N-STARCH)
 (A) 40% Fat level; Flb4. (B) 60% fat level; Flb6. Insert: DSC thermogram of all-purpose flour.

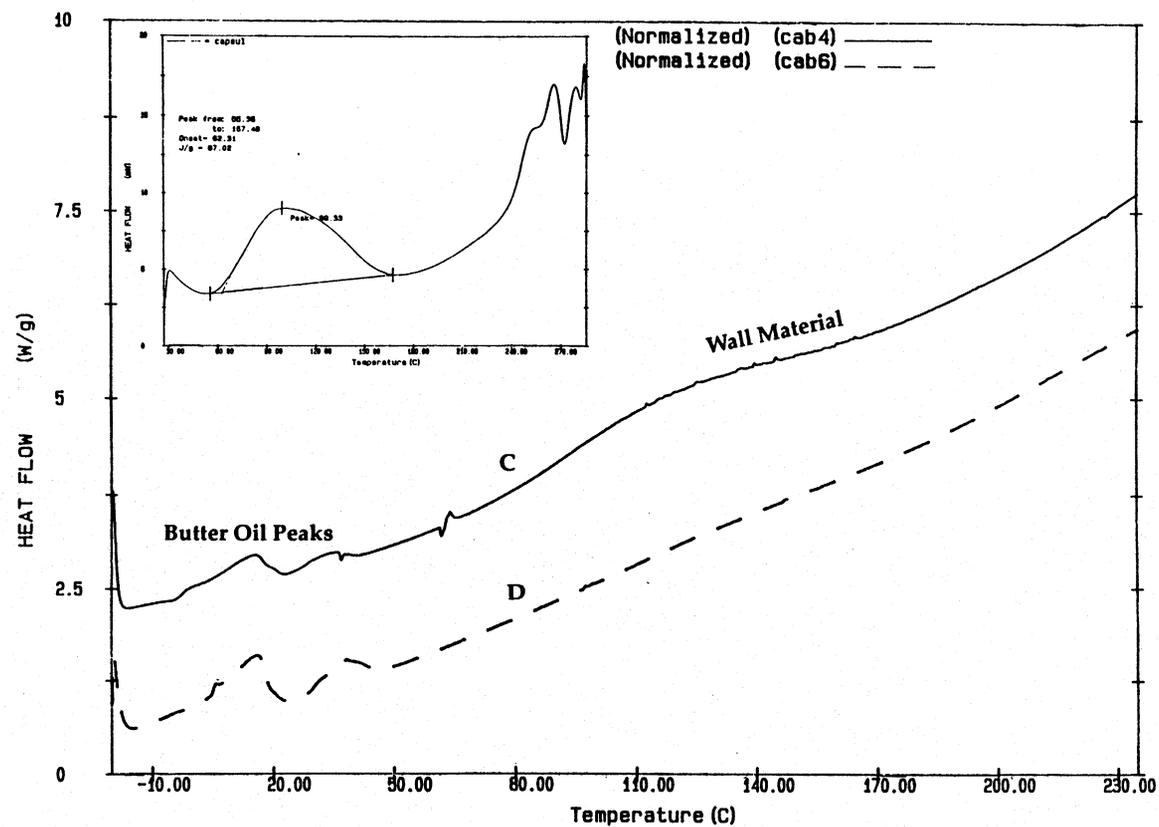


FIG. 2. DSC THERMOGRAMS OF BUTTER OIL ENCAPSULATED IN MODIFIED STARCH (M-STARCH)
 (C) 40% Fat level; CAB4. (D) 60% Fat level; CAB6. Insert: DSC thermogram of modified starch.

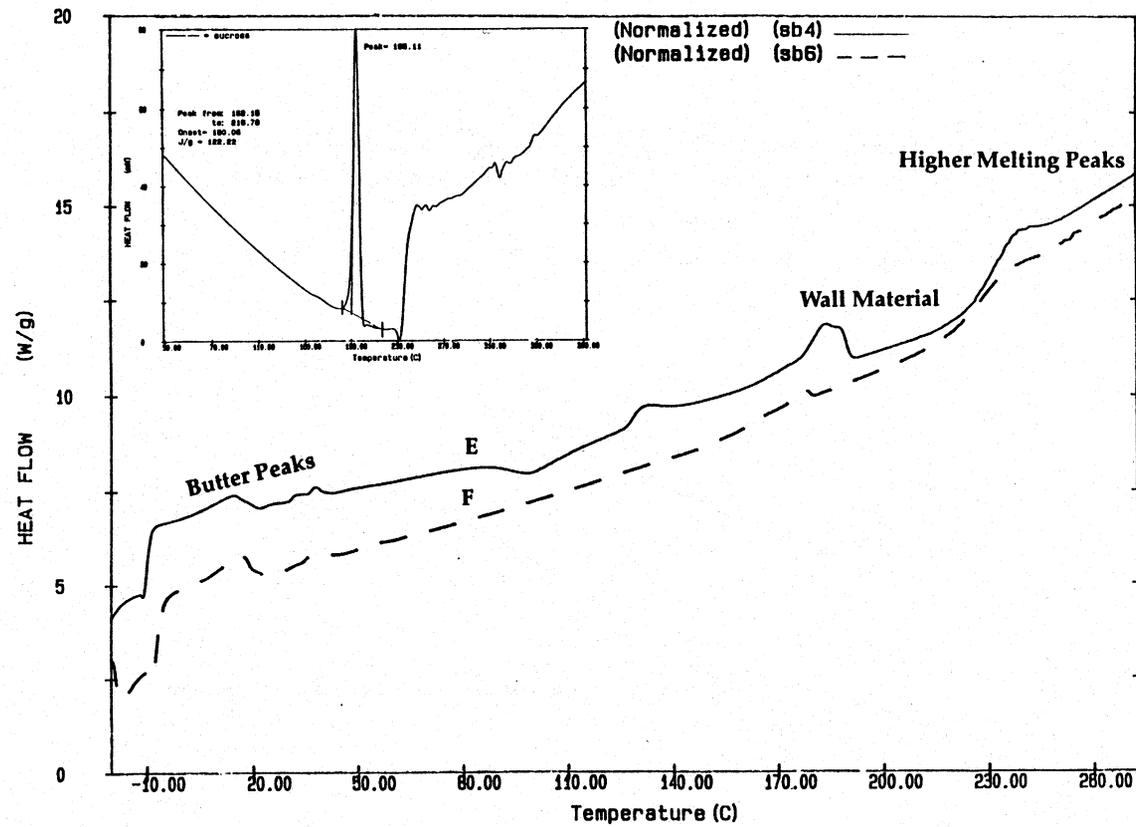


FIG. 3. DSC THERMOGRAMS OF BUTTER OIL ENCAPSULATED IN SUCROSE
 (E) 40% Fat level; SB4. (F) 60% Fat level; SB6. Insert: DSC thermogram of sucrose.

three fusion zones: surface fat peaks, 17–38C, sucrose peaks, 178–184C, and high temperature peaks above 220C. The capsules with sucrose and 40% fat show a disassociation product peak at 239C (Fig. 3E and Table 2); the sample with 60% fat disassociates at a maximum of 236C (Table 2). The thermal patterns of these powders are those of true capsules with defined event times for the fusion of the various components comprising the powders.

TABLE 2.
MELTING CHARACTERISTICS OF MILKFAT ENCAPSULATED IN
CARBOHYDRATE MATRICES¹

Product	Surface fat				Encapsulant load			
	Peak	ΔH	Peak	ΔH	Peak	ΔH	Peak	ΔH
-----	-----	$\Delta H = J/g$	-----	-----	Peak = C	-----	-----	-----
N-starch40	*	*	36.0	10.6	134.4	27.6	--	--
SD			0.0	2.1	2.6	0.4		
N-starch 60	4.0	25.2	39.1	13.6	148.5	19.6	--	--
SD	0.0	0.0	0.1	0.5	0.5	4.3		
M-starch 40	15.2	15.3	34.1	2.5	112.8	58.4	--	--
SD	0.2	0.2	0.1	0.8	0.2	4.1		
M-starch 60	15.8	24.9	36.1	8.3	96.7	9.6	--	--
SD	0.2	4.0	2.1	0.0	0.3	0.8		
Sucrose 40	17.6	14.5	38.0	4.9	183.8	42.5	239.1	23.9
SD	0.6	0.0	0.0	0.1	0.2	0.0	0.1	1.7
Sucrose 60	16.8	24.3	36.2	3.6	177.8	4.7	235.8	15.0
SD	0.2	2.0	0.2	0.2	0.2	2.4	0.2	1.9

*: Insignificant melting peaks.

--: No thermal products after carbohydrate peak.

N-starch = All-purpose flour and butter oil.

M-starch = Modified starch and butter oil.

40 and 60 = 40% and 60% milkfat.

SD = Standard Deviation

¹Moisture content of powders ranged from 1 to 3%.

Thermal properties of milkfat polymorphs and their crystallization properties have been studied in detail (van Beresteyn and Schaap 1971; Patel and Frede 1991). Solid fat indices and melting patterns were determined by the triglyceride structure and fatty acid composition. We made no attempt to identify the crystalline forms of the anhydrous milkfat in our powders; melting peaks (Table 2) for the six powders studied all fall within the known melting range for milkfat.

It is known that complexes formed in the presence of saccharides change the melting patterns of the components. Krog *et al.* (1989) reported a disassociation of amylose-lipid complex at 100–120C, with the heat of disassociation increasing in the presence of monoglycerides. Lipid-saccharose complexes appeared as high melting peaks. Starch degradation studies have shown that in the presence of sugar and emulsifiers, peak temperatures are increased (Buck and Walker 1988; Donovan 1977). In our study, the M-starch (modified starch) showed a peak temperature increase of 13C with a 40% fat content, whereas, with 60% fat, there was little change (2C) in peak temperature (Tables 1 and 2). In contrast, the N-starch (all-purpose flour) showed peak temperature increases of 16 and 30C for powders with 40 and 60% fat, respectively (Tables 1 and 2), suggesting that greater changes are occurring in the starch moiety of this encapsulant as a result of the association with fat. When sucrose was used as the encapsulant, maximum peak temperature decreased, with the greatest decrease (13C) observed in the powder with 60% fat (Tables 1 and 2). If encapsulated milkfat is to be used as a shortening in, for example, dry bakery mixes, upon reconstitution and subsequent baking, the capsule must rupture to deliver the shortening load at the appropriate time. Our results suggest that it might be possible to tailor capsule rupture temperature to the baking process by careful choice of encapsulant. In addition, the capsules must be able to withstand the mechanical stress of dry-mixing and blending to be shelf stable; milkfat completely enclosed in a competent capsule should be protected from oxidative deterioration during storage. Storage stability of milkfat encapsulated under our experimental conditions will be the subject of a future study.

To investigate the possibility of complex formation between sucrose and milkfat, as suggested by the appearance of a third high-melting peak in the thermograms of this formulation (Fig. 3E), samples encapsulated in sucrose were analyzed by nuclear magnetic resonance (NMR). NMR studies were not done on samples encapsulated in M-starch or N-starch, since these samples did not contain a high-melting fraction. A ¹³C CPMAS spectrum of a powder encapsulated with sucrose and 40% butter oil is presented in Fig. 4. The CPMAS spectrum shows a low crystalline order sucrose spectrum (110–50 ppm). The high resolution mass spectrum for butter oil in the same powder (Fig. 4, mobile phase) shows the presence of the fatty acid side chains (35–18 ppm), a glycerol peak (70–60 ppm), monounsaturates (130 ppm) and a carbonyl peak

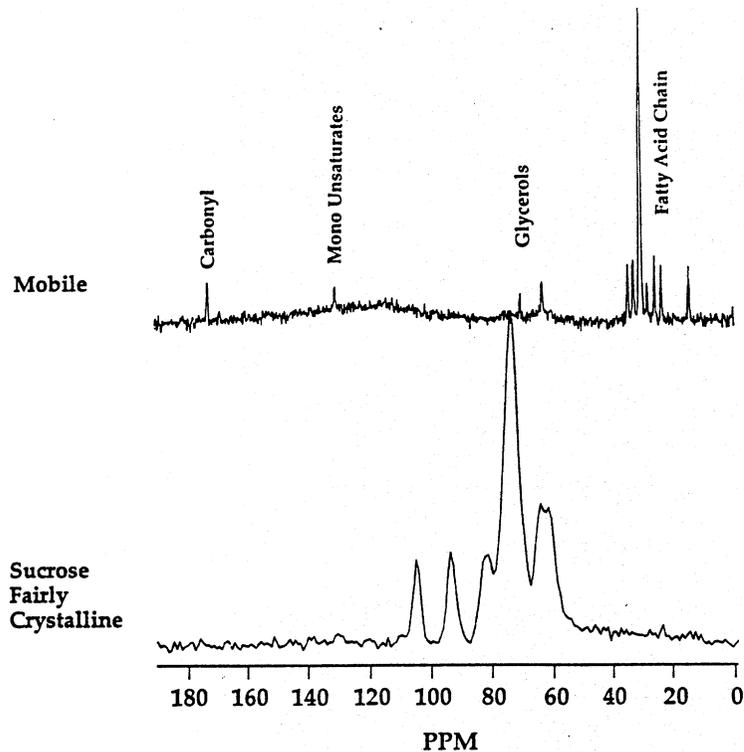


FIG. 4. ^{13}C NMR SPECTRUM OF POWDER WITH 40% BUTTER OIL ENCAPSULATED IN SUCROSE, SHOWING SOME CRYSTALLINE ORDER
Mobile phase shows intact triglyceride structure.

(170 ppm). The ^{13}C spectrum shows no evidence of thermal oxidation of the butter oil caused by the encapsulation process. NMR spectra of sucrose and other polysaccharides have been reported (Seino and Uchibori 1984; Akoh and Swanson 1987). The NMR spectra did not support the formation of sucrose-milkfat complexes such as ester linkages under our experimental conditions; the high melting peak present in the thermograms of sucrose/butter-oil powders still remains unidentified. Encapsulation may be stabilized by other interactions such as formation of fat-protein complexes by homogenization before drying.

Moisture uptake by the powders encapsulated with sucrose or M-starch and containing 40 or 60% anhydrous butter oil after exposure to 40% relative humidity at 25C for more than 200 h is plotted in Fig. 5. This demonstrates that the moisture sorption patterns were dependent on the type of encapsulant used. Sucrose/butter-oil powders showed initial moisture uptake and subsequent

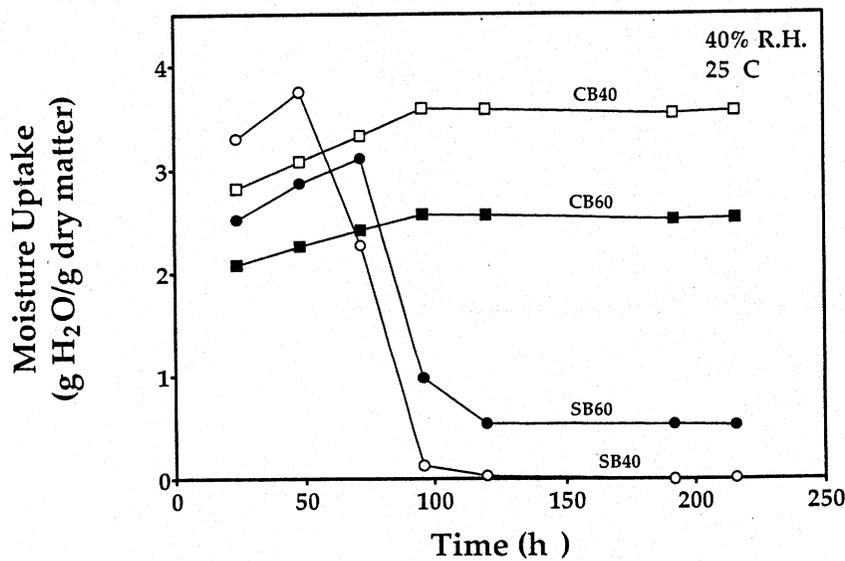


FIG. 5. UPTAKE OF MOISTURE AT 25C AND 40% RELATIVE HUMIDITY FOR SAMPLES WITH 40 OR 60% BUTTER OIL AND WITH SUCROSE OR MODIFIED STARCH (M-STARCH) AS ENCAPSULANT AFTER EQUILIBRATION FOR 200 H OVER ANHYDROUS POTASSIUM CARBONATE
 -○- = Sucrose 40 (SB40); -●- = Sucrose 60 (SB60); -□- = M-starch 40 (CB40);
 -■- = M-Starch 60 (CB60).

moisture loss after 100 h. This pattern of moisture uptake is typical of an amorphous powder which desorbs moisture upon crystallization. Sucrose in the amorphous form in a low humidity environment has been shown to recrystallize and lose moisture (Iglesias and Chirife 1978; Karel 1975). In contrast, the M-starch/butter-oil capsules showed a steady uptake of moisture until equilibrium was reached. There was no desorption of moisture even after 200 h. The moisture uptake patterns were similar to those of food gums that retain absorbed water. N-starch capsules imbibed negligible amounts of water under these conditions (data not shown). In both cases, samples with 60% anhydrous butter oil imbibed less water than did the samples with 40% fat.

Sorption isotherms of powders encapsulated in sucrose, N-starch and M-starch, with 40 or 60% butter oil are presented in Fig. 6. Sucrose/butter-oil powders show characteristic sorption patterns across the range of water activities examined. A similar break in the sorption isotherm between 40–50% relative humidity was reported for spray dried milk powders, attributed to the crystallization of α -lactose monohydrate (Berlin *et al.* 1969; Pisecky 1992). The sorption

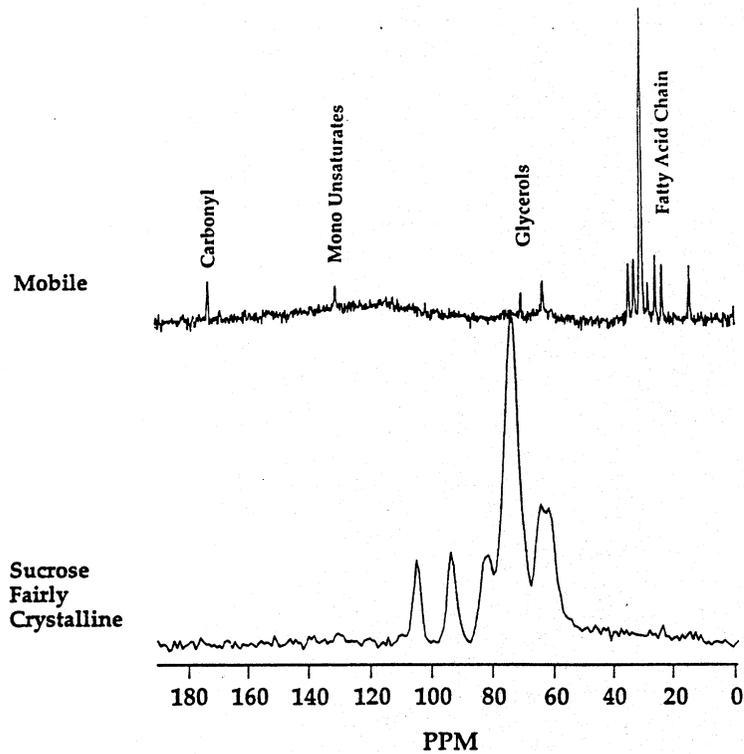


FIG. 4. ^{13}C NMR SPECTRUM OF POWDER WITH 40% BUTTER OIL ENCAPSULATED IN SUCROSE, SHOWING SOME CRYSTALLINE ORDER
Mobile phase shows intact triglyceride structure.

(170 ppm). The ^{13}C spectrum shows no evidence of thermal oxidation of the butter oil caused by the encapsulation process. NMR spectra of sucrose and other polysaccharides have been reported (Seino and Uchibori 1984; Akoh and Swanson 1987). The NMR spectra did not support the formation of sucrose-milkfat complexes such as ester linkages under our experimental conditions; the high melting peak present in the thermograms of sucrose/butter-oil powders still remains unidentified. Encapsulation may be stabilized by other interactions such as formation of fat-protein complexes by homogenization before drying.

Moisture uptake by the powders encapsulated with sucrose or M-starch and containing 40 or 60% anhydrous butter oil after exposure to 40% relative humidity at 25C for more than 200 h is plotted in Fig. 5. This demonstrates that the moisture sorption patterns were dependent on the type of encapsulant used. Sucrose/butter-oil powders showed initial moisture uptake and subsequent

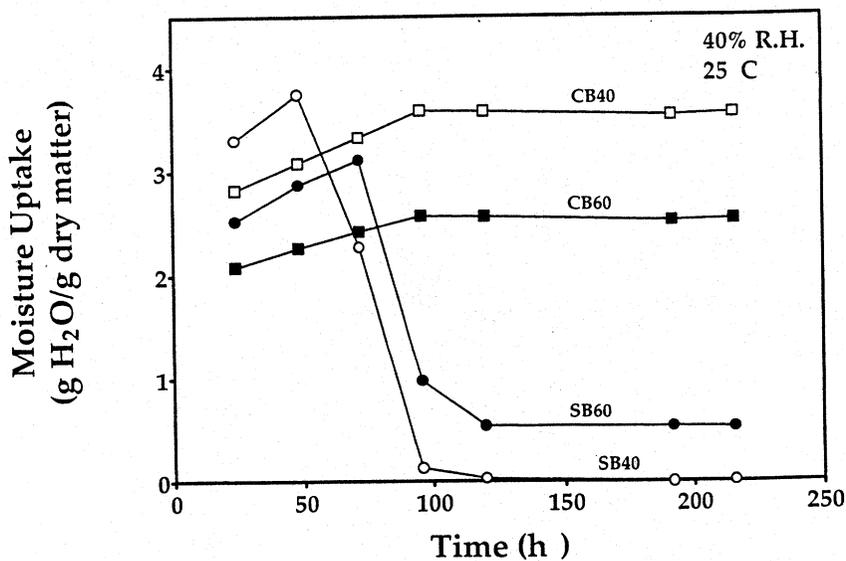


FIG. 5. UPTAKE OF MOISTURE AT 25C AND 40% RELATIVE HUMIDITY FOR SAMPLES WITH 40 OR 60% BUTTER OIL AND WITH SUCROSE OR MODIFIED STARCH (M-STARCH) AS ENCAPSULANT AFTER EQUILIBRATION FOR 200 H OVER ANHYDROUS POTASSIUM CARBONATE
 -○- = Sucrose 40 (SB40); -●- = Sucrose 60 (SB60); -□- = M-starch 40 (CB40);
 -■- = M-Starch 60 (CB60).

moisture loss after 100 h. This pattern of moisture uptake is typical of an amorphous powder which desorbs moisture upon crystallization. Sucrose in the amorphous form in a low humidity environment has been shown to recrystallize and lose moisture (Iglesias and Chirife 1978; Karel 1975). In contrast, the M-starch/butter-oil capsules showed a steady uptake of moisture until equilibrium was reached. There was no desorption of moisture even after 200 h. The moisture uptake patterns were similar to those of food gums that retain absorbed water. N-starch capsules imbibed negligible amounts of water under these conditions (data not shown). In both cases, samples with 60% anhydrous butter oil imbibed less water than did the samples with 40% fat.

Sorption isotherms of powders encapsulated in sucrose, N-starch and M-starch, with 40 or 60% butter oil are presented in Fig. 6. Sucrose/butter-oil powders show characteristic sorption patterns across the range of water activities examined. A similar break in the sorption isotherm between 40-50% relative humidity was reported for spray dried milk powders, attributed to the crystallization of α -lactose monohydrate (Berlin *et al.* 1969; Pisecky 1992). The sorption

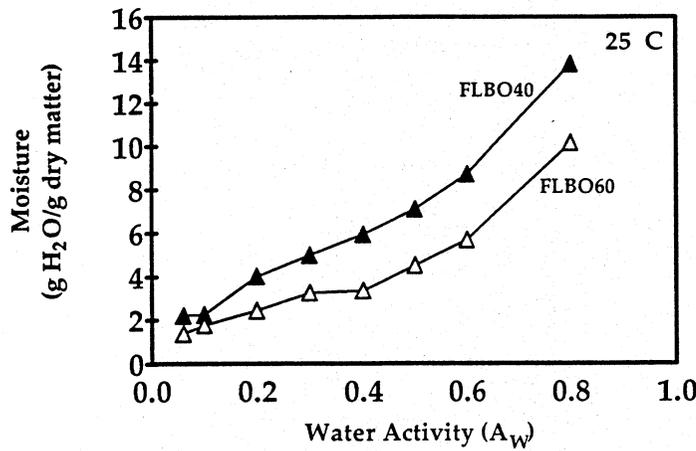
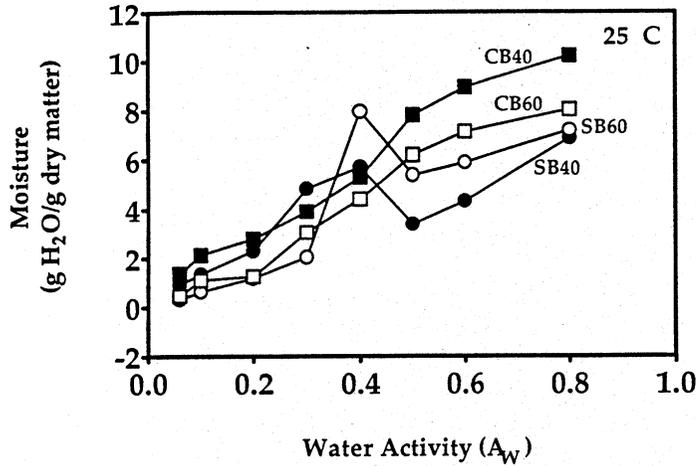


FIG. 6. MOISTURE SORPTION ISOTHERMS OF POWDERS WITH 40 OR 60% BUTTER OIL AND SUCROSE, MODIFIED STARCH (M-STARCH) OR ALL-PURPOSE FLOUR (N-STARCH) AS ENCAPSULANT

-●- = Sucrose 40 (SB40); -○- = Sucrose 60 (SB60); -■- = M-Starch 40 (CB40);
 -□- = M-Starch 60 (CB60); -▲- = N-Starch 40 (FLBO40); -△- = N-Starch 60 (FLBO60).

isotherm for crystalline sucrose differs from that of amorphous sucrose (Niediek 1988; Moreyra and Peleg 1981). Even though a small amount of lactose is present (about 1/20 of the total disaccharide present), we attribute the characteristic breaks in the isotherms of the sucrose/butter oil powders to crystallization of amorphous sucrose. It is highly likely that powders encapsulated with sucrose would crystallize eventually, even in low humidity, suggesting that these

powders must be protected from moisture uptake during storage by low-water-vapor-permeable packaging. M-starch/butter oil and N-starch/butter-oil isotherms showed patterns typical of water absorption for flours or gums, with steady increases in moisture sorption with increasing relative humidity. Oxidative stability may be expected for the sucrose/butter-oil powders between 0.1-0.2 A_w , and for M-starch/butter-oil and N-starch/butter oil powders between 0.2-0.4 A_w , based on the moisture monolayers (Karel 1975); this remains to be confirmed in future studies.

The amount of extractable fat ($\bar{Y}F$) at different relative humidities for each powder was measured, to determine the effect of high humidity on fat retention; results for sucrose/butter-oil and M-starch/butter-oil powders are shown in Fig. 7. $\bar{Y}F$ increased with increasing relative humidity at each fat level, for all encapsulated powders, up to the limit of fat encapsulated. This suggests that the uptake of moisture dissolved some of the encapsulating matrix, or ruptured the matrix as a result of particle swelling, exposing the enclosed fat. Previous studies (Onwulata *et al.* 1993a,b) had shown that the least amount of extractable fat (< 55%) was obtained from samples containing 40% butter oil encapsulated in sucrose.

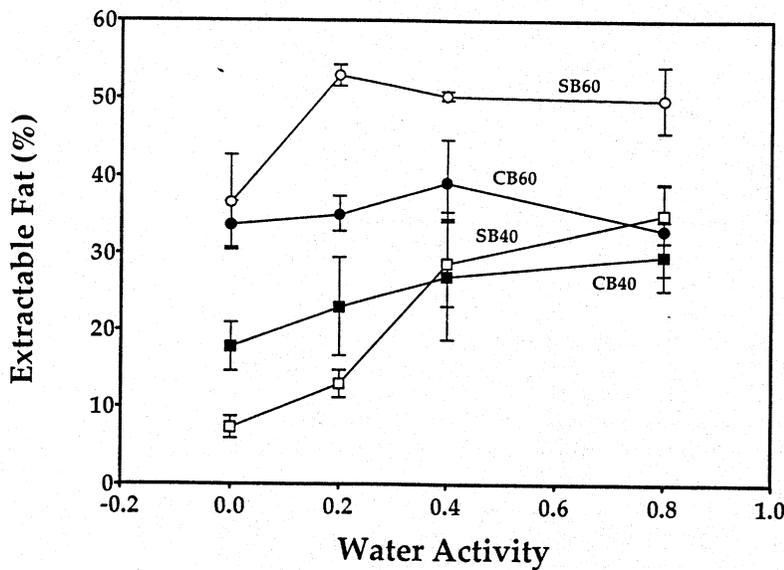


FIG. 7. INCREASE IN EXTRACTABLE FAT WITH INCREASING WATER ACTIVITY (A_w) OF POWDERS WITH 40 OR 60% FAT ENCAPSULATED IN SUCROSE OR MODIFIED STARCH (M-STARCH)
 -□- = Sucrose 40 (SB40); -○- = Sucrose 60 (SB60); -■- = M-Starch 40 (CB40);
 -●- = M-Starch 60 (CB60).

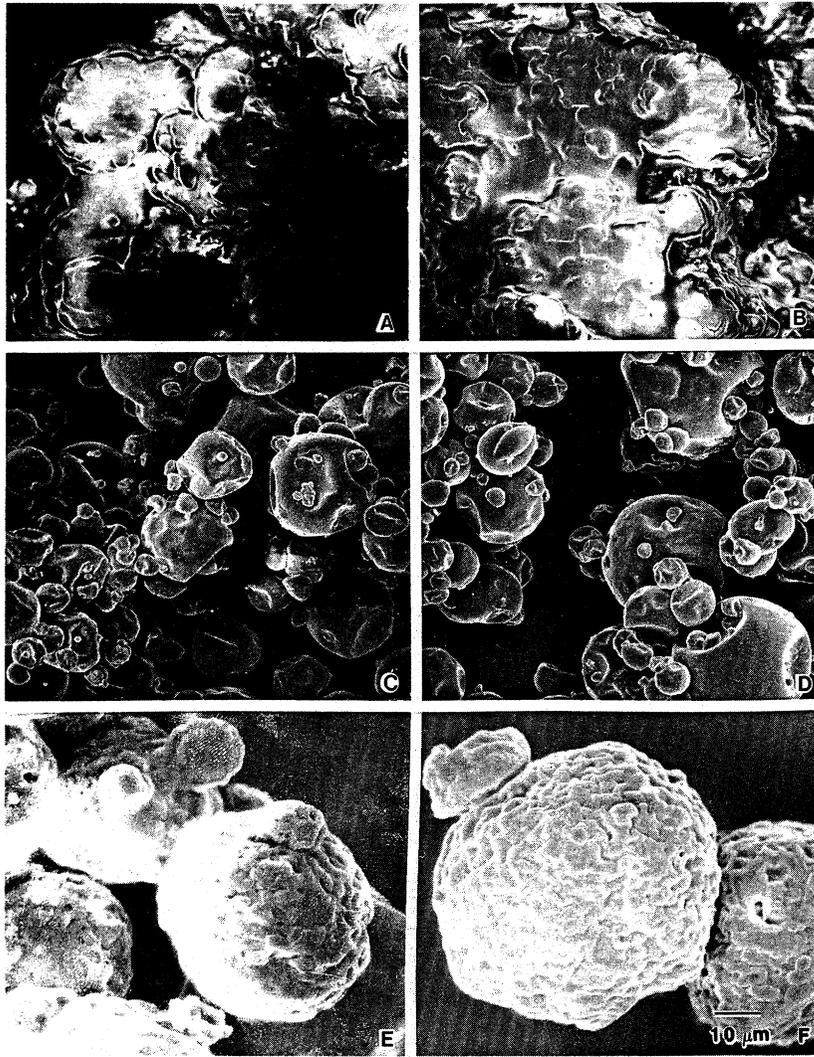


FIG. 8. SCANNING ELECTRON PHOTOMICROGRAPHS OF BUTTER OIL IN CARBOHYDRATE MATRICES (40% FAT)
 Sucrose at 20% relative humidity (8A); sucrose at 80% relative humidity (8B); modified starch (M-Starch) at 20% relative humidity (8C); M-Starch at 80% relative humidity (8D); all-purpose flour (N-Starch) at 20% relative humidity (8E); and N-Starch at 80% relative humidity (8F).

Based on ^{13}C CPNMR analysis, the sucrose comprising the microcapsule wall appeared to retain some crystalline order. However, isotherms done at 25C

(Fig. 5 and 6) showed that sucrose was mostly amorphous, only fully crystallizing after exposure to moisture. As shown by the data in Fig. 7, sucrose crystallization had an undesirable effect on fat retention within the capsule.

Scanning electron photomicrographs of the microcapsules containing 40% butter oil at 20 and 80% relative humidity are shown in Fig. 8A-F. Powders with sucrose as the encapsulant (8A) have absorbed sufficient moisture, even at 20% relative humidity to begin to lose their particulate identity. At 80% relative humidity (8B), the particles have fused and caked as a result of the crystallization of the sucrose. In contrast, photomicrographs of M-starch/butter-oil powders show typical spray dried powder particles at 20% relative humidity (8C); upon moisture imbibition, at 80% relative humidity, the particles have swelled slightly but have not lost their structural identity and appear to be intact (8D). N-starch/butter-oil powders show distinct surface ridges at 20% relative humidity (8E), but at 80% relative humidity, the ridges are partially reduced in size and appear smooth (8F). DSC analysis of milkfat extracted from these capsules by treatment with carbon tetrachloride shows partial dissolution of the capsule wall as a result of exposure to high relative humidity through presence of the encapsulant in the thermograms (data not shown). Based on these results, special packaging will be required to ensure structural integrity of the microcapsules if long shelf-life at ambient temperatures is to be attained.

CONCLUSIONS

Spray dried encapsulated milkfat powder shows potential for use as a food ingredient in such products as dry bakery mixes. Well-defined melting ranges are identifiable in DSC profiles; melting temperatures for capsule rupture and release of the fat load are associated with type of encapsulating agent chosen. Low levels of extractable fat show protection of the encapsulated butter oil, when sucrose is the encapsulant, which is essential in maintaining milkfat quality. Moisture uptake and sorption isotherms are also related to encapsulant and demonstrate the need for special packaging to prevent moisture imbibition during storage. Ease of moisture uptake can be advantageous in a batter when dry mixes are reconstituted for baking.

ACKNOWLEDGMENTS

The authors thank Dr. Peter Cooke for the scanning electron photomicrographs, Dr. Robert Dudley for the NMR spectral analyses and Dr. John Phillips for assistance with the experimental design.

REFERENCES

- AKOH, C.C. and SWANSON, B.G. 1987. One-stage synthesis of raffinose fatty acid polyesters. *J. Food Sci.* 52, 1570-1576.
- Anon. 1978. Analytical methods for dry milk products. Niro Atomizer Co., Copenhagen, Denmark.
- AOAC. 1984. *Official Methods of Analysis*, 14th Ed., Assoc. of Official Analytical Chemists, Washington, DC.
- BERLIN, E., ANDERSON, B.A. and PALLANSCH, M.J. 1969. Effect of temperature on water vapor sorption by dried milk powders. *J. Dairy Sci.* 53, 146-149.
- BUCK, J.S. and WALKER, C.E. 1988. Sugar and sucrose ester effects on maize and wheat starch gelatinization patterns by differential scanning calorimetry. *Starch* 40, 353-356.
- BUSHILL, J.H., WRIGHT, W.B., FULLER, C.H.F. and BELL, A.V. 1965. The crystallization of lactose with particular reference to its occurrence in milk powder. *J. Food Sci. Agric.* 16, 622-628.
- CHANG, S., PETERSON, R.J. and HO, C. 1978. Chemical reactions involved in the deep-fat frying of foods. *JAACS* 55, 718-727.
- DONOVAN, J.W. 1977. A study of the baking process by differential scanning calorimetry. *J. Sci. Food. Agric.* 28, 571-578.
- GEJL-HANSEN, F. and FLINK, J.M. 1977. Freeze-dried carbohydrate containing oil-in-water emulsions: Microstructure and fat distribution. *J. Food Sci.* 42, 1049-1055.
- IGLESIAS, H.A. and CHIRIFE, J. 1978. Delayed crystallization of amorphous sucrose in humidified freeze dried model systems. *J. Food Technol.* 13, 137-144.
- IMAGI, J., MURAYA, K., YAMASHITA, D., ADACHI, S. and MATSUNO, R. 1992. Retarded oxidation of liquid lipids entrapped in matrixes of saccharides or proteins. *Biosci. Biotechnol. Biochem.* 56(8), 1236-1240.
- KAREL, M. 1975. Stability of low and intermediate moisture foods. In *Freeze Drying and Advanced Food Technology*, (S.A. Goldblith, L. Rey and W.W. Rothmayr, eds.) pp. 643-674, Academic Press, New York.
- KEOGH, M.K. 1989. Anhydrous milk fat. *Irish J. Food Technol.* 13, 129-140.
- KIM, C.S. and WALKER, C.E. 1992. Effect of sugars and emulsifiers on starch gelatinization evaluated by differential scanning calorimetry. 1992. *Cereal Chem.* 69, 212-217.
- KROG, N., OLESEN, S.K., TOERNAES, H. and JOENSSON, T. 1989. Retrogradation of the starch fraction in wheat bread. *Cereal Foods World* 34(3), 281-285.

- LABROUSSE, S., ROOS, Y. and KAREL, M. 1992. Collapse and crystallization in amorphous matrices with encapsulated compounds. *Sci. Aliments* 12, 757-769.
- MISTRY, V.V., HASSAN, H.N. and ROBISON, D.J. 1992. Effect of lactose and protein on the microstructure of dried milk. *Food Microstruct.* 11, 73-82.
- MOREYRA, R. and PELEG, M. 1981. Effect of equilibrium water activity on the bulk properties of selected food powders. *J. Food Sci.* 46, 1918-1922.
- NIEDIEK, E.A. 1988. Effect of processing on the physical state and aroma sorption properties of carbohydrates. *Food Technol.* 42, 82-86.
- ONWULATA, C.I., SMITH, P.W., COOKE, P.H. and HOLSINGER, V.H. 1994a. Particle structures of encapsulated milkfat powders. *Food Struct.* (In Press).
- ONWULATA, C.I., SMITH, P.W., CRAIG, J.C., JR., and HOLSINGER, V.H. 1994b. Physical properties of encapsulated milkfat powders. *J. Food Sci.* 59, 316-320.
- PATEL, A.A. and FREDE, E. 1991. Studies on thermal properties of cow and buffalo milk fats. *J. Food Technol.* 24, 323-327.
- PISECKY, J. 1992. Water activity of milk powders. *Milk Sci. Int.* 47, 3-7.
- RIGANAKOS, K.A., DEMERTZIS, P.G. and KONTOMINAS, M.G. 1992. Effect of crystalline sucrose on the water sorption behavior of wheat flour as studied by inverse gas chromatography. *J. Food Technol.* 25, 389-404.
- ROCKLAND, L.B. and NISHI, S.K. 1980. Influence of water activity on food product quality and stability. *Food Technol.* 34, 42-59.
- ROOS, Y. and KAREL, M. 1991. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *J. Food Sci.* 56, 38-43.
- SALTMARCH, M. and LABUZA, T.P. 1980. Influence of relative humidity on the physicochemical state of lactose in spray-dried sweet whey powders. *J. Food Sci.* 45, 1231-1236.
- SEINO, H. and UCHIBORI, T. 1984. Enzymatic synthesis of carbohydrate esters of fatty acids. (1) Esterification of sucrose, glucose and sorbitol. *JAOCS* 61, 1761-1765.
- SHIMADA, Y., ROOS, Y. and KAREL, M. 1991. Oxidation of methylinoleate encapsulated in amorphous lactose-based food model. *J. Agric. Food Chem.* 39, 637-641.
- TANGEL, F.P., JR. 1977. Deep fat frying characteristics of butter oil. *J. Food Sci.* 42, 1110-1119.
- TAYLOR, M.W., NORRIS, G.E. and HAWKE, J.C. 1978. The thermal properties of bovine milk triglycerols. *N.Z.J. Dairy Sci. Technol.* 13, 236-241.

- VAN BERESTEYN, E.C.H. and SCHAAP, J.E. 1971. A study by differential thermal analysis of fat crystallization in emulsions. *Neth. Milk Dairy J.* 25, 274-277.
- WOOTTON, M. and BAMUNUA-RACHCHI, A. 1980. Application of differential scanning calorimetry to starch gelatinization. II. Effect of sucrose and sodium chloride. *Starch* 32, 126-129.
- YOUNG, S.L., SARDU, X. and ROSENBERG, M. 1993. Microencapsulating properties of whey proteins. 1. Microencapsulation of anhydrous milkfat. *J. Dairy Sci.* 76, 2868-2877.