ELSEVIER

International Journal of Pharmaceutics 171 (1998) 257–270

international journal of pharmaceutics

Solid state characterisation of a dry emulsion: a potential drug delivery system

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Accepted 5 June 1998

Abstract

Dry emulsions were prepared by spray drying liquid emulsions in a laboratory spray dryer. Lactose alone, and lactose in combination with maltodextrine, was used as a water soluble, solid carrier. Sodium caseinate was used as emulsifying agent and griseofulvin was used as an oil soluble model drug substance in very low concentration. Different fats were applied; soybean oil (liquid), hardened coconut oil (semisolid) and hardened rapeseed oil, being solid at room temperature. The surface of the powder particles was mainly made up of sodium caseinate, while the core was made up of fat dispersed in a carrier matrix of amorphous lactose. Amorphous lactose is very sensitive to moisture, and during moisture uptake recrystallisation of lactose takes place and the physical structure of the powder particle was changed. By addition of maltodextrine as carrier, the physical structure of the spray dried powders was tried to be maintained during recrystallisation of lactose. Reconstitution properties of the spray dried powders were investigated and correlated to solid state characterisation of the powders performed by Scanning Electron Microscope (SEM), Differential Scanning Calorimetry (DSC), X-ray powder diffraction and Electron Spectroscopy for Chemical Analysis (ESCA).

Keywords: Spray drying; Dry emulsion; Microencapsulation; ESCA; Lactose; Griseofulvin

1. Introduction

It is well known that the bioavailability of some drugs showing low and variable oral absorption can be improved by coadministration of fat in the form of a fatty meal or an emulsion (Bates and Sequeria, 1975; Chakrabarti and Belpaire, 1978; Ogunbona and Smith, 1985). For emulsions, an improved bioavailability of cyclosporine was obtained by reducing the droplet size (Tarr and Yalkowsky, 1989). The mechanism being responsible for the enhanced intestinal absorption of

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0378-5173/98/$ - see front matter
PII: S0378-5173(98)00197-5

some drugs when coadministered with fat is not fully understood, but several possible explanations are suggested in literature: (i) prolonged gastric residence of the drug due to reduced intestinal mobility improves the total amount of dissolved drug; (ii) improved bile salt secretion leading to favourable drug-fat-bile salt interactions, and thereupon improved wettability and facilitated diffusion of a drug from intestinal lumen to intestinal membrane; (iii) absorption via lipid absorption mechanisms; (iv) improved absorption via lymphatics with no liver presystemic first pass metabolism; and (v) a kind of protection of especially peptides and proteins from degradation and/or metabolism in lumen and in brush border region (Aungst, 1993). However, considering the physical and microbiological instability of emulsions, attempts have been made to formulate dry emulsions, being a powder, from which an emulsion can easily be reconstituted in vivo (Takeuchi et al., 1991a) or when exposed to an aqueous solution (Takeuchi et al., 1991b, 1992a; Vyas et al., 1992; Molina and Cadorniga, 1995; Shively and Thompson, 1995). Dry emulsions have been prepared by removing water from an ordinary emulsion containing a water-soluble (Vyas et al., 1992) or -insoluble (Richter and Steiger-Trippi, 1961) solid carrier, by rotary evaporation (Myers and Shively, 1992), lyophilisation (Lladser et al., 1968; Molina and Cadorniga, 1995) or spray drying (Takeuchi et al., 1991b; Mistry et al., 1992; Takeuchi et al., 1992a; Fäldt and Bergenståhl, 1995, 1996). In order to: (i) reduce oxidation of the fat; and (ii) to ensure a fast, easy and complete reconstitution of the liquid emulsion; that is the powder should easily sink, be wetted and dispersed in the reconstitution medium, it is desirable for the fat to be well encapsulated in the carrier in the dry emulsion. Improved chemical stability of some drug substances being dissolved in the oily phase might at the same time be obtained (Takeuchi et al., 1992b).

In this study, dry emulsions containing a drug substance were prepared by spray drying liquid emulsions containing lactose alone or in combination with maltodextrine as a water soluble solid carrier. Sodium caseinate was used as surface active ingredient, facilitating the emulsification of the liquid emulsion. Griseofulvin was chosen as a model drug substance, being dissolved in the fatty phase and, therefore, used in low concentration.

This type of dry emulsion, being powder particles, was seen to be made up of spherical not agglomerated particles where a solid dispersion of fat and amorphous lactose was under cover of a surface mainly made up of sodium caseinate (Fäldt and Bergenståhl, 1995, 1996). Lactose is sensitive to moisture, which induces recrystallisation of amorphous lactose formed during spray drying (White and Cakebread, 1966). This recrystallisation of lactose was seen to be accompanied by release of fat to the surface of the powder, thus degrading the fat encapsulation (Fäldt and Bergenståhl, 1995, 1996). The release of fat to the surface of the powders was, however, affected by the melting point of the fat. By applying crystalline fat, there was no release of fat to the surface during recrystallisation of lactose whereas release of fat to the powder surface was seen when semisolid or liquid fat was used (Fäldt and Bergenståhl, 1995).

In this study, fats being liquid, semisolid and solid at room temperature were applied, and attempts to prevent the release of fat to the surface by preventing recrystallisation of lactose were done by addition of maltodextrine to the solid carrier. Maltodextrine was seen to prevent recrystallisation of amorphous sucrose (Myers and Shively, 1993). The aim of the study was to understand the surface characteristics of the powder particles as a function of inner physical structure of the powder particles and how these parameters affect the reconstitution properties such as droplet size and degree of coalescence of the redispersed emulsions. In the solid state characterisation, the inner physical structure of the powder particles was verified by Differential Scanning Calorimetry (DSC), and X-ray powder diffraction, while the surface characteristics of the powder were studied by Scanning Electron Microscope (SEM) and Electron Spectroscopy for Chemical Analysis (ESCA).

2. Materials and methods

2.1. Materials

Griseofulvin micro cryst., supplied from Leo Pharmaceutical Products, Denmark. Specifications according to Ph.Eur. As fats were used soybean oil (m.p. −20°C), being liquid at room temperature, hardened coconut oil (h. coconut oil; m.p. 33°C), being semisolid at room temperature, and hardened rapeseed oil (h. rape seed oil; m.p. 59°C), being solid at room temperature. They were all obtained from Karlshamns AB, Sweden. The applied emulgator was sodiumcaseinate (Miprodan 31) obtained from MD Foods Ingredients amba, Viby J, Denmark. Lactose and lactose in combination with maltodextrine was used as carrier. Lactose (α-lactose monohydrate) was purchased from BDH Laboratory Supplies, UK, and maltodextrine, mw 3600 g/mol, (Maltodekstriini 22 Maltodekstriini DE-20 from Finnish Sugar) was purchased from Lyckeby Stärkelsen AB, Kristianstad, Sweden. As continuous phase in emulsions distilled water was used.

2.2. Preparation of dry emulsions

The load of solid material was 20%, and 500 ml emulsion was prepared. Lactose (41.8 g) or lactose and maltodextrine (33.5 and 8.36 g, respectively) were dissolved in 400 ml distilled water. pH was adjusted to 7.00 by the addition of 1.0 M NaOH using a PHM 80, portable pH meter from Radiometer, Copenhagen. Sodiumcaseinate (28.3 g) was added and dissolved by magnet stirring, and the solution was heated to 70°C. Griseofulvin (0.12 g) was dissolved in 30 g fat and preheated to 100–110°C. The two solutions were mixed, prehomogenised in a high speed Colloid mill, Ultraturrax (IKA, Germany) for 4 min at 24000 rpm and homogenised in a high pressure homogeniser, Mikro fluidizer, TM 110 (Microfluids, Newton, MA) at 1000 bar. Homogenisation was performed at 70°C, and the emulsion was recycled eight times.

The emulsion was spray dried in a laboratory spray dryer. The dimensions of the drying chamber were 0.5×0.15 m. The dryer operated co-currently and had a spray nozzle with an orifice having a diameter of 1 mm. Inlet air was approximately 180°C and outlet air was 80–90°C. Flow of drying air was 0.8 m^3/min and liquid feed was approximately 11 ml/min. The spray dried emulsions were stored in a dessicator over dry silica gel to prevent recrystallisation of lactose. The humid stored powders were obtained by storing a thin layer of the dry powders, being spread on glass plates, for 4 days in 75% relative humidity, created by a saturated NaCl-solution.

2.3. Reconstitution of liquid emulsion

Reconstitution of liquid emulsions was done from powders stored in dry and humid atmosphere. The solid phase constituted 20% of the total liquid emulsion, and reconstitution was performed by suspending 1.00 g of powder in 4.00 ml of distilled water in a 7-ml container (60 mm high and 15 mm in diameter). After 2 h of rotation at 30 rpm using a Heidolph Reax 2 rotamat, samples were withdrawn and further characterised.

2.4. Characterisation of liquid emulsion

Droplet size distribution of the emulsions before spray drying and after reconstitution of dry emulsions stored in dry and humid atmospheres was determined by light diffraction using a Mastersizer, Malvern, Instruments Ltd, Malvern, UK. For calculation of droplet size from the obtained scattering pattern, the instrument uses an approximated Mie-scattering theory, where the optical parameters, which means refractive index and absorptions coefficient, are necessary parameters. In this study, a relative refractive index (refractive index of oil/refractive index of water) of $1.46/1.33 \sim 1.095$ and an absorption value of 0.1 were used.

The droplet size distribution was determined on the basis of the volume average distribution and $d(v0.5)$, the volume weighted median diameter is used to express the obtained droplet size. The width of droplet size distribution is expressed in the SPAN value (Eq. (1)):

$$\text{SPAN} = \frac{(d(v0.9) - d(v0.1))}{d(v0.5)} \quad (1)$$

A Fourier optic lense with a 45-mm focal length was used, covering the size interval 0.1–80 μm. The degree of flocculation and coalescence was approximated by microscopy using a Zeiss, Axioplan, Germany, microscope at an appropriate magnification of 1200 times.

2.5. Solid state characterisation of dry emulsion

2.5.1. Characterisation of the surface of the powder particles

2.5.1.1. SEM. The outer macroscopic structure of the powder particles was examined by SEM, widely applied in studying spray dried milk and dairy products (Roetman, 1979; Saito, 1988). Scanning electron microscopy was performed using a Philips SEM 515, operating at 15 kV. A thin layer of the samples was placed on double adhesive tape, sticked on SEM-stubs. The samples were coated with gold/palladium by a Balzers SCD 050, Balzer Union AG sputter prior to microscopy.

2.5.1.2. ESCA. A quantitative analysis of the substances present at the surface of the powders was performed, using the ESCA technique (Fäldt et al., 1993). In this particular case, atomic concentrations of carbon, oxygen and nitrogen at the powder surface were analysed. From matrix formula, assuming a linear correlation between atomic concentrations and chemical substances, the concentrations of fat, lactose and sodiumcaseinate were calculated. An AXIS HS photoelectron spectrometer (Kratos Analytical, UK), with a monochromatic Al K_α X-ray source, was used. The pressure in the vacuum chamber during the analysis was less than 10^{-10} bar, and the take-off angle of the photoelectrons was perpendicular to the sample. The analyser operated with a pass-energy of 80 eV and the step size was 0.1 eV. Spectrum acquisition time depended upon the areas under the peaks. The area analysed was a circular region of a diameter of 1.3 mm.

2.5.2. Characterisation of inner physical structure of the powder particles

2.5.2.1. DSC. A Perkin Elmer differential scanning calorimeter type DSC 7 equipped with a Perkin Elmer instrument controller type TAC 7/PC was used. The samples (3.00–5.00 mg) were placed in 50 μl aluminium pans with holes, and dry nitrogen was used as effluent gas. The applied scanning rate was 10°C/min in the scan range 32–250°C. The instrument was calibrated towards zink and indium.

2.5.2.2. X-ray powder diffraction. To verify the molecular state of lactose in the spray dried emulsions, X-ray powder diffraction patterns were obtained using a Guinier camera type XDC 700 and a Phillips generator type PW 1720. Cr. $K_{\alpha 1}$ radiation was used. The obtained patterns were compared to the pattern obtained for pure α-lactose monohydrate and to a standard (Folen, 1975).

3. Results

3.1. Characterisation of liquid emulsion

The droplet size analysis as performed by light diffraction showed an almost identical size distribution for all the freshly prepared liquid emulsions whether they contained soybean oil, h. coconut oil or h. rapeseed oil, and whether maltodextrine was present or not. As seen in Table 1, the volume based median, $d(v0.5)$, was in the order of magnitude 0.30 μm. Span-values, expressing the width of the size distribution, were also in same order of magnitude. By light microscopy, all these emulsions were seen to be homogene and without flocculation and coalescence. In the case of h. rapeseed oil, crystals and few agglomerated crystals of fat were seen due to solidification of the fat at room temperature.

The reconstituted emulsions generally showed larger values of $d(v0.5)$. This was especially seen for the humid stored powders containing soybean oil and h. coconut oil. At the same time, a tendency to broader size distributions (larger values of span) was also observed. Considering the indi-

Table 1
Droplet size distribution of liquid emulsions before spray drying and after reconstitution

Product and storage conditions	Fat	Carrier	Droplet size	
			$d(v0.5)\mu$m	Span
Liquid emulsion before spray drying	Soybean oil	Lactose	0.29 ± 0	1.405 ± 0.01
	H. coconut oil		0.28 ± 0	1.385 ± 0.01
	H. rapeseed oil		0.29 ± 0	1.39 ± 0
	Soybean oil	Lactose	0.285 ± 0.01	1.40 ± 0.04
	H. coconut oil	+maltodextrine	0.285 ± 0.01	1.38 ± 0.01
	H. rape seed oil		0.30 ± 0	1.37 ± 0.02
Reconstituted emulsion from spray dried powders stored in dry atmosphere	Soybean oil	Lactose	0.31 ± 0	1.93 ± 0.26
	H. coconut oil		0.44	158.01
	H. rapeseed oil		0.37 ± 0.05	78.29 ± 100.0
	Soybean oil	Lactose	0.36 ± 0.08	64.1 ± 88.3
	H. coconut oil	+maltodextrine	0.39 ± 0.12	76.1 ± 105.4
	H. rapeseed oil		0.35 ± 0.05	95.1 ± 131.9
Reconstituted emulsion from spray dried powders stored in humid atmosphere	Soybean oil	Lactose	0.725 ± 0.01	7.60 ± 0.29
	H. coconut oil		0.91 ± 0.01	5.28 ± 0.33
	H. rapeseed oil		0.385 ± 0.01	4.82 ± 0.21
	Soybean oil	Lactose	0.50 ± 0.05	5.49 ± 0.12
		+maltodextrine	0.475 ± 0.01[a]	2.82 ± 0.02[a]
	H. coconut oil		0.43 ± 0	5.79 ± 0
			0.52 ± 0[a]	5.86 ± 0.03[a]
	H. rapeseed oil		0.345 ± 0.01	3.27 ± 0.06
			0.31 ± 0[a]	1.495 ± 0.01[a]

The values are average values of two determinations. The composition of the dry emulsions were 30% fat, 28% sodium caseinate and 42% carbohydrate (42% lactose or 34% lactose + 8% maltodextrine).
[a] Repeated experiment.

vidual size distributions, it was seen that during reconstitution bi- and tridisperse systems were obtained, explaining the larger $d(v0.5)$ and span values. In addition, from light microscopy it was seen that larger drops of fat were formed in the soybean oil containing emulsions due to coalescence during spray drying or during the reconstitution. This was also seen for those containing h. coconut oil, which also contained few small crystals of fat. In the case of h. rapeseed oil, no considerable difference in reconstitution properties was observed whether the powder was stored in dry or humid conditions, and by light microscopy crystals and agglomerated crystals of solid fat were seen. In all liquid emulsions, maltodextrine did not seem to have a remarkable effect on droplet size.

3.2. Solid state characterisation

3.2.1. Characterisation of the surface of the powder particles

3.2.1.1. SEM. The freshly prepared spray dried emulsions all consisted of well separated spherical particles with shallow dents, seen to be deeper and more abundant in those containing maltodextrine (Fig. 1(a), Fig. 2(a), Fig. 3(a), Fig. 4(a), Fig. 5(a) and Fig. 6(a)). As seen earlier (Fäldt and Bergenståhl, 1995), humid storage of the spray dried emulsions considerably changed the outer structure of the powders containing soybean oil and h. coconut oil. After humid storage, these powders were highly agglomerated (Fig. 1(b), Fig. 2(b), Fig. 4(b) and Fig. 5(b)), while well separated

powder particles still remained when h. rape seed oil was used (Fig. 3(b) and Fig. 6(b)). In powders containing maltodextrine, humid storage also induced agglomeration of those containing soybean oil and h. coconut oil (Fig. 4(b) and Fig. 5(b)), but the agglomeration was diminished as compared to those without maltodextrine (Fig. 1(b) and Fig. 2(b)).

3.2.1.2. ESCA. The surface composition of the spray dried powders with and without maltodextrine is presented in Fig. 7(a and b). The triangular phasediagrams show: (i) the total composition of the dry system; (ii) the chemical surface composition of the freshly prepared spray dried emulsions; and (iii) the chemical composition at the surface of the powder particles stored in humid atmosphere. In all spray dried powders, the concentration of fat present at the surface was very low, being in the range of 0–8%. The surface was mainly made up of sodium caseinate constituting approximately 65% of the surface (Fig. 7(a)). As seen earlier (Fäldt and Bergenståhl, 1995), the fat encapsulation was improved in succession; h. rapeseed oil, soybean oil and h. coconut. However, in the earlier study (Fäldt and Bergenståhl, 1995), the concentration of soybean oil and h. coconut oil was approximately 15% and 34%, respectively, at the surface compared to 5% and 8% in the present study. This difference might be due to: (i) different drying conditions such as different temperatures of liquid emulsions when

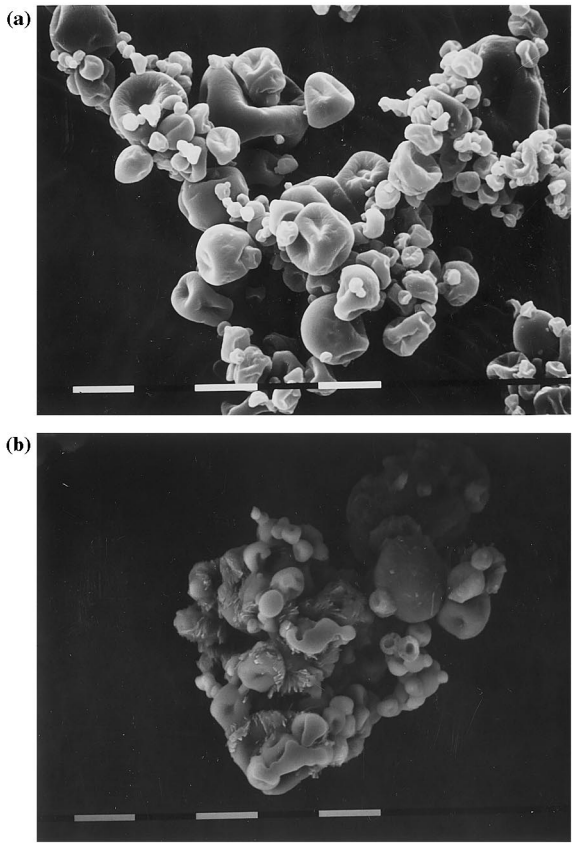

Fig. 1. Soybean oil without maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere; and (b) products stored in humid atmosphere. Bar = 10 μm.

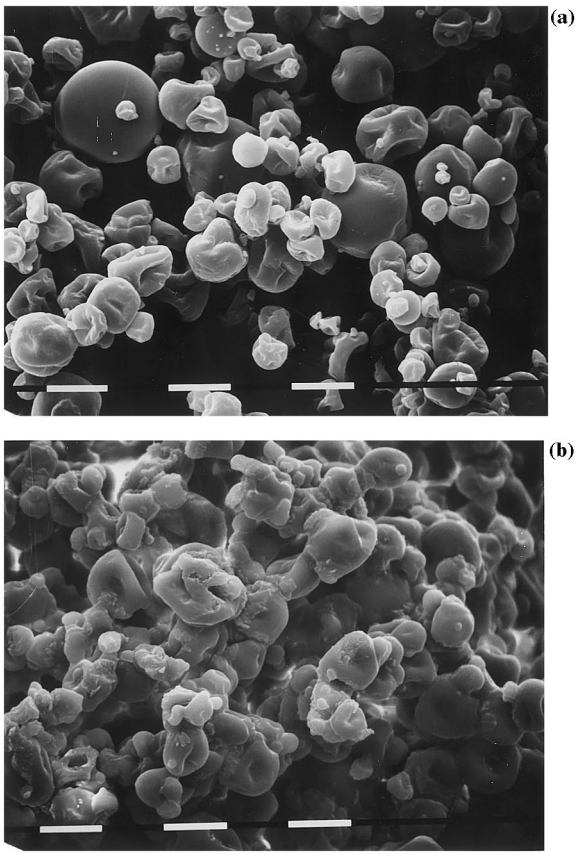

Fig. 2. H. coconut oil without maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere; and (b) products stored in humid atmosphere. Bar = 10 μm.

spray dried; 70°C or room temperature; or (ii) different concentrations of solid material in the liquid emulsions; 10% or 20%.

After humid storage, the concentration of fat at the surface was improved for the powders containing soybean oil and h. coconut oil whereas the fat encapsulation was maintained for those containing h. rapeseed oil (Fig. 7(a)). This is constituent with earlier observations (Fäldt and Bergenståhl, 1995).

Addition of maltodextrine as solid material did not alter the surface composition for the freshly prepared powders (Fig. 7(b)) as compared to those without maltodextrine. However, when stored in humid conditions, improved fat encapsulation was obtained for the powders containing maltodextrine (Fig. 7(b)) as compared to those without maltodextrine (Fig. 7(a)).

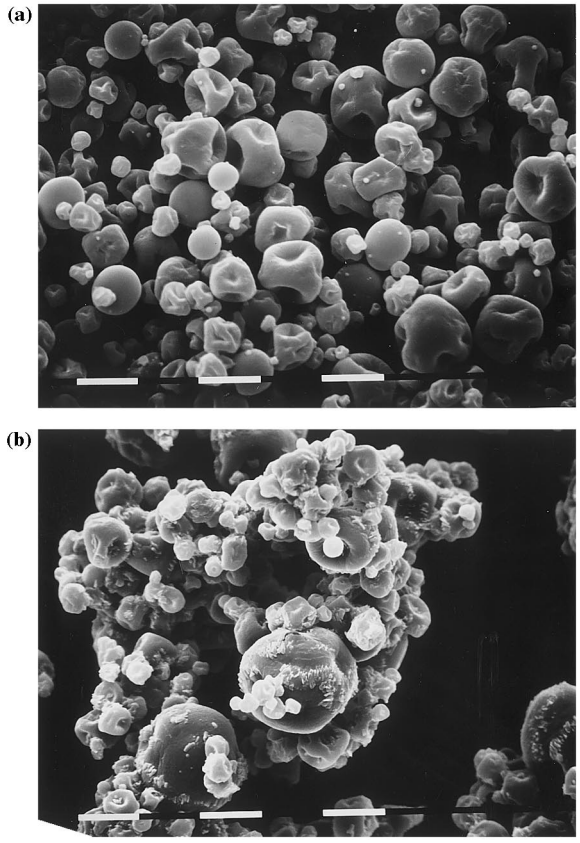

Fig. 3. H. rapeseed oil without maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere; and (b) products stored in humid atmosphere. Bar = 10 μm.

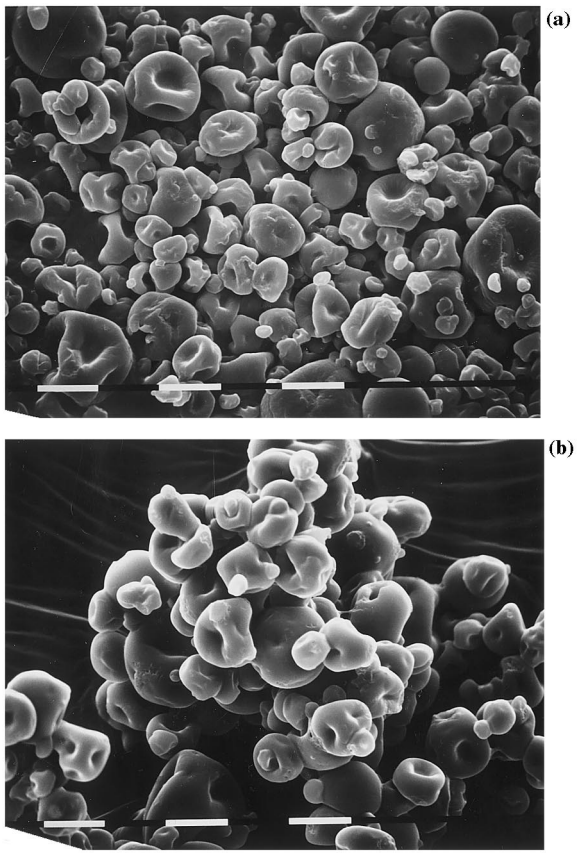

Fig. 4. Soybean oil with maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere; and (b) products stored in humid atmosphere. Bar = 10 μm.

3.2.2. Characterisation of inner physical structure of the powder particles

3.2.2.1. DSC. DSC profiles for spray dried emulsions, stored in dry and humid atmosphere, are shown in Fig. 8. The lack of endothermic events during scanning of the powders stored in dry conditions indicates lack of crystallinity of lactose in the powders. Also, no peaks due to exothermic events are seen, even though crystallisation of

amorphous lactose during scanning was expected. However, due to the lack of water vapour during the scanning, no water uptake took place, and no crystalline α-lactose monohydrate, being the common state of lactose, was formed. For powders containing h. rapeseed oil, an endothermic peak at approximately 60°C is seen because of melting of the solid fat.

After humid storage, it is evident from Fig. 8 that an alteration of the physical state of lactose in the powders had occurred. In all cases, a relatively sharp endothermic transition at approximately 120°C, representing the release of crystal water from α-lactose monohydrate, is seen. This transition is followed by a second endothermic transition at approximately 145°C. This peak is thought to represent melting of unstable α-lactose, which is reported to be formed when α-lactose monohydrate is heated, mostly in vacuo, at temperatures between 100 and 130°C (Buma and Wiegers, 1967; Lerk et al., 1984). The exothermic transition following this endothermic transition (Buma and Wiegers, 1967; Lerk et al., 1984) was not seen in this study, as is also the case for the peaks representing the melting of α-lactose at approximately 220°C. This is believed to be due to the multi-component system in the case of spray dried emulsions. During the DSC run,

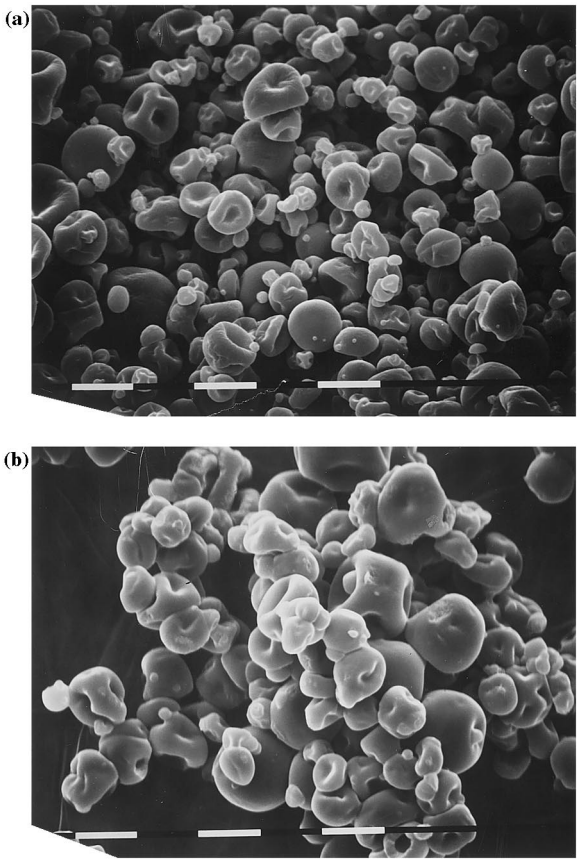

Fig. 5. H. coconut oil with maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere and (b) products stored in humid atmosphere. Bar = 10 μm.

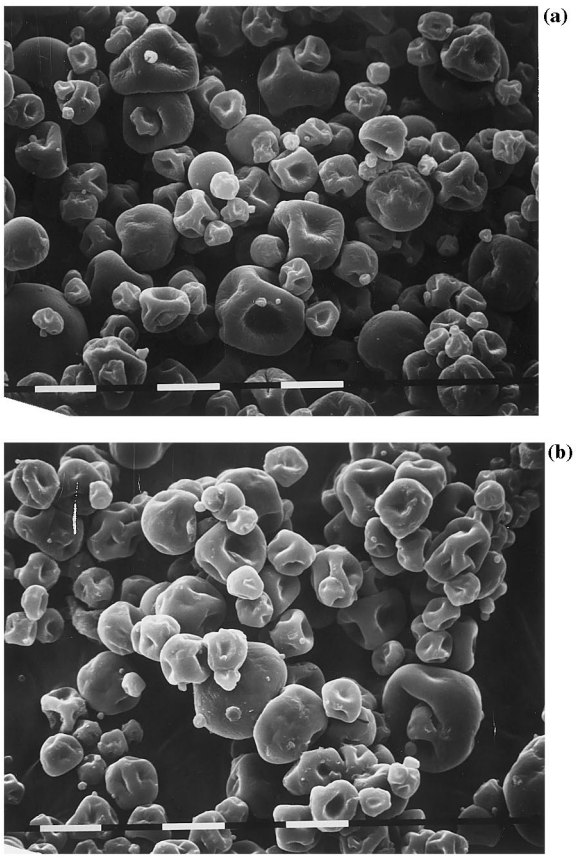

Fig. 6. H. rapeseed oil with maltodextrine. SEM micrographs of spray dried emulsions stored in dry and humid atmosphere. (a) Products stored in dry atmosphere and (b) products stored in humid atmosphere. Bar = 10 μm.

Fig. 7. Triangular phase diagrams showing the chemical composition at the surface of the powder particles as verified by ESCA. Fig. 7(a; left): spray dried emulsions without maltodextrine. Fig. 7(b; right): spray dried emulsions containing maltodextrine. Total composition of the spray dried powder, assuming even distribution of all ingredients throughout the entire powder (●); spray dried powder (■); and humid stored spray dried powder (○). Powders containing h. rapeseed oil (a); soybean oil (b); and h. coconut oil (c).

sodium caseinate and lactose might participate in Maillard reactions and, therefore, possible physical transitions of lactose were covered by other energy transitions. In addition to the endothermic transitions at approximately 120 and 145°C, the dry emulsions containing h. rapeseed oil show a third small endothermic transition at approximately 160°C.

Enthalpy of desorption of crystal water at approximately 120°C for all humid stored powders is summarised in Table 2. As is seen, the values are in same order of magnitude, indicating that the degree of crystallisation was in same order of magnitude for all the powders; that is, neither solid crystalline fat nor maltodextrine inhibited the recrystallisation of lactose during humid storage of the powders.

3.2.2.2. X-ray powder diffraction. From X-ray powder diffractograms in Fig. 9, the internal physical state of lactose in the spray dried emulsions is further verified. No peaks representing crystals of lactose are seen for the spray dried emulsions stored in dry atmosphere. The broad band at approximately $2\Theta = 28°$ represents average distances between molecules being in liquid or amorphous state.

After humid storage, it is seen from X-ray powder patterns that a change in the physical state of the powders had occurred and peaks corresponding to crystalline lactose are now present. There is no remarkable effect of maltodextrine as to inhibit recrystallisation of lactose; in all cases, peaks corresponding to α-lactose monohydrate are seen.

The three most characteristic peaks representing α-lactose monohydrate at approximately $2\Theta = 28.6°$, $2\Theta° = 29.2°$ and $2\Theta = 29.8°$ (Folen, 1975) are broader in the case of h. rapeseed oil compared to those containing h. coconut oil and soybean oil, verifying the predominantly formation of smaller crystals, when solid fat was present.

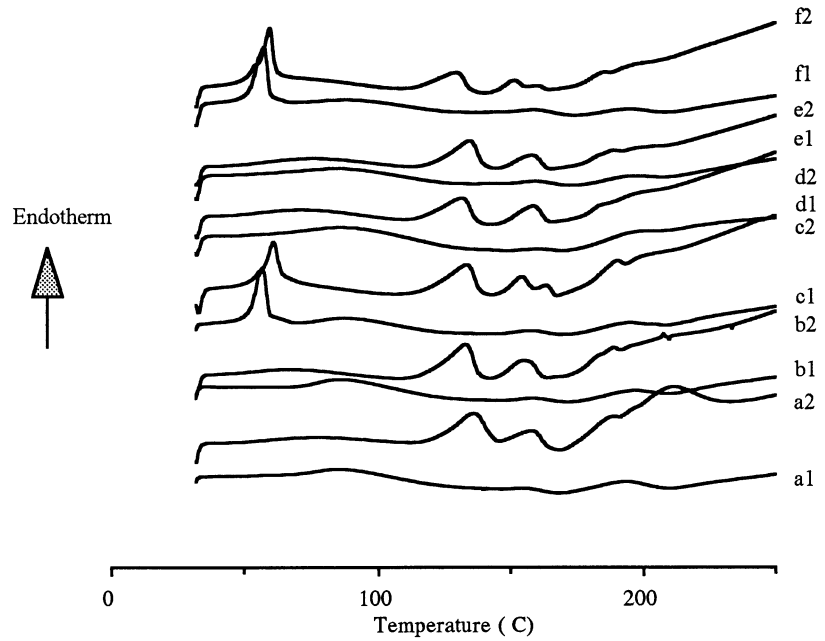

Fig. 8. DSC thermograms for spray dried emulsions stored in dry and humid atmosphere. Soybean oil without maltodextrine (a); h. coconut oil without maltodextrine (b); h. rapeseed oil without maltodextrine (c); soybean oil with maltodextrine (d); h. coconut oil with maltodextrine (e); and h. rapeseed oil with maltodextrine (f). (1) refers to products stored in dry atmosphere; and (2) refers to products stored in humid atmosphere, e.g. d1 refers to the dry emulsion containing soybean oil and maltodextrine, stored in dry atmosphere.

4. Discussion

4.1. Inner physical structure of the powder particles—effect of humid storage, the applied fat and the addition of maltodextrine

DSC measurements and X-ray powder diffraction showed that all the powders were in a high energy amorphous state in regard to lactose before humid storage whereas recrystallisation of lactose took place during humid storage. This confirms earlier studies (Fäldt and Bergenståhl, 1995, 1996) where ESCA and SEM observations were explained in the light of the physical state of lactose.

From DSC measurements, it is seen that the enthalpy of desorption of crystal water (Table 2) was in the same order of magnitude for all humid stored powders, verifying that the degree of crystallinity was equal. However, the X-ray powder diffraction patterns show that by applying h. rapeseed oil, broader peaks are obtained, verifying the formation of smaller crystals when solid fat was applied as compared to liquid or semisolid fat. From X-ray powder diffraction and DSC measurements there were no effect of maltodextrine on the recrystallisation behaviour of lactose in the spray dried emulsions.

4.2. Surface characteristics of the powder particles—effect of humid storage, the applied fat and the addition of maltodextrine

In all spray dried powders, the concentration of fat present at the surface was very low, being in the range of 0–8%. The surface was mainly made up of sodium caseinate constituting approximately 65% of the surface (Fig. 7(a)), and the fat encapsulation was improved in succession; h. rapeseed oil, soybean oil and h. coconut.

The freshly prepared spray dried emulsions all consisted of well separated spherical particles with

shallow dents. Humid storage of the spray dried emulsions considerably changed the outer structure of the powders containing soybean oil and h. coconut oil. After humid storage, these powders were highly agglomerated (Fig. 1(b), Fig. 2(b), Fig. 4(b) and Fig. 5(b)), while well separated powder particles still remained when h. rapeseed oil was used (Fig. 3(b) and Fig. 6(b)). This is constituent with earlier observations (Fäldt and Bergenståhl, 1995).

ESCA analysis also shows a remarkable effect of humid storage of the powders containing soybean oil and h. coconut oil. In these powders, the surface was dominated of fat, while the surface was still made up of sodium caseinate and lactose when h. rapeseed oil was applied.

By applying maltodextrine, the degree of particle agglomeration was diminished and the release of fat to the powder surface was decreased for the powders containing soybean oil and h. coconut oil.

4.3. Reconstitution properties—effect of humid storage, the applied fat and the addition of maltodextrine

Reconstitution of the emulsions from the spray dried powders was possible resulting in white homogene emulsions. Light diffraction showed that enlarged values of $d(v0.5)$ and span values were obtained for powders containing soybean oil and h. coconut oil, especially when stored in humid atmosphere, whereas $d(v0.5)$ and span values were almost preserved when h. rapeseed oil was used. There was no remarkable effect of maltodextrine on reconstitution properties.

Table 2
Results from differential scanning calorimetry of the spray dried powders stored in humid atmosphere. Calculation of enthalpy of desorption of crystal water.

Fat + maltodextrine	ΔH for desorption of crystal water (J/g)
soybean ÷ maltodextrine	99
H. coconut oil ÷ maltodextrine	107
H. rape seed oil ÷ maltodextrine	101
Soybean oil + maltodextrine	104
H. coconut oil + maltodextrine	101
H. rape seed oil + maltodextrine	74
α-Lactose monohydrate	103
α-Lactose monohydrate, humid storage	87

4.4. Surface characteristics, inner physical structure and reconstitution properties of the spray dried emulsion—effect of humid storage, the applied fat and the addition of maltodextrine

The spray dried powders were all made up of spherical hollow particles with fat drops or crystals dispersed in amorphous lactose. The surface of the powder particles was almost made up of sodium caseinate molecules. The liquid emulsions were easily reconstituted to white homogenous emulsions with almost preserved droplet size. Humid storage of the powder particles resulted in recrystallisation of amorphous lactose to crystalline α-lactose monohydrate. During this recrystallisation, lactose molecules accumulated and stress arised inside the powder particles. This stress induced a release of fat onto the surface of the powders and an agglomeration of powder particles occurred for those containing liquid and semisolid fat. For powders containing solid fat, no agglomeration took place and almost no release of fat onto the powder surface was seen. It is believed that the surface characteristics of the powder particles were preserved when solid fat was used, because the solid fat is more resistant to the stress induced by the recrystallising matrix. The firm solid fat particles most likely also reduced the growth of the lactose crystals reducing the agglomeration of the powder particles. Reconstitution of emulsions from humid stored powders gave white homogenous emulsions. The droplet size was enlarged for those containing liquid or semisolid fat, being also the powders where the surface characteristics were changed essentially. In contrast, droplet size was almost preserved when solid fat was applied, that is when the surface characteristics were preserved.

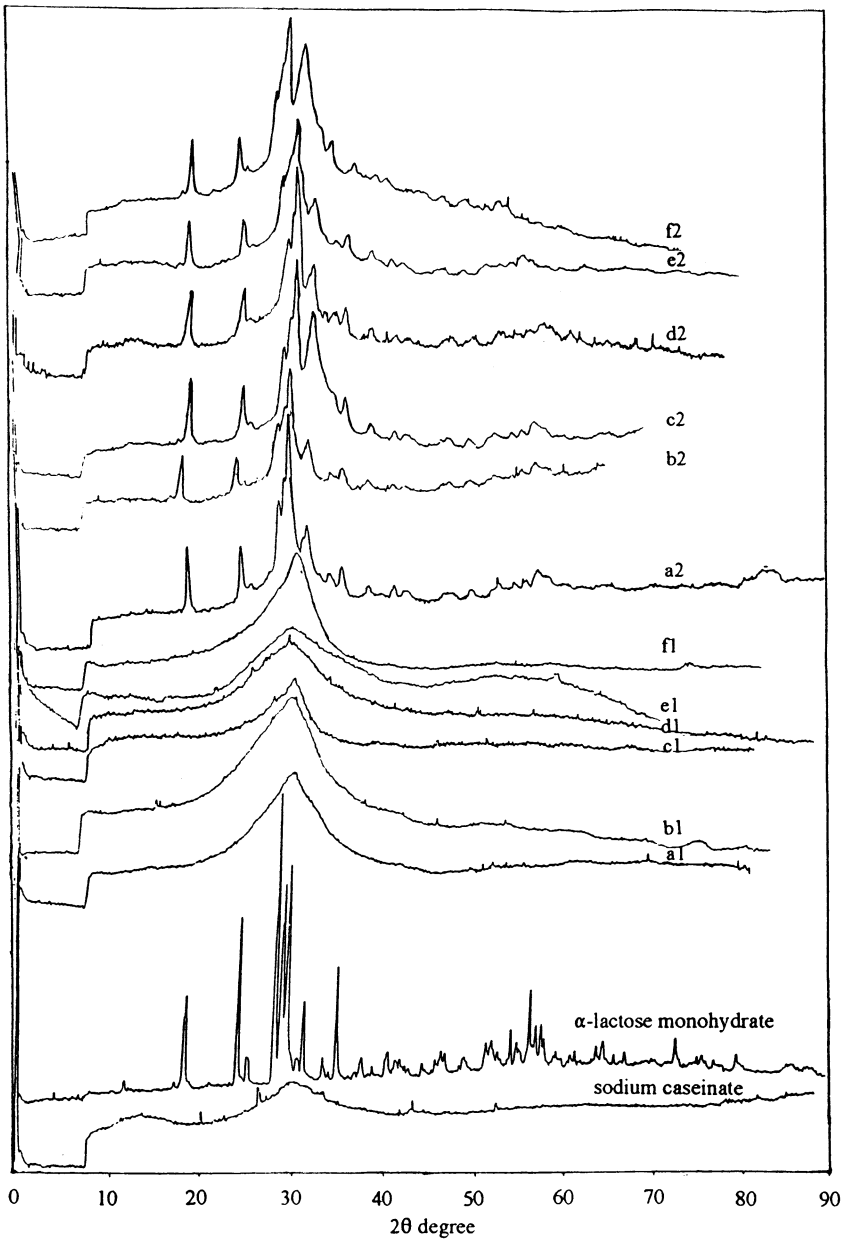

Fig. 9. X-ray powder diffractograms for spray dried emulsions stored in dry and humid atmosphere. Soybean oil without maltodextrine (a); h. coconut oil without maltodextrine (b); h. rapeseed oil without maltodextrine (c); soybean oil with maltodextrine (d); h. coconut oil with maltodextrine (e); and h. rapeseed oil with maltodextrine (f). (1) refers to products stored in dry atmosphere; and (2) refers to products stored in humid atmosphere, e.g. d1 refers to the dry emulsion containing soybean oil and maltodextrine, stored in dry atmosphere. In the bottom of the figure is shown X-ray powder diffractograms of pure α-lactose monohydrate and sodiumcaseinate.

Maltodextrine did affect the surface characteristics of the powders containing liquid or semisolid fat. The release of fat onto the powder surface and the degree of particle agglomeration were diminished during humid storage while there was no detectable effect of maltodextrine on reconstitution properties and the inner physical structure of the powder particles. One surprising result in this study is that change in surface characteristic was diminished without any significant reduction in the degree of lactose crystallisation or in the crystal size as verified by DSC measurements and X-ray powder diffraction. Hence the improving effect of maltodextrine might be related to an influence on the properties of the protein film covering the powder particles.

Acknowledgements

Griseofulvin was kindly supplied from Leo Pharmaceutical Products, Denmark. Thanks to Associate Professor, Ph.D. Alex Mehlsen Soerensen for benefiting discussions of the X-ray powder diffraction patterns.

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