MICROENCAPSULATION OF SOYBEAN OIL BY SPRAY DRYING AND FLUIDIZED BED AGGLOMERATION WITH SOY PROTEIN ISOLATE AND MALTODEXTRIN

PLENGSUREE THIENGNOI

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ABSTRACT

The aim of this study was to investigate the feasibility of microencapsulation of soybean oil serving as a model core material (25 or 50% w/w of dry matter) by spray drying using the wall system (20% w/w) consisting of soy protein isolate (either SPI 1 or SPI 2) and maltodextrins (MD) with different dextrose equivalent (DE) values (7.5 to 24), and then subjected to agglomeration by fluidized bed processing. For both SPIs, the properties of the core-in-wall emulsions and consequently the microencapsulation efficiency (MEE) of the resultant spray-dried microcapsules were adversely affected by an increase in the oil load levels. Even though emulsion oil droplet size was not significantly affected by DE, MEE of the resultant spray-dried microcapsules increased with increasing DE values of MD. Combinations of either SPI 1 or SPI 2 and high DE maltodextrins were found to be effective wall systems for microencapsulation of oil. Spray drying of the emulsions led to small particles (~20 μm) having poor handling and reconstitution properties. Agglomeration of the spray-dried microcapsules with maltodextrin as an aqueous binder solution using a fluidized bed agglomerator improved the handling and reconstitution properties of the powders. The optimum binder type and concentration was found to be 15% (w/v) maltodextrin of DE 14 which resulted in the largest particle size of the agglomerated powder (657 μm) having a very good flowability and low cohesiveness. The wettability (wetting time = 3 s) and dispersibility (98%) of this agglomerated powder were very satisfactory.

KEY WORDS: SOYBEAN OIL/ MICROENCAPSULATION/ SPRAY DRYING/
AGGLOMERATION/ FLUIDIZED BED

142 pages

การห่อหุ้มน้ำมันถั่วเหลืองด้วยสารโปรตีนสกัดจากถั่วเหลืองและมอลโตเด็กซ์ทริน โดยการทำแห้งแบบพ่นฝอยและการเกาะกลุ่มด้วยฟลูอิดไดซ์เบด

MICROENCAPSULATION OF SOYBEAN OIL BY SPRAY DRYING AND FLUIDIZED BED AGGLOMERATION WITH SOY PROTEIN ISOLATE AND MALTODEXTRIN

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คณะกรรมการที่ปรึกษาวิทยานิพนธ์ : มานพ สุพรรณธริกา, Ph.D., สิทธิวัฒน์ เลิศศิริ, Ph.D., อภิญญา อัศวนิก, Ph.D., ไพโรจน์ หลวงพิทักษ์, Dr.Arg.Chem.

บทคัดย่อ

งานวิจัยนี้ศึกษาถึงความเป็นไปได้ของการใช้สารห่อหุ้มน้ำมันถั่วเหลือง (ที่ปริมาณ 25 และ 50 เปอร์เซ็นต์ของน้ำหนักแห้ง) ด้วยวิธีการทำแห้งแบบพ่นฝอยในระบบของสารห่อหุ้ม (ความเข้มข้น 20 เปอร์เซ็นต์ น้ำหนัก/น้ำหนัก) ที่ประกอบไปด้วยโปรตีนสกัดจากถั่วเหลือง (SPI 1 หรือ SPI 2) กับมอลโตเด็กซ์ทรินที่มีค่าสมมูลเด็กซ์โทรสแตกต่างกัน (7.5-24) หลังจากนั้นจึงทำให้เกาะกลุ่มกันด้วยกระบวนการเกาะกลุ่มแบบฟลูอิดไดซ์เบด คุณสมบัติของระบบอิมัลชันและประสิทธิภาพในการห่อหุ้มด้วยสารของผงแห้งได้รับผลกระทบในทิศทางตรงกันข้ามกับการเพิ่มปริมาณน้ำมันถั่วเหลือง ถึงแม้ว่าขนาดอนุภาคของเม็ดไขมันในระบบอิมัลชันจะไม่ได้รับผลกระทบจากค่าความแตกต่างของสมมูลเด็กซ์โทรส แต่ประสิทธิภาพในการห่อหุ้มด้วยสารของผงแห้งเพิ่มขึ้น เมื่อค่าสมมูลเด็กซ์โทรสของมอลโตเด็กซ์ทรินเพิ่มขึ้น จากการศึกษาพบว่าของผสมระหว่างโปรตีนสกัดจากถั่วเหลืองชนิดใดชนิดหนึ่งกับมอลโตเด็กซ์ทรินที่มีค่าสมมูลเด็กซ์โทรสสูงจะมีประสิทธิภาพสูงในการห่อหุ้มน้ำมัน การทำแห้งอิมัลชันแบบพ่นฝอยทำให้ได้อนุภาคผงแห้งที่มีขนาดเล็ก (ประมาณ 20 ไมครอน) ซึ่งมีคุณสมบัติในการขนย้ายและการละลายกลับในน้ำต่ำ วิธีการเกาะกลุ่มด้วยฟลูอิดไดซ์เบดของน้ำมันถั่วเหลืองผง โดยใช้สารละลายมอลโตเด็กซ์ทรินเป็นสารช่วยจับระหว่างอนุภาคผงแห้งด้วยเครื่องเกาะกลุ่มแบบฟลูอิดไดซ์เบดสามารถปรับปรุงคุณสมบัติการละลายกลับในน้ำได้ จากการทดลองพบว่าชนิดและความเข้มข้นของสารละลายช่วยจับที่ให้ผลดีที่สุดคือ 15 เปอร์เซ็นต์ น้ำหนัก/ปริมาตรของมอลโตเด็กซ์ทรินที่มีค่าสมมูลเด็กซ์โทรสเท่ากับ 14 ซึ่งทำให้ได้เม็ดอนุภาคที่มีขนาดใหญ่ที่สุด (657 ไมครอน) และมีคุณสมบัติการไหลดีขึ้น รวมถึงเม็ดอนุภาคมีการเกาะตัวกันน้อยลง คุณสมบัติการเปียกน้ำของเม็ดอนุภาคดีขึ้น (เวลาที่เม็ดอนุภาคทั้งหมดเปียกน้ำเท่ากับ 3 วินาที) และคุณสมบัติการแพร่กระจายในน้ำ (98 เปอร์เซ็นต์) มีค่าสูง

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LIST OF ABBREVIATIONS

AOAC	Association of Official Analytical Chemists
ANOVA	Analysis of variance
CI	Carr index
DE	Dextrose equivalent
$d_{3,2}$	volume-surface area mean diameter
$d_{4,3}$	volume-weighted mean diameter
ed.	Edition
Ed. (Eds.)	Editor, editors, edited by
et al.	Et alii (Latin), and others
etc	Et cetera, and other similar things
e.g.	Exempli gratia (Latin), for example
GRAS	Generally recognized as safe
g	Gram
HR	Hausner ratio
Hz	Hertz
h	Hour
i.e.	Id est (Latin), that is
MD	Maltodextrin
MPa	Megapascal
MEE	Microencapsulation efficiency
MEY	Microencapsulation yield
mm	Millimeter
ml	Milliter
min	Minute
p.(pp.)	Page (pages)

LIST OF ABBREVIATIONS (cont.)

Pa	Pascal
R^2	Coefficient of determination
rpm	Round per minute
s	Second
SPI	Soy protein isolate
SD	Standard deviation
SNK	Student-Newman-Keuls
µm	Micrometer
WPI	Whey protein isolate
w/v	Weight by volume
w/w	Weight by weight
α	Alpha
&	And
°C	Degree Celsius
%	Percent
ε	Porosity
ρ_{bulk}	Bulk density
ρ_{particle}	Particle density
ρ_{tapped}	Tapped density

CHAPTER I
INTRODUCTION

Microencapsulation is a technique by which liquid droplets or solid particles of sensitive or bioactive materials are coated with a thin film of a microencapsulating agent. The structure formed by the microencapsulating agent around the microencapsulated material (the core) is called the wall system. The wall protects the core material against deterioration, limits losses of volatile materials and controls release of active materials (Rosenberg, Talmon, & Kopelman, 1988; Sheu & Rosenberg, 1995; Young, Sarda, & Rosenberg, 1993a, b). Microencapsulation is also used to transform liquids into dry, free-flowing powders, enhancing handling properties. Although many microencapsulation techniques have been developed, spray drying is the most commonly used to microencapsulate food ingredients (Rosenberg et al., 1988; Young et al., 1993a, b).

The wall material for microencapsulation by spray drying should exhibit high solubility, effective emulsification and film forming characteristics, efficient drying properties, and low viscosity at high concentrations (Sheu & Rosenberg, 1995; Young et al., 1993a, b). It is well recognized that gum arabic and proteinaceous materials such as sodium caseinate and whey protein are effective wall materials used alone or in combination with maltodextrin. Maltodextrin cannot be used as wall materials in the absence of a surface-active wall constituent because they generally have no emulsification properties, however, incorporating maltodextrin into the wall systems has been shown to improve the drying properties of the wall matrix probably by enhancing the formation of a dry crust around the drying droplets (Sheu & Rosenberg, 1995). A synergistic effect between protein and maltodextrin has been reported (Young et al., 1993b). The protein serves as an effective emulsifier, enabling the fine dispersion of oil in the wall system, whereas the maltodextrin acts as a filler that enhances the wall hydrophilicity, thus limiting the extraction of oil from interior parts of the microcapsule. A series of studies has indicated that a combination of gum arabic and maltodextrin (Fuchs, Turchiuli, Bohin, Cuvelier, Ordonnaud, Peyrat-Maillard, & Dumoulin, 2006; McNamee, O’Riordan, & O’Sullivan, 2001; Turchiuli, Fuchs, Bohin, Cuvelier, Ordonnaud, Peyrat-Maillard, & Dumoulin, 2005b), sodium caseinate and maltodextrin (Danviriyakul, McClements, Decker, Nawar, & Chinachoti, 2002; Hogan, McNamee, O’Riordan, & O’Sullivan, 2001a; Kagami, Sugimura, Fujishima, Matsuda, Kometani, & Matsumura, 2003), and whey protein and maltodextrin (Sheu & Rosenberg, 1995; Young et al., 1993b) exhibit excellent microencapsulating properties and are suitable for microencapsulation of volatile and non-volatile core materials.

Soy protein is an abundant, inexpensive, and renewable natural material. Soy protein was reported as an effective wall material for microencapsulation by spray drying (Molina Ortiz, Mauri, Monterrey-Quintero, Trindade, Santana, & Favaro-Trindade, 2009). However, the use of soy protein as wall material has been little explored. Moreover, there is no report on the evaluation of a combination of soy protein and maltodextrin as wall material for microencapsulation of oil.

The spray-dried powders usually have a small particle size, typically in the range of 10-100 μm, with poor handling and reconstitution properties. To alleviate these problems, the spray-dried powders are often agglomerated. Agglomeration is defined as the size enlargement process in which the starting material is fine particles join or bind with one another, resulting in an aggregate porous structure much larger in size than the original material, called agglomerates. Agglomerates are obtained by creating solid bridges between individual particles. The surface of particles is made sticky by wetting with water or a binder solution. Liquid bridges are formed when particles come into contact and consolidate during drying leading to solid bridges after solvent evaporation. Fluidized bed agglomeration is one of the most suitable processes leading to agglomerates with high porosity and good mechanical resistance for handling and packaging (Turchiuli, Eloualia, El Mansouri, & Dumoulin, 2005a). This process generally works by fluidizing the powder and then spraying water or a binder solution onto the bed of fluidized particles. There is very limited information available in the literature regarding the agglomeration of spray-dried microencapsulated powders (Buffo, Probst, Zehentbauer, Luo, & Reineccius, 2002; Fuchs et al., 2006; Turchiuli et al., 2005b). Moreover, these works were carried out on the spray-dried microcapsules with low core loads (5-20%) using gum arabic alone or in combination with maltodextrin as wall materials and mostly were agglomerated with water.

In this study, 2 types of soy protein isolate from different companies were selected to use as wall material. The reason for selecting them due to they characterized high solubility with low viscosity of the solution in order to allow the effective of spray drying. In order to validate the afore-stated research hypothesis, a research has been designed to investigate the microencapsulating properties of wall materials consisting soy protein isolate in combination with maltodextrin and to determine the characteristics of the agglomerated spray-dried microcapsules. The objectives of the research are:

1. To test the microencapsulating properties of each type of soy protein isolate in combination with maltodextrin which were used as wall materials. The effects of maltodextrin type (different DE values) and its proportion in the wall systems as well as the oil load levels on emulsion characteristics and microencapsulation efficiency were included.
2. To improve the physical properties, flow characteristics and reconstitution properties of spray-dried soybean oil powder by using fluidized bed agglomeration.
3. To investigate the effect of kinds of binder and binder concentrations on the agglomerated spray-dried powder in terms of physical, morphological, handling and reconstitution properties.

CHAPTER II
LITERATURE REVIEW

2.1 Emulsions

2.1.1 Definitions

An emulsion consists of two immiscible liquids (usually oil and water), with one of the liquids dispersed as small spherical droplets in the other. In most foods, the diameters of the droplets usually lie somewhere between 0.1 and 100 μm (Dickinson & Stainsby 1982; Walstra 1996b). Emulsions can be conveniently classified according to the distribution of the oil and aqueous phases. A system which consists of oil droplets dispersed in an aqueous phase is called an oil-in-water or O/W emulsion (e.g., mayonnaise, milk, cream, soups, and sauces). A system which consists of water droplets dispersed in an oil phase is called a water-in-oil or W/O emulsion (e.g., margarine, butter, and spreads). The substance that makes up the droplets in an emulsion is referred to as the dispersed or external phase. It is also possible to prepare multiple emulsions of the oil-in-water-in-oil (O/W/O) or water-in-oil-in-water (W/O/W) type (Dickinson & McClements 1995).

2.1.2 Emulsion formation

The formation of an emulsion or homogenization process usually requires a considerable amount of mechanical energy, to disperse one of the liquids in the form of small droplets in the continuous phase (Walstra, 1993; Walstra & Smulder, 1998). The formation of emulsion may involve a single step or a number of consecutive steps, depending on the nature of the starting material and the method used to create it. The process of converting two separate immiscible liquids into an emulsion, or of reducing the size of the droplets in a preexisting emulsion, is known as *homogenization.* In the food industry, this process is usually carried out using mechanical devices known as *homogenizers,* which subject the liquids to intense mechanical agitation. Depending on the nature of the starting material it is convenient to divide homogenization into two categories. The creation of an emulsion directly from two separate liquids will be defined as *primary* homogenization, whereas the reduction in size of the droplets in an already existing emulsion will be defined as *secondary* homogenization (Fig. 2.1). The creation of a particular type of food emulsion may involve the use of either of these types of homogenization, or a combination of them. In many food processing operations and laboratory studies it is more efficient to prepare an emulsion using two steps. The separate oil and water phases are converted to a coarse emulsion that contains fairly large droplets using one type of homogenizer (e.g., a high-speed blender), and then the size of the droplets is reduced using another type of homogenizer (e.g., a high-pressure valve homogenizer) (McClements, 2005).

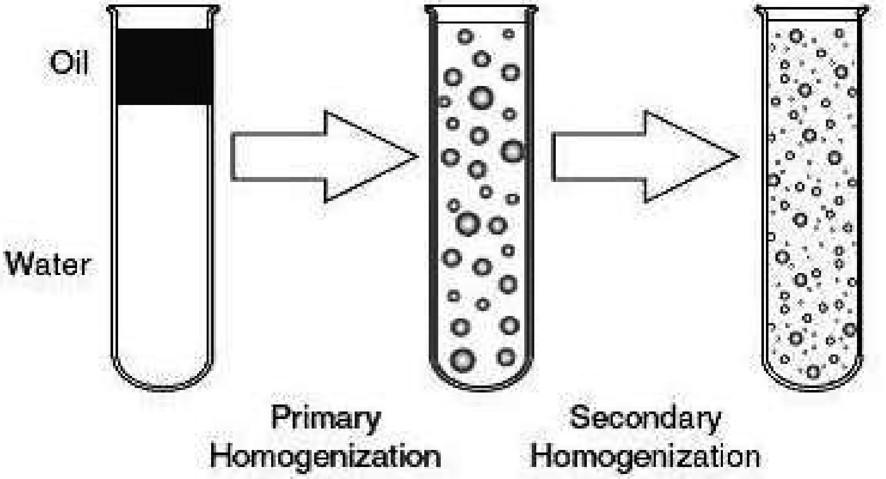

Figure 2.1 Homogenization can be conveniently divided into two categories: primary and secondary homogenization. Primary homogenization is the conversion of two bulk liquids into an emulsion, whereas secondary homogenization is the reduction in size of the droplets in an existing emulsion (McClements, 2005).

High-speed blenders are the most commonly used method for directly homogenizing oil and aqueous phases in the food industry (Brennan, Butters, Cowell, & Lilly, 1981; Fellows, 2000). In a batch process, the oil, water, and other ingredients to be homogenized are placed in a suitable vessel (Fig. 2.2), which may contain as small as a few cubic centimeters (for laboratory use) or as large as several cubic meters (for industrial use) of liquid, and are then agitated by a mixing head that rotates at high speed. The various ingredients may all be added at the beginning of the process or they may be added sequentially to improve dispersion and/or reduce homogenization times. The rapid rotation of the mixing head generates a combination of longitudinal, rotational, and radial velocity gradients in the liquids which disrupts the interfaces between the oil and water, causes the liquids to become intermingled, and breaks the larger droplets into smaller ones (Fellows, 2000). High-speed mixers are particularly useful for preparing emulsions with low or intermediate viscosities. The droplet size usually decreases as the homogenization time or the rotation speed of the mixing head is increased, until a lower limit is achieved which depends on the nature and concentration of the ingredients used and the power density of the mixer. Typically, the droplets produced by a high-speed mixer range between 2 and 10 µm in diameter (McClements, 2005).

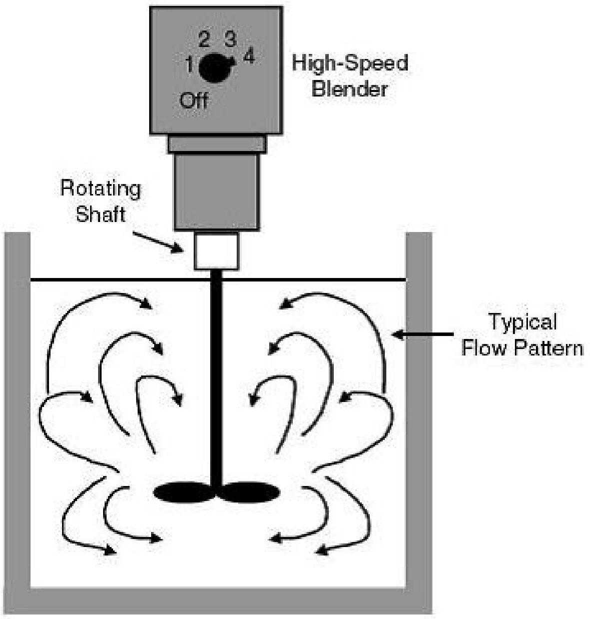

Figure 2.2 High-speed mixers are often used in the food industry to directly homogenize oil and aqueous phases (McClements, 2005).

High-pressure systems, are used to continuously produce fine-disperse emulsions, e.g. High-pressure valve homogenizers (Fig. 2.3). High-pressure valve homogenizers are probably the most common methods of producing fine emulsions in the food industry. They are more effective at reducing the size of the droplets in a preexisting emulsion, than at creating an emulsion directly from two separate liquids (Pandolfe, 1991; 1995). The homogenizer has a pump that pulls the coarse emulsion into a chamber on its backstroke and then forces it through a narrow valve at the end of the chamber on its forward stroke (Fig. 2.3). As the coarse emulsion passes through the valve it experiences a combination of intense disruptive forces that cause the larger droplets to be broken down to smaller ones. Some commercial devices use a “two-stage” homogenization process, in which the emulsion is forced through two consecutive valves. The first valve is at high pressure and is responsible for breaking up the droplets, while the second valve is set at a lower pressure and is mainly responsible for disrupting any “flocs” that are formed during the first stage (Phipps, 1985).

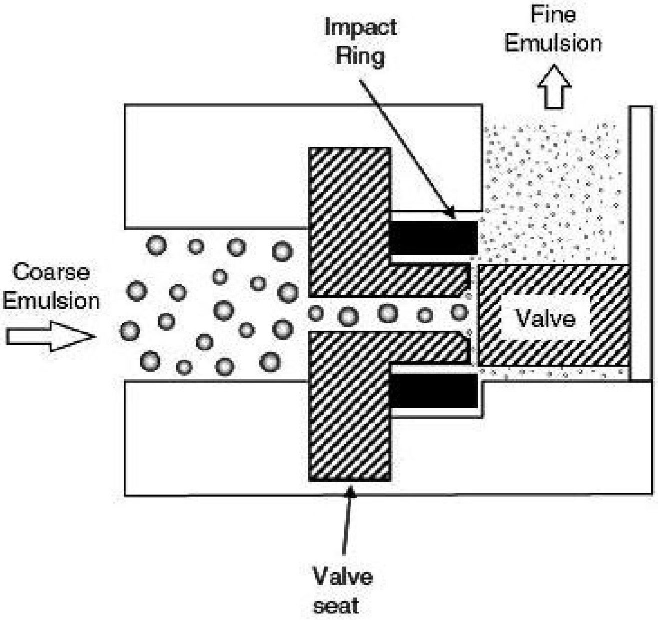

Figure 2.3 High-pressure valve homogenizers are used to produce emulsions with fine droplet sizes (McClements, 2005).

2.1.3 Particle size distribution as a property of emulsion

Many of the most important properties of emulsion-based food products are determined by the size of the droplets that they contain, for example, shelf life, appearance, texture, and flavor. The factors which influence the droplet size include emulsifier type and concentration, volumetric energy input during the homogenization, composition of component phases, and temperature. If all the droplets in an emulsion are of the same size it is referred to as a *monodisperse* emulsion, but if there is a range of droplet sizes present it is referred to as a *polydisperse* emulsion. The droplet size (x) of a monodisperse emulsion can be completely characterized by a single number, such as the droplet diameter (d) or radius (r). Monodisperse emulsions are sometimes prepared and used for fundamental studies because the interpretation of experimental measurements is much simpler than for polydisperse emulsions. Nevertheless, real food emulsions always contain a distribution of droplet sizes, and so the specification of their droplet size is more complicated than for monodisperse systems (McClements, 2005).

It is often convenient to represent the size of the droplets in a polydisperse emulsion by one or two numbers, rather than stipulating the full particle size distribution. The most useful numbers are the mean particle size, $\overline{x}$, which is a measure of the central tendency of the distribution, and the standard deviation, σ, which is a measure of the width of the distribution.

McClements (2005) mentioned that a widely used method of expressing the mean particle size is the surface-weighted mean diameter ($d_{3,2}$), which is related to the average surface area of droplets exposed to the continuous phase per unit volume of emulsion. This relationship is particularly useful for calculating the total surface area of droplets in an emulsion from knowledge of the mean diameter of the droplets and the disperse phase volume fraction. Another commonly used method of expressing the mean particle size of a polydisperse emulsion is the volume-weighted mean diameter ($d_{4,3}$), which is the sum of the volume ratio of droplets in each size-class multiplied by the mid-point diameter of the size-class. It should be noted that $d_{4,3}$ is more sensitive to the presence of large particles in an emulsion than $d_{3,2}$, hence it is often more sensitive to phenomenon such as flocculation. The $d_{3,2}$ and $d_{4,3}$ are given by the following expressions:

$$d_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \qquad \text{or} \qquad d_{4,3} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{2.1}$$

where n_i is the number of particles with diameter d_i.

2.2 Microencapsulation

2.2.1 Definition and objectives of microencapsulation

Microencapsulation can be defined as a “micropackaging” technique by which small liquid droplets, solid particles or gas compounds of an active material are packed into thin films of another material to form microcapsules (Arshady, 1993; Bhandari & Darcy, 1996; Dziezak, 1988; Gharsallaoui, Roudaut, Chambin, Voilley & Saurel, 2007; Shahidi & Han, 1993; Young, Sarda & Rosenberg, 1993a, b). The material inside the microcapsule is referred to as the core material, internal phase, active, or fill, whereas the wall is sometimes called shell, coating material, carrier, or membrane (Arshady, 1993; Augustin, Sanguansri, Margetts & Young, 2001; Gharsallaoui et al., 2007; Shahidi & Han, 1993) as shown in Fig. 2.4.

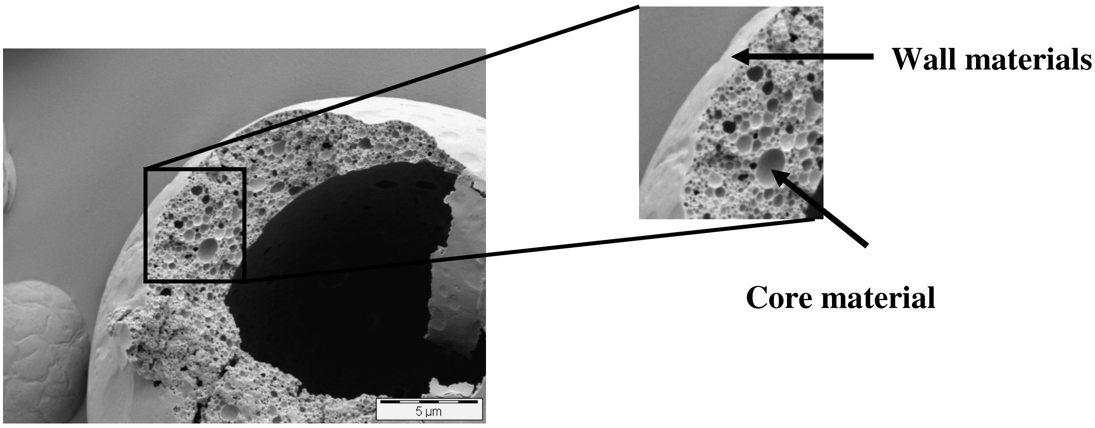

Figure 2.4 Example of the inner structure of spray-dried microencapsulated oil powder particle consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate/maltodextrin ratio of 1:3. Maltodextrin had a DE value of 18.

Comparison between a homogenized fat globule and a microencapsulated fat powder particle is shown in Fig. 2.5. Fat globules have a median particle size of 0.5 µm or less depending on the homogenization pressure and number of passes and an adsorbed protein layer that is 50 to 200 nm thick (Rosenberg & Lee, 1993). The prefix micro implies that all or at least 90% of the globules should be < 1 µm. By contrast, spray-dried microencapsulated fat powder particles have a median particle size of 35 to 75 µm or greater. The oil globules in the powder particles retain the layer of adsorbed emulsifier during drying, and in turn are embedded in a continuous phase of inert filler (Keogh, 2005). Spray-dried powder particles also contain a large central vacuole or hollow particle up to 15 µm or more in diameter with small to medium-sized vacuoles in the wall (Verhey, 1972).

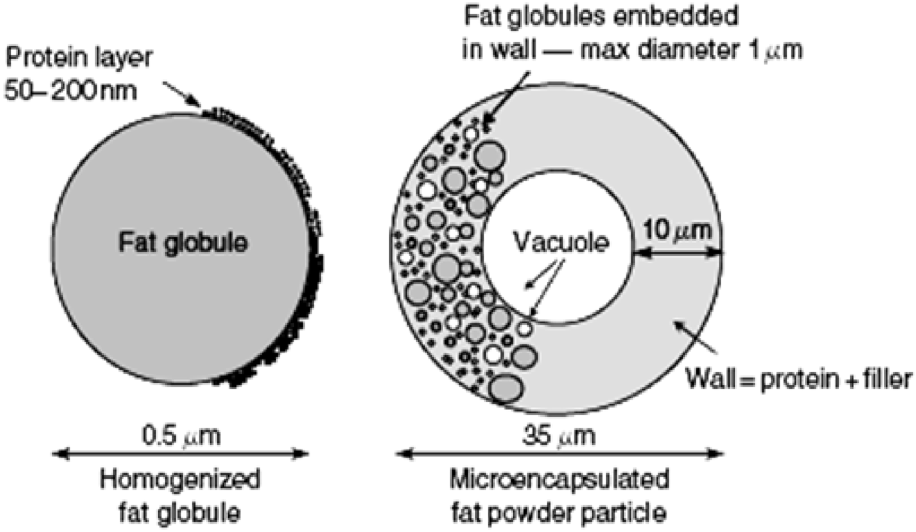

Figure 2.5 Comparison of homogenized and microencapsulated fat (Keogh, 2005).

Many food constituents are sensitive to environmental factors, such as, light, heat, and oxygen, which may cause deterioration of the food constituents. Some liquid form food ingredients are difficult to handle during processing and some may have objectionable flavor. Microencapsulation can change various active material properties. By microencapsulation, the active materials are protected by the wall systems, thus the shelf-life of unstable material can be improved, the volatile flavors can be retained and handling and flow properties of the products containing liquid ingredients can be improved, and the objectionable flavor can be masked (Augustin et al., 2001; Gibbs, Kermasha, Alli, & Mulligan, 1999; Jackson & Lee, 1991; Shahidi & Han 1993). Microencapsulation has been widely applied in the food industries. The major applications of microencapsulation in the food industries include: separate the reactive components within a mixture; protect unstable ingredients from degradation; provide controlled or delayed release until later during processing or storage, or during final preparation prior to consumption or ingestion; change the physical characteristics of the original material, such as, transforming liquid form into powder form to improve flowability and compression properties (Arshady, 1993; Bhandari & Darcy, 1996; DeZarn, 1995; Gibbs et al., 1999; Jackson & Lee, 1991; Shahidi & Han, 1993). Other applications of food encapsulation include: mask objectionable flavors; reduce hygroscopicity; reduce dustiness, modify handling properties; limit losses of volatile material; and alter surface properties of the material (Bakan, 1973; Bhandari & Darcy, 1996; Dziezak, 1988; Gibbs et al., 1999; Jackson & Lee, 1991; Karel & Langer, 1988; Onwulata, Smith, Craig & Holsinger, 1994; Rosenberg & Young, 1993).

2.2.2 Properties of microcapsules

Microcapsules referred to particles with size approximately between 0.2 μm and 5 mm in diameter (Jackson & Lee, 1991). The size of the capsules depends on the materials and the methods used in preparation of the capsules, as well as application purpose. Microcapsules can be many different shapes. They can be spherical, oblong or irregularly shaped, monolithic or aggregate (Gibbs et al., 1999; Jackson & Lee, 1991). The structure of the microcapsules can be a single-particle structure in which core material is completely surrounded by a uniform wall material. It can also be multi-walled structure in which the wall layers can have the same, or quite different composition (Shahidi & Han 1993; Gibbs et al, 1999). Microcapsule can also have a matrix structure, in which several distinct core particles or droplets are embedded in a wall matrix (multi-core) or numerous same core particles embedded in a continuous wall material matrix (Gibbs et al., 1999; Rosenberg & Young, 1993; Shahidi & Han, 1993; Sheu & Rosenberg, 1998). Microcapsules prepared by spray drying normally exhibit matrix form, such as spray-dried milk powder, in which numerous small core droplets are embedded in a continuous non-fat milk solid matrix (Aguilar & Ziegler, 1994a, b; Caric & Kalab, 1987). The thickness of a wall can be adjusted to alter permeability and stability of the microcapsules. The wall material usually represents about 1-70% weight of the microcapsules (Jackson & Lee, 1991).

2.2.3 Types of core material

Many valuable nutrients and sensitive ingredients, such as vitamins, minerals, anti-oxidants, flavours and oxygen-sensitive oil rich in omega-3 or omega-6 fatty acid, e.g. fish oil, need to be protected as they are unstable when in contact with other ingredients or the environment. Microencapsulation enables the incorporation of such ingredients into palatable and shelf-stable food products by affording protection to polyunsaturated oils and oxygen sensitive vitamins, during storage and processing (Augustin et al., 2001; Gharsallaoui et al., 2007).

There are many food ingredients were encapsulated by spray drying with either alone or in combination of wall material, such as, anhydrous milk fat (Young et al., 1993a, b; Danviriyakul, McClements, Decker, Nawar, & Chinachoti, 2002), ethyl caprylate (Sheu & Rosenberg, 1995, 1998), soya oil (Hogan, McNamee, O'Riordan, & O'Sullivan, 2001a, b; McNamee, O'Riordan & O'Sullivan, 2001), lycopene (Shu, Yu, Zhao, & Liu, 2006), cardamom oleoresin (Krishnan, Bhosale, & Singhal, 2005), D-limonene (Soottitantawat, Bigeard, Yoshii, Furuta, Ohkawara, & Linko, 2005a), cumin oleoresin (Kanakdande, Bhosale, & Singhal, 2007) and fish oil (Jafari, Assadpoor, Bhandari & He, 2008; Kagami, Sugimura, Fujishima, Matsuda, Kometani, & Matsumura, 2003; Keogh, O'Kennedy, Kelly, Auty, Kelly, Fureby, & Haahr, 2001; Serfert, Drusch & Schwarz, 2009).

2.2.4 Types of wall material

The choice of a wall material for microencapsulation by spray drying is very important for encapsulation efficiency and microcapsule stability. An acceptable microencapsulating agent must be safe, non-hazardous to the consumer health and bland or no flavor. It must be able to protect encapsulated cores from factors, such as oxygen, water, light or other compounds, which may cause its deterioration and also provide long-term stability. It should delay release of an active ingredient pending its use and prevent or limit evaporation of volatile molecules. Further, it should be able to transform liquid materials into dry powders. Additionally, the criteria for selecting a wall material are mainly based on the physico-chemical properties such as solubility, molecular weight, glass/melting transition, crystallinity, diffusibility, film forming, good drying properties, low viscosity of its concentrated solutions and emulsifying properties (Gharsallaoui, et al., 2007; Jackson & Lee, 1991; Onwulata et al., 1994; Reineccius, 1988; Rosenberg, 1997; Young et al., 1993b). Thus, judicious choice of encapsulating material according to the desired application is an important task. Depending on the core material and the characteristics desired in the final product, wall materials can be selected from a wide variety of natural and synthetic polymers. Since almost all spray-drying processes in the food industry are carried out from aqueous feed formulation, the wall material must be soluble in water at an acceptable level (Gouin, 2004). In addition to its high solubility, a wall material for microencapsulation by spray-drying should possess good properties of emulsification, film forming, and drying and the wall concentrated solutions should have low viscosity (Reineccius, 1988). Many available wall materials possess these properties but the number of materials approved for food uses is limited (Dziezak, 1988).

Numerous wall materials or microencapsulating agents are available for food application. Proteins, carbohydrates, lipids, gums, cellulose materials and inorganic materials are commonly used as wall materials either alone or in combination (Augustin et al., 2001; Kenyon, 1995; Reineccius, 1988; Shahidi & Han 1993). Due to, in some cases, one wall material cannot meet all the required properties and thus different constituents are combined to obtain the desired wall properties. There are many researches studied in combination of different wall materials, such as, whey proteins/lactose (Rosenberg & Sheu, 1996; Young et al., 1993a), whey proteins/carbohydrates (Young et al., 1993b), sodium caseinate/carbohydrates (Hogan et al., 2001a), gelatin/sucrose (Shu et al., 2006), gum arabic/modified starch/maltodetrin (Kanakdande et al., 2007; Krishnan et al., 2005; Soottitantawat et al., 2005a), gum arabic/modified starch (Shaikh, Bhosale & Singhal, 2006; Soottitantawat, Takayama, Okamura, Muranaka, Yoshii & Furuta, 2005b).

2.2.4.1 Soy protein isolate as wall materials

Soy protein isolate, or isolated soy protein, contains a minimum of 90% protein on a dry matter basis, processed from the same defatted soy flakes as defatted soy flour and soy protein concentrate, but soy protein isolate is processed one step beyond concentrates to remove not only the fat and soluble sugars but also the insoluble sugars and dietary fiber (Jordan & Golbitz, 2006; Taillie, 2006). Soy protein isolates are traditionally prepared from defatted soy meal using aqueous or mild alkali extraction (pH ~7-10) of proteins and soluble carbohydrates. The insoluble residue, mostly carbohydrate, is thus removed by centrifugation, followed by precipitation of soy protein at its isoelectric point (pH in the range of 4.5). The precipitated protein is separated by mechanical decanting, washed, and neutralized to a pH about 6.8 and then spray-dried (Hettiarachchy & Kalapathy, 1997). Soy protein isolates are typically light in color, bland in flavor, highly digestible and easy to use in food, beverage, and baking formulations (Egbert, 2004; Jordan & Golbitz, 2006). Furthermore, it is also an abundant, inexpensive and renewable raw material (Molina Ortiz, Mauri, Monterrey-Quinters, Trindade, Santana & Favaro-Trindade, 2009) including acceptability as a naturally occurring food component that is degradable by digestive enzymes (Chen, Remondetto & Subirade, 2006).

1) Basic structures of soy proteins

Approximately 90% of the proteins in soybeans exist as storage proteins, which mostly consist of β-conglycinin and glycinin. β-Conglycinin has the sedimentation coefficients (SC) of 7S, whereas glycinin has 11S (Koshiyama, 1965; Koshiyama & Fukushima, 1976; Mitsuda, Kusano & Hahegawa, 1965). The major storage proteins, namely, β-conglycinin and glycinin, possess a variety of functional properties physicochemically for food applications. These functional properties are ascribed to the intrinsic physicochemical characteristics which are based on the molecular structures (Fukushima, 2004).

β-conglycinin is a glycoprotein and a trimer which consists of three subunits with a molecular mass of 150-200 kDa. Major subunits are α', α, and β and their molecular weights are 72, 68, and 52 kDa, respectively. Besides these, there is a minor subunit called γ in β-conglycinin (Fukushima, 2004).

Glycinin is a hexamer with a molecular mass of 300-380 kDa. Each subunit is composed of acidic (~35 kDa) and basic (~20 kDa) polypeptides, which are linked together by a disulfide bond. In glycinin, five subunits are identified as $A_{1a}B_{1b}$ (53.6 kDa), A_2B_{1a} (52.4 kDa), $A_{1b}B_2$ (52.2 kDa), $A_5A_4B_3$ (61.2 kDa) and A_3B_4 (55.4 kDa), which are classified into group I ($A_{1a}B_{1b}$, A_2B_{1a} , $A_{1b}B_2$) and group II ($A_5A_4B_3$, A_3B_4) by the extent of the homology (Fukushima, 2004; Nielsen, 1985).

2) The physicochemical properties of soy proteins

Functional properties of proteins can be defined as the physicochemical properties and their interactions with other food components (Hettiarachchy & Kalapathy, 1997). Functional properties of proteins connote those physicochemical properties which affect the behavior of proteins in food systems during preparation, processing, storage and consumption (Kinsella, 1979). Functional properties are important not only in determining the quality of the final product but also in facilitating processing.

The physicochemical functions of proteins depend upon their three-dimensional structures substantially. The polypeptide chains of the protein molecules are unfolded through the heat treatment of soybeans and as a result the amino acid side residues buried inside a molecule are exposed on the surface. The exposed -SH or hydrophobic residues combine the protein molecules through -SH, -SS- interchange reaction or hydrophobic bonding, respectively. In this case, it is very important that these active residues are present at an accessible location of the molecules. The larger numbers of SH groups and their topology in glycinin make glycinin gel much harder and more turbid in comparison with β-conglycinin gel, whereas the higher hydrophobicity and more easily unfolded structure in β-conglycinin make its emulsifying ability much stronger than that of glycinin (Utsumi, Matsumura & Mori, 1997).

Soy protein isolate was chosen as microencapsulating agent in this research because of its useful functional properties for microencapsulation, such as emulsification, solubility, film-forming and water binding capacity. In addition, soy protein isolate is recognized as safe (GRAS) (Boyacioglu, 2006; Egbert, 2004; Hettiarachchy & Kalapathy, 1997). These properties make soy protein isolate a very attractive wall material for the microencapsulation of bioactive compounds. Moreover, the use of soy protein as microencapsulating agent or wall material has been little explored.

2.2.4.2 Carbohydrates as wall materials

Maltodextrins and corn syrup solids are produced by partially hydrolyzing starch, usually corn, with acid or enzymes or with a combination of acid and enzymes. Maltodextrins are nonsweet nutritive polysaccharides consisting of α-(l,4)-linked D-glucose that have dextrose equivalence (DE) less than 20. Corn syrup solids are dried glucose syrups in which have the DE of 20 or higher. Both maltodextrins and corn syrup solids are recognized as safe (GRAS) (Kenyon 1995; Reineccius, 1991). The average molecular weight of maltodextrins and corn syrup solids is approximately 3600 for 5 DE, 1800 for 10 DE, 1200 for 15 DE and 900 for 20 DE, respectively. Compared to original starch (approximately 2,000,000), these hydrolysates are much smaller polymers (Kenyon & Anderson, 1988). Maltodextrins and corn syrup solids demonstrated good solubility when solids content ranges 30-45% at 5 DE, 45-55% at 10 DE, 50-60% at 15 DE, and 60-75% at 20 DE (Kenyon, 1995). Viscosity and solubility properties are two very important factors for an encapsulation matrix ingredient. In spray-dried encapsulations, increase soluble solids at a low viscosity increases the efficiency of production (Reineccius, 1988). Normally, maltodextrins and corn syrup solids are used at higher dryer feed solids.

Maltodextrins and corn syrup solids are widely used as microencapsulating agent by spray drying for flavor retention as well as for preventing lipid oxidation (Hogan et al., 2001a; McNamee et al., 2001; Reineccius, 1988; 1991; Rosenberg, Kopelman, & Talmon, 1990) with low cost, bland in flavor, high water solubility and low viscosity of solutions (Gharsallaoui, et al., 2007; Loksuwan, 2007; Turchiuli, Fuchs, Bohin, Cuvelier, Ordonnaud, Peyrat-Maillard, & Dumoulin, 2005b). Maltodextrins and corn syrup solids have virtually no emulsification properties, they produce coarse emulsion that results in poor flavor retention during drying (Kenyon, 1995; Reineccius, 1991; Sheu & Rosenberg, 1995; Turchiuli et al., 2005b). In addition, they have no film-forming property (Sheu & Rosenberg, 1998). In encapsulation of ingredients, the wet encapsulation matrix must form a film around the droplets of active material and effectively retain them during the drying process while losing the water (Reineccius, 1991; Risch & Reineccius, 1988). So they are usually combined with other emulsifying matrix materials such as gum arabic, modified starches, or proteins to achieve the necessary emulsion stability (Danviriyakul et al., 2002; Hogan et al., 2001a; McNamee et al., 2001; Sheu & Rosenberg, 1995).

Many researches have used hydrolyzed starches in conjunction with other wall materials or emulsifying agents to improve their emulsifying characteristics. Mixtures of maltodextrins or corn syrup solids with whey proteins were reported as effective wall materials for microencapsulation of ethyl caprylate (Sheu & Rosenberg, 1995). A blend of gum arabic: maltodextrins: modified starch at a 4/6:1/6:1/6 was reported to provide a better protection of cardamom oleoresin than gum arabic alone (Krishnan et al., 2005). It has found that blending maltodextrin with either modified starch or gum arabic or proteins can significantly reduce costs of the wall materials without reducing the encapsulating ability (Hogan et al., 2001a; McNamee et al., 2001; Sheu & Rosenberg 1995).

2.2.5 Microencapsulation by spray drying

Spray drying is the most widely used method in the food industry, particularly for flavor encapsulation (Augustin et al., 2001; DeZarn 1995; Dziezak, 1988; Gibbs et al., 1999; Jackson & Lee, 1991; Reineccius, 1991; Risch, 1995; Shahidi & Han 1993). It is also one of the oldest encapsulation methods, being used in the 1930s to prepare the first encapsulated flavors with gum acacia as the microencapsulating agent (Dziezak, 1988). Spray drying is a mass and heat transfer process that can be defined as a gas-solid contact interaction, removing solvent (commonly water) from the solids phase during the drying process (Masters, 1991). The process of spray drying is economical and flexible. The required equipment is readily available and the production cost is lower than most other microencapsulation methods (Gibbs et al., 1999; Jackson & Lee, 1991 ; Risch 1995; Shahidi & Han 1993). Shahidi & Han (1993) suggested that the microencapsulation by spray drying involves four stages: preparation of the dispersion or emulsion; homogenization of the dispersion; atomization of the infeed emulsion; and dehydration of the atomized particles.

The first stage is the formation of a fine and stable emulsion of the core material in the wall solution. The mixture to be atomized is prepared by dispersing the core material, which is usually of hydrophobic nature, into a solution of the coating agent with which it is immiscible. The dispersion must be heated and homogenized, with or without the addition of an emulsifier depending on the emulsifying properties of the coating materials due to some of them have themselves interfacial activities (Gharsallaoui, et al., 2007). The obtained oil-in-water emulsion is then atomized into a heated air stream supplied to the drying chamber and the evaporation of the solvent, usually water, consequently leads to the formation of microcapsules. As the sprayed particles fall through the gaseous medium, they assume a spherical shape with the oil encased in the aqueous phase (Dziezak, 1988). The short time exposition and the rapid evaporation of water keep the core temperature below 40 °C, in spite of the high temperatures generally used in the process (Gharsallaoui, et al., 2007).

The main factors known to affect the efficiency of the encapsulation by spray drying include wall material properties, wall material concentration, molecular weight and vapor pressure of core, core-to-wall ratio, the concentration of the solids in the emulsion, the viscosity of emulsion, the drying properties of the wall material, particle size of emulsion, the degree of homogenization, and the spray drying conditions (Bhandari & Darcy, 1996; Jackson & Lee 1991 ; Kenyon, 1995; Liu, Zhou, Zeng, & Ouyang, 2004; Reineccius, 1989; Shahidi & Han 1993). High infeed of solids reduces the time necessary to form a semi-permeable membrane around the droplet, therefore, increasing retention of core. When moisture at the droplet surface decreases to about l0%, the surface of the droplet forms a semi-permeable film (Reineccius, 1989). Flavor molecules cannot diffuse through the surface film, while most water molecules can continue to diffuse through this surface film (Bhandari & Darcy, 1996; Gibbs et al., 1999; Reineccius, 1989). Most of the flavor losses occur before the formation of the semi-permeable film (Bhandari & Darcy, 1996; Bhandari, Dumoulin, Richard, Noleav, & Lebert, 1992). Most work suggested that higher infeed of solids has advantage as long as the solids are soluble (Kenyon, 1995; Shahidi & Han 1993). The molecular weight of the core material is directly related to the diffusion coefficient (Bhandari & Darcy, 1996; Dziezak, 1988), The small molecules with low boiling points are more vulnerable to loss during drying process (Dziezak, 1988;

Shahidi & Han 1993). Higher core to wall ratio generally result in greater loss of core in spray drying, due to the particle shrinkage and cracking during drying (Reineccius, 1989). Lower viscosity of the emulsion will result in slower formation of the semi-permeable film, which causes low retention of core. However, oil droplets should be rather small and viscosity should be low enough to prevent air inclusion in the particle (Drusch, 2007). Emulsion viscosity and particle size distribution have significant effects on microencapsulation by spray-drying. High viscosities interfere with the atomization process and lead to the formation of elongated and large droplets that adversely affect the drying rate (Rosenberg et al., 1990).

Reineccius (1989) thought that effect of particle size of the emulsion on the retention of the flavor depends on the infeed solids load. If high infeed of solids are used, the effect of particle size is insignificant. The degree of homogenization mainly affects the particle size of the emulsion, which may affect the core retention (Risch & Reineccius, 1988). Drying conditions such as inlet air and outlet air temperatures mainly affect the drying rate. Relatively high drying inlet temperature allows rapid formation of "ballooning" of the drying droplet (Bhandari & Darcy, 1996; Rosenberg et al., 1990). Ballooning occurs when steam is formed in the interior of the droplet (a very rapid expansion of air) at high inlet temperature, which may result in thin-walled hollow particles, therefore, lower flavor retention (Rosenberg & Young, 1993). In some cases, some cracks may be formed due to the rapid expansion of the capsules, therefore causing high surface oil (Sheu & Rosenberg, 1998).

Reineccius (1988) reported that the greatest loss of the volatiles during microencapsulation by spray-drying takes place at early stages of drying, prior to the formation of a dry crust at the surface of the drying particles. However, the use of some specific compounds can modify the drying properties of microcapsules. Indeed, the addition of lactose to the whey protein-based system appeared to enhance crust formation by improving the drying properties of the wall. This positive effect of lactose has been attributed to the formation of a continuous glass phase of lactose in which the protein chains are dispersed (Rosenberg & Sheu, 1996). In addition, the lactose glass phase increases the hydrophilic nature of the wall matrix and limits the diffusion of the solvent through the wall (Moreau & Rosenberg, 1993). Microencapsulation efficiency can be increased by increasing wall solution solids concentration which can be related to the effect of wall solids concentration on the formation of surface core prior to the formation of crust around the drying droplets (Young, Sarda & Rosenberg, 1993b).

The main limitation of the spray drying technique in microencapsulation is the limited number of wall materials available and that must have a good solubility in water (Gharsallaoui et al., 2007). Another disadvantage for spray drying that should be considered is that it produces a fine microcapsules powder, typically in the range 10-100 µm in diameter. This small particle size may result in poor reconstitution properties, product separation during shipping and handling (when mixed with other ingredients), poor handling properties, and dusting problems in manufacturing. To relieve these problems, spray-dried powders can be agglomerated (Buffo, Probst, Zehentbauer, Luo, & Reineccius, 2002; Fuchs et al., 2006; Gharsallaoui et al., 2007; Jones, 1988; Turchiuli et al., 2005b).

2.3 Spray drying

2.3.1 Definition and objectives of spray drying

Spray-drying is a unit operation by which a lipid product is atomized in a hot gas current to instantaneously obtain a powder. The gas generally used is air or more rarely an inert gas as nitrogen (Gharsallaoui et al., 2007). The feed can either be a solution, suspension, emulsion or paste. The resulting dried product conforms to powders, granules or agglomerates, the form of which depends upon the physical and chemical properties of the feed and the dryer design and operation (Masters, 1991). Spray-drying produces, depending on the starting feed material and operating conditions, a very fine powder (10-50 µm) or large size particles (2-3 mm) (Gharsallaoui et al., 2007).

Spray-drying is generally used in food industry to ensure a microbiological stability of products, avoid the risk of chemical and/or biological degradations, reduce the storage and transport costs, and finally obtain a product with specific properties like instantaneous solubility for example (Gharsallaoui et al., 2007; Masters, 1991; Shaw, 1997).

There are several reasons why the technology of spray drying has found many applications in numerous industries. As long as liquid feed can continue to be supplied to the drying system the spray-dried product will continue to be produced. Due to spray drying is a continuous process and can be operated for months without interruption. The spray drying process, is economical and flexible, uses equipment that is readily available, and produces particles of good quality. In addition, this process can be fully automated. Spray drying also has some limitations. It is not typically well suited for producing granules with mean particle size more than 200 µm. It also has poor thermal efficiency at lower inlet temperatures and the exhaust air stream contains heat, which often required sophisticated heat exchange equipment for removal. (Augustin et al., 2001; Çelik & Wendel, 2005; Dziezak, 1988; Masters, 1991; Zeller, Saleeb, & Ludescher, 1998).

2.3.2 Theory of spray drying

Spray drying, the unique process involving both particle formation and drying, is the only process that directly converts a liquid into a dry powder in a single step. This method removes moisture instantly and converts pumpable liquid into dry powder (Masters, 1991; Shaw, 1997). Dry solid particles are obtained by hot air drying of liquid droplets, which could also be solution, emulsion or suspension, produced at the top of the drying chamber. Drying occurs during their fall to the bottom of the chamber due to contact with drying air flowing either co- or counter- currently. Residence times of particles in the chamber are very short ensuring low particle temperature despite their contact with hot air (Turchiuli et al., 2005b). The actual spray-drying process is very rapid, with the major portion of the evaporation taking place in less than a few seconds. This minimal exposure time combined with evaporative cooling, creates a very lenient process relative to thermal effects. As a result, spray drying is well suited for heat-sensitive products (Shaw, 1997)

2.3.3 Spray drying processes

Spray drying involves atomization of feed into a spray, and contact between spray and drying medium resulting in moisture evaporation. The drying of the spray proceeds until the desired moisture content in the dried particles is obtained, and the product is then recovered from the air. These four stages are illustrated by reference to the open-cycle, co-current spray dryer layout (Fig. 2.6), the most common type of spray dryer in industry (Master, 1991; Shaw, 1997)

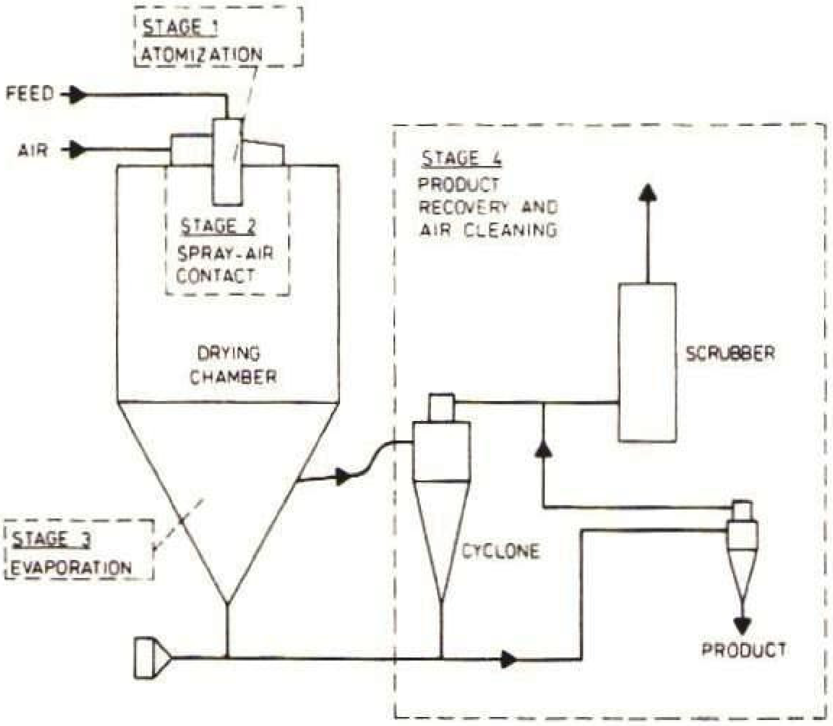

Figure 2.6 The process stages of spray drying illustrated by the open-cycle co-current layout (Masters, 1991).

The spray drying process is carried out in four fundamental stages as shown in Fig. 2.6

2.3.3.1 Atomization of feed into a spray

The atomization stage in spray drying produces from liquid bulk a spray of droplets having a high surface-to-mass ratio. The dried product that results from moisture evaporation of atomized spray can be made to possess the desired particle size distribution through control of the atomization variables. The selection and operation of the atomizer is of supreme importance in achieving economic production of top-quality products. The atomization stage must create a spray for optimum evaporation conditions leading to a dried product of required characteristics (Masters, 1991)

Rotary atomizers (Fig. 2.7) and nozzles (Fig. 2.8) are used to form sprays. With rotary atomizers centrifugal energy is utilized, whereas pressures, kinetic, or sonic energy is utilized in nozzle atomization. Feed capacities per nozzle are lower than per rotary atomizer, leading to nozzle duplication to meet high feed-rate requirements (Gharsallaoui et al., 2007; Masters, 1991). Regardless of the kind of atomizer used, the emulsion particles gain a spherical shape during spray drying because of the surface tension. Atomization parameters have an effect on some important properties of the final products including bulk density, shape and size distributions of powder particles, occluded air content, and moisture content (Masters, 1991; Reineccius, 1989). The rotary atomizer is normally selected due to its greater flexibility and use of operation. Rotary atomizers are used to produce a fine to medium-coarse product (mean size 20-150 μm), whereas, nozzle atomizers are used to produce a coarse product (mean size 150-300 μm) (see Table 2.1) (Masters, 1991). The aim of this stage is to create a maximum heat-transferring surface between the dry air and the liquid in order to optimize heat and mass transfers. The choice upon the atomizer configuration depends on the nature and viscosity of feed and the desired characteristics of dried product. The higher the provided energy is, the finer are formed droplets. For the same energy amount, the size of formed particles increases with increasing feed rate. However, the size of particles increases when both viscosity and surface tension of the initial liquid are high (Gharsallaoui et al., 2007)

Figure 2.7 Atomizer in operation (Rotary atomizer) (http://www.niroinc.com/images/technologies/rotary_atomizer_technology.jpg).

Figure 2.8 Atomizer in operation (Nozzle atomizer) (http://www.niroinc.com/images/technologies/technology_nozzle_atomizer.jpg).

Both rotary atomizer and pressure nozzle atomizer have their own advantages and disadvantages as presented in Table 2.2.

Table 2.1 Guidelines for droplet/particle size and atomizer operation (for low viscosity, Newtonian liquids) (Masters, 1991).

Rotary atomizer

Wheel peripheral velocity (m/s)	Mean size (µm)
> 180	20-30
150-180	30-75
125-150	75-150
75-125	150-275

Pressure nozzle

Pressure (atm)	Mean size (µm)
> 100	15-30
50-100	30-50
25-50	50-150
15-25	150-350

Table 2.2 Atomizer features (Masters, 1991).

Rotary atomizer	Pressure nozzle
Easy control of particle size	Less easy control of particle size
Large flow areas	Small flow areas
Single atomizer for low and high capacities	Nozzle duplication for high capacities
Handles slurries and crystalline feedstocks	Fine feed filtering required
Particle size virtually independent of feed rate	Narrow operating feed rate range
Capacity independent of feed pressure	Capacity proportional to square root of pressure
Large particles dried only in large-diameter drying chambers	Large particles dried in smaller diameter drying chambers
Unit cost with pump comparable	Unit cost with pump comparable
Low-pressure feed system	High-pressure feed system
Fine-medium size particles individual, mean size up to 200 µm	Coarse free-flowing particles (individual), mean size up to 350 µm
Deposit tendencies on wall at wheel level	Less tendency to deposit on wall

2.3.3.2 Spray-air contact

Once the liquid is atomized it must be brought into intimate contact with the heated gas for evaporation to take place equally from the surface of all droplets. This contact step takes place within a vessel called the drying chamber. The heated gas is introduced into the chamber by an air disperser, which ensures that the gas flows equally to all parts of the chamber. The contact takes place during atomization and initiates the drying stage. Spray-air contact is determined by the position of the atomizer in relation to the drying air inlet. The spray can be directed into hot air entering the drying chamber as shown in Fig. 2.9.

According to the atomizer emplacement compared to the hot air spreader, one can distinguish co-current one. In co-current process the apparatus, hot air inlet temperature is typically 150-200 °C, evaporation occurs instantaneously and for which dry powders will be exposed to moderate temperatures (typically 50-80 °C) which limits thermal degradations. This arrangement is widely used, especially if heat-sensitive products are involved. Spray evaporation is rapid, the drying air cools accordingly, and evaporation times are short. Whereas, during counter-current drying, the liquid is sprayed in the opposite direction of the flow of hot air and for which the dry product is exposed to high temperatures which limits the applications of this process to thermo-sensitive products. This arrangement offers dryer performance with excellent heat utilization, but it does subject the driest powder to the hottest air stream.

There are dryer designs that incorporate both co-current and counter-current layouts, i.e. mixed-flow dryers. In the upward firing or fountain-type system, coarse free-flowing powder can be produced in dryer chambers of relatively small size, but the powder is subjected to higher particle temperatures. A mixed flow system can be integrated with a fluid-bed drying chamber when lower particle temperatures are necessary (Çelik & Wendel, 2005; Gharsallaoui et al., 2007; Masters, 1991; Shaw, 1997).

Temperature to which dry and semi-dry particles are subjected in co-, counter-current and mixed-flow drying chambers can be more readily appreciated from the air temperature profile characteristics show in Fig. 2.10.

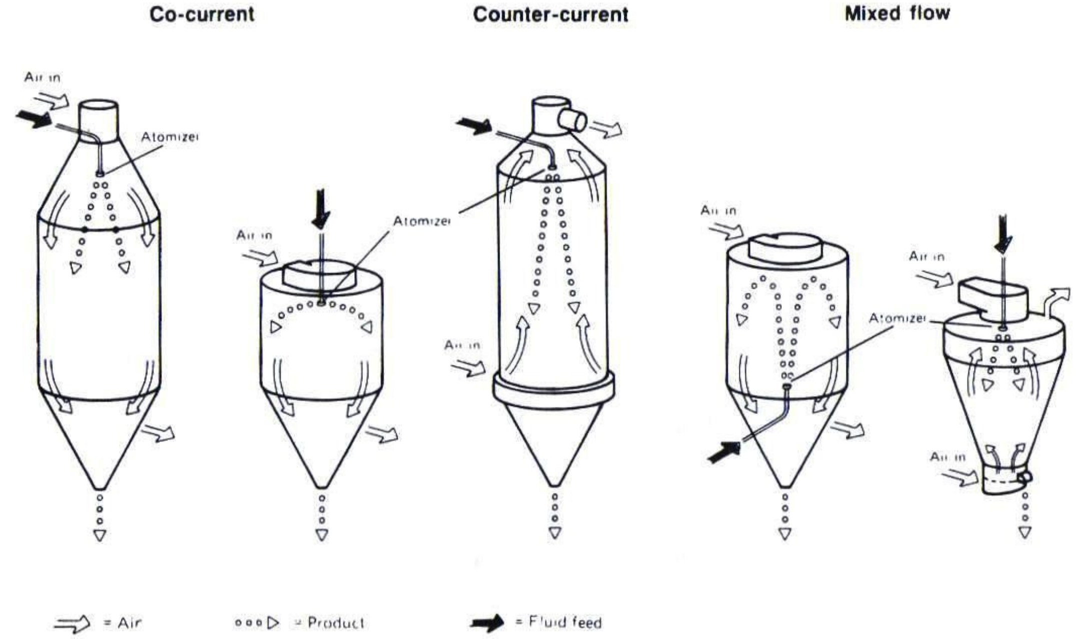

Figure 2.9 Product-air flow in spray dryers (Masters, 1991).

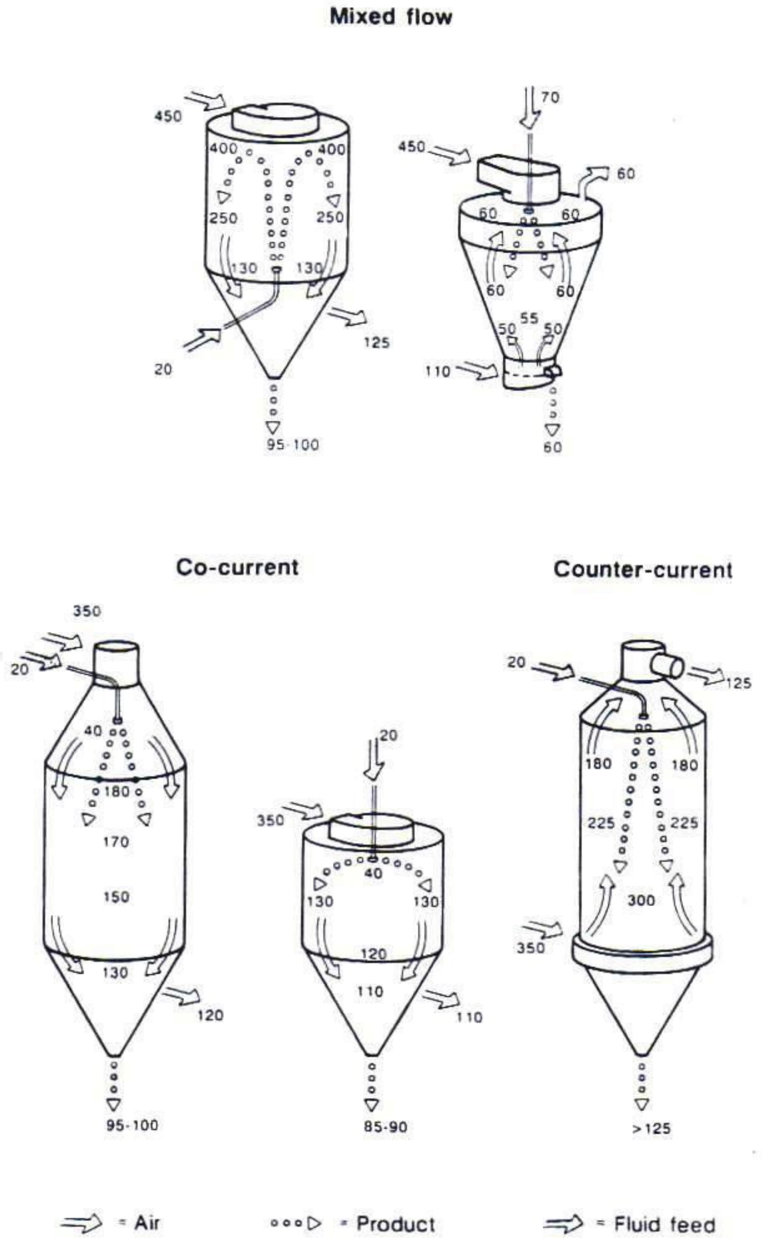

Figure 2.10 Temperature profiles in spray dryer chambers (Masters, 1991).

2.3.3.3 Drying of spray

Drying process of spray was described by Gharsallaoui et al. (2007) and Masters (1991). At the time of droplets-hot air contact, balances of temperature and vapor partial pressure are established between liquid and gas phase. Thus, heat transfer is carried out from air towards the product as a result of temperature difference whereas water transfer is carried out in the opposite direction due to the vapor pressure difference. Evaporation takes place in two stages. At first stage, is termed the constant rate period of first period of drying, there is sufficient moisture within the droplet to replenish that lost at the surface. The rate of water diffusion from the droplet core to its surface is usually considered constant and equal to the surface evaporation rate, evaporation takes place at a constant rate. When the moisture content becomes too low to maintain saturated conditions, the so-called critical point is reached and a dried shell forms at the droplet surface. Evaporation is now dependent upon the rate of moisture diffusion through the dried surface shell. The thickness of the dried shell increases with time, causing a decrease in the rate of evaporation. This is termed the falling rate period or second period of drying. After the evaporation has ceased, the temperature of the particle rises to the general temperature of the drying chamber. This stage is associated with increasing droplet temperature, which can cause detrimental effects on core retention. Balloning occurs at this stage since high evaporation rate accelerates the formation of a crust around the droplet surface (Masters, 1991; Reineccius, 1988; Rosenberg & Young, 1993).

These two steps have different durations depending on both product nature and air inlet temperature. In fact, if the air inlet temperature is high, the dry crust is rapidly formed because of the high water evaporation rate. This fact due to the large surface to volume ratio of the atomized droplets, drying of formed droplets in the hot atmosphere is a very rapid process. Thus a substantial part of the droplet evaporation takes place when the droplet surfaces are saturated and cool. Drying chamber design and air flow rate provide a droplet residence time in the chamber, so that the desired droplet moisture removal is completed and product removed from the dryer before product temperatures can rise to the outlet drying air temperature of the chamber. Hence, there is little likelihood of heat damage to the product.

During evaporation, the atomized spray distribution undergoes change. Different products exhibit different evaporation characteristics. Some tend to expand, others collapse, fracture or disintegrate, leading to porous, irregularly shaped particles (Fig. 2.11). Others maintain a constant spherical shape or even contract, so that the particles become denser. The extent of any change in particle shape, and hence the dried-powder characteristics, are closely connected to the drying rate. The drying rate must be given to the drying chamber design in order to meet desired powder characteristics.

Formation of hollow particles within the powders can be occured during microencapsulation by spray drying. The tendency towards expansion and formation of hollow particles plays an important role in the final bulk density of dried product. Hollow particles can be formed from four mechanisms, that is,

1. A surface layer, semi-impervious to vapour flow, forms at the droplet surface. The droplet puffs out as vapour is formed within the droplet and expands with the increase in droplet temperature.
2. Moisture evaporates at a rate faster than the diffusion of solids back into the droplet interior. On completion of evaporation, air voids are present, especially in the case of crystalline products.
3. Liquid flows with accompanying solids to the droplet surface by capillary action. This leaves the centre of the droplet as a void. This mechanism is applicable to clay slip feeds.
4. Air entrained in the feed contributes to air spaces within the droplet.

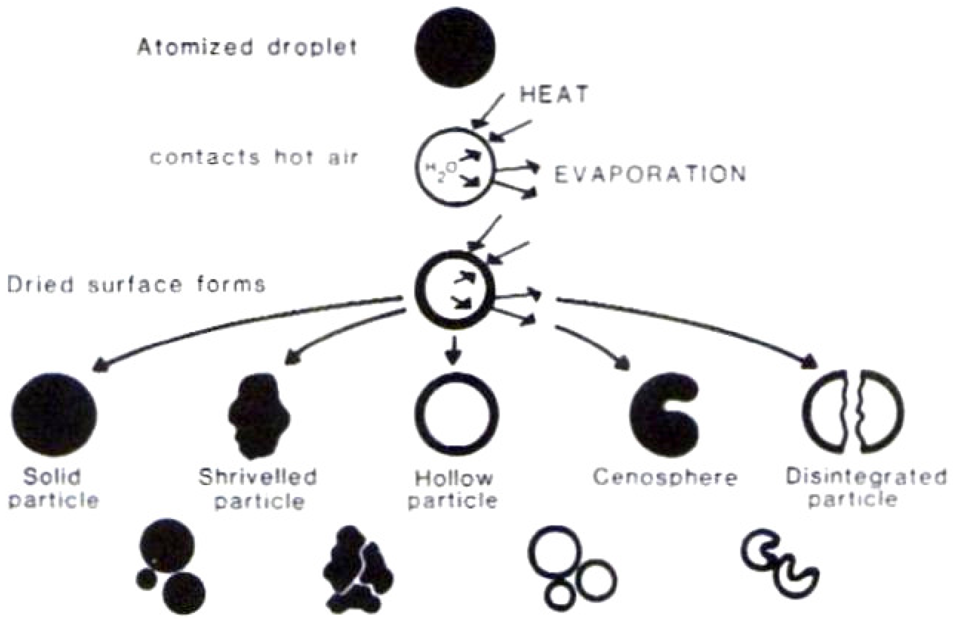

Figure 2.11 Mechanism of droplet drying illustrated in simplified manner. Droplets dry to single, misshapen and agglomerated particles (Masters, 1991).

2.3.3.4 Separation and recovery of dried product

The fourth and last stage of the spray drying operation is the separation of dried product from the air. Separation of dried product can be carried out firstly at the chamber base (primary product separation) followed by recovery of fines in collecting equipment (secondary product separation). The amount of primary product separation depends upon the chamber design, atomization of product and drying-air flow. Product is separated out of the air either by the cyclonic air flow set up at a conical chamber base, or by the ability of particles to fall out of the air flow to a flat chamber base. Whatever method of separation is used, some form of collection equipment is required after the drying chamber. Collection equipment can be dry or wet types, e.g. cyclones, bag filters, scrubbers, electrostatic precipitators. Choice of equipment is based primarily on cost, collection efficiency and treatment of the product undergoing separation. Separation of dried product from the air influences powder properties by virtue of the mechanical handling involved during the separation stage. Excessive mechanical handling can produce powders with a high percentage of fines (Çelik & Wendel, 2005; Masters, 1991)

2.4 Agglomeration

2.4.1 Definition and objectives of agglomeration

Agglomeration ,also known as granulation, pelletisation or balling, is the process of agglomerating particles together into larger, semi-permanent aggregates (granules) in which the original particles can still be distinguished (Ortega-Rivas, 2005; Parikh & Mogavero, 2005; Snow, Allen, Ennis & Litster, 1997) and the spheroidal ensemble of particles is called a agglomerate, granule, pellet, or ball (Kadam, 1991). In wet agglomeration processes, this is performed by spraying a liquid binder onto the particles as they are agitated in a tumbling drum, fluidized bed, high shear mixer or similar device. The liquid binds the particles together by a combination of capillary and viscous forces until more permanent bonds are formed by subsequent drying, sintering or cooling (Iveson, Litster, Hapgood & Ennis, 2001; Tan, Salman & Hounslow, 2006). Agglomeration is an example of particle design. The desired attributes of the agglomerate are controlled by a combination of the formulation and the process design (Parikh, 2005). Agglomeration finds application in a wide range of industries including mineral processing, agricultural products, detergents, pharmaceuticals, foodstuffs and specialty chemicals (Iveson et al., 2001). These industries employ agglomeration techniques (Kadam, 1991; Parikh, 2005; Schwartz, 1991) :

- To improve dispersibility and solubility characteristics of product in water.
- To make a dust-free product that reduces handling hazards and losses.
- To improve flow properties & the appearance of the product.
- To reduce the tendency of materials, generally hygroscopic, to form lumps or cakes on storage.
- To produce useful structural forms and shapes.
- To densify the material for shipment or storage.
- To produce hydrophilic surfaces.

In the food industry, agglomeration is used for instant products such as coffee, milk, or cocoa that disperse and/or dissolve quickly in liquids like water or milk (Carić, 2003; Schubert, 1993; Schuchmann, 1995). The reconstitution properties such as wettability, sinkability, dispersibility, and solubility are enhanced. These properties depend on the type of agglomeration process and on the operating conditions during agglomeration (Jinapong, Suphantharika & Jamnong, 2008).

The commonly used agglomeration processes can be divided into three groups: (a) pressure agglomeration (e.g. tableting); (b) growth agglomeration (e.g. fluidized bed, jet agglomeration, pelletizing); and (c) agglomeration during drying (e.g. spray drying, drum drying). Depending on whether or not a binder liquid is involved in the process, groups (a) and (b) can be subdivided into wet and dry agglomeration methods. Wet growth agglomeration is the most suitable method for encapsulated spray-dried flavours because the wall materials used in flavour systems are readily dissolved and form strong interparticle bridges on re-drying. This is done by introducing a liquid, either in the form of condensing vapour, as liquid spray, or a mixture of both (Buffo et al., 2002). Fluidized bed agglomeration is one of the most suitable processes leading to agglomerates with high porosity and good mechanical resistance for handling and packaging (Turchiuli, Eloualia, El Mansouri, & Dumoulin, 2005a). This process generally works by spraying binder liquid onto a bed of fluidized particles, where upon wetting, the particles will be bound together by liquid bridges. Depending on the type of binder used, the liquid bridge will either solidify with cooling or dry with heating to form a solid bridge (Parikh, Bonck, & Mogavero 1997; Tan et al., 2006).

2.4.2 Theory of fluidized bed agglomeration

The principle of fluidization is to maintain particles in suspension in a closed area by blowing air upward through the powder bed resting on a porous gas distributor plate (Fig. 2.12). Fluidized bed agglomeration, as shown in Fig. 2.13, is a process by which granules are produced in a single piece of equipment by spraying a binder solution on to a fluidized powder bed. The fluid bed agglomeration process has received considerable attention within the pharmaceutical industry; however, other process industries, such as food, agro-chemical, dyestuffs, and other chemical industries, have adopted the fluid bed agglomeration process to address particle agglomeration, dust containment, and material handling (Parikh & Mogavero, 2005). Parikh et al. (1997) and Parikh & Mogavero (2005) mentioned that, in this process, the fluidizing air plays a critical role in the agglomeration of particles. The light unagglomerated particles are carried by the fluidizing air to a point where they come in contact with the fine droplets of the binder liquid in the spray zone. Agglomeration occurs as the wetted heavier particles move to the lower part of the bed owing to increased weight. In this manner, the agglomerates continuous to go through the wetting and drying cycles caused by the liquid spray addition and the drying action by the fluidizing air, both occurring concurrently. The fluidizing air passes through an exhaust filter assembly allowing the air to escape to the outer environment while trapping the fine particles within the agglomerating chamber. During the entire process, the exhaust filters are subjected to an intermittent shake cycle to allow for the trapped particles to return to the fluidizing bed.

The granule growth continues until all of the liquid binder is consumed. Once all the binder liquid has been consumed, the agglomerated mass enters the drying phase as the moisture from the surface of the agglomerates continues to leave the surface. Eventually, when the agglomeration reaches the desired level of moisture, the fluidization is stopped and the process is complete (Gore, 1991)

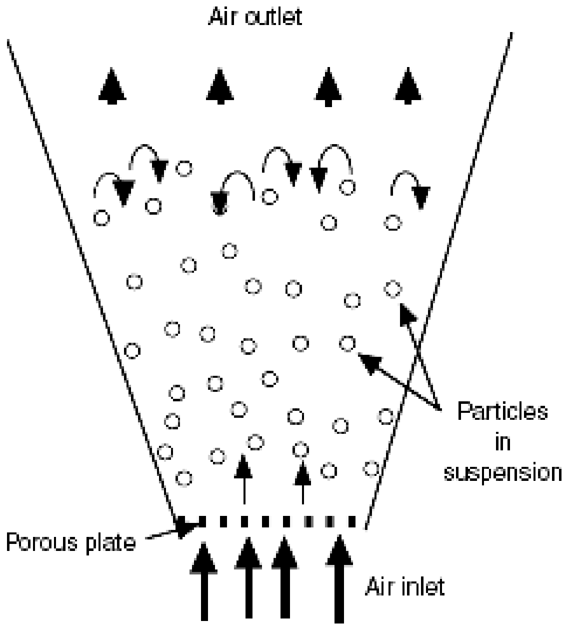

Figure 2.12 Principle of fluidization (Teunou & Poncelet, 2005).

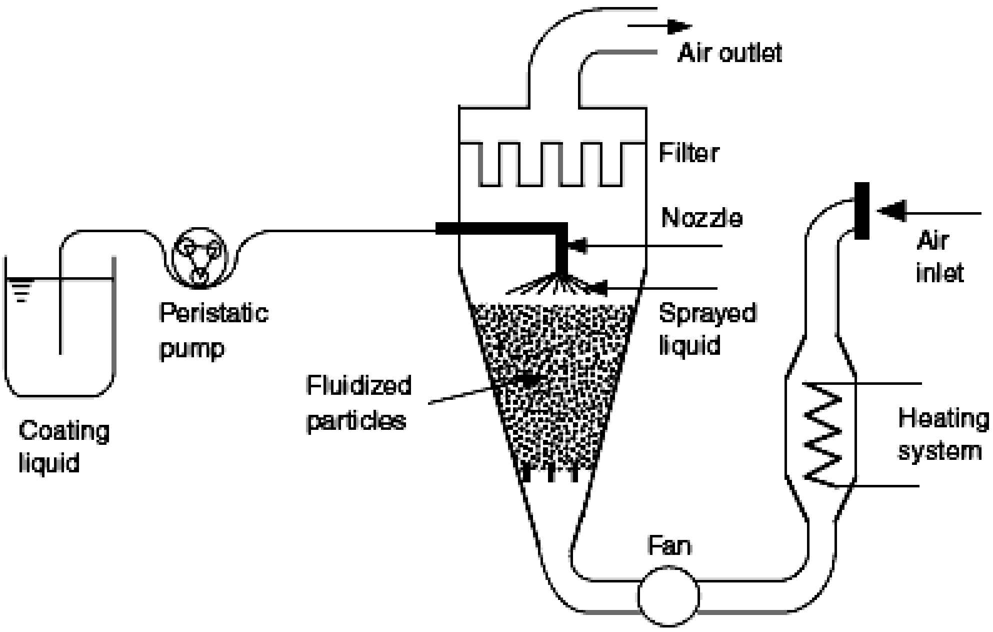

Figure 2.13 Principal features of a batch fluid bed agglomerator (Teunou & Poncelet, 2005).

2.4.3 Agglomeration processes

Iveson et al. (2001); Snow et al. (1997) and Tardos, Irfan-Khan & Mort (1997) described that there are fundamentally only three sets of rate processes which are important in determining wet agglomeration behaviour (Fig. 2.14). These are:

1. Wetting and nucleation, where the liquid binder is brought into contact with a dry powder bed, and is distributed through the bed to give a distribution of nuclei granules.
2. Consolidation and growth, where collisions between two granules, granules and feed powder, or a granule and the equipment lead to granule compaction and growth.
3. Attrition and breakage, where wet or dried granules break due to impact, wear or compaction in the granulator or during subsequent product handling.

Once these processes are sufficiently understood, then it will be possible to theoretically predict the effect of formulation properties, equipment type and operating conditions on agglomeration behaviour, provided that these can be adequately characterized.

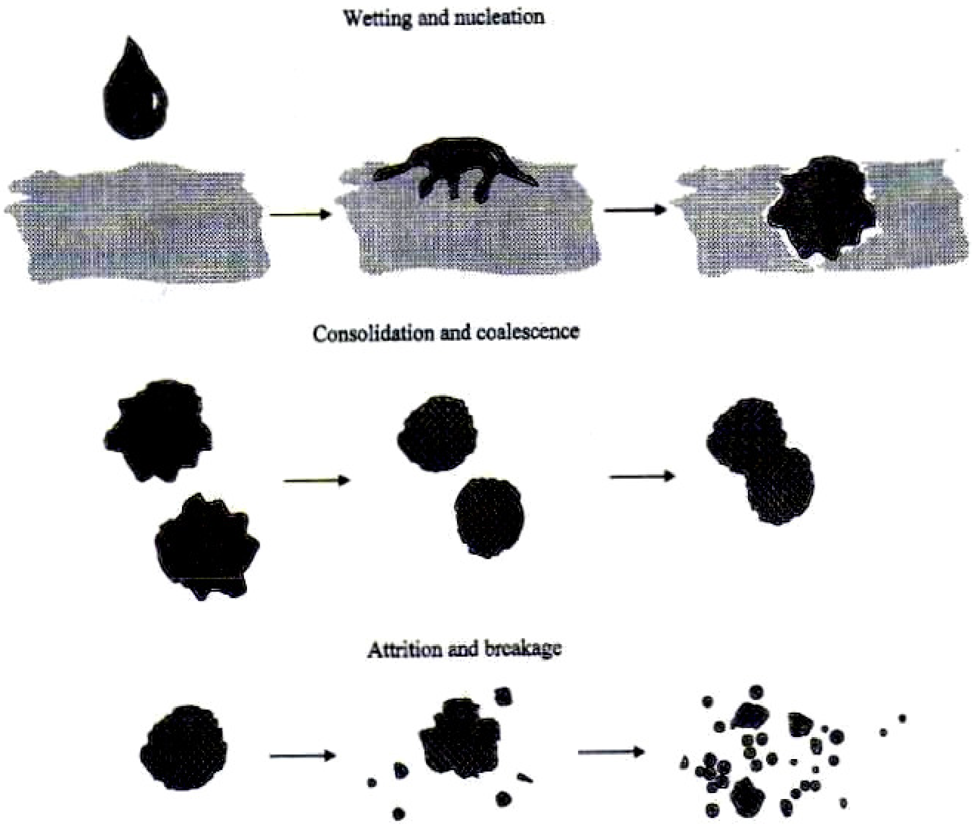

Fig. 2.14 A classification of agglomeration rate processes (He, Liu & Litster, 2005).

2.4.3.1 Wetting and nucleation

Wetting and nucleation is the process of bringing liquid binder into contact with dry powder and attempting to distribute this liquid evenly throughout the powder. It is regarded as an important stage in granulation processes (Snow et al., 1997). Poor wetting results in drop coalescence, and in fewer, larger nuclei with unagglomerated powder and overwetted masses, leading to broad nuclei distributions.

1) Mechanics of the wetting rate process

As outlined previously, wetting is the first stage in wet granulation involving liquid binder distribution to the feed powder. There are two extremes:

1.1) liquid drop size is large compared to unit or primary particle size of the feed; and

1.2) particle size is large compared to the drop size.

As depicted in Fig. 2.15 for the first case of fine feeds compared to drop size, the wetting process consists of several important steps. First, droplets are formed related to spray distribution, or spray flux defined as the wetting area of the bed per unit time. Important operating variables include nozzle position, spray area, spray rate, and drop size. Second, droplets impact and coalesce on the powder bed surface if mixing or wet-in time is slow. Third, droplets spread and penetrate into the moving powder bed to form loose nuclei, again coalescing if wet-in is slow. In the case of high-shear processes, shear forces break down overwet clumps, also producing nuclei.

For the second case of small drop size compared to the primary particle size, the liquid will coat the particles as depicted in Fig. 2.16 Coating is produced by collisions between the drop and the particle followed by spreading of the liquid over the particle surface. If the particle is porous, then liquid will also be sucked into the pores by capillary action. The wetting dynamics control the distribution of coating material, which has a strong influence on the later stages of growth as well as coating quality.

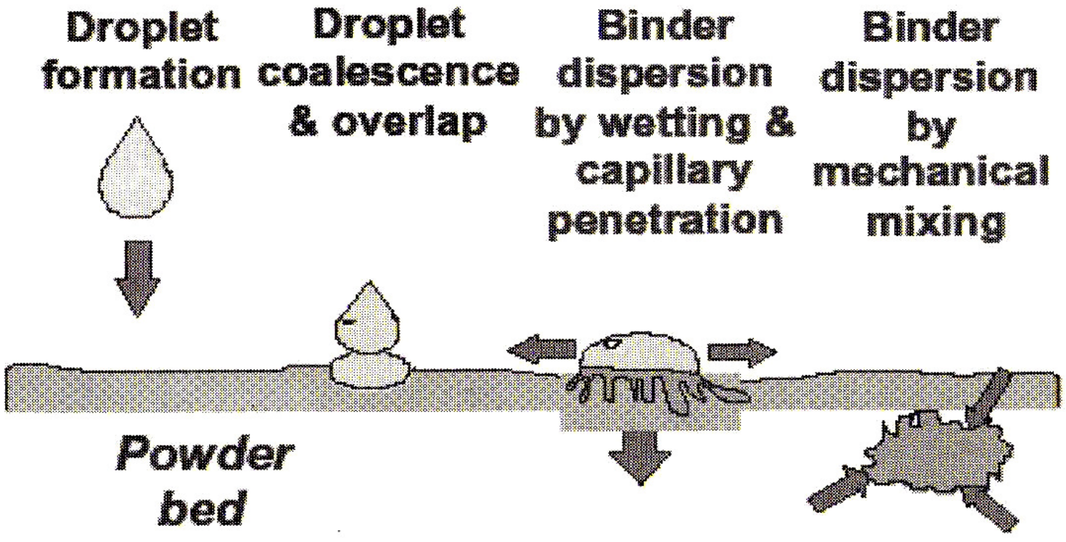

Figure 2.15 Stages of wetting for fine powder compared to drop size (Ennis, 2005).

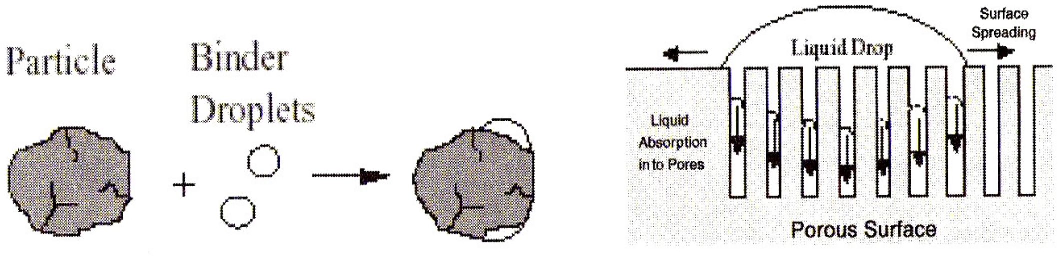

Figure 2.16 Stages of wetting for coarse powder compared to drop size (Ennis, 2005).

In this rate process (wetting and nucleation) on wet agglomeration nucleation and binder dispersion processes, Iveson et al. (2001) focus on the nucleation zone, also called the wetting zone. They defined this as the area where the liquid binder and powder surface first come into contact and form the initial nuclei. The size distribution of these initial nuclei depends critically on the processes happening in the nucleation zone, although other processes in the rest of the granulator, such as mechanical mixing, may subsequently alter this distribution. Two processes are important in the nucleation zone. Firstly, there is nuclei formation, which is a function of wetting thermodynamics and kinetics. Secondly, there is binder dispersion, or effective mixing of the powder and binder, which is a function of process variables. Choosing a poor combination of powder and binder or using an inefficient binder dispersion method both produce a product that is difficult to control and reproduce.

2) Nucleation regime map

Nucleation is a combination of single drop behaviour (e.g. the penetration time controlled by contact angle and other material properties) and multiple drop interactions (e.g. the spray flux controlled by the spray zone characteristics and other operating variables). Depending on the particular formulation properties and operating conditions, different mechanisms may dominate. Ennis (2005); Lister, Hapgood, Michaels, Sims, Roberts, Kameneni, & Hsu (2001) postulated that three nucleation regimes exist: drop controlled, mechanical dispersion controlled and intermediate regime. In the drop controlled regime, the controlling property is the droplet size. The binder droplets penetrate into the powder bed pores almost immediately, and the nuclei distribution reflects the drop size distribution. In this region, one drop tends to form one granule provided that two key conditions are met:

2.1) The powder flux through the spray zone must be fast enough that drops which hit the powder surface do not overlap (low Ψ_a). For small spray flux, drops will not overlap on contact and will form separate discrete nuclei for fast penetration time. For large spray flux, however, significant drop overlap occurs, forming nuclei much larger than drop size, and in the limit, independent of drop size.

2.2) The drop must wet into the bed completely before bed mixing brings it into contact with another partially absorbed drop on the bed surface (fast drop penetration time).

Powder mixing characteristics relative to capillary pressure and binder viscosity should dominate in the mechanical dispersion regime. Viscous or poorly wetting binders are slow to flow through the powder pores and form nuclei. Drop coalescence on the powder surface (also known as “pooling”) may occur and create a very broad nuclei size distribution. In this regime, nucleation and binder dispersion occur by mechanical mixing and agitation, and the solution delivery method (drop size, nozzle height etc.) has a minimal effect on the nuclei size distribution, though interfacial properties may affect nuclei and final granule strength.

In the intermediate regime, both drop penetration dynamics and shear force dispersion are significant. Clumps of unevenly distributed binder will form if the binder addition rate exceeds the binder dispersion rate. Wetting kinetics compared to binder flux and exposure time should control the nucleation. In other words, an intermediate regime exists for moderate drop penetration times and moderate spray flux, with the resulting nuclei regime narrowing with decreases in both. This regime would be most difficult to control. Based on this idea, Ennis (2005); Iveson et al. (2001) proposed a preliminary version of the nucleation regime map, shown in Fig. 2.17. Testing is in the early stages and the exact positions of the regime limit lines are currently unknown. On the vertical axis is drop penetration time (t_p), indicating single drop behaviour and material properties. The penetration time is made dimensionless by the particle circulation time (t_c). The horizontal axis is the dimensionless spray flux, which takes into account multiple drop behaviour. The map centres around the drop-controlled regime, where one drop makes one nuclei, provided the drop penetrates fast enough and the drops are well separated from each other. If validated, this nucleation regime map will allow the effect of changing formulation properties or operating conditions to be predicted beforehand.

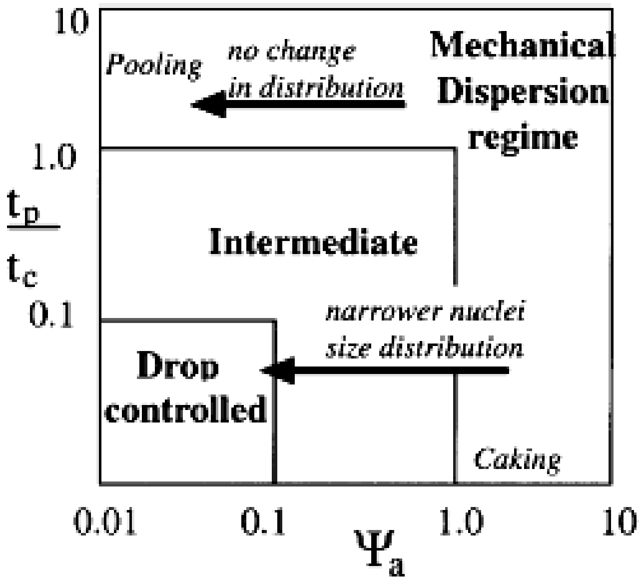

Fig. 2.17 Nucleation regime map. In the drop controlled regime, one drop tends to form one granule as the spray droplets penetrate quickly into the powder and are well dispersed. In the mechanical dispersion regime, one or both of these conditions are not met, and binder dispersion occurs instead by mechanical mixing and shear forces (Iveson et al., 2001).

2.4.3.2 Consolidation and growth

Granule growth occurs whenever material in the granulator collides and sticks together. For two large granules this process is traditionally referred to as *coalescence*, whereas the sticking of fine material onto the surface of large pre-existing granules is often termed *layering*. However, the distinction between these two processes is arbitrary depending on the cut-off size used to demarcate fine from granular material. These growth processes may begin as soon as liquid is added to an agitated powder mass and may continue on well after liquid addition has been completed. In some systems, however, insufficient liquid is added to promote further growth, and the granule size is determined purely by the nucleation conditions.

Whether or not a collision between two granules results in permanent coalescence depends on a wide range of factors including the *mechanical properties* of the granules and the *availability of liquid binder* at or near the granule surfaces. During agitation, granules gradually consolidate which increases their liquid pore saturation and alters their mechanical properties. Hence, consolidation often has a pronounced effect on granule growth behaviour and must be considered in conjunction with it.

1) Mechanical properties of liquid-bound granules

Granules can exist in a number of different states of liquid saturation. These were described by Augsburger and Vuppala (1997) and Iveson et al. (2001) and are shown in Fig. 2.18. The mechanism of agglomeration can be considered as a gradual change from a triphasic stage (air-liquid-solid) in which most granules are in pendular and funicular states, to a biphasic (liquid-solid) particulate assembly, in which the granules will be in the capillary and droplet states. In the *pendular* state particles are held together by liquid bridges at their contact points (pendular bonds). The *capillary* state occurs when a granule is saturated, all the voids are filled with liquid and the surface liquid is drawn back into the pores under capillary action. The *funicular* state is a transition between the pendular and capillary state where the voids are not fully saturated with liquid. The *droplet* state occurs when the particles are held within or at the surface of a liquid drop. It is also possible to have a *pseudo-droplet* state where unfilled voids remain trapped inside the droplet. This is more likely to occur in poorly wetting systems. During agglomeration, it is possible for the saturation state of the granules to shift from the pendular state through to the droplet state, either due to the continuous addition of liquid binder and/or due to consolidation reducing the granule porosity.

A granule initially consists of moist particles that have partly coalesced to form loose aggregates held together by pendular bonds. The kneading action of the granulator brings the particles closer together so that the internal pore space in the aggregates is reduced and, if the moisture content is sufficient, the pores eventually become saturated, From geometric considerations of smooth spheres on close proximity, Flemmer (1991) reported the levels of moisture content (%MC by volume) for the three stages of granule growth:

Pendular regimen: $0 < \%MC < 13.6$
Funicular regimen: $13.6 < \%MC < 100$
Capillary regimen: $\%MC = 100$

The characteristics of the granules from various stages of the granulation are given in Table 2.3.

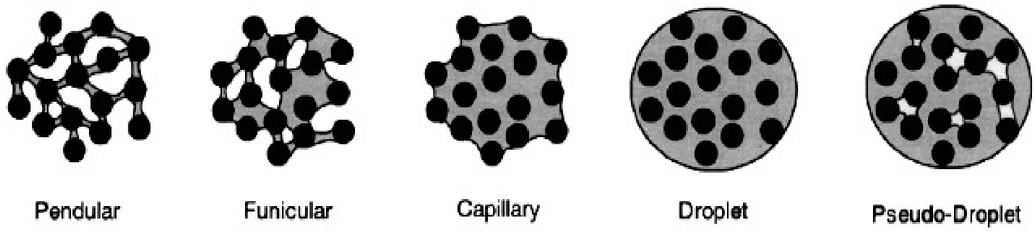

Figure 2.18 The different states of saturation of liquid-bound granules (Iveson et al., 2001).

Table 2.3 Characteristics of the granules from different stages of granulation (Augsburger & Vuppala, 1997).

Aggregate type	Characteristics
Pendular	Typically nonspherical, “dry” surface, soft, low density
Funicular	More nearly spherical, “dry” surface, firm, denser than pendular
Capillary	Tend to be spherical, surface normally wet, dense, plastic
Kneaded capillary	Maximal density and consistency

2) Granule consolidation

Iveson et al. (2001) remarked that as granules collide with other granules and equipment surfaces they gradually consolidate. This reduces their size and porosity, squeezes out entrapped air and may even squeeze liquid binder to their surface. Porosity controls granule strength. Granules with high porosity are weak and friable. These granules will break and generate dust during handling which is undesirable in most cases. However, for many products it also desirable that the granules be porous in order to facilitate fast dispersion and dissolution. Hence, granule porosity is an important product property to control and optimise.

Granule porosity is also important in controlling granule growth mechanisms. In many systems, granules experience a long period of little growth, variously referred to as the “nuclei”, “no growth”, “induction” or “compaction” phase. If consolidation eventually squeezes liquid binder to the surface, then rapid coalescence growth may follow. Consolidation also has a complex effect on the mechanical properties of granules. Granule yield stress generally increases as granule porosity decreases. This decreases the amount of deformation when two granules collide which decreases the likelihood of coalescence. However, consolidation also increases the pore saturation, which in turn increases granule plasticity and the availability of liquid at the granule surface. Both of these effects will aid coalescence. If granules become fully saturated, then the frequent impacts they experience may cause them to liquefy which would further aid coalescence. Hence, the net effect of consolidation on granule growth is uncertain and will probably depend strongly on the formulation and binder properties.

3) Granule growth behaviour

Consolidation of granules determines *granule porosity* or *voidage*, and hence *granule density*. Granules may consolidate over extended times and achieve high densities if there is no simultaneous drying to stop the consolidation process (Ennis, 2005). Augslurger & Vuppala (1997); Iveson et al. (2001); Parikh et al. (1997) mentioned that the evolution of the granule size distribution during granulation is usually reported by plotting average granule size (usually mass-mean or mass-median) vs. time (e.g. Fig. 2.19). These plots show a number of characteristic regions:

1. *Nucleation* during which nuclei agglomerates are first formed as the liquid binder is added.
2. *Induction period* (also known as the “nuclei region” or “compaction stage”) during which the nuclei agglomerates are consolidated but do not grow substantially.
3. *Coalescence growth* (or the transition region) occurs if granules are sufficiently deformable to coalesce without the presence of surface liquid or else when the agglomerates have consolidated sufficiently to squeeze moisture to the surface.
4. Then there may be a final slow *ball growth* region where growth occurs slowly by a combination of crushing and layering, abrasion transfer or coalescence. A maximum granule size may or may not be reached.
5. *Breakage and attrition* may follow in systems where the granules dry out and become weakened.

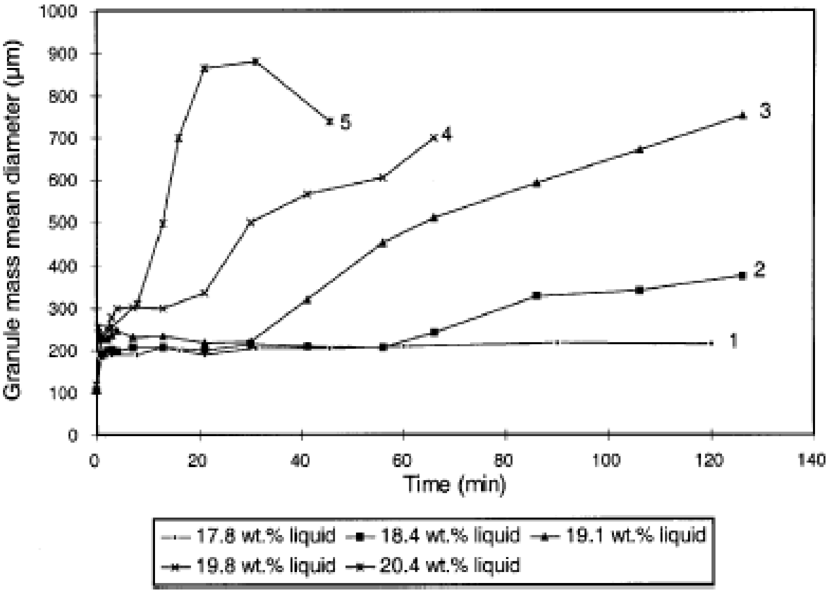

Fig. 2.19 Effect of liquid content on the growth behaviour of sodium sulphate and cellulose mixtures during batch granulation in a lödige high shear mixer: (1) Nucleation only; (2–4) Induction time followed by rapid growth; (5) rapid growth followed by breakage (Hoornaert, Wauters, Meesters, Pratsinis, & Scarlett, 1998).

There is not always a clear demarcation between these regions. Moist coarse feed may quickly densify and pass rapidly through the nucleation, induction and transition regions. Fine ground powders usually show all of the first four regions quite clearly. These behaviours have been observed in a range of granulation equipment types including fluidised beds, drums and high-shear mixers. It should be noted, that although widely used, these plots do not fully describe granule growth behaviour. The average size conceals the shape of the size distribution which may be important if the binder has been poorly distributed. These plots also do not reveal the underlying growth mechanisms. These subtleties can only be revealed by examining the full granule size distributions and through the use of tracer studies.

For closely sized materials, the growth rate (rate of increase of average granule size) has been found to be more or less constant with time. However, for more broadly sized materials the growth rate increases as the system moves from the nucleation region through the transition region, before dropping off again. This was speculated to be because for broadly sized particles the increasing appearance of water at the granule surface due to consolidation dominates the decrease in granule deformability.

4) Granule growth regimes

Iveson et al. (2001) proposed that there are two broad categories of granule growth behaviour: *steady growth* systems where granule size increases linearly with time and *induction growth* systems where there is a delay period during which little growth occurs. These two classes of behaviour have been observed in both tumbling drum granulators and high shear mixers.

Steady growth occurs in systems with weak, deformable granules (low strength and/or high impact forces). Granules grow by either the crushing and layering mechanism or else they deform, creating a large contact area during impact which promotes coalescence. Steady growth is generally exhibited by relatively coarse, narrowly sized particles with low viscosity binders.

Induction growth occurs in systems which are relatively strong. The granules do not deform sufficiently during impact to coalescence without the presence of liquid at the surface. Hence, after the initial nuclei form, there is a delay period during which little growth occurs. If the granules consolidate sufficiently to squeeze liquid to the surface, then they will begin to grow quickly until a critical size is reached, above which the torque experienced by dumbbell pairs becomes too large for further coalescence growth. Induction growth is generally seen in systems with fine, widely sized particles and/or viscous binders. Induction growth has not been reported in fluidized beds, probably because the impact forces are too low to cause significant granule consolidation.

2.4.3.3 Breakage and attrition

Iveson et al. (2001) mentioned that there are really two separate phenomena to consider:

- Breakage of wet granules in the granulator; and
- Attrition or fracture of dried granules in the granulator, drier or in subsequent handling.

Breakage of wet granules will influence and may control the final granule size distribution, especially in high shear agglomerators. In some circumstances, breakage can be used to limit the maximum granule size or to help distribute a viscous binder. On the other hand, attrition of dry granules leads to the generation of dusty fines. As the aim of most granulation processes is to remove fines, this is generally a disastrous situation to be avoided.

1) Breakage of wet granules

Few investigators have described or studied wet granule breakage in granulation processes. Some preferential growth mechanisms in tumbling granulation may involve attrition or breakage of weak granules (crushing and layering, abrasion transfer). However, breakage is much more likely in higher intensity mixer and hybrid granulators. The limited work on wet granule breakage focuses on these types of equipment. Wet granule breakage is potentially an important process affecting binder distribution and granule size in high intensity processes. Therefore it is important to establish the conditions under which breakage will occur.

There is very little quantitative theory or modeling available to predict conditions for breakage, or the effect of formulation properties on wet granule breakage. However, controlling wet granule breakage gives the opportunity to give a narrow granule size distribution by growing granules up to a breakage limit. This has been the driving force in the development of some newer granulator designs. It is important to note that size distribution control will also depend on the impact velocity distribution and turnover of granules through the high impact region (impeller or chopper). Granulators with broad impact velocity distributions and small, uncontrolled turnover through the high impact region are unlikely to ever yield narrow granule size distributions.

2) Attrition and fracture of dry granules

Ennis (2005); Iveson et al. (2001) described that most granulation processes involve drying granules either simultaneously (fluidised bed and spouted bed granulators) or immediately after granulation in a separate drier. Attrition or fracture of the granules during granulation, drying or subsequent handling is generally undesirable. Therefore understanding the attrition process and the parameters which affect it is important.

2.1) Fracture properties of dry granules

From the point of view of breakage, we can consider a dry granule as a non-uniform physical composite rather than an agglomerate of primary particles. The composite possesses certain macroscopic mechanical properties including a yield stress. Instead of porosity, we see an inherent distribution of cracks and flaws. Dry granules fail in brittle or semi-brittle fashion i.e. they fail in tension by the propagation of pre-existing cracks which concentrate stress. Thus, the fracture stress may be much less than the inherent tensile strength of bonds between particles in the granule. Consider a semi-brittle material failing by crack propagation (Fig. 2.20). The tensile stress concentrates near the crack tip and is much higher than the applied stress leading to local yielding near the crack tip (the process zone). The crack will propagate from the edge of the process zone. The process zone size is a measure of the yield stress or plasticity of the material in comparison to its brittleness. Yielding within the process zone may take place either plastically or by diffuse microcracking, depending on the brittleness of the material.

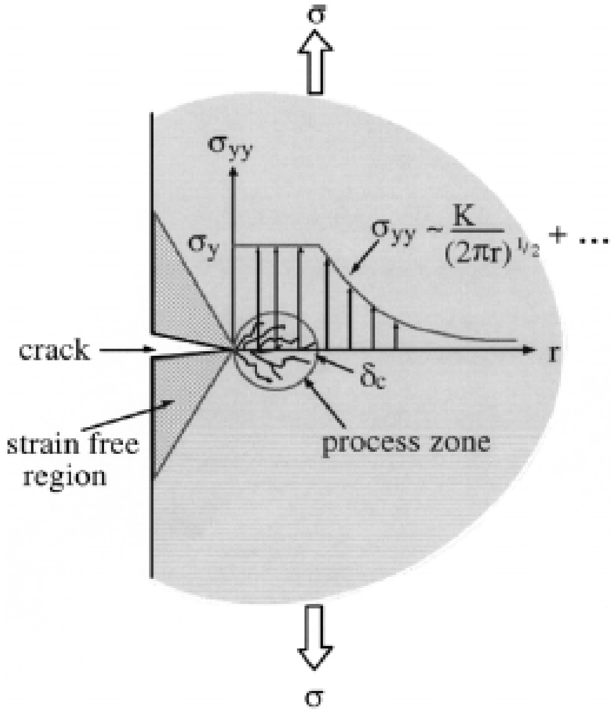

Fig. 2.20 Fracture of a semi-brittle material by crack propagation (Iveson et al., 2001).

2.2) Breakage mechanisms for dry granules

The process zone plays a large role in determining the mechanism of granule breakage. Agglomerates with small process zones in comparison to granule size break by a brittle fracture mechanism into smaller fragments (Fig. 2.21a), called *fragmentation* or *fracture*. However, for fracture to occur the granule must be able to concentrate enough elastic energy to propagate gross fracture during collision. This is harder to do as the process zone size increases. For well defined compacts under controlled stress testing conditions, it can be shown both theoretically and experimentally that fracture will only occur when the specimen size is significantly larger than the process zone size. For many agglomerate materials, the process zone size is of the order of the granule size. These granules will break by *wear, erosion* or *attrition* brought about by diffuse microcracking (Fig. 2.21b) leading to the generation of fine dust rather than a few fragments (Ennis, 2005; Iveson et al., 2001).

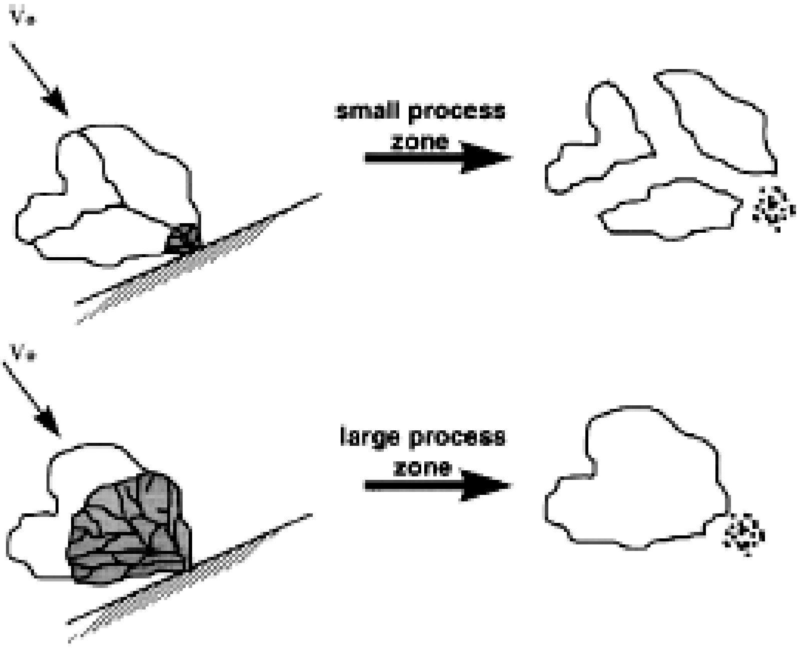

Fig. 2.21 Schematic of breakage by (a) fracture, and (b) erosion/attrition depending on process zone size (Iveson et al., 2001).

CHAPTER III
MATERIALS AND METHODS

3.1 Materials

Soybean oil was purchased from a local supermarket and was used as a model core material. Soy protein isolates (SPI) containing 92.5% protein (Supro670, the Solae Company, St. Louis, MO), and 90.3% protein (ISP500, Cargill Sample Product, Wayzata, MN) (designated: SPI 1 and SPI 2, respectively), maltodextrins (MD) with dextrose equivalent (DE) values of 7.5 (MD7.5), 18 (MD18), and corn syrup solids having a DE of 24 (MD24) (Cerestar USA, Inc., Hammond, IN) were used as a wall material for spray-dried microencapsulation of soybean oil. Maltodextrins with DE values of 10 (MD10), 14 (MD14) and 18 (MD18) (Siam Modified Starch Co., Ltd., Pathum Thani, Thailand) were used as a binder for agglomeration of the spray-dried microcapsules.

3.2 Emulsion preparation

A wall solution containing 20% (w/w) solids consisting of SPI/MD combination with a weight ratio of 1:3 or 1:7 were prepared in deionized water at room temperature (25 °C). Soybean oil was emulsified into the wall solutions at a proportion of 25% or 50% (w/w of total dry matter) (Table 3.1). Emulsification was carried out by first preparing a coarse emulsion using an Ultra Turrax® T18 basic homogenizer (IKA® Werke GmbH & Co. KG, Staufen, Germany) operated at 22,000 rpm for 30 s followed by four successive homogenization steps using a high-pressure homogenizer (type Panda, Niro-Soavi S.p.A., Parma, Italy) operated at 50 MPa.

Table 3.1 Composition of the investigated systems in each type of SPI

Systems	SPI (%)[1]	Maltodextrin (%)[2]			Soybean oil (%)[4]	SPI/MD[5]
		DE[3] 7.5	DE 18	DE 24		
1	2.5	17.5			25	1:7
2	2.5		17.5		25	1:7
3	2.5			17.5	25	1:7
4	2.5	17.5			50	1:7
5	2.5		17.5		50	1:7
6	2.5			17.5	50	1:7
7	5	15			25	1:3
8	5		15		25	1:3
9	5			15	25	1:3
10	5	15			50	1:3
11	5		15		50	1:3
12	5			15	50	1:3

[1] Concentration (% w/w) of soy protein isolate in wall solution

[2] Concentration (% w/w) of maltodextrin in wall solution

[3] Dextrose equivalent of the maltodextrin

[4] Core, soybean oil load, in the investigated systems (% w/w)

[5] Ratio (w/w) of soy protein isolate to maltodextrin in the wall solution

3.3 Spray drying

The emulsions were fed into a spray dryer (Mobile Minor Spray Dryer, Niro A/S, Soeborg, Denmark) by a peristaltic pump, and atomized to small droplets by a centrifugal vaned atomizer wheel with a rotational speed of 23,000 rpm (0.4 MPa air pressure) in a co-current air flow system. In all cases, the inlet and exit air temperatures were kept at 160 ± 5 °C and 80 ± 5 °C, respectively. All the powders were collected from the bottom of the dryer's cyclone and were kept in glass jars in desiccators at 25 °C.

3.4 Fluidized bed agglomeration

Agglomeration of the spray-dried soybean oil powders was performed in a top-sprayed fluidized bed granulator and dryer (Strea-1, Fluid Bed Laboratory, Aeromatic-

Fielder AG, Bubendorf, Switzerland) with 2 l vessel capacity. In this study, aqueous solutions (10%, w/v) of maltodextrin with a different DE value of 10, 14, and 18 were used as binders to investigate their effect on agglomeration. To study the effect of binder concentration, the chosen maltodextrin was prepared to various concentrations, i.e. 0%, 5%, 10%, 15%, and 20% (w/v). The spray-dried powder weighing 200 g was placed in the product container, and fluidized by means of an upward flowing air stream. The temperature of the inlet fluidizing air entering the bed was set at 50 °C. The binder solution (200 ml) was fed by a peristaltic pump at a flow rate of 8 ml/min to a two-fluid spray nozzle where the binder was sprayed onto the fluidized bed of the soybean oil powder. The air pressure on the nozzle was 0.15 MPa. During agglomeration, it was necessary to regularly increase the fluidizing air flow to maintain a good fluidization of the growing agglomerates. When the binder solution was consumed, the product was dried for 10 min at a temperature of 50 °C.

3.5 Methods of analysis

3.5.1 Determination of surface load of protein on emulsion droplets.

In order to investigate the adsorption of proteins at the oil-water interface, a modification of the procedures reported by Cano-Ruiz & Richter (1997) and by Patton & Huston (1986) was developed. The method allowed recovering protein-coated lipid droplets and removing proteins that were only loosely associated with the interface.

3.5.1.1 Separation and washing of cream layer

A sample (5 ml) of emulsion was placed under a layer of 25 ml of deionized water in a 50-ml centrifuge tube by using a 5-ml syringe. Placing the emulsion below the water layer provided conditions that promoted the “washing” of the oil droplet, by the overlay water, during centrifugation. Loaded tubes were centrifuged at 10,000 rpm for 1 h at 20 °C using a Marathon 21 K/R centrifuge (Fisher Scientific, Pittsburgh, PA). Following centrifugation, the aqueous phase was removed and the top cream layer was washed and then re-suspended in deionized water to the original volume of the emulsion. The centrifugation were repeated 2 more times at the same conditions. The cream obtained after the third centrifugation was collected and analyzed for moisture content, oil content and protein content.

3.5.1.2 Moisture content

Moisture content of the separated cream was determined gravimetrically after 12 h of vacuum drying at 65 °C and 6.7 kPa (Young et al., 1993a, b).

3.5.1.3 Protein content

The crude protein content was determined according to the Kjeldahl method using a multiplying factor of 6.25 (AOAC, 2000). In the Kjeldahl procedure, proteins and other organic food components in a sample are digested with sulfuric acid in the presence of catalysts (Potassium sulfate – K_2SO_4 and Cupric sulfate - $CuSO_4.5H_2O$). The total organic nitrogen is converted to ammonium sulfate. The digest is neutralized with alkali and distilled into a boric acid solution. The borate anion formed is titrated with standardized HCl acid (0.02N for the control and 0.1N for the investigate systems), which is converted to nitrogen in the sample. The result of the analysis represents the crude protein content of the food since nitrogen also comes from non-protein components.

3.5.1.4 Oil content

The Oil content was determined using a modification of the Roese-Gottlieb method (Bradley, Arnold, Barbano, Semerad, Smith, & Vines, 1993). A sample (about 0.4 g) of the separated cream was placed into a 50-ml tube containing 2 ml of ethanol. Then, 10 ml mixture of 37% HCl and water at 25:11 (v/v) was added into the tube. The mixture was heated at 100 °C for 3 h, cooled to room temperature. The mixture was added with 10 ml ethanol and then transferred into a Mojonnier oil extraction flask. Lipids were first extracted using a mixture of 25 ml ethyl ether and 25 ml petroleum ether and then a mixture of 15 ml ethyl ether and 15 ml petroleum ether was used for additional 2 successive extraction steps. The mixtures were combined, the solvent was removed at 100 °C, the solvent-free extracts were dried at 100 °C under vacuum for 30 min. Afterthat, the solvent-free extracts were cooled to room temperature in a desiccator and the extracted oil was determined gravimetrically.

3.5.1.5 Calculation of surface excess

Surface excess was defined as the amount (mg) of protein adsorbed per unit surface area at the surface of lipid droplets (Sharma et al., 1996). Based on the specific surface area and the oil and the protein content of the washed cream, surface excess (mg protein / m^2 oil surface area) was calculated according to the following equation :

$$\text{Surface excess} = \frac{\text{Protein content per gram cream}}{(\text{Oil content per gram cream / Oil density}) \times \text{Specific surface area}} \quad (1)$$

Oil density 0.915 g / ml at 20 °C is used. Specific surface area was obtained from particle size analysis using a laser diffraction particle size analyzer (Mastersizer MS20, Malvern Instruments, Ltd., Worcestershire, UK) in terms of square meters of lipid surface per milliliter of lipid (m^2 / ml).

3.5.1.6 Particle size measurement

For the emulsion, particle size distribution, volume-weighted mean diameter ($d_{4,3}$), surface-weighted mean diameter ($d_{3,2}$) and specific surface area (m^2 surface area/ml droplet) of the oil droplets in the emulsion were investigated using a laser diffraction particle size analyzer (Mastersizer MS20, Malvern Instruments, Ltd., Worcestershire, UK). Measurements were carried out with a 2-mW He-Ne laser beam (633 nm) and a 45-mm focus lens. The surface-weighted ($d_{3,2}$) and the volume-weighted ($d_{4,3}$) mean diameter were calculated as follows:

$$d_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (2)$$

$$d_{4,3} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (3)$$

where n_i is the number of particles with diameter d_i.

3.5.2 Microcapsule analysis

3.5.2.1 Chemical analysis

Moisture content of the spray-dried powders and agglomerated powders were determined gravimetrically after 12 h of vacuum drying at 65°C and 6.7 kPa (Young et al., 1993a, b). The crude protein content was determined according to the Kjeldahl method using a multiplying factor of 6.25 (AOAC, 2000) (see 3.5.1.3). The oil content was determined using a modification of the Roese-Gottlieb method (Bradley et al., 1993) (see 3.5.1.4) and was expressed as grams of oil per 100 grams of powder, which was defined as the microencapsulated oil load. The microencapsulation yield (MEY) was defined as the ratio (expressed as percentage) of microencapsulated oil load to the oil load in the emulsion (Young et al., 1993a). With the exception of moisture content the chemical composition was expressed as percentage (w/w) of total dry matter.

Microencapsulation efficiency (MEE) parameter was defined as the percentage of oil that could not be extracted from the test sample by petroleum ether using a method described by Young et al. (1993a) with a slight modification. One gram of spray-dried powder was weighed into a glass extraction flask and 25 ml of petroleum ether were added. The extraction flask was placed on a shaker and the extraction was carried out for 5 min at 25 °C. The mixture was filtered, the solvent was evaporated over a water bath at 70 °C, and the solvent-free extract was dried under vacuum at 100 °C and 6.7 kPa. The amount of extracted oil was then determined gravimetrically. The MEE was calculated as follows:

$$\text{MEE (\%)} = 100 - \text{extracted oil (g/100 g oil content)} \tag{4}$$

3.5.2.2 Particle size measurement

For the spray-dried soybean oil powders, the particle size distribution, the $d_{3,2}$ value and the $d_{4,3}$ value were measured by the dry method in a laser diffraction particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK) fitted with a Scirocco 2000 dry powder feeder unit.

For the agglomerated soybean oil powders, due to their much larger particle sizes, sieve analysis using a vibratory sieve shaker (Model Octagon Digital 2000, Endecotts Ltd., London, UK) with a series of eight sieves was used to determine their particle size distributions. The aperture sizes of sieves were 125, 180, 250, 355, 500, 710, 1000, and 1400 μm. The agglomerated soybean oil powder (50 g) was put on the sieve's series and shaken at a vibration speed of 3,000 min^{-1} with a displacement amplitude of approximately 3 mm for 15 min. Due to their high oil contents, the agglomerated powders remained on the first sieve and aggregated into big balls. Addition of aluminum sodium silicate (Sigma-Aldrich Chemie GmbH, Germany) as a free flowing agent at a level of 1% (w/w) improved flowability of the sample through sieves (Early, 1992; Hall & Hedrick, 1975; Perez-Munoz & Flores, 1997). This agent covered the surface of powder particles, the adhesion among them was reduced and this reduced the possibility of wet bridges formation (Carić, 2003). The geometric mean particle size and the geometric standard deviation of the agglomerated powders were determined by graphical method using a log-probability plot (Jinapong, Suphantharika, & Jamnong, 2008).

3.5.2.3 Morphological study

The inner and outer structures of the spray-dried microcapsules were studied by scanning electron microscopy. For examination of the outer structure, microcapsules were attached to stubs using a two-sided adhesive tape. In order to examine the inner structure of the microcapsules, the microcapsules were fractured by moving a razor blade perpendicularly through a layer of microcapsules attached by doubled sided adhesive tape to a specimen holder. In all cases, the specimens were subsequently coated with gold using a Polaron sputter coater (model 5100; Bio Rad, San Jose, CA) and studied microscopically using a scanning electron microscope (FEI XL30 SFEG, PHILIPS, Hillsboro, OR) operating at 5 kV.

The appearance, size, and shape of the agglomerated samples were investigated by placing the agglomerates on aluminum stubs using a double-sided adhesive tape. The samples were then coated with gold and were examined with a scanning electron microscope (SEM S-2500, Hitachi Science Systems, Ibaraki, Japan) operating at 15 kV accelerating voltage.

3.5.2.4 Bulk and tapped densities

Bulk and tapped densities reflected the quality of the microcapsules. Density is defined as the unit mass per unit volume and is of fundamental use for material properties' studies and industrial processes in adjusting storage, processing, packaging, and distribution conditions. Bulk density is regarded as the weight per unit volume and is expressed as g/cm^3. Bulk density includes the volume of the solid and liquid materials, and all pores closed or open to the surrounding atmosphere. Whereas, tapped density results after a volume of powder has been tapped or vibrated under specific conditions and it is most useful to describe powder behavior during compaction. The relatively low density of powders has several practical implications. It is undesirable as it leads to higher packaging, storage and transportation costs (Barbosa-Cánovas & Juliano, 2005; Carić, 2003).

Powder was gently loaded into a 100 ml tared graduated cylinder to the 100 ml mark and weighed. The volume read directly from the cylinder was then used to calculate the bulk density (ρ_{bulk}) according to the relationship: mass/volume. For the tapped density (ρ_{tapped}), the cylinder was tapped 1250 times, using a VanKel tap density tester (ASTM Version, Varian, Inc., Cary, NC) with a displacement amplitude of 3 ± 0.3 mm. The volume of the sample was then read and used in the calculation. The results were calculated from three replicate measurements.

3.5.2.5 Particle density

Particle density (ρ_{particle}) of the powder sample was analyzed according to A/S Niro Atomizer (1978c) with some modifications. The powder sample (1 g) was transferred into a 10 ml measuring cylinder with a glass stopper. Then 5 ml of petroleum ether was added and the measuring cylinder was shaken until all the powder particles were suspended. Finally, all the powder particles on the wall of the cylinder were rinsed down with a further 1 ml of petroleum ether (6 ml in total) and the total volume of petroleum ether with suspended powder was read. The particle density was calculated as follows:

$$\rho_{\text{particle}} = \frac{\text{weight of powder (g)}}{\text{total volume of petroleum ether with suspended powder (ml)} - 6} \qquad (5)$$

3.5.2.6 Porosity

Porosity (ε) of the powder samples was calculated using the relationship between the tapped (ρ_{tapped}) and particle (ρ_{particle}) densities of the powder as shown below (Jinapong et al., 2008):

$$\varepsilon = \frac{(\rho_{\text{particle}} - \rho_{\text{tapped}})}{\rho_{\text{particle}}} \times 100 \qquad (6)$$

3.5.2.7 Friability

Friability measurement of the agglomerated soybean oil powders was performed using the vibratory sieve shaker, which is the same as that used for particle size analysis, according to the procedure described in the literature (Turchiuli et al., 2005a; Utsumi, Hirono, Mori, Tsubaki, & Maeda, 2002) with some modifications. The test samples (10 g) were hand-sieved with a 355-µm sieve, taking care that attrition did not occur during sieving, and the fine particles, which included any fragments already abraded, were removed. A 5 g fraction of the sieved sample was placed into 300-µm sieve with three glass balls having a diameter of 15 mm and weighing 5 g each. The sample was shaken at a vibration speed of 3,000 min^{-1} for 5 min. The amount retained on the sieve was weighed and the friability percentage was calculated as follows:

$$\text{friability (\%)} = \frac{\text{weight of powder passing through the sieve (g)}}{\text{total weight of powder (g)}} \times 100 \qquad (7)$$

3.5.2.8 Flowability and cohesiveness

Flowability and cohesiveness of the powder were evaluated in terms of Carr index (CI) (Carr, 1965) and Hausner ratio (HR) (Hausner, 1967), respectively. Both CI and HR were calculated from the bulk (ρ_{bulk}) and tapped (ρ_{tapped}) densities of the powder as shown below:

$$\mathrm{CI} = \frac{(\rho_{\mathrm{tapped}} - \rho_{\mathrm{bulk}})}{\rho_{\mathrm{tapped}}} \times 100 \qquad (8)$$

$$\mathrm{HR} = \frac{\rho_{\mathrm{tapped}}}{\rho_{\mathrm{bulk}}} \qquad (9)$$

Classification of the flowability and cohesiveness of the powder based on the CI and HR values are presented in Tables 3.2 and 3.3, respectively.

Table 3.2 Classification of powder flowability based on Carr Index (CI) (Carr, 1965).

CI (%)	Flowability
<15	Very good
15-20	Good
20-35	Fair
35-45	Bad
>45	Very bad

Table 3.3 Classification of powder cohesiveness based on Hausner ratio (HR) (Hausner, 1967).

HR	Cohesiveness
<1.2	Low
1.2-1.4	Intermediate
>1.4	High

3.5.2.9 Wettability

Wettability of the powder sample was determined according to A/S Niro Atomizer (1978a) with some modifications. An amount of distilled water (100 ml) at 25 ± 1 °C was poured into a 250 ml beaker. A glass funnel held on a ring stand was set over the beaker with the height between the bottom of the funnel and the water surface of 10 cm. A test tube was placed inside the funnel to block the lower opening of the funnel. The powder sample (1 g) was placed around the test tube and then the tube was lifted while the stop watch was started at the same time. Finally, the time was recorded for the powder to become completely wetted (visually assessed as when all the powder particles penetrated the surface of the water).

3.5.2.10 Dispersibility

Dispersibility measurement was performed according to the procedure described in A/S Niro Atomizer (1978b) with some modifications. Distilled water (10 ml), at 25 ± 1 °C, was poured into a 50 ml beaker. The powder (1 g) was added into the beaker. The stop watch was started and the sample was stirred vigorously with a spoon for 15 s making 25 complete movements back and forth across the whole diameter of the beaker. The reconstituted solution was poured through a sieve (212 µm). The sieved solution (1 ml) was transferred to a weighed and dried aluminum pan and dried for 4 h in a hot air oven at 105 ± 1 °C. The dispersibility of the powder was calculated as follows:

$$\text{dispersibility}\,(\%) = \frac{(10 + a) \times \%\,\text{TS}}{a \times \dfrac{100 - b}{100}} \qquad (10)$$

where a is the amount of powder (g) being used, b is the moisture content in the powder, and % TS is the dry matter in percentage in the reconstituted solution after it has been passed through the sieve.

3.6 Statistical analysis

All measurements were performed in triplicate at least, and the mean values were presented in respective table. A one-way analysis of variance (ANOVA) and Student-Newman-Keuls (SNK) ($p \leq 0.05$) were used to establish the significance of differences among the mean values of the physical, handling, and reconstitution properties of the spray-dried and agglomerated soybean oil powders. The data were analyzed using SigmaStat (2004) version 3.1 Windows program (Systat Software, Inc., San Jose, CA).

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of liquid emulsions

Emulsion physical properties were monitored in terms of oil droplet size distribution (Figs. 4.1 and 4.2 for SPI 1 and SPI 2-based emulsions, respectively) and volume-weighted ($d_{4,3}$) mean droplet diameter (Tables 4.1 for SPI 1 and SPI 2-based emulsions). Both of SPI-based emulsions, $d_{3,2}$ and $d_{4,3}$ were significantly affected by composition of emulsions. For the SPI 1-based emulsion systems (Fig. 4.1), the emulsions with low oil load (25%) had monomodal droplet size distribution ranged from 0.1-2.0 µm, whereas the ones with high oil load (50%) exhibited a shoulder or bimodal distribution with additional larger size ranges (2-10 µm). These results were reflected by their $d_{4,3}$ values, in which the $d_{4,3}$ values of the 50% oil emulsions (0.9-1.3 µm) were about twice as big as those of the 25% oil emulsions (~0.5 µm) regardless of the wall systems as shown in Table 4.1. This could be due to the reduced availability of protein to stabilize the oil/water interface during emulsification, so the emulsion oil droplets became larger. These bimodal distributions of the emulsions with high oil load (50%) suggested destabilization of the emulsion and formation of clusters consisting of several small oil droplets (Dickinson, 1997; McClements, 2005). These clusters could not be disintegrated by continuous stirring and high pressure homogenizer. This, and the relatively low surface excess of the emulsions suggested that the overall repulsive forces that stabilized the oil droplets in the emulsions were relatively weak resulted in destabilization and enhancement of the attractive forces between droplets, probably due to the exclusion of colloidal particles from a narrow depletion region that surrounded each soybean oil droplet (Dickinson, 1997; McClements, 2005). Altogether, these phenomena promoted clustering, that was manifested by the increase in mean particle size (Table 4.1), and resulted in the bimodal distributions of the oil droplets population (Fig. 4.1). It has to be noted that the mechanical input during particle size analysis did not result in disruption of the clusters and thus each of the clusters was determined as a single large particle during particle size analysis. These findings are consistent with those reported by McNamee et al. (2001) who encapsulated soybean oil with a wall system consisting of gum arabic and maltodextrins of various DE values. It has been reported that the emulsions with a mean oil droplet size of 1.0 μm or 1.2 μm were not as stable as the one with 0.5 μm mean droplet diameter and creaming was observed even before spray drying (Danviriyakul et al., 2002). The instability led to poor spray-dried powder properties and poorer encapsulation efficiency. In the case of SPI 2-based emulsion systems (Fig. 4.2), all of the emulsions had monomodal droplet size distribution ranged from 0.1-2.0 μm, in which their $d_{4,3}$ values ranged from 0.4-0.8 μm, regardless of the wall systems (Table 4.1). These monomodal distribution indicated that consistent small oil droplets were produced and no clusters occurred during processing. In general, the oil droplet sizes of less than 1 μm were recommended by several workers (Fuchs et al., 2006; Turchiuli et al., 2005b). In this study, the spray-dried powders obtained from the high oil load emulsions reflected the decreasing ability of the wall systems to encapsulate high oil loads as evidenced by lower MEE values. Although, the protein content used in this experiment is similar but the differences of particle size distribution between SPI 1 and SPI 2-based emulsions were obtained. It could be attributed to the fact that the physicochemical properties of the whole proteins contained in soybeans considerably differ depending upon soybean cultivars which were used to produce soy protein isolate. As already described in chapter II, the physicochemical properties of each component of soy proteins are quite different not only between *β*-conglycinin and glycinin, but also among the subunits of *β*-conglycinin or glycinin molecule. Further, both the ratio of *β*-conglycinin to glycinin and the subunit compositions of *β*-conglycinin or glycinin molecules are fairly different among soybean cultivars. This is the reason why the physicochemical properties differ among soybean cultivars. Additionally, the other reason is 2 types of soy protein isolate might differ because of the differences in the manufacturing process, such as, pH and concentration of solvent, and period of time for extraction, etc.

Emulsion physical properties were also monitored in terms of volume-surface area ($d_{3,2}$) mean droplet diameter for SPI 1- and SPI 2-based emulsions (Table 4.1).

The mean particle size ($d_{3,2}$) of soybean oil in these emulsions ranged from 0.32-0.52 µm for SPI 1 and 0.32-0.42 µm for SPI 2. Results also indicated that oil load had an effect on $d_{3,2}$ in the emulsions. At a given SPI/MD ratio, both SPI 1 and SPI 2, mean particle size ($d_{3,2}$) proportionally related to the oil load in the emulsion. In all cases, results showed that $d_{3,2}$ was increased when oil load increased. With increasing oil load, the number of oil droplets and their overall surface area increases. Under these conditions, the availability of protein to stabilize the oil/water interface during emulsification was limited, so the emulsion oil droplets became larger. The larger mean droplet diameter (in case of 50% high oil load) were not as stable as the one with the smaller mean droplet diameter (in case of 25% oil load) and affected lower MEE values. As shown in Tables 4.4 and 4.5 for SPI 1 and SPI 2, respectively, in all cases, the 50% oil load presented lower MEE values than the 25% oil load for the same combination. In all case except the system containing SPI 1/MD7.5 ratio of 1:3 at the oil load of 50%, both SPI 1 and SPI 2 containing emulsions had mean particle sizes less than 0.5 µm. Regardless of composition of emulsions, in all cases, fine emulsion with $d_{3,2} < 0.6$ µm were obtained that has been reported to be desired in oil encapsulation by spray drying (Young et al., 1993a, b). For each emulsion, the $d_{4,3}$ value was much higher than the $d_{3,2}$ value. The reason for this difference is that the former is more sensitive to the presence of large particles, whereas the latter is more sensitive to the majority of the droplets (McClements, 2005). Therefore, the $d_{4,3}$ value can give a better indication of droplet aggregation than the $d_{3,2}$ value.

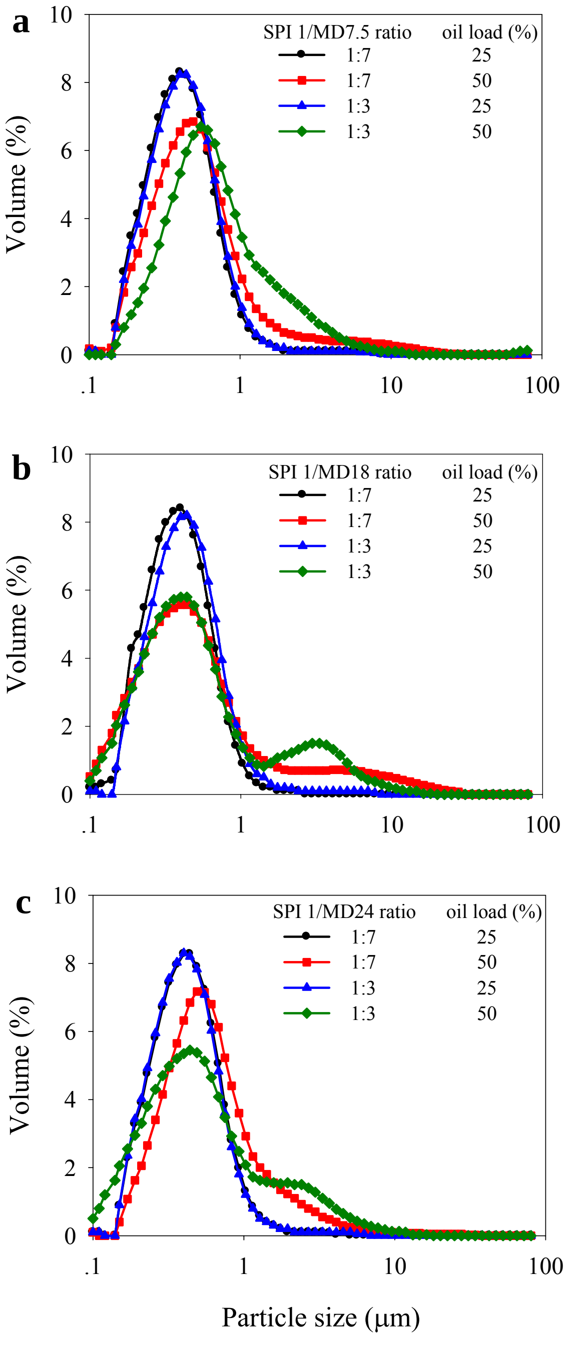

Fig. 4.1 Effects of types of wall system (SPI 1/MD) and oil loads on oil droplet size distribution of emulsions containing maltodextrin with a DE value of 7.5 (a), 18 (b), and 24 (c). All emulsions contained 20% (w/w) wall solids.

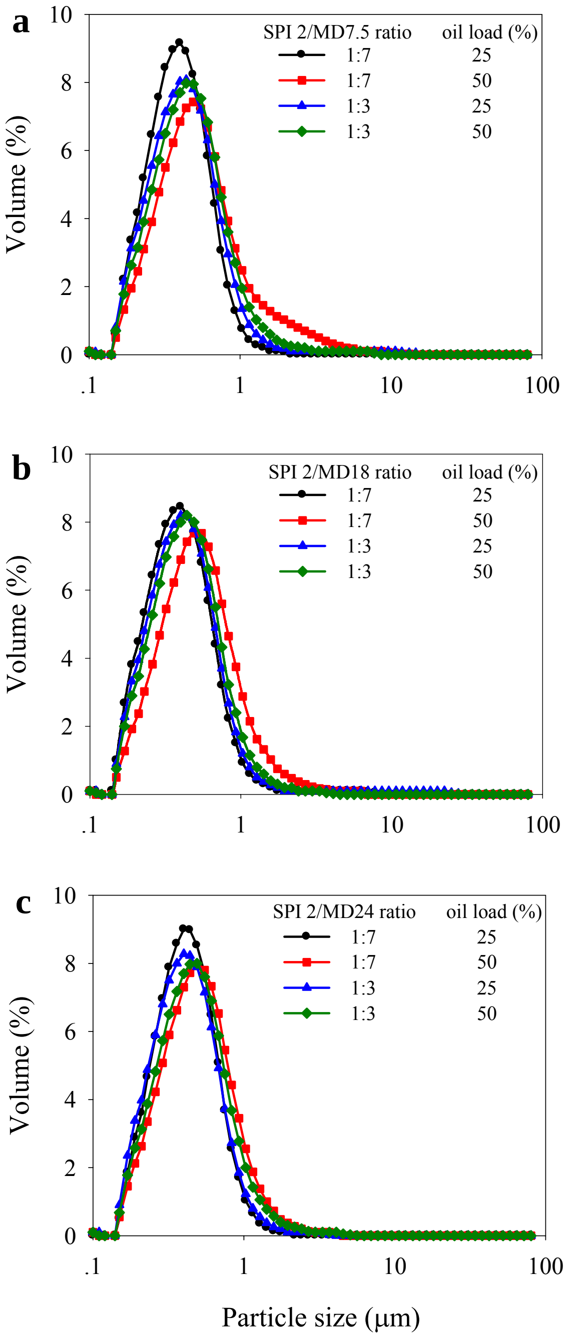

Fig. 4.2 Effects of types of wall system (SPI 2/MD) and oil loads on oil droplet size distribution of emulsions containing maltodextrin with a DE value of 7.5 (a), 18 (b), and 24 (c). All emulsions contained 20% (w/w) wall solids.

Table 4.1 Effects of wall material type and oil load on properties of soy protein isolate (SPI 1 and SPI 2)/maltodextrin-based, soybean oil-containing emulsions.

SPI 1/MD ratio	Oil load (% w/w)	DE value	SPI 1		SPI 2	
			Emulsion droplet size, (µm)		Emulsion droplet size, (µm)	
			$d_{3,2}$	$d_{4,3}$	$d_{3,2}$	$d_{4,3}$
1:7	25	7.5	$0.34 \pm 0.01^{\text{b E}}$	$0.48 \pm 0.01^{\text{a C}}$	$0.33 \pm 0.00^{\text{b FG}}$	$0.44 \pm 0.01^{\text{a D}}$
		18	$0.32 \pm 0.00^{\text{c F}}$	$0.49 \pm 0.02^{\text{a C}}$	$0.32 \pm 0.01^{\text{b G}}$	$0.46 \pm 0.01^{\text{a D}}$
		24	$0.34 \pm 0.01^{\text{a E}}$	$0.49 \pm 0.05^{\text{a C}}$	$0.35 \pm 0.01^{\text{a DE}}$	$0.49 \pm 0.07^{\text{a D}}$
1:7	50	7.5	$0.39 \pm 0.01^{\text{b C}}$	$0.95 \pm 0.11^{\text{b B}}$	$0.42 \pm 0.01^{\text{a A}}$	$0.75 \pm 0.03^{\text{a A}}$
		18	$0.34 \pm 0.00^{\text{c E}}$	$1.27 \pm 0.07^{\text{a A}}$	$0.42 \pm 0.01^{\text{a A}}$	$0.62 \pm 0.01^{\text{b B}}$
		24	$0.45 \pm 0.01^{\text{a B}}$	$0.87 \pm 0.07^{\text{b B}}$	$0.40 \pm 0.01^{\text{b B}}$	$0.60 \pm 0.03^{\text{b BC}}$
1:3	25	7.5	$0.35 \pm 0.01^{\text{a DE}}$	$0.50 \pm 0.01^{\text{a C}}$	$0.35 \pm 0.01^{\text{a DE}}$	$0.77 \pm 0.00^{\text{a A}}$
		18	$0.35 \pm 0.00^{\text{a DE}}$	$0.52 \pm 0.03^{\text{a C}}$	$0.34 \pm 0.00^{\text{b EF}}$	$0.60 \pm 0.00^{\text{b BC}}$
		24	$0.34 \pm 0.00^{\text{b E}}$	$0.49 \pm 0.04^{\text{a C}}$	$0.34 \pm 0.01^{\text{b EF}}$	$0.49 \pm 0.03^{\text{c D}}$
1:3	50	7.5	$0.52 \pm 0.01^{\text{a A}}$	$1.16 \pm 0.39^{\text{a AB}}$	$0.37 \pm 0.01^{\text{a C}}$	$0.55 \pm 0.02^{\text{a C}}$
		18	$0.36 \pm 0.01^{\text{b D}}$	$1.04 \pm 0.06^{\text{a B}}$	$0.36 \pm 0.01^{\text{b CD}}$	$0.49 \pm 0.01^{\text{b D}}$
		24	$0.36 \pm 0.01^{\text{b D}}$	$0.90 \pm 0.04^{\text{a B}}$	$0.37 \pm 0.01^{\text{a C}}$	$0.55 \pm 0.03^{\text{a C}}$

Assays were performed in triplicate.

$^{\text{a-c}}$ For a given DE values, mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

$^{\text{A-C}}$ For all treatments, mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

Table 4.2 Effects of wall material type and oil load on properties of soy protein isolate (SPI 1)/maltodextrin-based, soybean oil-containing emulsions.

SPI 1/MD ratio	Oil load (% w/w)	DE value	Specific surface area (m^2 / ml)	Protein content (% w/w)	Oil content (% w/w)	Surface excess (mg protein / m^2)
1:7	25	7.5	17.89 ± 0.08^{b}	0.20 ± 0.03^{a}	1.50 ± 0.06^{c}	0.67 ± 0.10^{ab}
		18	18.76 ± 0.06^{a}	0.39 ± 0.08^{a}	2.07 ± 0.15^{b}	0.92 ± 0.20^{a}
		24	17.56 ± 0.14^{c}	0.22 ± 0.12^{a}	2.95 ± 0.11^{a}	0.39 ± 0.21^{b}
1:7	50	7.5	15.18 ± 0.17^{b}	0.70 ± 0.29^{a}	6.38 ± 0.20^{c}	0.66 ± 0.28^{a}
		18	17.58 ± 0.12^{a}	0.70 ± 0.06^{a}	8.13 ± 0.49^{b}	0.45 ± 0.04^{a}
		24	13.33 ± 0.32^{c}	0.49 ± 0.12^{a}	11.59 ± 0.17^{a}	0.29 ± 0.07^{a}
1:3	25	7.5	17.38 ± 0.07^{b}	1.42 ± 0.04^{a}	1.55 ± 0.17^{b}	4.83 ± 0.14^{b}
		18	17.27 ± 0.08^{b}	1.57 ± 0.05^{a}	1.14 ± 0.11^{c}	7.33 ± 0.23^{a}
		24	17.77 ± 0.07^{a}	1.10 ± 0.18^{b}	3.03 ± 0.17^{a}	1.87 ± 0.31^{c}
1:3	50	7.5	11.69 ± 0.08^{b}	1.25 ± 0.12^{a}	6.03 ± 0.57^{c}	1.62 ± 0.16^{a}
		18	16.83 ± 0.34^{a}	1.18 ± 0.03^{a}	8.13 ± 0.03^{b}	0.79 ± 0.02^{b}
		24	16.67 ± 0.19^{a}	0.74 ± 0.16^{b}	11.38 ± 0.20^{a}	0.36 ± 0.08^{c}

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

Table 4.3 Effects of wall material type and oil load on properties of soy protein isolate (SPI 2)/maltodextrin-based, soybean oil-containing emulsions.

SPI 2/MD ratio	Oil load (% w/w)	DE value	Specific surface area (m^2 / ml)	Protein content (% w/w)	Oil content (% w/w)	Surface excess (mg protein / m^2)
1:7	25	7.5	18.02 ± 0.06^b	0.40 ± 0.04^b	2.56 ± 0.23^b	0.80 ± 0.07^b
		18	18.49 ± 0.05^a	0.16 ± 0.02^c	1.53 ± 0.30^c	0.50 ± 0.05^c
		24	17.23 ± 0.32^c	0.80 ± 0.12^a	3.91 ± 0.30^a	1.09 ± 0.17^a
1:7	50	7.5	14.27 ± 0.18^b	0.54 ± 0.06^a	7.00 ± 0.50^b	0.49 ± 0.05^a
		18	14.47 ± 0.17^b	0.63 ± 0.07^a	5.49 ± 0.12^c	0.73 ± 0.09^a
		24	15.15 ± 0.20^a	0.94 ± 0.29^a	8.96 ± 0.18^a	0.63 ± 0.19^a
1:3	25	7.5	17.00 ± 0.35^b	1.52 ± 0.16^a	2.97 ± 0.13^a	2.75 ± 0.28^a
		18	17.52 ± 0.09^a	1.41 ± 0.15^a	2.20 ± 0.10^b	3.34 ± 0.35^a
		24	17.72 ± 0.20^a	1.01 ± 0.19^b	1.54 ± 0.07^c	3.39 ± 0.62^a
1:3	50	7.5	16.09 ± 0.13^b	1.20 ± 0.10^a	4.47 ± 0.05^a	1.53 ± 0.12^a
		18	16.82 ± 0.12^a	1.06 ± 0.20^a	5.05 ± 0.24^a	1.12 ± 0.21^b
		24	16.08 ± 0.16^b	0.61 ± 0.15^b	4.97 ± 0.09^a	0.70 ± 0.17^c

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

4.2 Properties of the emulsions consisting of SPI and maltodextrins

4.2.1 Properties of the emulsions consisting of SPI 1 and maltodextrins

4.2.1.1 Specific surface area

The calculated specific surface area of these emulsions, which indicates emulsification capacity, ranged from 11.69-18.76 m^2/ml. As expected, specific surface area of soybean oil droplets was inversely related to the particle size ($d_{3,2}$) of the droplets (Table 4.2). Specific surface area was increased with the decrease in particle size ($d_{3,2}$). Addition of maltodextrin with different DE values into the emulsions caused significant change of specific surface area (Table 4.2).

4.2.1.2 Protein content in the separated and washed cream

Protein content in the separated and washed cream could be assumed to represent proteins that were strongly associated with the oil/water interface. Differences in protein content among these creams reflected differences in the amount of proteins absorbed at the oil/water interfaces of these emulsions. Protein content at the oil/water interface in separated and washed cream obtained from SPI 1-based emulsion is presented in Table 4.2. Homogenizing soybean oil into the mixture of SPI 1 and maltodextrin with different DE values resulted in 0.2-0.7% and 0.7-1.6% protein content in the separated and washed cream containing SPI 1/MD ratio of 1:7 and 1:3, respectively. Maltodextrin DE values didn’t affect protein content at the oil/water interface in separated and washed cream in the wall systems consisting of SPI 1/MD ratio of 1:7 at the oil loads of 25% and 50%. Significant decrease of protein content was observed after addition maltodextrin with higher DE values into the wall systems consisting of SPI 1/MD ratio of 1:3 at the oil loads of 25% and 50%. Consistently, regardless of oil load and DE values, SPI 1/MD ratio of 1:7 always presented lower interfacial protein content than the SPI 1/MD ratio of 1:3 which increase from 0.27 (range from 0.20-0.22%) to 1.36 (range from 1.42-1.10%) at the oil load of 25% and 0.63 (range from 0.70-0.49%) to 1.06 (range from 1.25-0.74%) at the oil load of 50%, respectively (Table 4.2). Due to the lower protein content presented the reduced availability of protein content in the separated and washed cream to stabilize the oil-in-water interface.

4.2.1.3 Oil content in the separated and washed cream

Oil content in the separated and washed cream obtained from SPI 1-based emulsion is shown in Table 4.2. Regardless of the wall systems, the oil contents of the cream obtained from 50% oil emulsions were significantly higher than those obtained from the 25% oil emulsions. Regardless of the oil loads, the oil contents increased with the DE values of maltodextrins. It could be noted that the smaller molecular weight carbohydrate (high DE value) could lead to a better of emulsion than the higher molecular weight carbohydrate (lower DE value).

4.2.1.4 Surface excess

Surface excess obtained from SPI 1-based emulsions are presented in Table 4.2. Surface excess ranged from 0.3-0.9 mg protein/m^2 and ranged from 0.4-7.3 mg protein/m^2 in the emulsions prepared from SPI 1/MD ratio of 1:7 and 1:3, respectively. Results indicated that increasing protein content in the emulsions from 2.5% w/w (SPI 1/MD ratio of 1:7) to 5% w/w (SPI 1/MD ratio of 1:3) increased the surface excess in all cases. The results of the effect of protein content on surface excess agreed with those reported by Hunt & Dalgleish (1994). Hunt & Dalgleish (1994) reported that surface excess in whey protein isolate (WPI)-stabilized oil/water emulsions (20% soybean oil) increased from 1.5 to 3.0 mg protein/m^2 when WPI concentration was increased from 0.3 to 2.5%. Brun & Dalgleish (1999) reported that when surface excess of milkfat droplet was lower than 2.0 mg protein/m^2, only a monolayer could be formed and that whey proteins were spread at the oil/water interface. It was reported that the maximum monolayer adsorption by WPI corresponded to a surface excess of 2.0 mg protein/m^2 (Dalgleish, 1996). In this study, as protein content increased from 2.5% to 5%, in some cases, surface excess increased but not more than 2 mg protein/m^2 which corresponded to maximum monolayer adsorption (Dalgleish, 1996). In some cases, when increasing protein content to 5%, surface excess higher than 2 mg protein/m^2 was obtained and thus indicated the formation of a soy protein-based multi-layer at the oil/water interface (Hunt & Dalgleish, 1994; Dalgleish, 1996).

Research indicated that during emulsification of oil into a mixture of protein and carbohydrate, the effect of carbohydrate on the adsorption of protein to the interface depended on both protein and carbohydrate concentrations (Pavlovskaya et al., 1993; Semenova et al., 1999). At low protein (<0.6%) and carbohydrate (<4%) concentrations, the characteristic of emulsions prepared from protein solution alone did not differ from those of emulsions stabilized by mixtures of protein and carbohydrates (Pavlovskaya et al., 1993). At higher polysaccharide content, the polysaccharide may influence the hydrophobic and hydrophilic balance of the protein. Semenova et al. (1999) indicated that in a mixture solution of protein and maltodextrin, a weak attractive interaction between protein and maltodextrin occurred due to the hydrogen bonding. This weak attractive interaction can increase the protein hydrophilicity and decrease the protein surface activity. This may be the reason why addition of maltodextrin at higher content (SPI 1/MD ratio of 1:7) into the SPI solution led to an decrease of the surface excess when compared to addition of maltodextrin at lower content (SPI 1/MD ratio of 1:3) into the SPI solution.

4.2.2 Properties of the emulsions consisting of SPI 2 and maltodextrins

4.2.2.1 Specific surface area

The calculated specific surface area of these emulsions, which indicates emulsification capacity, ranged from 14.27-18.49 m^2/ml. As being expected, specific surface area of soybean oil droplets (Table 4.3) in the emulsions followed the opposite trend of $d_{3,2}$ (Table 4.3). Specific surface area increased when $d_{3,2}$ decreased. Addition of maltodextrin with different DE values into the emulsions caused significant change of specific surface area.

4.2.2.2 Protein content in the separated and washed cream

Protein content at the oil/water interface in separated and washed cream obtained from SPI 2-based emulsion is presented in Table 4.3. Homogenizing soybean oil into the mixture of SPI 2 and maltodextrin with different DE values resulted in 0.2-

0.9% and 0.6-1.5% protein in the cream containing SPI 2/MD ratio of 1:7 and 1:3, respectively. Maltodextrin DE values didn't affect protein content at the oil/water interface in the separated and washed cream of the emulsions consisting of SPI 2/MD ratio of 1:7 at the oil loads of 50%. However, significant increase of protein content with increasing DE values was found for the emulsions consisting of SPI 2/MD ratio of 1:7 at the oil loads of 25%. Significant decrease of protein content with increasing DE values was observed for the emulsions consisting of SPI 2/MD ratio of 1:3 at the oil loads of 25% and 50%. Similar to what was obtained with the emulsions prepared with SPI 1, regardless of oil load and DE values, SPI 2/MD ratio of 1:7 always presented lower interfacial protein content than the SPI 2/MD ratio of 1:3 which increase from 0.45 (range from 0.40-0.80%) to 1.31 (range from 1.52-1.01%) at the oil load of 25% and 0.70 (range from 0.54-0.94%) to 0.96 (range from 1.20-0.61%) at the oil load of 50% (Table 4.3). Due to the limited availability of protein content which presented in SPI 2/MD ratio of 1:7.

4.2.2.3 Oil content in the separated and washed cream

Oil content in the separated and washed cream obtained from SPI 2-based emulsion is shown in Table 4.3. Regardless of the wall systems, the oil contents of the cream obtained from the 50% oil emulsions were significantly higher than those obtained from the 25% oil emulsions. The systems with SPI 2/MD ratio of 1:7 exhibited a significant increase in oil content of the cream with increasing the DE values of maltodextrin regardless of the oil load, whereas the systems with SPI 2/MD ratio of 1:3 showed no effect of the DE values on the oil content at 50% oil load, but significantly decreased with increasing DE values at 25% oil load.

4.2.2.4 Surface excess

Surface excess obtained from SPI 2-based emulsions are presented in Table 4.3. Surface excess ranged from 0.5-1.1 mg protein/m^2 and 0.7-3.4 mg protein/m^2 in the emulsions prepared from SPI 1/MD ratio of 1:7 and 1:3, respectively. Results indicated that increasing protein content in the emulsions from 2.5% w/w (SPI 2/MD ratio of 1:7) to 5% w/w (SPI 2/MD ratio of 1:3) increased the surface excess in all cases. These results were similar to those of the SPI 1-based emulsions which were previously discussed.

For subsequent experiments, all treatments (both SPI 1 and SPI 2-based emulsions) were used to produce the microcapsules by spray drying. All of the spray-dried microcapsules were determined the microencapsulating properties of wall materials consisting of each type of soy protein isolate in combination with maltodextrin on microstructure, microencapsulation efficiency and microencapsulation yield of the spray-dried microcapsules.

4.3 Microstructure of spray-dried microcapsules

In this part of the research, the results revealed the outer topography, especially, surface indentation of the microcapsules, and inner structure of the microcapsules prepared from various composition of emulsions. Generally, results (Figs. 4.3-4.10) indicated that the microstructure of microcapsule was affected by type of maltodextrin and a much less extent by its proportion in the wall. The smoothness of the powder surface increased with increasing DE values of maltodextrin. The oil load also affected the microcapsule structure. The powders tended to agglomerate when the oil load was increased. In all cases, the outer topography revealed that the spherical microcapsules were free of visible cracks or pores, and almost no surface dents could be detected except for most of the SPI/MD7.5-based systems, which exhibited a very high extent of surface indentations. The powder particles containing 25% oil load appeared as discrete particles and showed little evidence of agglomeration. However at 50% oil load, the powder particles appeared highly agglomerated which suggests that the lower MEE of this powder (Tables 4.4 and 4.5) may be due to high levels of surface oil (Hogan et al., 2001). Other work (Keogh & O'Kennedy, 1999) has already shown that the higher level of oil load increased the surface oil on the powder particles as measured by electron spectroscopy for chemical analysis (ESCA).

The inner structure of the microcapsules indicated that in all cases the core material was in the form of small droplets embedded in the wall matrix. It was noted that in all samples, microcapsules had a central void. Central voids have been reported to characterize spray-dried microcapsules and were attributed to effect of thermal expansion within the drying particle during late stages of drying (Rosenberg et al., 1988; Sheu & Rosenberg, 1995).

In the case of 25% oil load systems, the wall thickness of the microcapsules and the oil droplet size decreased with increasing DE values of MD. This was possibly due to a lack of thermal stabilization effect of a larger molecular weight maltodextrin (MD7.5 in this case) on the surface activity of protein leading to a significant increase in average oil droplet size upon spray drying and in turn a significant decrease in MEE value of the microcapsule (Tables 4.4 and 4.5) as pointed out by Danviriyakul et al. (2002). Additionally, the observed structural differences may attribute to the changes in physical state of these materials from liquid to rubbery and eventually to glassy state due to an increase in viscosity during drying. Since the highest glass transition temperature is expected for MD7.5, the sample would turn glassy earlier followed by MD18 and then MD24 (Bhandari & Howes, 1999). A more rapid increase in viscosity at the early stage of drying in the presence of MD7.5 may retard the formation of impermeable microregions entrapping the core material (Danviriyakul et al., 2002). With a lower viscosity, structural collapse in the higher DE samples (MD18 and MD24) could lead to a formation of a denser wall matrix around the oil droplets preventing the accessibility of oil by the solvent and therefore increased the MEE values of the samples (Tables 4.4 and 4.5). It was found that at a given solid concentration and drying conditions used in this study, the increasing oil load led to larger oil droplet size and thinner wall layers around each droplet. This was not surprising because it was shown earlier (Tables 4.1) that the increase oil load resulted in a major increase in average oil droplet size in liquid emulsions due to the limited availability of protein. The accessibility of the microencapsulated oil by the solvent would be high and therefore lowering the MEE of the samples (Tables 4.4 and 4.5).

Specifically, microstructural properties of both the outer topography and inner structure of the spray-dried microcapsules consisting of SPI 1/MD and SPI 2/MD as wall materials are presented in Figs. 4.3-4.6 and Figs. 4.7-4.10, respectively. In all cases, regardless of the wall composition and oil load in the microcapsules, spherical microcapsules, ranging in diameter from about 2 to about 60 µm, were obtained and some small particles were deposited on the larger particle (Figs. 4.3-4.10). These results reveals only a slight apparent degree of agglomeration among the individual spray-dried particles. In general, microcapsules exhibited microstructural features similar to those reported for microcapsules with wall matrices consisting of SPI-based (Kim & Morr, 1996; Molina Ortiz, Adriana Mauri, Monterrey-Quintero, Trindade, Santana & Favaro-Trindade, 2009).

Results indicated that DE value of maltodextrin significantly affected the outer topography and surface indentation of the microcapsules, regardless of SPI types. In the SPI 1 systems, when the DE of maltodextrin was 7.5, regardless of SPI content and oil load in the microcapsules, the microcapsules exhibited more deep dents, wrinkled and cracked surface than in the microcapsules made from MD18 and MD24. These surface indentation may expose the microencapsulated oil to the outside environment, which may result in fast oil oxidation. As the DE value of the maltodextrin in the microcapsules increased to 18, the existence of surface indentation, in most of the microcapsules, was almost diminished and had fewer surface dents than that of MD7.5 (Figs. 4.3a, c - 4.6a, c). As DE of the maltodextrin in the microcapsules was further increased to 24, most of the microcapsules presented spherically shaped, smoothed surfaced particles and were free of visible dents and holes (Figs. 4.3e - 4.6e).

When the microcapsules were prepared from SPI 2-based, effect of DE value on the outer topography of the microcapsules, similar to that described above, was observed (Figs. 4.7a, c, e - 4.10a, c, e). More wrinkled, and deep dented surface were found in the microcapsules prepared from MD7.5 (Figs. 4.7a - 4.10a) than in the microcapsules made from MD18 (Figs. 4.7c - 4.10c) or MD24 (Figs. 4.7e - 4.10e). Most of the microcapsules prepared with MD18 and MD24 exhibited spherical shape, and in some cases, slight surface wrinkles were observed on some of the microcapsules containing MD18, but were very limited on MD24-based microcapsules. Results also indicated that, microcapsules prepared from SPI 2-based exhibited similar outside topography to those prepared from SPI 1-based.

The inner structure of all the investigated microcapsules (Figs. 4.3b, d, f - 4.6b, d, f for SPI 1 microcapsules and Figs. 4.7b, d, f - 4.10b, d, f for SPI 2 microcapsules) was not affected by wall composition. Small soybean oil droplets ranging in diameter from about 0.1 to about 2 μm in SPI 1- and SPI 2-based microcapsules were evenly embedded throughout the wall matrices. In all cases of SPI 1 and SPI 2 microcapsules, a central void was found. The formation of the central void can be caused by the expansion of entrapped air, or entrapped steam pocket within the drying particle (Rosenberg, et al., 1988; Rosenberg & Young, 1993). Central void or hollow vacuoles are surrounded by porous walls of ~10 µm in thickness. These structure features were in agreement with those reported for spray-dried microcapsules consisting of WPI/maltodextrin, caseinate/maltodextrin, WPC, and SPI, reported by Kim & Morr (1996), Sheu & Rosenberg, (1998), Hogan et al. (2001), and Danviriyakul et al. (2002).

The relationships between surface dents and DE values of maltodextrin were in agreement with the findings of Danviriyakul et al. (2002); Rosenberg (1997) and Sheu & Rosenberg (1998) regarding spray-dried particles consisting of carbohydrate. These results indicated that carbohydrate type significantly affected the drying rate and rheological properties of the matrix, which are associated with the formation surface dents. It has been suggested that dent formation is related to uneven shrinkage of the atomized droplets at the early stages of spray drying (Rosenberg et al., 1985, 1988; Sheu & Rosenberg, 1998). At high drying rate, the thermal expansion of the air inside the drying particle can erase the dents. Thus, the effectiveness of dent smoothing is dependent on the drying rate and the viscoelastic properties of the wall matrix. Expansion of hot air and smoothing out of dents can occur only prior to solidification of the matrix when the wall matrix is elastic enough to allow hot air to erase the dents (Rosenberg, et al. 1985). Carbohydrates with different DE have different molecular weight. The difference of molecular weight resulted in differences in drying rate and elasticity of the wall matrix during spray drying (Danviriyakul et al. 2002; Sheu & Rosenberg, l998). As DE value increased, the proportion of low molecular weight carbohydrate increased and the average molecular weight decreased (Kenyon & Anderson, 1988). Low DE maltodextrin has high viscosity than high DE maltodextrin at the same concentration and temperature (Kenyon & Anderson, 1988). At the early stage of the drying, with the loss of water, a more rapid increase in viscosity in high molecular weight carbohydrate resulted in the fast formation of a dry crust at the surface of microcapsules. If the wall matrix was solidified before the expansion of the hot air, the hot air inside the drying particles could not erase the dents. Small molecular weight carbohydrate exhibited slower drying rates of the wall matrix due to the slow increase in viscosity of the wall matrix, and the wall materials was still elastic enough and allowed the hot air or water to erase the dents (Danviriyakul et a1.2002; Rosenberg et al., 1985, Sheu & Rosenberg, 1998). These results were in agreement with the surface-tension-driven, viscous flow mechanism suggested by Alexander & King (1985). Alexander & King (1985) suggested that a critical viscosity for folding exists, below which surface tension forces are sufficient to smooth out surface indentations or irregularities. This mechanism assumes a critical role of the viscoelastic properties of the drying matrix, which in turn is affected by the composition. The results suggested the importance of carbohydrate molecular weight in the wall system to the ultimate structural characteristics of the microcapsules.

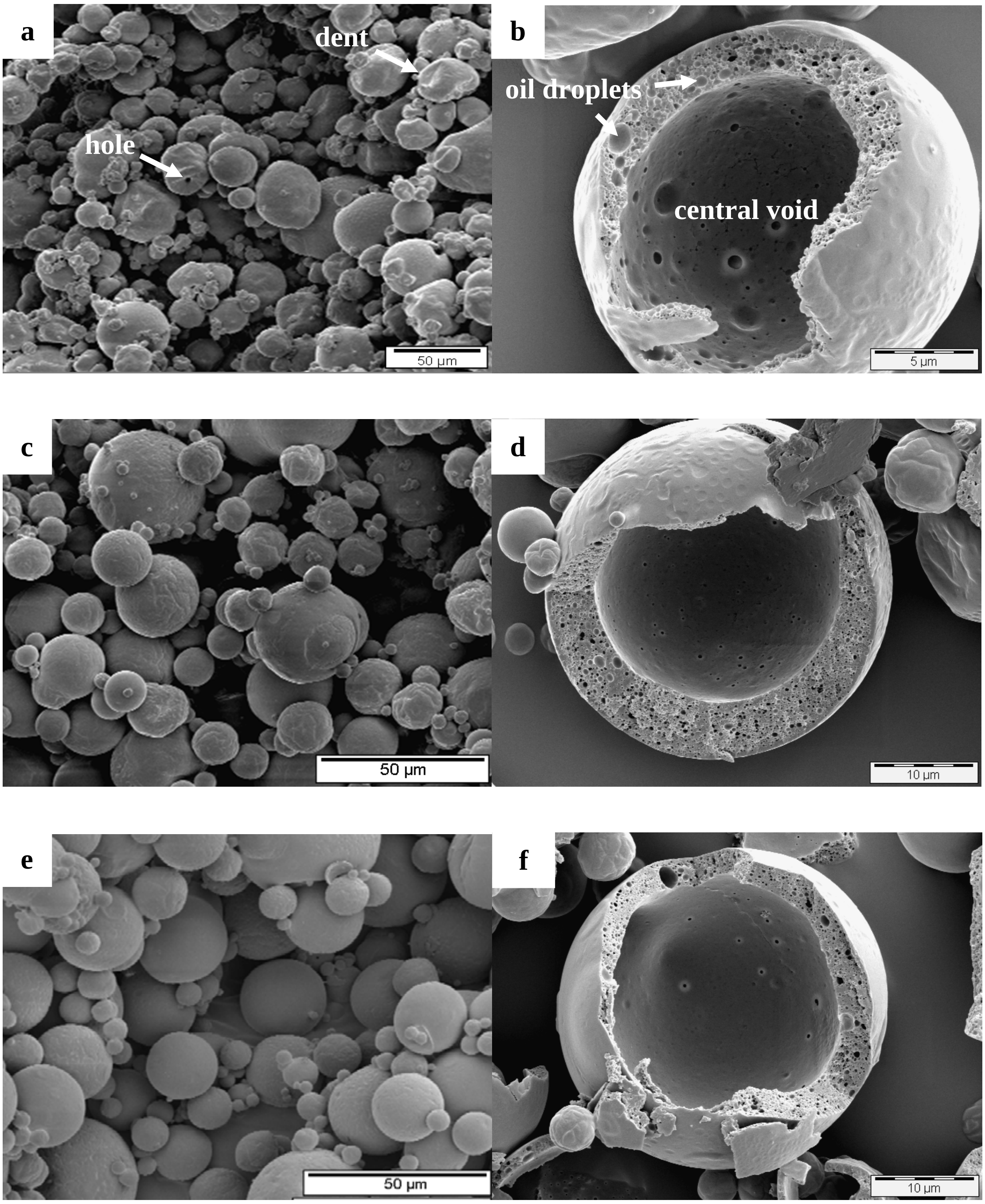

Fig. 4.3 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 25% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 1) /maltodextrin ratio of 1:7. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

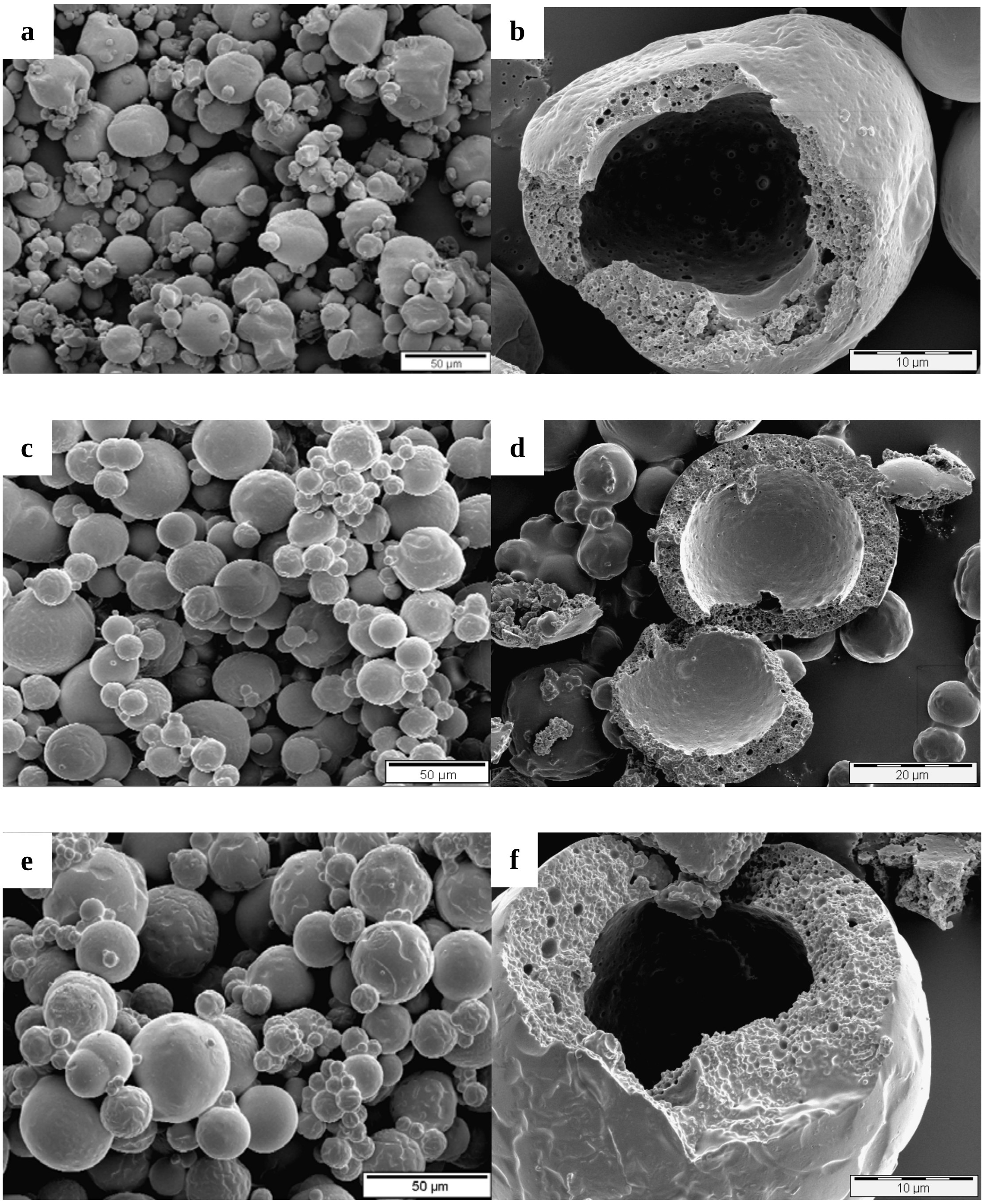

Fig. 4.4 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 1) /maltodextrin ratio of 1:7. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

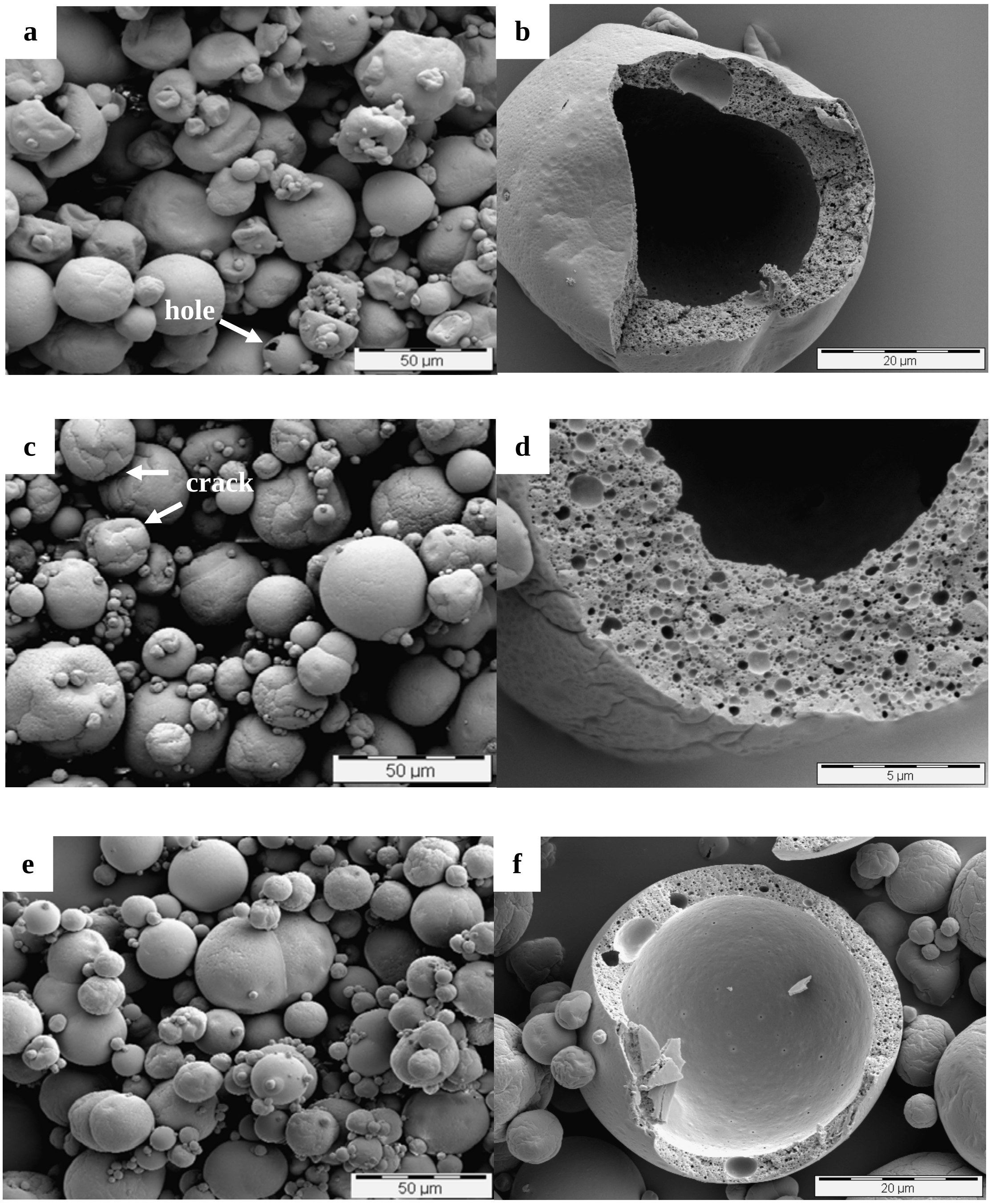

Fig. 4.5 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 25% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 1) /maltodextrin ratio of 1:3. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

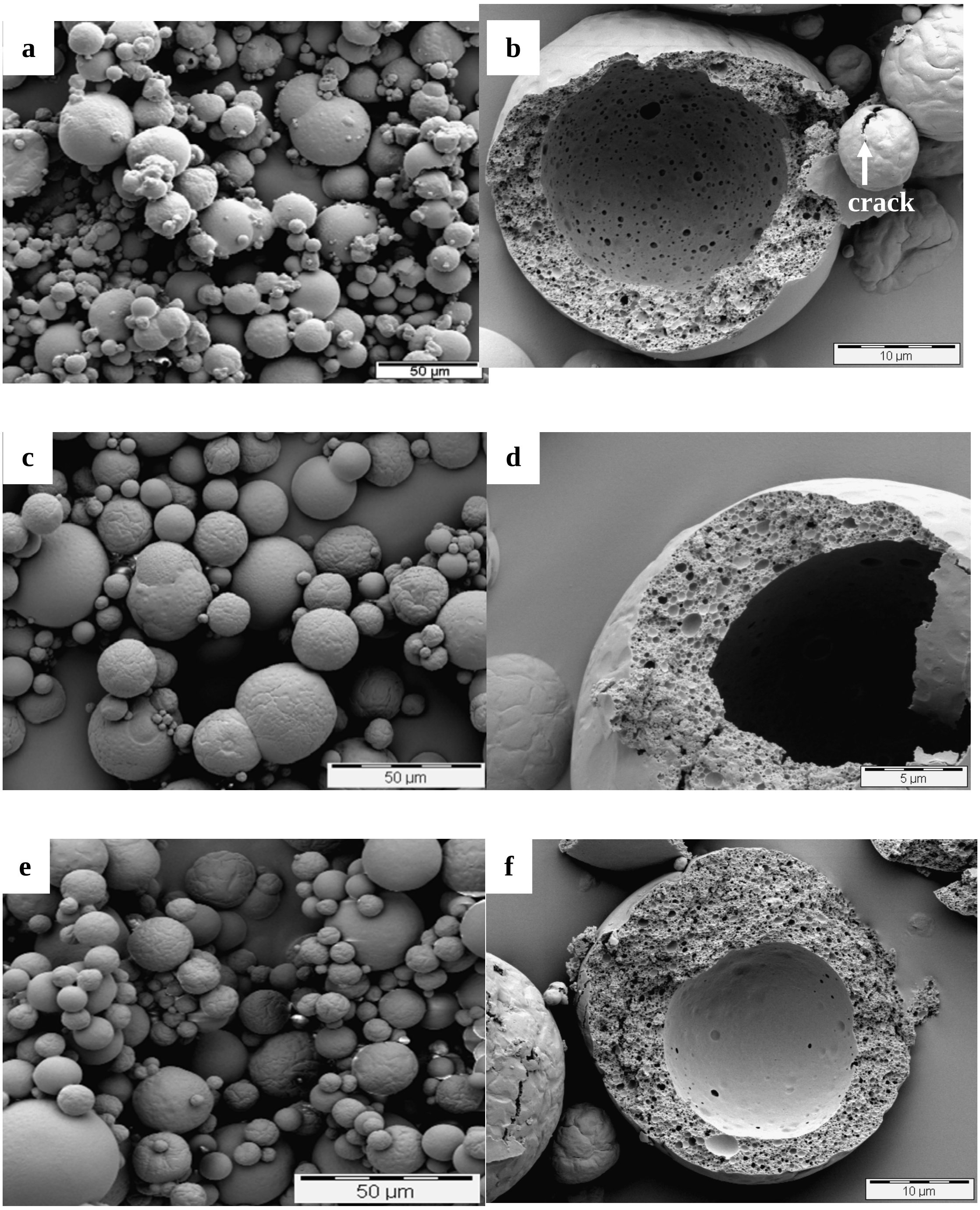

Fig. 4.6 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 1) /maltodextrin ratio of 1:3. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

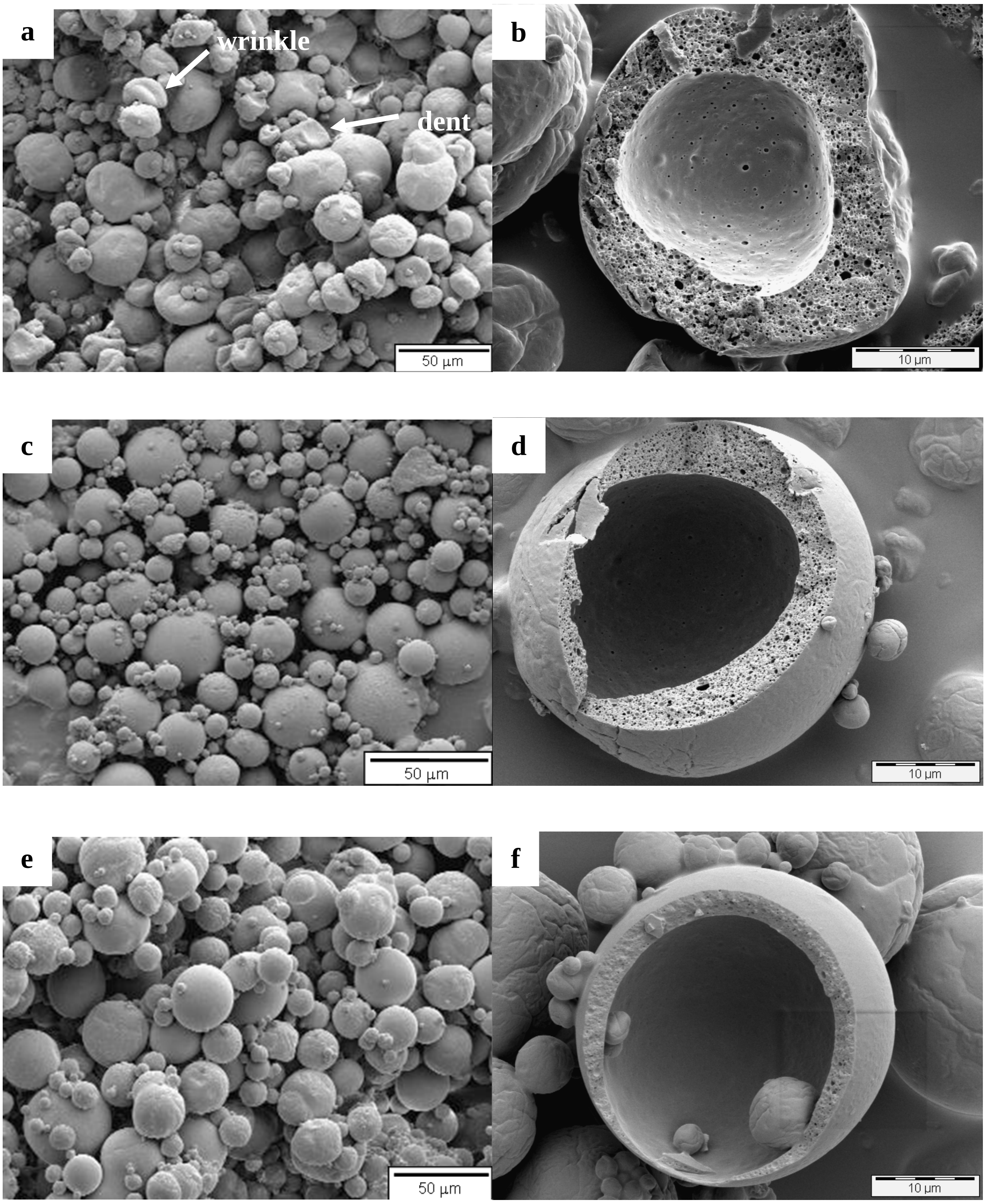

Fig. 4.7 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 25% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 2) /maltodextrin ratio of 1:7. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

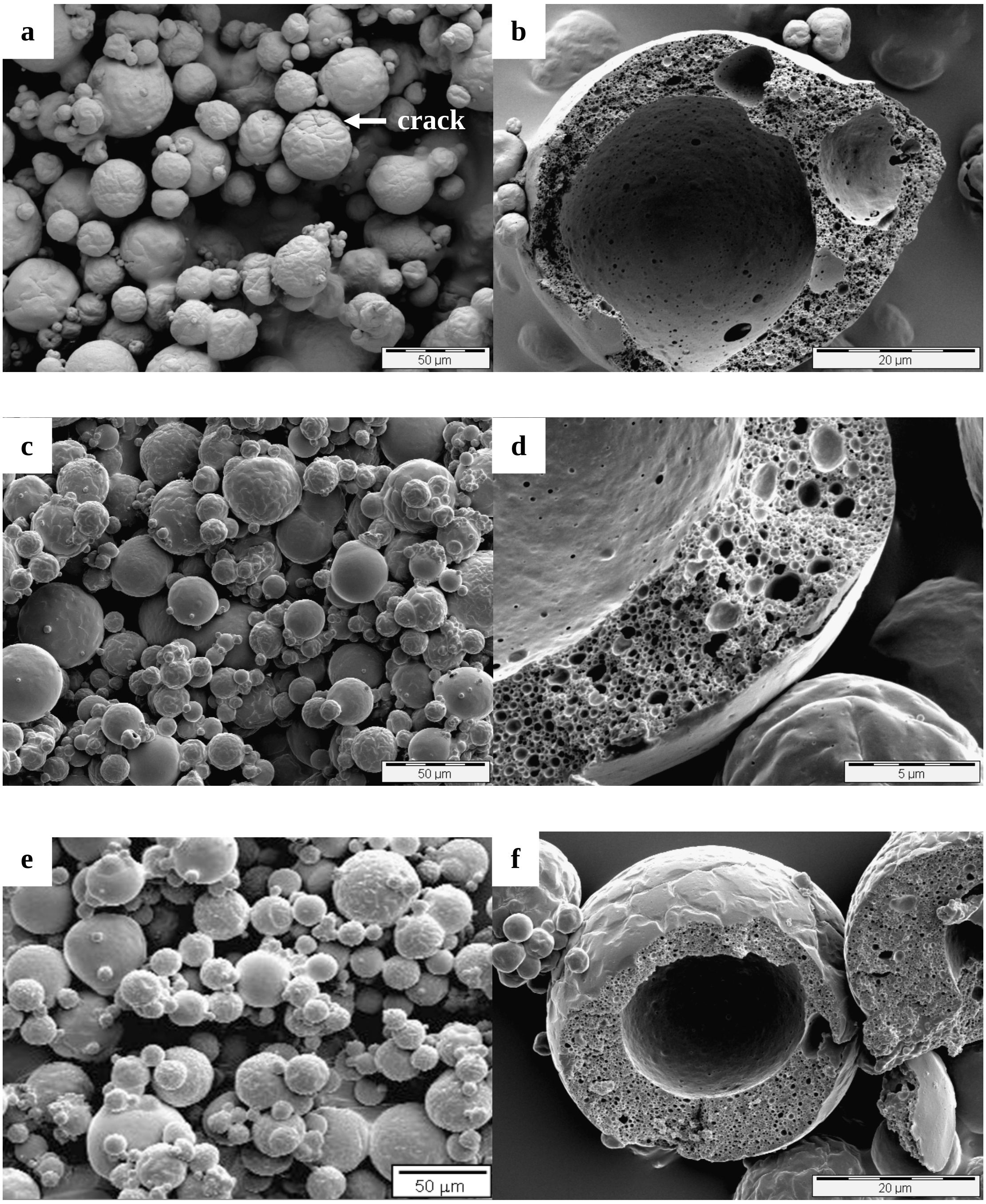

Fig. 4.8 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 2) /maltodextrin ratio of 1:7. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

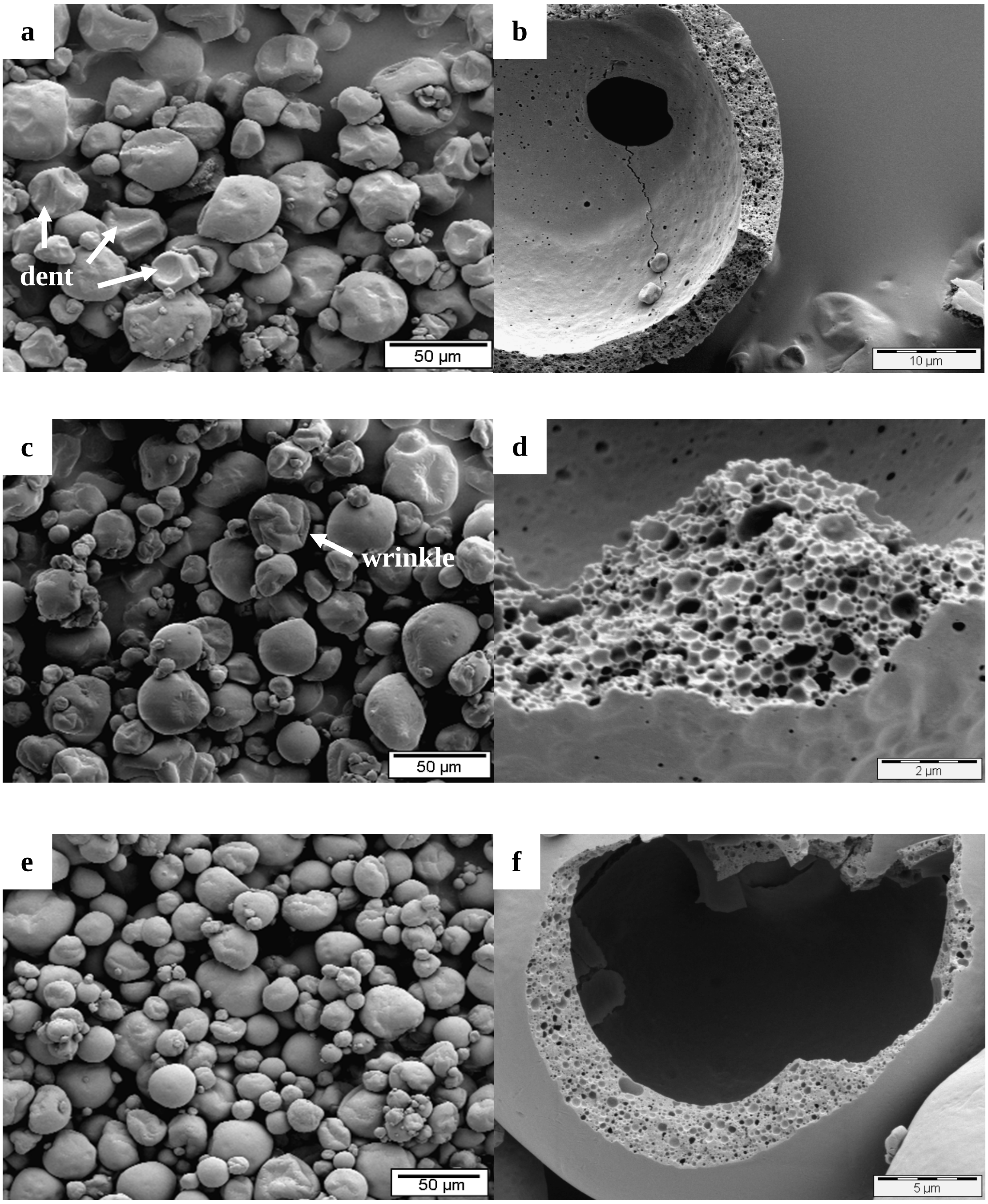

Fig. 4.9 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 25% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 2) /maltodextrin ratio of 1:3. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

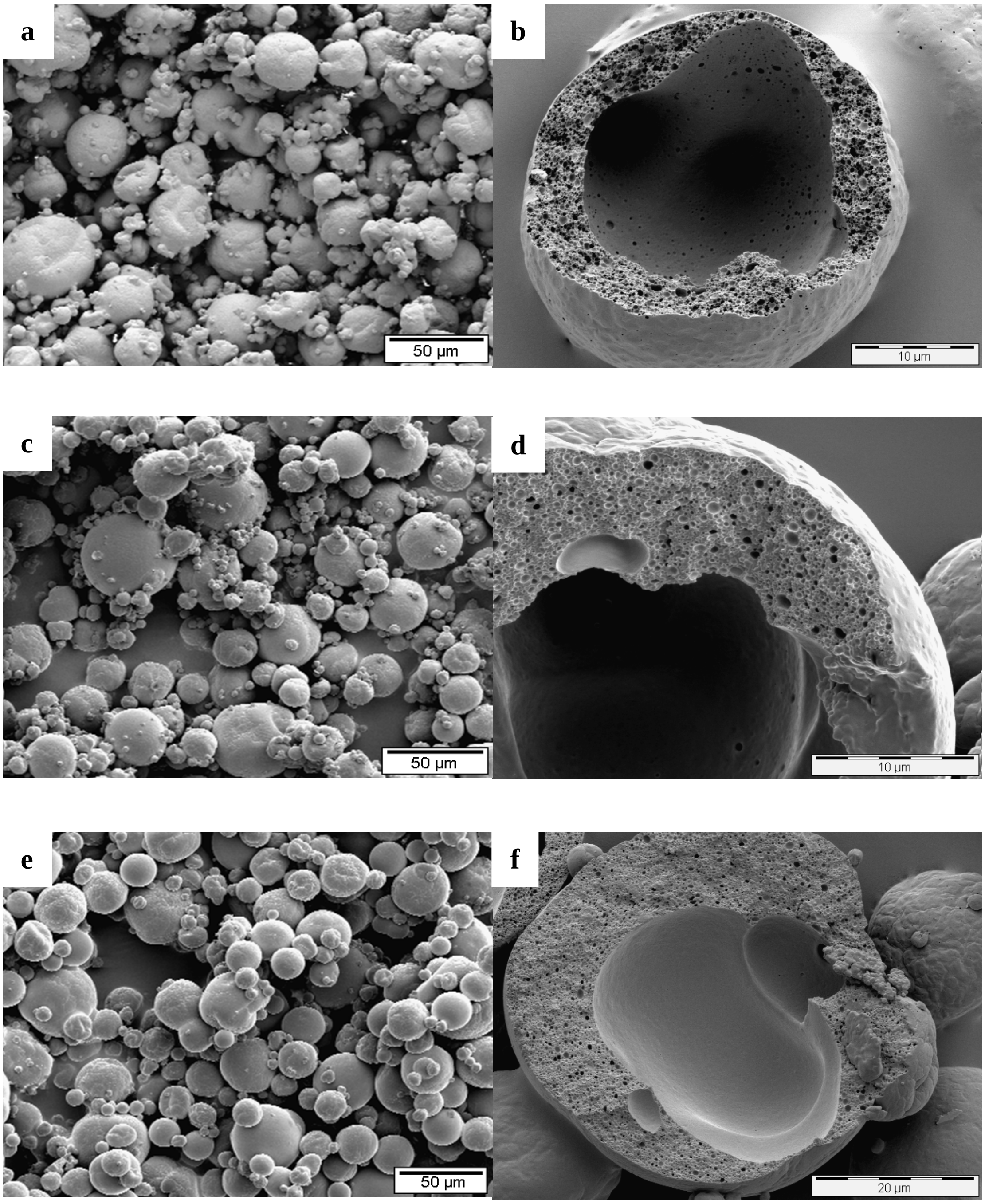

Fig. 4.10 Representative micrographs depicting the outer topography (a, c, e) and inner structure (b, d, f) of spray-dried microcapsules consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate (SPI 2) /maltodextrin ratio of 1:3. Maltodextrin had a DE value of 7.5 (a, b), 18 (c, d), and 24 (e, f).

4.4 Microencapsulation yield (MEY)

The retention of the core material during microencapsulation by spray drying is affected by the properties and composition of the emulsion, and by the influence of atomization and drying conditions (Moreau & Rosenberg, 1993; Reineccius, 1988; Rosenberg, Kopelman, & Talmon, 1990; Rosenberg & Young, 1993; Sheu, & Rosenberg, 1995). Theoretically, with nonvolatile core, an ideal microencapsulation process should result in no core loss during the process. Soybean oil is non-volatile material, but some losses did occur during spray drying. This loss due to soybean oil droplets were removed from the surface of the drying particles at an early stage of drying. The presence of soybean oil droplets on the outer surfaces of the particles related to atomization process and internal mixing within the drying particles at an early stage of drying (Young et al., 1993a, b). In order to understand the main factors that affect the core retention, it is important to understand the different phases during spray drying process. The first phase can be described as a steady-state process or a constant rate phase during water is removed, by a hot air, from the surface of the drying particles. Once a moisture content at the surface drops below saturation, an outer surface starts to dry until a crust is formed and signals the beginning of the second phase of spray drying, that is, a decreasing rate phase. A driving force that determined a drying rate during the first stage is the moisture content of the hot air and its flow rate around the drying particles. The second phase of the spray drying process is controlled by the rate of water diffusion from interior parts of the particle to the surface. This stage is influenced by the hindered diffusivity of water through the wall matrix. It has to be noted that due to the formation of moisture gradient from the surface of the drying particle inward, the drying rate during this stage exhibits an exponential decrease with time (Reineccius, 1988; Rosenberg et al., 1990). The high drying rates lead to rapid crust formation around the drying particles and then, the core retention increases. It has been suggested that core losses occur mainly prior to the formation of the dry crust, at the end of the constant drying rate phase of spray drying (Rosenberg et al., 1990).

The core retention, or the microencapsulation yield (MEY), was defined as the ratio (expressed as percentage) of microencapsulated oil load to the oil load in the emulsion (Young et al., 1993a). The effects of wall composition and oil load on the

MEY of the microcapsules prepared from SPI 1 and SPI 2-based systems are shown in Tables 4.3 and 4.4, respectively. The MEY higher than 70% was obtained with both of the investigated SPI 1 and SPI 2-based microcapsules. Results indicated that the effect of maltodextrin with different DE values on the MEY was significantly varied. These differences could be explained by a variety of reason. It could be explained as the difference of maltodextrin molecular weight. Maltodextrins with a higher DE value presents a smaller molecular weight than a lower DE maltodextrins. The higher MEY at the lower DE value was due to the higher viscosity of emulsion, with the higher molecular weight, led to slower drying rate, its influence on an internal mixing was more significant. The higher viscosity limited the internal mixing and thus promoted the MEY. Nevertheless, the higher MEY at the higher DE value was affected as carbohydrate enhances the drying rate and thus, led to a rapid formation of dry crust and therefore, to increase the core retention (Rosenberg, 1997).

Table 4.4 Effects of wall material type (SPI 1/MD) and oil load on properties of spray-dried microcapsules.

SPI 1/MD ratio	Oil load (% w/w)	DE value	MEY (%)	MEE (%)	Moisture content (% w/w)	Protein content (% w/w)	Oil content (% w/w)
1:7	25	7.5	71.24 ± 4.07^{a}	87.85 ± 0.43^{c}	0.26 ± 0.04^{a}	8.41 ± 0.37^{a}	17.81 ± 1.02^{a}
		18	75.07 ± 9.30^{a}	91.79 ± 0.41^{b}	0.30 ± 0.09^{a}	8.54 ± 0.07^{a}	18.77 ± 2.33^{a}
		24	83.25 ± 1.75^{a}	93.26 ± 0.29^{a}	0.24 ± 0.01^{a}	7.90 ± 0.27^{a}	20.81 ± 0.44^{a}
1:7	50	7.5	73.97 ± 5.36^{b}	54.13 ± 2.77^{b}	0.26 ± 0.06^{b}	5.61 ± 0.39^{a}	36.98 ± 2.68^{b}
		18	87.55 ± 2.11^{a}	83.32 ± 1.21^{a}	0.30 ± 0.02^{b}	6.00 ± 1.06^{a}	43.77 ± 1.05^{a}
		24	72.77 ± 6.07^{b}	83.69 ± 0.44^{a}	0.44 ± 0.04^{a}	6.51 ± 0.58^{a}	36.38 ± 3.04^{b}
1:3	25	7.5	78.24 ± 4.16^{b}	87.78 ± 0.84^{c}	1.28 ± 0.10^{a}	16.52 ± 0.08^{a}	19.56 ± 1.04^{b}
		18	88.96 ± 0.89^{a}	98.05 ± 0.49^{a}	0.72 ± 0.08^{b}	17.06 ± 0.79^{a}	22.24 ± 0.22^{a}
		24	81.06 ± 3.49^{b}	93.89 ± 0.23^{b}	0.87 ± 0.11^{b}	15.88 ± 1.22^{a}	20.27 ± 0.87^{b}
1:3	50	7.5	77.94 ± 5.28^{ab}	48.40 ± 1.61^{b}	1.05 ± 0.20^{a}	12.25 ± 0.32^{a}	38.97 ± 2.64^{ab}
		18	75.77 ± 2.33^{b}	93.19 ± 0.36^{a}	0.20 ± 0.08^{b}	12.19 ± 0.86^{a}	37.89 ± 1.17^{b}
		24	83.58 ± 2.32^{a}	93.87 ± 0.54^{a}	0.18 ± 0.01^{b}	11.99 ± 0.56^{a}	41.79 ± 1.16^{a}

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

Table 4.5 Effects of wall material type (SPI 2/MD) and oil load on properties of spray-dried microcapsules.

SPI 2/MD ratio	Oil load (% w/w)	DE value	MEY (%)	MEE (%)	Moisture content (% w/w)	Protein content (% w/w)	Oil content (% w/w)
1:7	25	7.5	83.35 ± 1.55^{b}	93.28 ± 0.85^{b}	0.77 ± 0.10^{b}	8.95 ± 0.07^{a}	20.84 ± 0.39^{b}
		18	82.69 ± 1.81^{b}	91.10 ± 0.39^{c}	2.17 ± 0.17^{a}	8.52 ± 0.29^{a}	20.67 ± 0.45^{b}
		24	89.99 ± 2.12^{a}	96.85 ± 0.18^{a}	0.88 ± 0.26^{b}	8.33 ± 0.30^{a}	22.50 ± 0.53^{a}
1:7	50	7.5	86.76 ± 1.81^{a}	74.41 ± 2.75^{c}	0.38 ± 0.07^{b}	6.58 ± 0.28^{a}	43.38 ± 0.91^{a}
		18	79.59 ± 1.73^{b}	89.11 ± 0.69^{b}	0.16 ± 0.07^{c}	6.36 ± 0.28^{a}	39.79 ± 0.86^{b}
		24	89.21 ± 1.94^{a}	93.00 ± 0.24^{a}	0.58 ± 0.14^{a}	5.89 ± 0.61^{a}	44.61 ± 0.97^{a}
1:3	25	7.5	84.88 ± 0.82^{a}	91.25 ± 1.12^{b}	0.90 ± 0.28^{a}	18.10 ± 0.55^{ab}	21.22 ± 0.20^{a}
		18	83.05 ± 1.52^{a}	96.40 ± 0.20^{a}	0.62 ± 0.10^{a}	15.65 ± 0.37^{c}	20.76 ± 0.38^{a}
		24	86.44 ± 6.68^{a}	95.53 ± 0.39^{a}	1.08 ± 0.16^{a}	17.48 ± 0.76^{bc}	21.61 ± 1.67^{a}
1:3	50	7.5	86.29 ± 5.12^{a}	71.44 ± 1.48^{b}	0.73 ± 0.03^{a}	11.58 ± 0.56^{a}	43.15 ± 2.56^{a}
		18	89.97 ± 2.79^{a}	93.17 ± 0.13^{a}	0.21 ± 0.00^{c}	12.28 ± 0.64^{a}	44.99 ± 1.39^{a}
		24	78.67 ± 3.12^{b}	93.91 ± 0.32^{a}	0.40 ± 0.08^{b}	10.93 ± 0.34^{a}	39.33 ± 1.56^{b}

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

4.5 Microencapsulation efficiency (MEE)

Microencapsulation efficiency (MEE) is an important parameter that have been used to evaluate the quality of microencapsulated products. The MEE, as determined in this work, represents not only the proportion of oil present on the microcapsule surfaces but also a fraction of the microencapsulated oil extracted from the interior parts of the capsules by a leaching process (Young et al., 1993a). The effects of wall composition and oil load on MEE are presented in Tables 4.4 and 4.5 for SPI 1 and SPI 2-based systems, respectively. Increasing the DE values of MD resulted in higher MEE in all cases, for both of SPI-based systems, which is consistent with the previous reports (Danviriyakul et al., 2002; Hogan et al., 2001; Sheu & Rosenberg, 1995; Young et al., 1993b). The lowest MEE values were observed in the SPI/MD7.5-based systems which significantly increased as a function of DE value up to DE18, followed by a slight increase up to DE24. These results are consistent with those reported for WPI/carbohydrate and caseins/carbohydrate wall systems (Danviriyakul et al., 2002; Hogan et al., 2001; Sheu & Rosenberg, 1995; Young et al., 1993b). This effect was more pronounced at the high oil load. Increasing the oil load resulted in a decrease in MEE, regardless of the wall material used; however, the SPI/MD7.5-based systems were more sensitive to the oil load than the other systems and showed a more profound decrease in MEE as a function of oil load. This is in agreement with those reported by Young et al. (1993a). The explanation for these phenomena could be made mainly based on the outer and inner structure of the spray-dried microcapsules as discussed earlier. MEE decreased with an increase in oil load. At a given wall composition, increasing core content increased the number of core droplets embedded in a unit volume of wall matrix. This resulted in thinner wall layers separating core droplets from each other. The thinner matrix layer represented a shorter diffusional path and the overall amount of core could be extracted increased and led to a lower MEE.

MEE reflected the presence of oil on powder particle surfaces and the degree to which the wall matrix could prevent extraction of internal oil by a leaching process (Moreau & Rosenberg, 1993; Young et al., 1993b). High DE maltodextrins, which presented small molecule, exhibited high MEE, suggesting that the chain length of the polysaccharide significantly affected the physicochemical properties and structural of the powders. Powders containing smaller polysaccharide molecules (high DE value) normally had smoother surfaces and uniform models than powders containing larger polysaccharide molecules (low DE value) (Sheu & Rosenberg, 1995). In most cases, powders containing high molecular weight carbohydrates exhibited cracks and holes on the surface, which exposed the microencapsulated oil to the extracting solvents (Sheu and Rosenberg, 1995). In addition, powders made from polysaccharide containing high proportion of high molecular weight constituents exhibited deep folds and wrinkles in contrast to the fold and wrinkle-free powders made from small molecular weight carbohydrates. This kind of surface imperfection damaged the surface integrity of the spheres and may have increased the actual surface area compared to smooth sphere in the powder made from small molecular weight polysaccharides, and subsequently, facilitated the access of the extracting solvent to the core material and increased the extractable oil content (Caric & Kalab, 1987). During spray drying, the viscosity of the emulsion increased because of the loss of water, which changed the physical state of drying material from liquid to rubber and eventually to glass state. With a lower viscosity, structural collapse in the presence of small molecular weight carbohydrate could lead to a formation of a dense wall matrix around the oil droplets, preventing the accessibility of oil to the solvents and therefore reducing the amount of extractable oil. A more rapid increase in viscosity, at the early stage of spray drying, in the presence of a higher molecular weight polysaccharide may retard the formation of impermeable micro-regions entrapping the encapsulated material. It has also been indicated that the presence of high proportion of low molecular weight carbohydrates led to the formation of a glassy phase upon spray drying (Grattard, Salaun, Champion, Roudaut, & Le Meste, 2002). This phase demonstrated resistance to solvent diffusion and led to lower core extractability resulting in higher MEE.

Che Man, Irwandi, & Abdullah (1999) mentioned that differences in DE value suggested differences in the hydrophilic nature of maltodextrins. It could be supposed that MD24 exhibited higher hydrophilic properties than MD7.5 and MD18, therefore, it was more resistant to be accessible by the non-polar solvent. During spray drying, it was also found that the powder made with MD24 tended to stick to the wall of the spray dryer, this was attributed to the greater hygroscopicity of the powder made with MD24 than that of the powders made with low DE value.

4.6 Physicochemical properties of spray-dried microcapsules

Moisture, protein, and oil contents of the microcapsules obtained from all treatments are presented in Tables 4.4 and 4.5 for SPI 1- and SPI 2-based systems, respectively. Moisture contents of the spray-dried microcapsules varied, from 0.2% to 1.3% for SPI 1- based system and 0.2% to 2.2% for SPI 2-based system, and were not affected by any of the treatments. This is consistent with the observations of Hogan et al. (2001), who found that moisture content was not affected by type of wall material or oil load. As expected, both of the SPI-based systems, the systems with higher SPI/MD ratio exhibited higher protein content than those with lower SPI/MD ratio. The systems with higher oil load had lower protein contents regardless of the wall type due to dilution effect of the oil. It was not surprising that the oil contents of the systems with 50% oil load (37-44% and 39-45% for SPI 1- and SPI 2-based systems, respectively) approximately doubled those of the 25% oil load systems (18-22% and 21-23% for SPI 1- and SPI 2-based systems, respectively). In all cases, however, these oil contents were significantly lower than the corresponding initial oil loads (MEY < 100%), indicating some losses did occur during microencapsulation process. Even though soybean oil is not a volatile material, some losses have been reported to occur during spray drying. This can most probably be attributed to the oil droplets that were present at the surface of emulsion droplets leaving the atomizer, or those that migrated to the surface prior to the formation of dry crust around the drying particles, were swept off the particle surface. This could be the result of the combined effect of the high air turbulence around the drying particles and of water vapors leaving the outer surfaces of these particles (Young et al., 1993a).

In this study, the system consisting of SPI 1/MD18 ratio of 1:3 and 50% oil load was chosen for subsequent experiments due to its high MEE (93%) and oil load. Using the highest possible oil load that provides high MEE is advantageous because the effect of wall materials (after reconstitution of microcapsules) on physicochemical characteristics of the product could be minimized. The MD18 would probably be selected as the most suitable wall component in combination with SPI 1 as it has high solubility, bland in flavor, low sweetness, and hygroscopicity (McNamee et al., 2001).

4.7 Physical properties of spray-dried microcapsules

Physical properties of the chosen spray-dried microcapsules are presented in Table 4.5. The spray-dried microcapsule exhibited a monomodal particle size distribution (Fig. 4.11). Mean particle size of the microcapsules was very small (20 μm) and can be classified as very fine particles (Masters, 1991), which is a typical characteristic of the powders obtained from small scale spray dryers (Jinapong et al., 2008). The particle density (ρ_{particle}) was lower than that of the other spray-dried products reported in our previous work (Jinapong et al., 2008), confirming the existence of a large central void in each microcapsule (Fig. 4.4d).

In terms of handling properties, a large difference between the bulk (ρ_{bulk}) and tapped densities (ρ_{tapped}) of the microcapsules resulted in a high Carr index (CI) and Hausner ratio (HR), indicating its poor flowability and high cohesiveness as classified in Tables 3.2 and 3.3, respectively. This poor flowability at small particle sizes is due to the large surface area per unit mass of powder. There is more contact surface area between powder particles available for cohesive forces, in particular, and frictional forces to resist flow (Fitzpatrick, 2005; Fitzpatrick, Iqbal, Delaney, Twomey, & Keogh, 2004). Moreover, the spray-dried microcapsules obtained in this study contained 38% oil (Table 4.3). This high oil content also caused the powder to have very poor flowability (Fitzpatrick et al., 2004). Due to when the fat content increased, the uncoated fat increased that acted as a binder, and cohesiveness increased, producing lumpy chunks and poorer flowability (Onwulata, 2005).

In terms of reconstitution properties, dried milk products were used as a reference of this study due to they were used as a universal model for most of food powders. The recommended values of dried milk products are less than 15 s for the wettability value (A/S Niro Atomizer, 1978a) and are not less than 85% for the dispersibility value (Barbosa-Cánovas, Ortega-Rivas, Juliano, & Yan, 2005). From our results, the spray-dried microcapsules exhibited very poor wettability with a wetting time of 147 s and a fairly good dispersibility of 93%. In general, it is known that water wets very fine powders poorly because of its high surface tension (Schubert, 1993). Additionally, the high levels of surface oil in the case of high oil load microcapsules could also cause poor wettability. A bed of powder remained on the surface of water, with a viscous layer stopping capillary flow in the interparticle porosity (Vu, Galet, Fages, & Oulahna, 2003).

It can be concluded that the spray-dried microcapsules had poor handling and reconstitution properties which could be improved by further agglomeration.

Table 4.6 Properties of soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules.

Properties	
Particle size, $d_{4,3}$ (μm)	20.43 ± 0.34
ρ_{bulk} (g/cm^3)	0.27 ± 0.01
ρ_{tapped} (g/cm^3)	0.45 ± 0.00
ρ_{particle} (g/cm^3)	1.11 ± 0.01
Porosity (%)	60.84 ± 1.16
CI (%)	39.26 ± 2.57
HR	1.65 ± 0.07
Wetting time (s)	146.67 ± 19.09
Dispersibility (%)	93.12 ± 2.21
Friability (%)	N/A[1]

[1] N/A = not applicable.

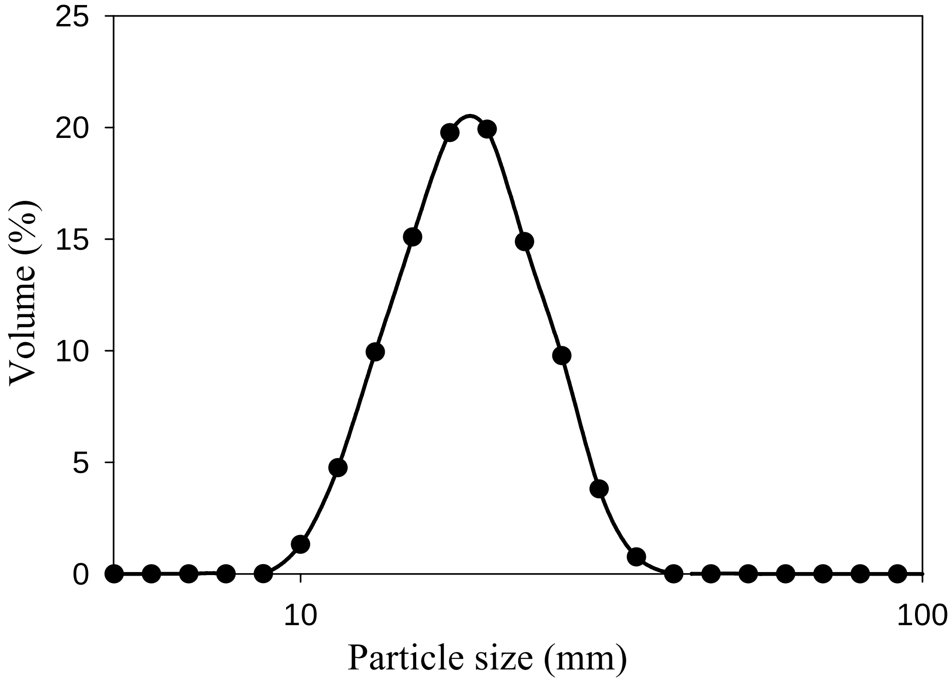

Fig. 4.11 Particle size distribution of spray-dried soybean oil powder.

4.8 Effect of kinds of binder on physical, morphological characteristics, handling and reconstitution properties of agglomerated microcapsules

4.8.1 Physical and morphological characteristics of agglomerated microcapsules

Physical properties of the agglomerated spray-dried microcapsules as a function of kinds of binder are presented in Table 4.7. After fluidized bed agglomeration, larger agglomerates were obtained with a geometric mean diameter ranged from 363 to 685 μm depending on the kinds of binder used (Table 4.7). The size distributions were generally found to be in good agreement with the log-normal distribution (R^2 = 0.957-0.988) (see Tables A 1-A 3 and Figs. A 1-A 3). The particle size distributions of the agglomerates obtained with different kinds of binder are presented in Fig. 4.12. In all cases, the agglomerates exhibited a similar monomodal size distribution with different geometric standard deviations (Table 4.7) and negligible amounts (<5%) of the fine particles (<125 μm) retained on the pan. This result indicates that the kinds of binder affected both the mean particle sizes and particle size distributions of the resultant agglomerated powders which in turn influenced their physical and reconstitution properties.

Results show that the moisture contents of agglomerated powders were significantly higher than that of the corresponding spray-dried powders, implying a more complex structure of the large agglomerates. The agglomeration of the spray-dried powder also occurred by using distilled water, indicating that a part of the powder dissolved during agglomeration which eventually acted as a binder.

The bulk densities of the agglomerated powders were comparable to that of the spray-dried powders (0.27 g/cm^3), whereas the tapped densities were significantly lower (~0.35 vs 0.45 g/cm^3). The reason for the lower tapped density observed for the agglomerates with small percentage (<5%) of fine particles is simply that there are not enough fine particles to fill the voids in between the large particles. The fines percentage which gives maximum tapped density is in the range of 20-40% (Abdullah & Geldart, 1999; Jinapong et al., 2008). The intergranular porosities of the agglomerates were slightly higher than that of the spray-dried powders (61%), reflecting their lower tapped densities. The exception is the agglomerates prepared using MD10 as a binder which exhibited porosity lower than that of the spray-dried powders, resulting in the highest tapped density. In most cases, the particle densities of the agglomerates were lower than that of the spray-dried powder (1.11 g/cm^3), indicating a more porous structure of the agglomerates.

The agglomerate prepared with water as a binder had the highest friability compared with those obtained using MD as a binder, indicating the strengthening of solid bridge by MD during agglomeration process.

Table 4.7 Physical properties of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different kinds of binder.

Treatments	Moisture (%)	Particle size (µm)	ρ_{bulk} (g/cm^3)	ρ_{tapped} (g/cm^3)	ρ_{particle} (g/cm^3)	Porosity (%)	Friability (%)
Distilled water	1.74 ± 0.20^c	362.59 ± 2.36	0.26 ± 0.01^c	0.33 ± 0.01^c	0.83 ± 0.06^c	60.69 ± 3.91^b	49.58 ± 1.46^a
MD10	3.78 ± 0.18^a	685.38 ± 1.65	0.34 ± 0.01^a	0.40 ± 0.00^a	0.98 ± 0.12^{bc}	58.68 ± 4.57^b	28.76 ± 0.74^d
MD14	3.00 ± 0.11^b	508.76 ± 1.79	0.26 ± 0.00^c	0.31 ± 0.00^d	1.14 ± 0.06^{ab}	72.48 ± 1.39^a	44.18 ± 1.25^b
MD18	3.48 ± 0.13^a	668.83 ± 1.59	0.30 ± 0.00^b	0.36 ± 0.00^b	0.99 ± 0.14^{bc}	63.14 ± 5.39^b	31.56 ± 1.20^c

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

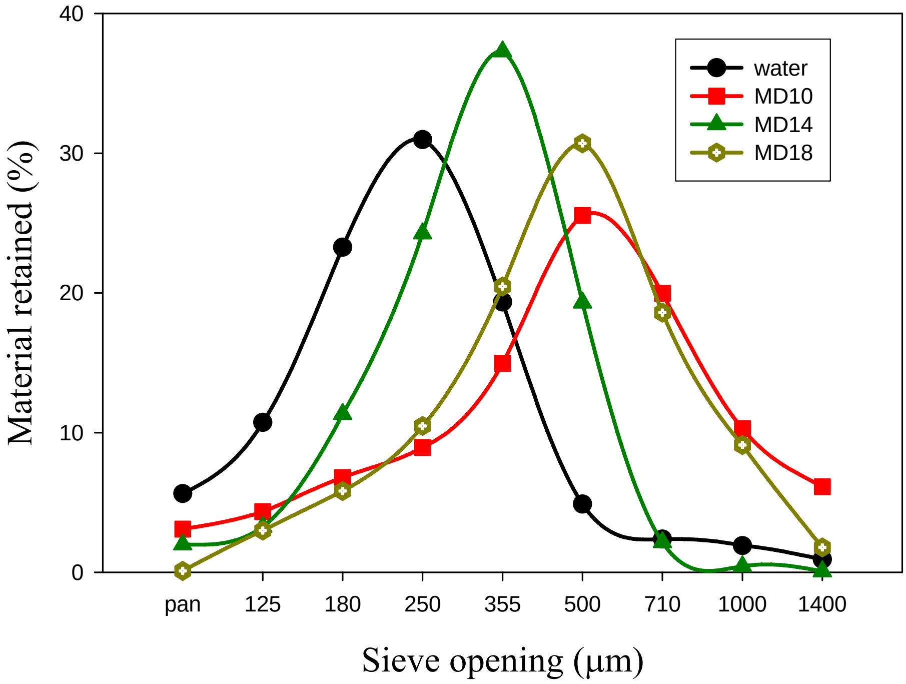

Fig. 4.12 Particle size distributions of agglomerated spray-dried microcapsules produced from emulsion consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate/maltodextrin (DE18) ratio of 1:3. Agglomeration was performed by using an aqueous solution of different kinds of maltodextrin as a binder.

4.8.2 Handling and reconstitution properties of agglomerated microcapsules

The handling and reconstitution properties of the agglomerates obtained with different kinds of binder are presented in Tables 4.8 and 4.9, respectively. In all cases, the Carr index (CI) and Hausner ratio (HR) of the agglomerates (Table 4.8) were significantly lower than those of the spray-dried powder (Table 4.6). This can be interpreted mainly as the effect of size enlargement. Size enlargement by agglomeration seemed to improve flow characteristics of the powders. As particle size increased, the cohesiveness of powder was expected to decrease due to their weaker interparticle forces (Abdullah & Geldart, 1999). Results also show that the CI and HR values of agglomerates significantly decreased with increasing geometric mean diameter of agglomerates prepared by different kinds of binder. However, the kinds of binder had no significant effect on CI and HR of the agglomerates. It has been reported that the mean particle size and particle size distribution had a major influence on powder flowability (Jinapong et al., 2008). The coarser powder in the absence of the fine particles flowed better, as expected.

From the reconstitution properties data (Table 4.9), it can be inferred that the fluidized bed agglomeration markedly improved the wettability of the powders from the wetting time of 147 s for the spray-dried powder (Table 4.6) to a satisfactory level ranged from 4 to 5 s for the agglomerates obtained with different kinds of binder. The dispersibility also increased from 93% for the spray-dried powder (Table 4.6) to 93-98% for the agglomerates. It is known that size enlargement by agglomeration not only increases the rate of water penetration into the space between the agglomerates, but also the capillary-driven flow of water into the fine pores within the agglomerates and consequently shortens the wetting time (Carić, 2003; Schubert, 1993). From the point of view of dispersibility, the particle adhesion within the agglomerates should be strong enough to avoid abrasion during packaging and transportation, but should largely dissolve in an aqueous environment, preferably with minimum mechanical energy. In the reconstituted dispersion, the particles should neither float to the surface nor sediment to the bottom of the container within a certain time period (Schubert, 1993). In this study, the kinds of binder had no significant effect on wettability of the resultant agglomerates. Whereas, the system containing MD14 as a binder presented the highest dispersibility and were considered to be excellent. This can possibly due to their large particle sizes (>500 μm) with negligible amounts of the fine particles (< 5%). From these reasons, this system was chosen for subsequent experiments.

Table 4.8 Flow characteristics (Carr index, CI, and Hausner ratio, HR) of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different kinds of binder.

Treatments	CI (%)	HR
Distilled water	19.96 ± 2.04^a	1.25 ± 0.03^a
MD10	16.67 ± 1.44^a	1.20 ± 0.02^a
MD14	16.03 ± 1.86^a	1.19 ± 0.03^a
MD18	15.74 ± 1.60^a	1.19 ± 0.02^a

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

Table 4.9 Reconstitution properties (wettability and dispersibility) of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different kinds of binder.

Treatments	Wetting time (s)	Dispersibility (%)
Distilled water	4.83 ± 0.75^a	95.13 ± 0.67^b
MD10	4.67 ± 0.58^a	92.52 ± 1.24^b
MD14	3.50 ± 0.55^a	97.95 ± 2.06^a
MD18	4.00 ± 0.00^a	93.21 ± 1.06^b

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

4.9 Effect of binder concentrations on physical, morphological characteristics, handling and reconstitution properties of agglomerated microcapsules

4.9.1 Physical and morphological characteristics of agglomerated microcapsules

Physical properties of the agglomerated spray-dried microcapsules as a function of binder concentrations are presented in Table 4.10. All the physical properties of agglomerates were significantly affected by the binder concentration. After fluidized bed agglomeration, larger and more irregular agglomerates were obtained (Fig. 4.13) with a geometric mean diameter ranged from 363 to 657 μm depending on the binder concentrations used (Table 4.10). The size distributions were generally found to be in good agreement with the log-normal distribution (R^2 = 0.929-0.988) (see Tables A 2, A 4-A7 and Figs. A 2, A 4-A 7). The particle size distributions of the agglomerates obtained with different binder concentrations are presented in Fig. 4.14. In all cases, the agglomerates exhibited a similar monomodal distribution with different geometric standard deviations (Table 4.10) and negligible amounts (<6%) of the fine particles (<125 μm) retained on the pan. This result indicates that the binder concentrations affected both the mean particle sizes and particle size distributions of the resultant agglomerated powders which in turn influenced their physical and reconstitution properties.

Results show that the moisture contents of agglomerated powders were significantly higher than that of the corresponding spray-dried powders, implying a more complex structure of the large agglomerates. The agglomerate sizes increased, whereas the friability decreased as the concentration of binder solutions was increased from 0% up to 15%. However, a further increase in the binder concentrations up to 20% resulted in smaller and more friable agglomerates. The agglomeration of the spray-dried powder also occurred by using distilled water, i.e. 0% binder concentration, indicating that a part of the powder dissolved during agglomeration which eventually acted as a binder. It is possible that optimum binder concentration is reached at the 15% level, which can be in correlation with the largest particle size of agglomerates (657 µm) and its lowest friability (33%). From the geometric standard deviation data, it can be inferred that the particle size distributions became narrower as the binder concentration was increased from 0 to 15%. Beyond this binder concentration, a wider size distribution was observed. These results could be interpreted that at lower binder concentrations, the particles were coated with only a small proportion of binder which bonded the powder particles together, while at higher binder concentrations exceeding the optimum level, the binder started to spread over the particles in several layers and the cohesion of binder molecules to each other was such that the powder particles were not bonded to each other by a binder bridge (Jinapong et al., 2008; Planinšek, Pišek, Trojak, & Srčìč, 2000; Rohera & Zahir, 1993; Tüske, Regdon, Erős, Srčìč, & Pintye-Hódi, 2005). Therefore, when the amount of binder added to the powders was increased beyond the optimum level, the friability of the agglomerates became higher. Also, at the equilibrium agglomeration state, the weight of the agglomerates exceeded the strength of the interparticle bond. The gravitational force due to the weight of agglomerates along with forces of shearing among the particles and between particles and fluidizing chamber, induced by the fluidizing air, caused the agglomerates to break apart, consequently, reduced the particle size (Jinapong et al., 2008; Rohera & Zahir, 1993; Turchiuli et al., 2005a).

The bulk densities of the agglomerated powders were comparable to that of the spray-dried powders (0.27 g/cm^3), whereas the tapped densities were significantly lower (~0.33 vs 0.45 g/cm^3). The reason for the lower tapped density observed for the agglomerates with small percentage (<6%) of fine particles is simply that there are not enough fine particles to fill the voids in between the large particles. The fines percentage which gives maximum tapped density is in the range of 20-40% (Abdullah & Geldart, 1999; Jinapong et al., 2008). The intergranular porosities of the agglomerates were slightly higher than that of the spray-dried powders (61%), reflecting their lower tapped densities. In most cases, the particle densities of the agglomerates were lower than that of the spray-dried powder (1.11 g/cm^3), indicating a more porous structure of the agglomerates (Fig. 4.13). A morphological study revealed that all the agglomerates produced with the different binder concentrations exhibited a loose, porous structure and an irregular shape (Fig. 4.13). The particle sizes estimated from the visual inspection of the micrographs are consistent with those determined by the sieve analysis.

4.9.2 Handling and reconstitution properties of agglomerated microcapsules

The handling and reconstitution properties of the agglomerates obtained with different binder concentrations are presented in Tables 4.11 and 4.12, respectively. In all cases, the Carr index (CI) and Hausner ratio (HR) of the agglomerates (Table 4.11) were significantly lower than those of the spray-dried powder (Table 4.6). This can be interpreted mainly as the effect of size enlargement. Size enlargement by agglomeration seemed to improve flow characteristics of the powders. As particle size increased, the cohesiveness of powder was expected to decrease due to their weaker interparticle forces (Abdullah & Geldart, 1999). Results also show that the CI and HR values of agglomerates significantly decreased with increasing the binder concentrations up to 15% and then increased with further increments up to 20%. This means that the agglomerate having the largest particle size and narrowest size distribution obtained with 15% binder concentration (Table 4.10) exhibited a very good flowability and low cohesiveness as classified by its lowest CI (14%) and HR (1.16) values given in Tables 3.2 and 3.3, respectively. It has been reported that the mean particle size and particle size distribution had a major influence on powder flowability (Jinapong et al., 2008). The coarser powder in the absence of the fine particles flowed better, as expected.

From the reconstitution properties data (Table 4.12), it can be inferred that the fluidized bed agglomeration markedly improved the wettability of the powders from the wetting time of 147 s for the spray-dried powder (Table 4.6) to a satisfactory level ranged from 3 to 5 s for the agglomerates obtained with different binder concentrations. The dispersibility also increased from 93% for the spray-dried powder (Table 4.5) to 95-98% for the agglomerates. It is known that size enlargement by agglomeration not only increases the rate of water penetration into the space between the agglomerates, but also the capillary-driven flow of water into the fine pores within the agglomerates and consequently shortens the wetting time (Carić, 2003; Schubert, 1993). From the point of view of dispersibility, the particle adhesion within the agglomerates should be strong enough to avoid abrasion during packaging and transportation, but should largely dissolve in an aqueous environment, preferably with minimum mechanical energy. In the reconstituted dispersion, the particles should neither float to the surface nor sediment to the bottom of the container within a certain time period (Schubert, 1993). In this study, the binder concentrations ranged from 5 to 20% had no significant effect on both wettability and dispersibility of the resultant agglomerates. The wettability (wetting time = 3.0-3.5 s) and dispersibility (97-98%) of these agglomerates were considered to be excellent. This can possibly due to their large particle sizes (>400 μm) with negligible amounts of the fine particles (< 6%).

Table 4.10 Physical properties of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different binder concentrations.

Treatments[1]	Moisture (%)	Particle size (µm)	ρ_{bulk} (g/cm^3)	ρ_{tapped} (g/cm^3)	$\rho_{particle}$ (g/cm^3)	Porosity (%)	Friability (%)
0[2]	1.74 ± 0.20^d	362.59 ± 2.36	0.26 ± 0.01^c	0.33 ± 0.01^b	0.83 ± 0.06^b	60.69 ± 3.91^b	49.58 ± 1.46^b
5	2.22 ± 0.05^c	453.13 ± 1.94	0.26 ± 0.00^c	0.33 ± 0.00^b	0.94 ± 0.05^b	64.82 ± 1.88^b	42.00 ± 2.67^c
10	3.00 ± 0.11^b	508.76 ± 1.79	0.26 ± 0.00^c	0.31 ± 0.00^c	1.14 ± 0.06^a	72.48 ± 1.39^a	44.18 ± 1.25^c
15	3.24 ± 0.02^a	656.63 ± 1.60	0.31 ± 0.00^a	0.35 ± 0.00^a	0.94 ± 0.06^b	62.48 ± 1.63^b	32.58 ± 0.89^d
20	3.30 ± 0.07^a	425.38 ± 2.03	0.28 ± 0.00^b	0.33 ± 0.00^b	0.89 ± 0.05^b	61.93 ± 2.62^b	53.86 ± 2.05^a

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

[1] Treatments are different binder concentrations (%)

[2] 0% binder concentration is distilled water.

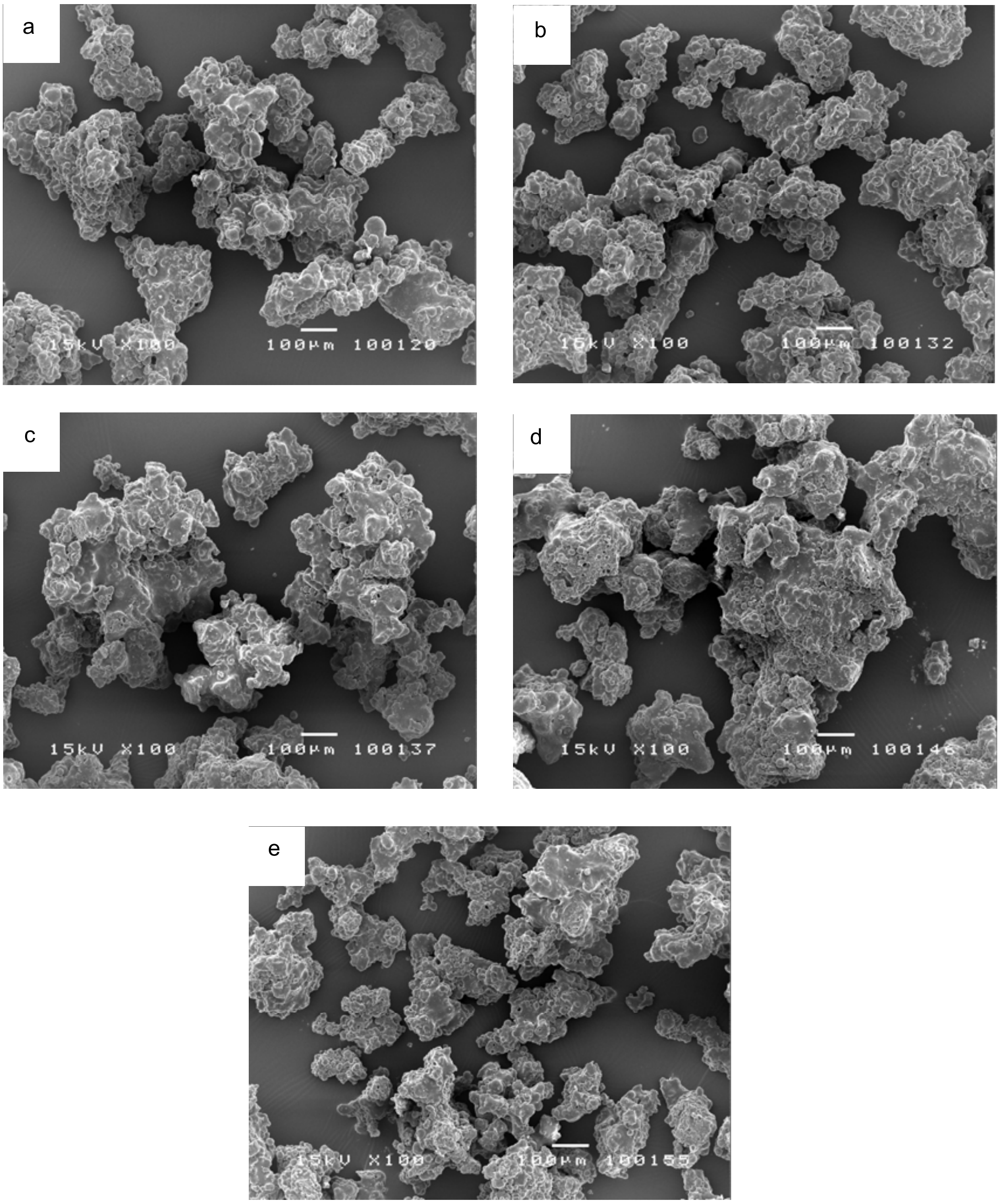

Fig. 4.13 Scanning electron micrographs of agglomerated spray-dried microcapsules produced from emulsion consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate/maltodextrin (DE18) ratio of 1:3. Agglomeration was performed by using an aqueous solution of maltodextrin (DE14) with different concentrations as a binder: 0% (a), 5% (b), 10% (c), 15% (d), and 20% (e).

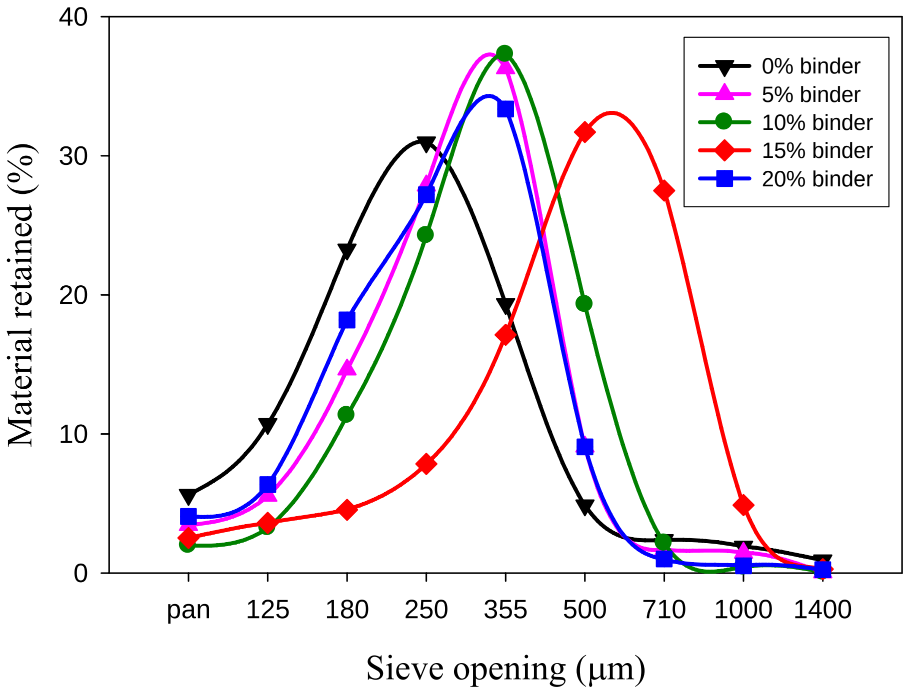

Fig. 4.14 Particle size distributions of agglomerated spray-dried microcapsules produced from emulsion consisting of 50% (w/w) oil load and 20% (w/w) wall solids with a soy protein isolate/maltodextrin (DE18) ratio of 1:3. Agglomeration was performed by using an aqueous solution of maltodextrin (DE14) with different concentrations as a binder.

Table 4.11 Flow characteristics (Carr index, CI, and Hausner ratio, HR) of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different binder concentrations.

Treatments[1]	CI (%)	HR
0[2]	19.96 ± 2.04^{a}	1.25 ± 0.03^{a}
5	21.21 ± 0.00^{a}	1.27 ± 0.00^{a}
10	16.03 ± 1.86^{b}	1.19 ± 0.03^{bc}
15	14.15 ± 0.23^{b}	1.16 ± 0.00^{c}
20	17.80 ± 2.72^{ab}	1.22 ± 0.04^{ab}

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

[1] Treatments are different binder concentrations (%)

[2] 0% binder concentration is distilled water.

Table 4.12 Reconstitution properties (wettability and dispersibility) of agglomerates produced from soy protein isolate/maltodextrin-based, soybean oil-containing, spray-dried microcapsules with different binder concentrations.

Treatments[1]	Wetting time (s)	Dispersibility (%)
0[2]	4.83 ± 0.75^a	95.13 ± 0.67^a
5	3.33 ± 0.58^b	97.42 ± 1.08^a
10	3.50 ± 0.55^b	97.95 ± 2.06^a
15	3.00 ± 0.00^b	97.63 ± 1.97^a
20	3.00 ± 0.00^b	96.95 ± 1.00^a

Assays were performed in triplicate. Mean ± SD values in the same column with different superscripts are significantly different ($p \leq 0.05$).

[1] Treatments are different binder concentrations (%)

[2] 0% binder concentration is distilled water.

CHAPTER V

CONCLUSIONS

The variety of GRAS wall materials approved for use in food applications is relatively limited and thus a need to discover and introduce new, food grade, encapsulating agents exists. One of the most desirable applications of the soy proteins as microencapsulating agents is their use for microencapsulation of non-volatile oil (e.g.soybean oil) in many food industries. Usefulness of non-volatile oil in various food systems is limited by its susceptibility to oxidation and its handling difficulties. The success of microencapsulation process could transform oil into a free flowing, dry and stable powder and thus could solve these problems.

The research studied on microencapsulation of soybean oil by spray drying in the wall systems consisting of soy protein isolate (SPI 1 or SPI 2) and maltodextrin with different DE values. Two types of SPI presented the difference in particle size distribution emulsion droplets. However, in all cases, fine emulsions with $d_{3,2} < 0.6$ µm were obtained that has been reported to be desired in oil encapsulation by spray drying. The results, of both SPIs, revealed that the MEE of the spray-dried microcapsules increased with increasing DE values and decreased with increasing the levels of oil load. Microstructure of the spray-dried microcapsules was affected by the DE of the maltodextrins. Higher DE value resulted in microcapsules with spherical shape and smooth surface, while low DE value was associated with a relatively high proportion of microcapsules with deep surface indentation. These results indicate that combination of soy protein isolate and maltodextrins were effective microencapsulating agents.

However, the spray-dried microcapsules were small particles (~20 µm) having poor handling and reconstitution properties. Size enlargement by fluidized bed agglomeration could improve these properties. Results indicated that the aqueous solutions of maltodextrin binders promoted size enlargement and improved handling and reconstitution properties of the spray-dried microcapsules. The system containing 15% maltodextrin with DE value of 14 was found to be optimum giving the agglomerated powder of the highest particle size (657 µm) and in turn excellent handling and reconstitution properties. Nevertheless, additional studies investigating chemical analysis, for example, oxidative stability, shelf-life, etc. can provide more detailed information about microencapsulation of oil.

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APPENDIX

Appendix: Particle size measurement of agglomerated soybean oil powders

Mass-weighted geometric mean diameter and standard deviation of the agglomerated soybean oil powders can be calculated as the followings:

Log normal mean size $= \chi(50)$

Log normal standard deviation $= \dfrac{\chi(84.13)}{\chi(50)}$

Where $\chi(50)$ = equivalent weight diameter at 50% cumulative weight

$\chi(84.13)$ = equivalent weight diameter at 84.13% cumulative weight

1. Agglomerated soybean oil powder with MD10 as a binder

Table A 1: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with MD10

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	6.12	0.9388
1000	10.28	0.8360
710	19.96	0.6364
500	25.54	0.3810
355	14.96	0.2315
250	8.93	0.1421
180	6.79	0.0743
125	4.34	0.0309
Pan	3.09	0.0000

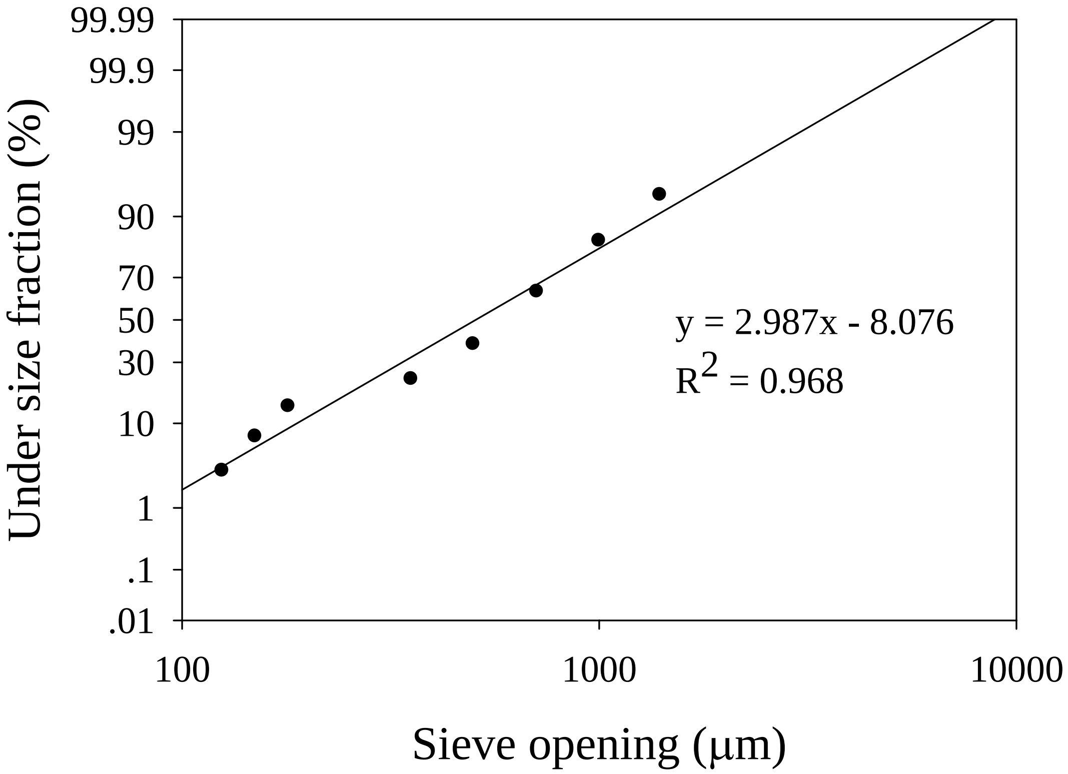

Figure A 1: The log-probability plots between under size fraction (%) and sieve opening (μm) of agglomerated soybean oil powders with MD10 as a binder.

According to y = 2.987x – 8.076, $\chi(50)$ can be calculated as the following:

50 = 2.987x – 8.076

x = 19.44 μm

$\chi(84.13)$ can be calculated as the following:

84.13 = 2.987x – 8.076

x = 30.87 μm

Therefore, Log normal mean size $= \chi(50)$

= 19.44 μm

Log normal standard deviation $= \dfrac{\chi(84.13)}{\chi(50)}$

$= \dfrac{30.87}{19.44}$ = 1.59

2. Agglomerated soybean oil powder with MD14 as a binder

Table A 2: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with MD14

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	0.06	0.9994
1000	0.42	0.9952
710	2.14	0.9737
500	19.30	0.7808
355	37.27	0.4080
250	24.25	0.1655
180	11.32	0.0523
125	3.25	0.0198
Pan	1.98	0.0000

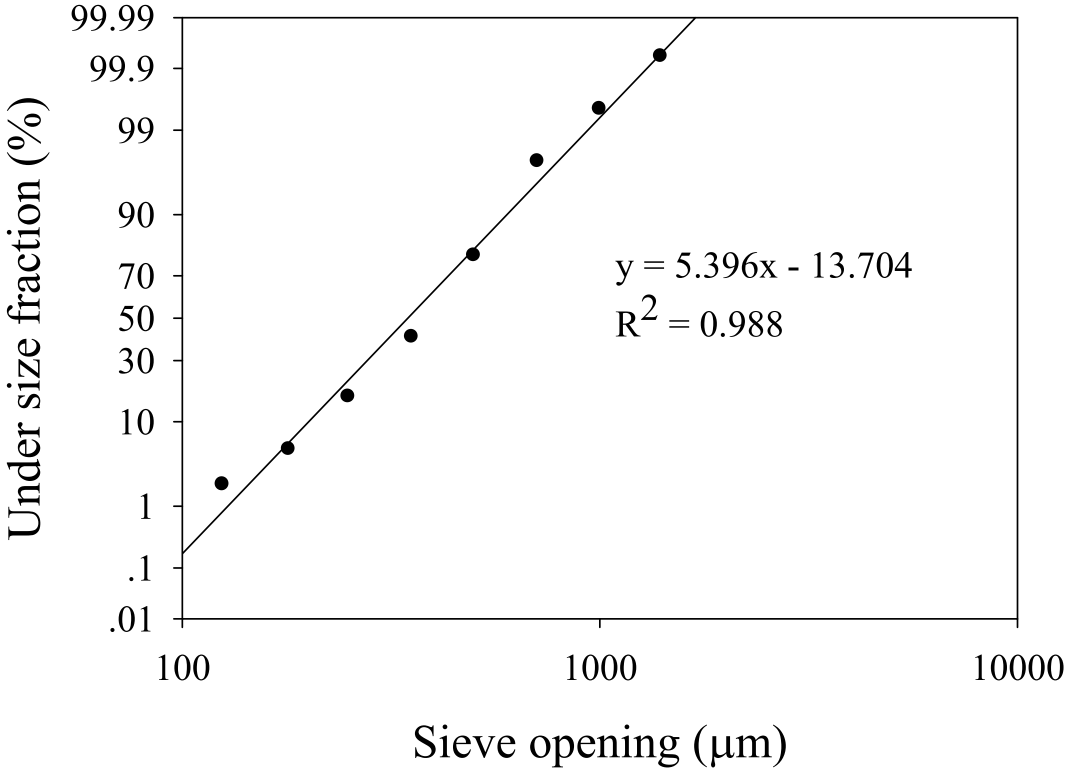

Figure A 2: The log-probability plots between under size fraction (%) and sieve opening (μm) of agglomerated soybean oil powders with MD14 as a binder.

3. Agglomerated soybean oil powder with MD18 as a binder

Table A 3: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with MD18

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	1.78	0.9822
1000	9.10	0.8912
710	18.59	0.7053
500	30.70	0.3983
355	20.45	0.1938
250	10.48	0.0890
180	5.81	0.0309
125	2.99	0.0010
Pan	0.10	0.0000

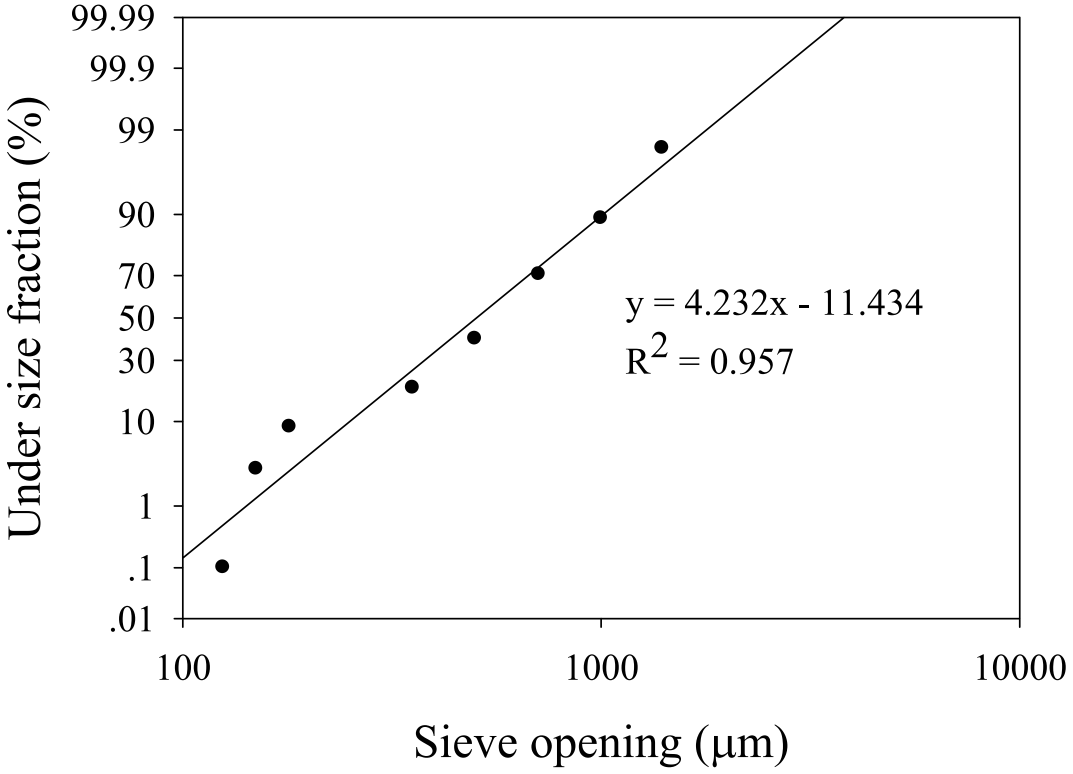

Figure A 3: The log-probability plots between under size fraction (%) and sieve opening (μm) of agglomerated soybean oil powders with MD18 as a binder.

4. Agglomerated soybean oil powder with 0% binder concentration

Table A 4: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with 0% binder

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	0.92	0.9908
1000	1.91	0.9717
710	2.37	0.9480
500	4.87	0.8993
355	19.34	0.7059
250	30.97	0.3962
180	23.27	0.1635
125	10.73	0.0562
Pan	5.62	0.0000

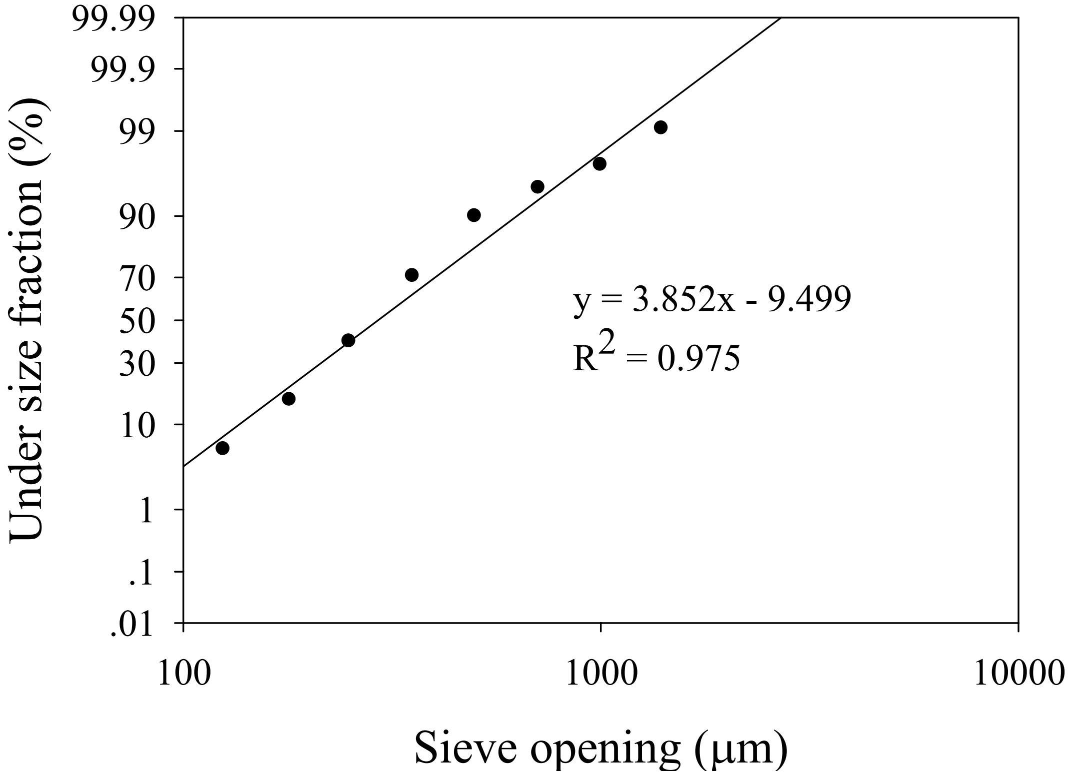

Figure A 4: The log-probability plots between under size fraction (%) and sieve opening (µm) of agglomerated soybean oil powders with 0% binder concentration.

5. Agglomerated soybean oil powder with 5% binder concentration

Table A 5: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with 5% binder

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	0.04	0.9996
1000	1.45	0.9851
710	1.69	0.9682
500	9.07	0.8775
355	36.28	0.5147
250	27.85	0.2362
180	14.63	0.0899
125	5.55	0.0344
Pan	3.44	0.0000

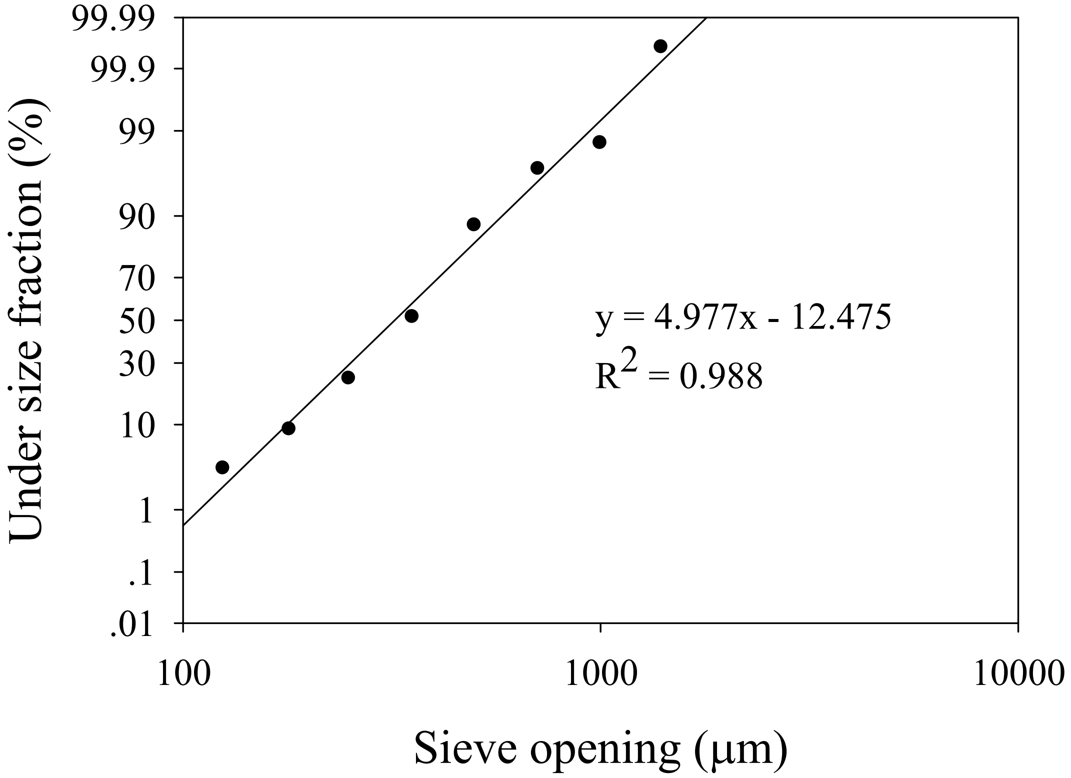

Figure A 5: The log-probability plots between under size fraction (%) and sieve opening (µm) of agglomerated soybean oil powders with 5% binder concentration.

6. Agglomerated soybean oil powder with 15% binder concentration

Table A 6: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with 15% binder

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	0.28	0.9972
1000	4.89	0.9483
710	27.49	0.6734
500	31.70	0.3564
355	17.13	0.1851
250	7.85	0.1067
180	4.55	0.0612
125	3.60	0.0252
Pan	2.52	0.0000

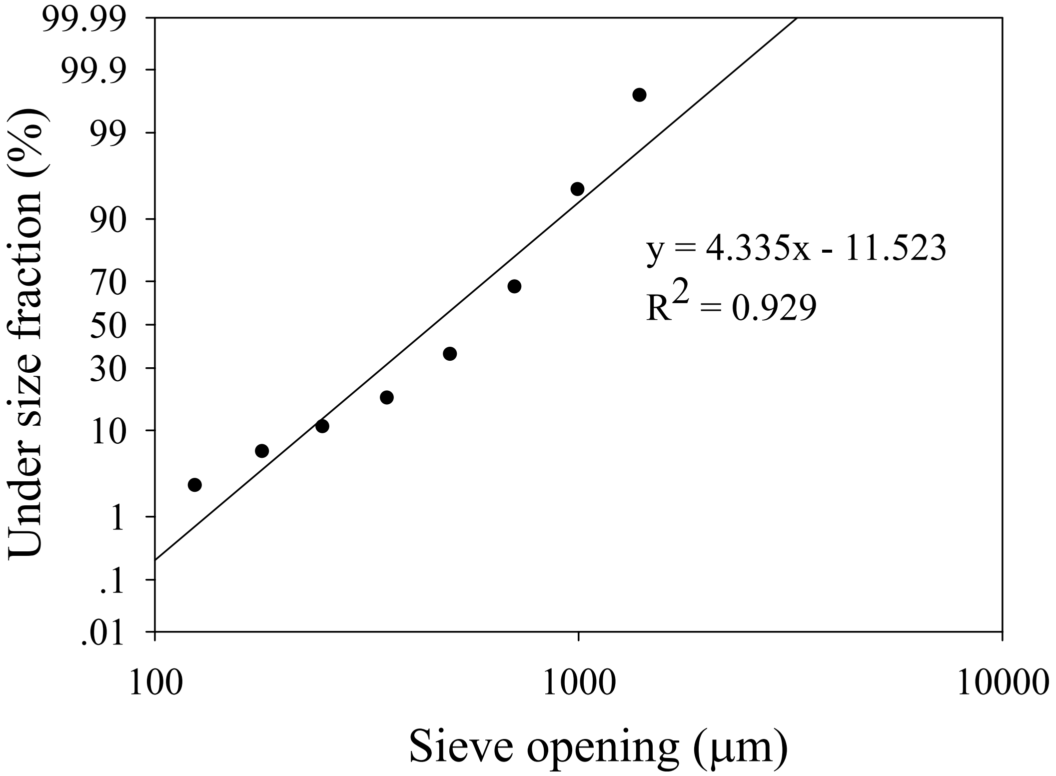

Figure A 6: The log-probability plots between under size fraction (%) and sieve opening (µm) of agglomerated soybean oil powders with 15% binder concentration.

7. Agglomerated soybean oil powder with 20% binder concentration

Table A 7: Cumulative sieve analysis of agglomerated soybean oil powder produced from spray-dried with 20% binder

Screen opening (D_{pi})	Mass fraction (%)	Cumulative fraction smaller than D_{pi}
More than 1400	-	1.0000
1400	0.24	0.9976
1000	0.52	0.9924
710	1.01	0.9823
500	9.07	0.8916
355	33.35	0.5580
250	27.20	0.2861
180	18.19	0.1042
125	6.36	0.0406
Pan	4.06	0.0000

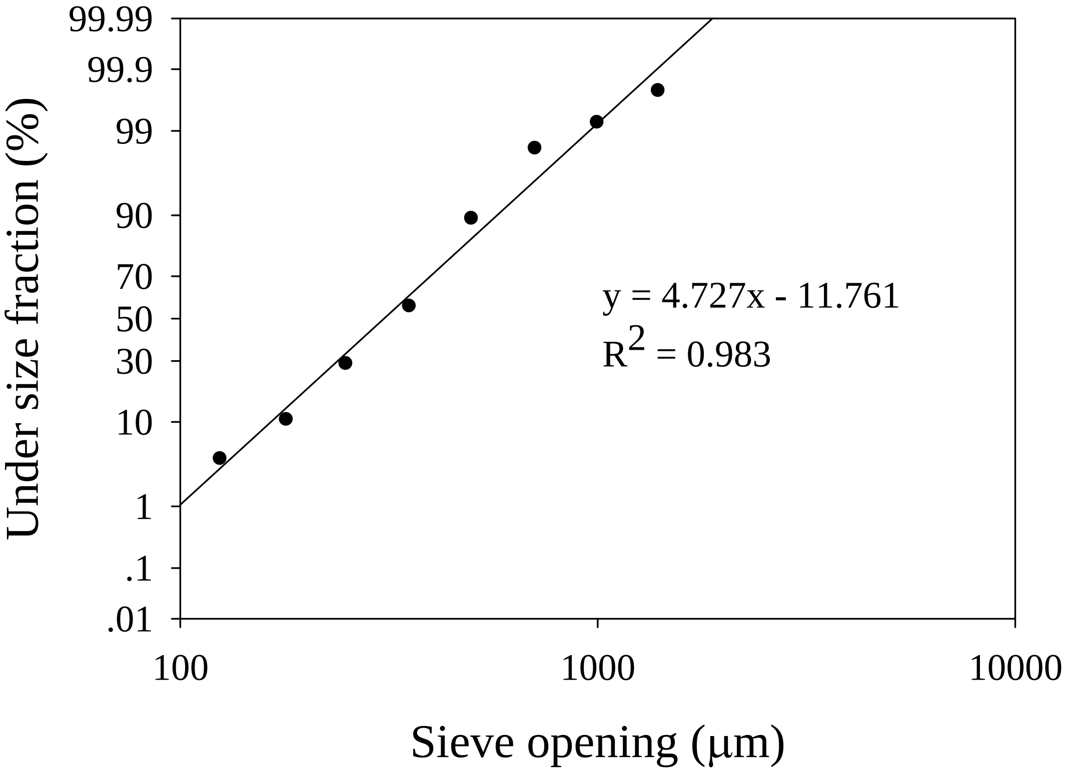

Figure A 7: The log-probability plots between under size fraction (%) and sieve opening (µm) of agglomerated soybean oil powders with 20% binder concentration.

BIOGRAPHY

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PRESENTATIONS

1. Thiengnoi, P., Rosenberg, M., & Suphantharika, M. (2007, June 20-21). Microencapsulation by spray drying soy oil in isolated soy protein and carbohydrates wall systems. Oral presented at The 3rd Naresuan Agriculture Conference, Naresuan University, Phitsanuloke, Thailand.
2. Thiengnoi, P., Rosenberg, M., & Suphantharika, M. (2007, November 6-7). Effect of maltodextrin on core retention and microencapsulation efficiency of encapsulated soy oil. Oral presented at Starch Update 2007: The 4th International Conference on Starch Technology, Queen Sirikit National Convention Center, Bangkok, Thailand.
3. Thiengnoi, P., & Suphantharika, M. (2008, June 15-19). Development of handling and reconstitution properties of spray-dried microencapsulated soybean oil powder using fluidized bed agglomeration. Oral presented at IHC 2008: The 9th International Hydrocolloids Conference, Rasa Sentosa Resort, Sentosa, Singapore.