CHAPTER 1

Introduction and review of literature
1.1. Preamble

The nature and structure of a food material are the inherent properties that dictate the suitability of application in a particular product. Powdery food materials are frequently used for convenience in applications during transportation, handling, processing and for product formulations (Ghosal, Indira and Bhattacharya, 2010). A variety of food powders from different sources are used to serve specific purposes including improving sensory appeal and nutritional status of finished products. Occasionally, there is a need to modify the structure of food to achieve certain specific characteristics and convenience in use. Therefore, it is desirable to look into such processes that modify the native structure of powder. Among the various frequently used processes, the food powders undergo the steps like agglomeration, compaction, instantisation and encapsulation. These are practiced to get products with specific purposes and for convenience. Agglomeration, in general, can be defined as a process during which primary particles are joined together so that bigger porous secondary particles (conglomerates) are formed by short-range physical or chemical forces among the particles (Palzer, 2005). This phenomenon is triggered by specific processing conditions, or binders and substances those adhere chemically or physically to the solid surfaces to form a bridge between particles (Pietsch, 2003). Bonding mechanisms responsible for inter-particle forces operating during and after agglomeration are van der Waals forces, electrostatic forces, liquid bridges, solid bridges, and interlocking bonds (Schuchmann, Hogekamp and Schubert, 1993).

The main purpose of particle size enlargement by agglomeration is to regulate certain physical properties of food powders such as density, flowability, to improve dispersion and dissolution characteristics, reduce the tendency of caking and dust formation (Mukherjee and Bhattacharya, 2006). The process of agglomeration can be applied to many food and non-food items. The non-food applications include the manufacture of ceramic objects formed by granular materials from kaolin, feldspar, silica and silicon carbide, fish and mammal feeds, household products (detergents for fabrics, dish and hard surface cleaning), microbiological products (enzyme, yeast and bacterial granules) and a number of pharmaceutical products like feed stock for tabletting, pellets and encapsulates. The agglomeration of food powders is of recent interest in which
control of porosity and density of material is the main interest. These have practical applications like dispersability, wettability, sinkability and solubility. The process of agglomeration may be conducted by several ways in conjunction with other unit operations such as spraying, steaming and drying. The selection of a specific agglomeration process depends on several factors including physical and chemical properties, average particle sizes of initial raw material(s) and product requirement, thermal sensitivity, and on the requirement of special properties like instant solubility, easy flowability, etc.

1.2. Applications in food system
In various industries fine powders are produced in an agglomerated form in order to improve their flowability, avoid lumping during rehydration and to improve the appearance of the product (Palzer, 2011). In the context of instantisation, the technique of tumble/growth agglomeration is frequently used in the food industries to improve reconstitution properties of a number of products including flour, cocoa powder, instant coffee, dried milk powder, sweeteners, fruit beverage powder, instant soup and spice mixes (Barbosa-Canovas et al., 2005). The number of available patents reflects the application of agglomeration in food industries. The patented processes include the production of instant powder (Strommen, Eikevik and Alves Filho, 2001), compositions and methods for binding agglomeration of proteins (Grossman, Kryukov and Zeiler, 2007), agglomerated starch product which has improved flow properties and disintegrates at substantially the same rate in media of varying pH (Cunningham, 2007), and a free-flowing granular dried soup mix (Haefliger et al., 2001). The list of products also includes fish and dairy products of commercial importance, microbial products and enzyme granules. Many more food products can be developed to satisfy specific needs and requirements. The approximate price of selected agglomerated products per kilogram is around ‘800-1000 and ‘400-600 for instant coffee granule and chocolate, respectively.
1.3. Turmeric

Turmeric is the rhizome of the plant *Curcuma longa* Linn, a tropical herb of the *Zingiberaceae* family and native to southern Asia. It is primarily consumed in the form of powdered rhizomes mainly for colouring (because of its yellow colour) and its associated medicinal properties. It also imparts the characteristic flavour and preserves the freshness of the product prepared. The rhizomes contain curcuminoids (3-6%), which are responsible for the yellow colour. The curcuminoid pigments and volatile oils, which are the major secondary metabolites of turmeric, have been shown to be largely responsible for the pharmacological activities of turmeric powder, extracts and oleoresins. In Asian countries, fresh and dry turmeric rhizomes as well as ground turmeric is used for vegetable and meat dishes and soup-like products. Turmeric is commercially available as a whole dried rhizome powder, curcuminoids, essential oils and oleoresin. Oleoresin extracted from turmeric is used in brine pickle, mayonnaise, non-alcoholic beverages and other similar products (Govindarajan and Stahl, 1980).

In recent years, the evaluation of antioxidant potential of foods has received much attention. Several studies have been carried out on the antioxidant and related anti-cancer activities of compounds derived from turmeric rhizomes. In Ayurvedic system, turmeric has been used internally as a stomachic, tonic and blood purifier, and externally in the prevention and treatment of skin diseases (Anon, 2001). The main biological activities of turmeric rhizome reported are anti-inflammatory, hepato-protective, anti-microbial, anti-fungal, anti-viral, wound healing, anti-cancer, anti-tumour, anti-inflammatory and anti-venom agents (Jayaprakasha, Rao and Sakariah, 2005; Negi *et al*., 1999; Ferreira *et al*., 1992). Over the past few years, there has been an increasing interest in turmeric due to its medicinal properties.

The microencapsulated turmeric oleoresin powder can be obtained by spray drying of oleoresin using edible gum as a matrix (Kshirsagar *et al*., 2009). One of the demerits of spray-dried powders is their small particle size, 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 (e.g., flow and quantification), and dusting problems during manufacturing (Buffo *et al*., 2002). To overcome this problem, turmeric powder can be
agglomerated directly. Obviously, this concept will be an alternate process compared to the existing process of extraction of oleoresin in addition to encapsulation in a carrier matrix followed by agglomeration.

1.4. Scope of work
The process of agglomeration involves physical and chemical changes; hence, there is a need for detailed investigation of the process of agglomeration of food powders. The possible approaches include the use of a model system that is simple, cost effective and is easily available. Latter, the results obtained from such studies may be extrapolated for a real food system (e.g., spice powder such as turmeric). The studies on the powder rheology, flowability, dispersability and density parameters will provide an insight of the physico-chemical changes in the agglomerated products. The chemical characterisation may comprise studies on the kinetics, sorption isotherm, gelatinisation, stability, and changes in volatile oil, its chemical composition and curcuminoids with particular reference to turmeric powder.

1.5. Objectives
The overall objective of the present investigation is to understand the process of agglomeration. The specific objectives are

A. Study of the physico-chemical properties and microstructural changes during agglomeration using a model system

B. To study
   1. Interaction of chemical constituent viz. volatiles and non-volatiles of turmeric in the agglomeration process.
   2. Role of starch in agglomeration process.

Keeping the objectives in mind, the present investigation has been subdivided into several chapters. Chapter 1 entitled ‘Introduction and review of literature’ deals with a brief general discussion of agglomeration process and turmeric to provide a concise idea about the area of the research undertaken. It also includes a review of the literature to give an insight into the process of agglomeration, its application to food powders and
provides an up-to-date development in this field through a survey of literatures and patents. Chapter 2 entitled ‘Characterisation of starch in turmeric rhizome and changes during processing’ describes the characteristics of turmeric powder and isolated starch to understand their suitability for agglomeration. Chapter 3 entitled ‘Effect of processing on volatiles and non-volatiles in turmeric rhizome’ presents the chemical characterisation of volatiles and non-volatiles of turmeric rhizome. Chapter 4 entitled ‘Physico-chemical and microstructural changes in model system due to agglomeration’ has been divided into two sections. Section 4.1 describes the effect of binder on corn starch powder and section 4.2 shows the compaction characteristics of corn starch in the presence of selected binders. Chapter 5 entitled ‘Agglomeration of turmeric powder and its effect on physico-chemical and chemical characteristics, and stability’ deals with the agglomeration of turmeric powder. It also provides an insight into the changes in its physico-chemical properties and chemical composition. Summary and conclusions section highlights the important findings and scope for application of the obtained results. The present investigation has been supplemented with bibliography and outcome of the research (viz., published papers, presented posters and submitted patent).

1.6. Review of literature

Powdery food materials are frequently used for convenience in applications. Powders are characterised in terms of size, shape and their functionality, while there is a lack of knowledge about their behaviour under various processing conditions (e.g., temperature, moisture). Large quantities of different powders (e.g., beverage powder, table salt, spice powders, cereal and pulse flours, etc) are produced in food industries. Hence, there is a need for detailed information about their handling and processing characteristics. Food powders are occasionally used as such though their main use lies in further processing for developing different products (Table 1.1). Agglomeration process is employed to get products with specific features for convenience to consumers.

1.6.1. Agglomeration

Agglomeration is basically a physical phenomenon and can be described as the sticking of particulate solids, which is caused by short-range physical or chemical forces among
the particles as a result of physical or chemical modifications of the surface of the solid (Palzer, 2005). According to this definition, even caking of hygroscopic raw materials during storage can be regarded as a kind of undesired agglomeration. The bonding mechanisms responsible for inter-particle forces in agglomeration are intermolecular forces. These intermolecular attractive forces between particles are inversely proportional to the seventh power of their separation distance. The roughness of the surface increases the effective separation distance between the particles, which in turn decreases the magnitude of van der Waals and electrostatic forces in granulating systems. Absorbed liquid binder layers on the particle surface have the effect of smoothing out surface roughness and thus particle separation distances tend to decrease leading to an increase in intermolecular forces. The mobile liquid bonds have an important role during the granulation process. An increase in the quantity of liquid thus changes the nature of the bonds and influences the overall granule strength. Particles containing liquid bonds at the contact point between individual particles is stated to be in the pendular state; an increase in the liquid content gives rise to the funicular state, and finally to the capillary state in which the inter-particle space is saturated with liquid. Though theory on the binding of particles by liquid is available, the same is not true on solid bridges between particles. The strength of such bridges depends on the amount of material present and its structure. A finer crystal structure results in stronger bonds and there exists some correlation between bond strength and higher drying temperatures. Granule strength is a function of the structure and physical properties of the binder used (Smith, 2003).

In agglomeration processes, granules grow by the successive addition of primary particles to agglomerate that is already formed; this happens when two particles or two granules are brought into contact with sufficient liquid binder. In tumbling bed of powder, two colliding particles/agglomerates are kneaded together by the tumbling action of the mixer to form near spherical shaped granules. Subsequent growth occurs by a crushing and layering mechanism in which larger ones crush the smallest and weakest granules, and the material becomes redistributed around the surface of the large granule in a uniform layer (Smith, 2003).
<table>
<thead>
<tr>
<th>Details of function</th>
<th>Raw materials</th>
<th>Specific applications</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food, food additive, taste or flavour enhancer</td>
<td>Salt, spice, sugar, milk and beverage powder</td>
<td>Spray or drum dried milk powder, baby foods, instant coffee and tea powders</td>
<td>Bergquist, Lorimor and Wildy (1992); Hogekamp, Schubert and Wolf (1996); Nasirpour, Scher and Desobry (2006); Sherwood, Jenkins and Rittmanic (2008)</td>
</tr>
<tr>
<td>Developing granulated and compacted items</td>
<td>Cereal starch/flour, puffed cereals and pulses</td>
<td>Bouillon cubes, compressed bars/cubes, chocolate bars, granulated products and soup mix</td>
<td>Snow et al. (1999); Kimura and Teraunchi (1999); Haefliger et al. (2001); Pietsch (2005)</td>
</tr>
<tr>
<td>Coating material to add taste and flavour (sweet/salty, chocolate), anti sticking agent, to improve appearance, and adding nutrients</td>
<td>Cereal/pulse flour, sugar, salt, maltodextrin, spices, vitamins/minerals, Chocolate, artificial sweeteners and herb/plant extracts</td>
<td>Sweet/salt-spicy snacks, confectionery and sugar coated products</td>
<td>Teunou and Poncelet (2002); Kowalska and Lenart (2005); Jinaong, Suphantharika and Jammong (2008); Camp and Fischbach (1990).</td>
</tr>
<tr>
<td>Increasing consistency and for gelling</td>
<td>Starches, hydrocolloids like crude gelatin, gums and pectin</td>
<td>Snacks, jams, jellies, desserts, soups, and sauces</td>
<td>Casper et al. (2001); Zhao and Bertrand (2007)</td>
</tr>
<tr>
<td>Suitable as a food component only after significant processing</td>
<td>Corn flour/starch, rice/wheat gelatin, protein concentrates/isolates, modified starches, casein and egg powder</td>
<td>Soup mix, traditional product like pancake, dosa/idli, high protein foods like meat analogues</td>
<td>Pietsch (2005); Cunningham (2007); Takeiti, Kieckbusch and Collares-Queiroz (2008)</td>
</tr>
<tr>
<td>Microbial culture in dried form</td>
<td>Yeast media, bacterial culture and enzymes</td>
<td>Formulations containing lactic acid bacteria and yeast powder</td>
<td>Harkonen et al. (1993)</td>
</tr>
<tr>
<td>Natural and synthetic flavours/colours</td>
<td>Cheese, spices, extracted and natural colours</td>
<td>Cheese flavoured extruded snacks, mixed spice flavour and coloured ice cream/jam/jelly</td>
<td>Fuchs et al. (2006); Buffo et al. (2002); Stahl (2005)</td>
</tr>
<tr>
<td>Adds specific fruit and vegetable taste</td>
<td>Dehydrated fruits and vegetables</td>
<td>Onion/garlic/potato/tapioca/mango powders, fruit-based beverage powder, potato flakes and granules</td>
<td>Pietsch (2005); Cremer et al. (2008); Stahl (2005)</td>
</tr>
<tr>
<td>Provides a non-sticky surface</td>
<td>Cereal starches/flour</td>
<td>Breadcrumb, Rolling /sheeting Machines</td>
<td>Takeiti et al. (2008)</td>
</tr>
</tbody>
</table>
The classification of the different materials according to their molecular polarity and their supra-molecular structure enables to understand the behaviour of the powder particles in different agglomeration processes. Depending on their polarity, particles made of amorphous materials can be plasticized using either polar or apolar liquids. They have viscoelastic behaviour and their mechanical properties are strongly dependant on plasticizer content, temperature and deformation speed. Particles have been classified into hydrophilic/hydrophobic amorphous and hydrophilic/hydrophobic crystalline materials. Hence, while agglomerating food and allied powders, it is important to know their physical properties particularly the flow characteristics (Palzer, 2009). Depending on the type of particle, different agglomeration processes are used, which means different binder solutions and different process conditions are required (Palzer, 2011).

1.6.2. Applications

The major applications of agglomeration in food include easy flow table salt, dispersible milk powder and soup mix, instant chocolate mix and beverage powder, compacted cubes for the nutritional intervention program, health bars using expanded/puffed cereals, etc (Table 1.1). A major application of the agglomeration process is in the production of instant products in which primary particles are agglomerated to give a granule shaped product with improved wettability, dispersability and dissolution characteristics compared to the original primary particles. Agglomeration process in the manufacturing of baby food powders causes an increase in the mean diameter of particles, which improves the flowability and decreases the bulk density of the agglomerated baby food (Szulc and Lenart, 2010). Table 1.2 shows the various applications of agglomeration processes in food and allied industries.

Food particulates are encapsulated to increase shelf life, masking taste or odour, and for improving the appearance. Agglomerated encrust granules are produced for controlled release of constituents the particle by providing a coating which dissolves at a given rate in a particular temperature or pH, or to protect unstable ingredients from degradation by heat, moisture or light (Teunou and Poncelet, 2002; Dewettinck and Huyghebaert, 1998).
The materials used for coating in food industries are mainly water soluble biopolymers, lipids (Eichler, 1996), milk or corn proteins, gums such as locust bean gum, carboxymethylcellulose, sodium alginate and kappa-carrageenan, protein concentrates (sodium caseinate, lysozyme), blood plasma concentrate (Dewettinck et al., 1998), gelatin and starch hydrolysates (Dewettinck et al., 1999). As an example, the flow chart for the production of instant agglomerated soymilk powder is presented in Fig 1.1, which shows the use of maltodextrin as a binder (Jinapong et al., 2008).
Processes for the production of granular cocoa (Kimura and Teranchi, 1999), a gelling aid consisting of particulate sugar (Caspers et al., 2001), production of instant powder (Strommen et al., 2001), infusing flavours into cereal grains and the agglomeration of grains into a unitary food product (Capodieci, 2002) and granular protein rich fraction of flour (Berizzi, 2004) have been patented in which agglomeration is a critical processing step. Applications of agglomeration also include the production of artificial sweeteners (Fotos and Bishay, 2001) and a granular flavouring for chewing gum that facilitates flavour retention (Hyodo et al., 2003). Zhao and Bertrand (2007) have developed a method for producing instantly dispersible pre-gelatinised starches for different food products.

### 1.6.3. Agglomeration processes

The process of agglomeration may be conducted by several ways in conjunction with other unit operations such as spraying, steaming and drying. The selection of a specific agglomeration process depends on several factors including physical and chemical properties, average particle sizes of initial raw material(s) and product, thermal sensitivity, and on the requirement of special properties like instant solubility, easy flowability, etc. The technologies applied thus also vary widely in their process conditions and adhesion principles to bind the primary particles together.
commonly used agglomeration processes can be divided into three groups (Hogekamp et al., 1996; Schuchmann, 1995) like pressure agglomeration (e.g., tableting), growth agglomeration (e.g., granulation) and agglomeration by drying (e.g., spray drying). Depending on whether or not a binder liquid is involved in the process, it can be subdivided into ‘wet’ and ‘dry’ agglomeration methods. Each method exploits certain binding mechanisms for granulation (Ennis, Tardos and Pfeffer, 1991). The subsequent sections describe the different processes of agglomeration that are frequently used in agro-food processing industries.

1.6.3.1. Pressure agglomeration
Dry granulation is of particular interest in the industry as the final product requires no liquid binder and drying process, and therefore costs less to operate as it requires simpler equipment (Augsburger and Vuppala, 1997). Compaction agglomeration is one such process, where post-process drying is an optional process depending on the binders used. Compaction is a process whereby small particles are bound together by mechanical force to form larger cohesive masses (compacted mass of given porosity) in which the original particles can still be identified (Snow et al., 1999). In order to achieve the desired compact properties, the powders are mixed with other ingredients having specific functions. Understanding the compaction process requires knowledge of the flow behaviour of powders, the densification mechanisms (which depend on the contact interactions between particles), the formation of bonds that give strength to compacts and the understanding of the response of a porous compact during unloading, ejection and post-compaction operations (Pitt and Sinka, 2007).

Pressure agglomeration is carried out using the equipment like the piston and moulding presses, tableting presses and roll presses. The success of compaction process depends on the effective utilisation and transmission of the applied external force, and on the ability of the material to form and maintain inter-particle bonds during pressure compaction (Snow et al., 1999). Various densification mechanisms operate during powder compaction. One of the most common binding mechanisms in these processes are caused by the short-range molecular attraction forces, i.e., electrostatic and van der Waals forces (Pietsch, 1999). Mukherjee and Bhattacharya (2006) and Ghosal et al. (2010) reported the inter-relationship between rheology of powder and texture of the compacted mass using model food powder systems in presence of selected binders. The advantages of compaction agglomeration include an
increase in product density and the requirement of a small amount of liquid binder (Snow et al., 1999). This process has special advantages for handling of moisture sensitive material (Yusof, Smith and Briscoe, 2005).

1.6.3.2. Extrusion agglomeration
Pressure or press agglomeration using an extruder is possible for commercial applications of size enlargement by agglomeration. In the extrusion agglomeration process, powder mixture is blended with binder liquid, additives or dispersants and then extruded at low pressure followed by drying, cooling and crumbling to get the final instant product (Pietsch, 1999). Many food products such as snack bars and confectioneries are processed and/or finished by pressure agglomeration, mainly extrusion (Pietsch, 2005). Extrusion has also been used to encapsulate flavours, vitamin C and colours (Dziezak, 1988). The major advantage of extrusion is its outstanding protection of flavours against oxidation (Barbosa-Canovas et al., 2005) while being a commercially viable continuous processing technique offering a reduced cost of production.

1.6.3.3. Tumbling of powders (rewetting agglomeration)
The tumbling agglomeration involves both disintegration of weaker bonds and re-agglomeration by abrasion transfer and coalescence of larger units. Coalescence occurs at contact points and additional growth of the agglomerate may proceed by further coalescence, or by layering, or both. The particles to be agglomerated are larger; however, the particle-to-particle adhesion needs to be increased by the addition of binders, such as water or other more viscous liquids, depending on the properties of the particles being agglomerated and the required strength of the agglomerate structure. The whole process, tumble/growth agglomeration first renders weak agglomerates known as green products. Surface tension and capillary forces of the liquid binder temporarily bond these wet agglomerates. This is the reason why, in most cases, tumble/growth agglomeration requires some sort of post treatment. Drying and heating, cooling, screening, adjustment of product characteristics by crushing, conditioning, and recirculation of undersize material are some processes that have been used as a post-treatment in tumble/growth agglomeration (Barbosa-Canovas et al., 2005).
In food industries, most units use static and vibrating fluidised beds to mix the powder, promote inter-particle collisions and dry the granules (Coucoulas, 1992). Granules are formed by shear processing in planetary mixers, ribbon blenders, Z-blade units and high-speed intensive mixers. For example, granulated enzyme products can be manufactured by mixing enzyme solution with a suitable filler to form dough, which is then pressed into fine granules. The granules are then sprayed with a suitable binder and further dried in a fluidised bed dryer (Harkonen et al., 1993). Sometimes, a large amount of fine products is reprocessed, causing an economical burden to this technology.

1.6.3.4. Straight through agglomeration
A liquid concentrate is used in this process. When powders are produced by spray dryer, the agglomeration process can be accomplished in a fluidised bed connected directly to the spray dryer. There the operating conditions can be controlled so that the partially dried particles formed in the upper part of the dryer are still sticky. Fine particles, either from recycle or the drying chamber, are fed into an external fluidised bed dryer to undergo cluster formation. Sometimes, steam or atomised water can be injected into the fluidised bed to assist in the agglomeration process. Final drying and cooling are also accomplished in the bed, and agglomerated product is removed for storage or packaging. This procedure is more adequate for coffee and baby foods (Masters and Stoltze, 1973), skim and whole milk, non-caking whey, milk replacer and ice cream mix.

1.6.3.5. Spray-bed dryer agglomeration
A fluidised bed is integrated into a spray dryer chamber by combining spray dryer with a fluidised bed agglomeration unit. Particles formed in the spray drying-zone enter the integrated fluidised bed at the bottom of the dryer with high moisture content, and become agglomerated in the bed where they are vigorously agitated by high fluidisation velocity (Gong et al., 2008; Quek, Chok and Swedlund, 2007). An external fluidised bed is connected to the integrated fluidizer for final product drying and cooling. This type of dryer is most suitable for small to medium sized plants and can produce agglomerated powder with excellent properties. As an example, the flowchart for the production of granular encapsulated flavour powder has been cited
in Fig 1.2 where maltodextrin/gum acacia/modified starch have been used as a carrier of flavour (Buffo et al., 2002).

Carriers (maltodextrin/gum acacia/modified starch)
\[\text{Dissolved in water}\]
Dispersion containing carrier substances
\[\text{Stands overnight}\]
Hydrated carrier + flavour
\[\text{Emulsification}\]
Carrier-flavour emulsion (1:4)
\[\text{Spray drying}\]
Spray dried encapsulated flavour powder
\[\text{Agglomeration}\]
Agglomerated encapsulated flavour powder

Figure 1.2. Flowchart for flavour encapsulation employing agglomeration
(Source: Buffo et al., 2002)

1.6.3.6. Atomiser wheel agglomeration
This method is used when powder cannot withstand a forceful agglomeration process or where small sized agglomerates are desired. The layout closely resembles the agglomerating tube method. The only difference is that a rotary atomiser replaces the agglomerating tube. The powder falls around the rotating atomising wheel and is sprayed with water or binder solution. This system is used for certain baby foods, beverage whiteners and cocoa/sugar mixtures (Jinapong et al., 2008; Masters and Stoltze, 1973).

1.6.3.7. Steam jet agglomeration
Steam jet agglomeration is a continuous process, which has been used in the food industries for several years to produce agglomerates with favourable instant properties from fine powders. Turbulent free jets of steam wet the free falling particles. The colliding wet particles can form agglomerates provided, their relative kinetic energy are dissipated by the viscous liquid layers on the particle surfaces (Schuchmann et al., 1993). Steam jet agglomeration involves many process variables and product
characteristics. Of the process variables, the most important are the feed conditions (solids flow, steam flow) and the drying conditions (temperature and residence time in the dryer). With respect to product characteristics, it is of fundamental importance to know the particle size and distribution, the moisture content and the intrinsic characteristics of the material (chemical composition and proportion of soluble components) in addition to the powder flow properties (Vissotto et al., 2010). The material to be agglomerated should preferably be water-soluble; insoluble or water-repellent substances can be processed if mixed with a sufficient amount of water-soluble material such as sucrose or a monosaccharide. A typical application is instant beverages intended for reconstitution with water or milk (Schuchmann et al., 1993).

1.6.3.8. Agglomeration by heat/sintering

Sintering is a process in which the particles in a powder mass can be bonded in solid state at elevated temperatures below the melting or softening temperature of the materials. The driving force for sintering is a diminution of surface area of the assembly of original particles. Therefore, sintering occurs with a reduction in total surface energy and accordingly, the total free energy of the powder decrease with sintering. At a certain elevated temperature, atoms and molecules begin to migrate across the interface where particles touch each other in solid state. Depending on temperature, time and intensity of contact, diffusion of matter forms bridge-like structures between the surfaces, which solidify upon cooling. This may result in a densification of the compact, which is due to an elimination of pores and associated shrinkage (Pietsch, 2002a). A typical example for agglomeration by sintering is reported by Omobuwajo et al. (2000) to develop instant chocolate beverage granules.

1.6.4. Binders

Binders are adhesives that provide the cohesiveness that is essential for the bonding of solid particles during the process of agglomeration. In the wet granulation process, binders promote size enlargement and thereby improve flowability of the blend during the manufacturing process. During wet massing, the binder may be dissolved in the granulating solvent, which is then added to the powder, or mixed dry with the powder and the granulating solvent (generally water) (Barbosa-Canovas et al., 2005).

In food system, binders are used in aqueous solution of lactose or dextrose, gelatin or a food gum. In product, the nature of the binder is a major factor that
determines the granule strength, attrition resistance and granule dustiness. It affects the dispersion and dissolution properties, ingredient release rate and chemical stability of the ingredients (Knight, 2001). Binders are classified as natural polymers, synthetic polymers, or sugars (Barbosa-Canovas et al., 2005).

In the agglomeration process, the binder provides capillary and viscous forces that give the wet granules mechanical strength and particularly with high shear mixer granulation (Mills et al., 2000; Keningley, Knight and Marson, 1997). The factors influencing the binder efficiency are concentration, viscosity, and mechanical properties of the binder, inter-particulate interactions between the binder and the substrate, and binder distribution. Glucose or sucrose can be applied as syrups in concentrations above 50% in wet granulation processes exhibiting good bonding properties, although sucrose produces hard and brittle bridges (Barbosa-Canovas et al., 2005). Multidimensional model enables the study of critical parameters in binder granulation such as reaction rate (solidification of binder) and size of the added binder droplets, which demonstrates its promising potential (Braumann et al., 2007).

1.6.5. Characterisation of agglomerated products
The knowledge and characterisation of raw materials and products are essential to select appropriate method and machine, optimise processes, functionality, product formulation and reduce cost of product. The bulk properties of food powders are the function of physical and chemical properties of the material, the geometry, size and surface characteristics of the individual particles as well as the whole system. Parameters that determine the properties of agglomerates include those related to primary particles and agglomerates. Thus, the measurement of powder property is important because these properties intrinsically affect powder behaviour during storage, handling and processing.

1.6.5.1. Physical properties of agglomerates
**Bulk density and porosity:** The density is of primary importance in applications involving bulk flow of air around the particles like in fluidisation, of liquid as sedimentation, or flow through packed beds. Measurement of bulk density is of fundamental use by the industry to adjust storage, processing, packaging and distribution conditions. Bulk density is the mass of the particles that occupies unit
volume of a bed, whereas porosity is defined as the volume of the voids within the bed divided by the total volume of the bed. There are several types of bulk density based on the method of volume determination. The bulk density ($\rho_b$) of powders is the mass of the particles that occupies unit volume of a bed. It is determined by particle density, which in turn is determined by solid density, particle internal porosity, and also by spatial arrangement of the particles in the container. Bulk density includes the volume of the solid and liquid materials, and all pores. Compact or compacted density is determined after compressing the powder by use of mechanical pressure and impact(s). Tap or tapped density results after a specific volume of powder has been tapped or vibrated under specific conditions. Loose bulk density is measured after a powder is freely poured into a container. Aerated bulk density is used for testing under fluidised conditions or during pneumatic conveying. The volume fraction of air over the total bed volume is called porosity (Barbosa-Canovas and Juliano, 2005).

**Flowability:** Powder flow is defined as the relative movement of a bulk of particles among the neighbouring particles or along the container wall surface (Peleg, 1978). The forces involved in powder flow are gravity, friction, cohesion (inter-particle attraction), and adhesion (particle-wall attraction). Particle surface properties, particle shape, size distribution and the geometry of the system are factors that affect the flowability. It is, therefore, quite difficult to have a general theory applicable to the flow of all food powders in all possible conditions that may be developed in practice (Peleg, 1978). The practical objective of powder flowability determination is to provide both qualitative and quantitative knowledge of powder behaviour, which can be used in the designing of equipment. In order to flow, the powder strength must be less than the load put on them (Barbosa-Canovas *et al.*, 2005).

### 1.6.5.2. Structural features of agglomerates

**Particle size and shape:** Particle size is one of the most important physical characteristics of particles. In the case of simple shapes such as the sphere or cylinder, one or several dimensions explicitly determine the size. However, particles are of irregular shape so that a large number of dimensions are required to describe the size and shape. To determine the particle size, in principle, any measurable physical property which correlates with characteristic geometric dimensions or
equivalent dimensions can be used (Schubert, 1987). The bulk density, compressibility and flowability of food powders are highly dependent on particle size and its distribution. The common convention considers that for a particulate material to be considered a powder, its approximate median size (50% of the material is smaller than median size and 50% larger) shall be less than 1 mm. A significant number of food powders may be considered to be in the fine range. Methods for measuring particle size are sieving, microscope counting technique, sedimentation and stream scanning. The median particle sizes in common food commodities have been indicated by Barbosa-Canovas et al. (2005).

Particle shape influence the factors such as flowability of powder, packing, interaction with fluids, and coating of powders such as pigments (Barbosa-Canovas et al., 2005). Generally the particle shapes are defined as acicular (needle shape), angular (roughly polyhedral shape), crystalline (freely developed geometric shape in a fluid medium), dentritic (branched crystalline shape), fibrous (regular or irregular thread-like), flaky (plate-like), granular (approximately equi-dimensional irregular shape), irregular (lacking any symmetry), modular (rounded irregular shape), and spherical (global shape), etc.

Solid and liquid bridges: In general, interaction between particles is regulated by the relationship between the strength of the attractive (or repulsive) forces and gravitational forces. For all particles in the amorphous rubbery state (or above glass transition temperature), forces causing primary particles to stick together are inter-particle attraction forces (van der Waals or molecular forces and electrostatics forces), liquid bridges and solid bridges (Seville, Willett and Knight, 2000; Hartley, Parfitt and Pollack, 1985). Inter-particle forces are inversely related to the particle size (Adhikari et al., 2001; Rennie et al., 1999). Van der Waals forces and electrostatic attraction are not as high as the inter-particle connecting force coming from liquid bridges (Schubert, 1987). Van der Waals forces arise from electron motion among dipoles and act over very short distances within the material structure, becoming prevalent when the particle size is less than 1 μm (Hartley et al., 1985). Electrostatic forces are long ranging forces that arise through surface differences on particles and are present when the material does not dissipate electrostatic charges.

Solid bridge is formed as a result of sintering, solid diffusion, condensation, or chemical reaction and arises from the material deposited between the agglomerated particles. Solid bridges can also be built up by chemical reaction, crystallisation of
dissolved substances, hardening of binders, and solidification of melted components (Loncin and Merson, 1979). Liquid bridges are related to chemical interactions between particle components and result from the presence of bulk liquid (generally unbound water or melted lipids) between the individual particles. In liquid bridges, the force of particle adhesion arises either from surface tension of the liquid/air system (as in the case of a liquid droplet) or from capillary pressure. Composition of the liquid in the bridge varies in different food materials. The ‘bridging potential’ or ‘stickiness’ is related to factors such as powder moisture, fat or low-molecular-weight sugar content and shape of particles (Barbosa-Canovas et al., 2005).

1.6.5.3. Instant properties
The instantaneous properties of agglomerates are the most desirable properties of agglomeration processes and they can be measured by the following four dissolution properties when agglomerates are spread on the surface of liquid (Schubert, 1987). These are wettability (liquid penetration into a porous agglomerate system due to capillary action), sinkability (the sinking of agglomerates below the liquid surface), dispersability (the dispersion of agglomerates with little stirring) and solubility (dissolving of soluble agglomerates in the liquid). The wetting of solid food materials plays an important role for a number of practical applications such as agglomeration, granulation, coating, drying, dissolution and dispersion. Important factor affecting the reconstitution process of agglomerate is related to the amount of energy required to breakdown the agglomerates to individual particles or aggregates (Forny, Marabi and Plazer, 2011).

The ability of the bulk powder to imbibe a liquid under the influence of capillary forces is called wettability (Freudig, Hogekamp and Schubert, 1999) and it is the ability of the powder particles to overcome the surface tension between themselves and liquid (Fang, Selomulya and Chen, 2008). The wettability of powders, an important parameter to qualify instant foods, tends to decrease with the presence of hydrophobic components at the particles surface and wetting agents (Kim et al., 2002; Hogekamp et al., 1996). The conditions favouring good wettability are large particles with large pores in between, high porosity as long as a critical porosity is not exceeded and small contact angle (Freudig et al., 1999).

Sinkability is defined as the falling of powder particles below the surface of an aqueous phase or liquid (Thomas et al., 2004). It depends mainly on the particle size
and density, since larger and denser particles usually sink faster than finer and lighter ones. A higher particle density combined with a lower quantity of air content enclosed within powder particle results in faster sinking rate (Caric and Milanovic, 2002). However, swelling can strongly inhibit sinking (Freudig et al., 1999).

Dispersability describes the ease with which the powder may be distributed as single particles over the surface and throughout the bulk of the reconstituting water. In dispersability measuring test, it is essential to assume that following a short period of dispersing, soluble particles are completely dissolved and suspended particles are regarded as residual material (Galet et al., 2004; Vu et al., 2003).

Solubility refers to the rate and extent to which the components of the powder particles dissolve in water. Solubility depends mainly on the chemical composition of the powder and its physical state. Solubility is the final step of powder dissolution and is possibly the key determinant of the overall reconstitution quality.

1.6.6. Spice

1.6.6.1. Introduction

Spices are the important agricultural products that are produced throughout the world. Spices are widely used in food products to create the distinctive flavour and character that is representative of different cuisines for culinary, medicinal use and also for food flavouring, colouring and preservation. In addition, spices possess several medicinal properties and hence are used in the preparation of a number of medicinal formulations (Risch, 1996). Spices come from different parts of plants like bark (cinnamon), buds (cloves), berries (black pepper), fruit (chilli), bulb (garlic, onion) pistil (saffron), kernel (nutmeg), seeds (ajowan, aniseed), rhizomes (ginger, turmeric) and leaves (basil, bay leaf, mint, curry leaf).

Spices contain several active chemical compounds that impart flavour, fragrance and sharp taste. Most spices owe their flavouring properties to volatile oils and in some cases to fixed oils and resin, which are known as oleoresins. A mixture of compounds such as alcohols, phenols, esters, terpenes, organic acids, resins, alkaloids, and sulphur containing compounds are responsible for the flavour of spices (Manay and Shadaksharaswami, 1997). Besides these flavouring components, every spice contains the usual components such as protein, carbohydrates, fibre, minerals, tannins or polyphenols. Turmeric being the most commonly used spice for its distinct colour and flavour, and pharmacological applications; it has been selected to conduct
the agglomeration trials with an intention to modify its physico-chemical and
functional properties. The subsequent sections show an insight into the chemistry and
application of turmeric rhizomes.

1.6.6.2. Turmeric rhizomes

Turmeric belongs to the *Curcuma* genus of the Zingiberaceae family. Several species
of *Curcuma* are called turmeric but *C. longa* L. represents the “turmeric” of
commercial importance, and currently more than 50 cultivars are known in India.
India is the major producer and exporter of turmeric. Its rhizomes are oblong, ovate,
pyriform and often short- branched (Eigner and Scholz, 1999). Turmeric belongs to
the group of aromatic spices and has been used as a food additive in curries to
improve the storage condition, palatability, appearance and preservation of food.
Turmeric is used as whole cured-dried (cooking in excess of water and dried in shade)
rhizome, ground powder, or as an oleoresin. Turmeric powder is stored in bulk in
containers such as fibre hard drums, multi-wall bags and tin containers in which
moisture absorption and light exposure is prevented suitably lined or coated to prevent
moisture absorption, loss of flavour and colour (Sasikumar, 2001). The product is
stable for up to 6 months. Turmeric oleoresin is a mixture of compounds: volatile oils
and non-volatile fatty and resinous material, among others. Oleoresin is used mainly
as a food colour and secondarily as spice. Turmeric oleoresin is essentially used in
institutional cooking in meat and fish products and in certain processed products such
as mustard paste, pickles, frozen fish fillets, frozen potato croquettes, butter,
beverages and cheese. Oleoresin is used in the range of 2 to 640 ppm (Buescher and
Yang, 2000; Govindarajan and Stahl, 1980).

Turmeric rhizomes contain protein (6.3-9.7%), crude fibre (2.6-5.8%),
carbohydrates (50.4-69.4%), ash (3.5-6.0%) and moisture (8.1-13.1%). Apart from
the common plant constituents, the characteristic components of the turmeric are
curcuminoids (3-6%), responsible for its deep yellow colour, and the volatile oil (3.2-
5.8%) responsible for its aroma (Govindarajan and Stahl, 1980). The major portion of
carbohydrates is starch and is around 50-60% of the rhizome. Studies on isolation of
starch from turmeric rhizome and its characterisation are limited. Jyothi, Moorthy
and Vimala (2003) have extracted starch from two species of curcuma such as
*Curcuma zedoaria* and *Curcuma malabarica*; no significant differences have been
reported between these two species in respect of granule shape, size and amylose
content. Elliptical granule shape with an average granule size of about 35 µm has been reported. Leonel, Sarmento and Cereda (2003) have extracted starch from two curcuma species (Curcuma longa and Curcuma zedoaria). Microscopic examination has revealed a flat triangular shape while the viscoamylographic investigation has indicated the pasting (gelatinisation) temperature to be 81 and 78°C for Curcuma longa and Curcuma zedoaria, respectively. Braga, Moreschi and Meireles (2006) have reported that turmeric rhizomes contain about 40% starch. The general conclusion that is derived from all of these studies is that starch from curcuma species is different from conventional sources like cereal, pulse and tuber crops with respect to physical and physico-chemical characteristics.

1.6.6.3. Chemistry of turmeric

Volatile components: Turmeric owes its characteristic aromatic taste and odour to the volatile oil (essential oil) present in the rhizome. Volatile oil present in rhizome are extracted by hydrodistillation of turmeric powder, contains all the volatile aroma components of the spice. The yield of volatile oil from turmeric varies from 3 to 7%. It is light orange-yellow in colour with an odour reminiscent of turmeric powder (Balakrishnan, 2007). Analysis of turmeric oil has been studied extensively using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Volatile oil is mainly contains oxygenated sesquiterpenes, along with small quantities of sesquiterpene hydrocarbons, monoterpenene hydrocarbons, oxygenated monoterpenes and alcohols (Fig 1.3). The main components are the ar-turmerone (30-40%), α-turmerones (8-10%) and β-turmerone (15-18%). α-Turmerone is unstable in the presence of air, yielding its dimmer or the most stable ar-turmerone (Su et al., 1982). The flavour components of turmeric are mainly ketones and sesquiterpene alcohols (Silva et al., 2005).

Manzan et al. (2003) have extracted turmeric oil using supercritical fluid extraction unit under optimised condition. They have reported to yield a high amount of ar-turmerone, α-turmerones and β-turmerone. The major compounds in volatile oil are ar-turmerone, zingiberene, turmerone and curlone. Beside these major components, there are several low-boiling terpenes, d-sabinene, α-phellandrene, cineole, borneol, p-cymene, β-sesquisphellandrene, and the higher-boiling sesquiterpene, zingiberene in substantial amounts.
Figure 1.3. Structure of components in volatile oil from *Curcuma longa*
Negi et al. (1999) have isolated turmeric oil from spent turmeric oleoresin. The turmeric oil fractions are analysed by GC and GC-MS; ar-turmerone, turmerone and curlone are found to be the major compounds present in these fractions along with other oxygenated compounds. The essential oil from the rhizome of turmeric grown in Pakistan has been isolated by the hydro-distillation in which 17 components are identified and reported (Naz et al., 2011). The three oxygenated sesquiterpenes viz. ar-turmerone, α-turmerones and β-turmerone are extracted by supercritical carbon dioxide and purified column chromatography. Latter, they have been quantified and identified by NMR and HPLC (Chang et al., 2006). The quantity and relative composition of volatile vary with the geographic origin and climatic conditions (Usman et al., 2009).

Volatile compounds present in turmeric leaves are isolated by hydro distillation, and twenty chemical constituents have been identified using GC and GC-MS (Garg et al., 2002). Predominant chemical groups are monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons and oxygenated sesquiterpenes. The ar-turmerone is used in pharmaceutical applications for its insect repellent, anti-fungal, anti-bacterial, antioxidant, anti-mutagenic and anti-carcinogenic activities (Gowda, Malathi and Sugalanthi, 2004; Jayaprakasha et al., 2002; Aratanechemuge et al., 2002; Negi et al., 1999; Roth, Chandra and Nair, 1998).

Non-volatile component: The non-volatile extract of turmeric rhizome mainly contains diarylheptanoids, which are belongs to a class of natural compounds. The turmeric colour is attributed primarily to a group of related compounds designated as curcuminoids with curcumin [1, 7-bis-(4-hydroxy,3-methoxy phenyl) hepta-1, 6-diene-3, 5-dione] as the principal component with its two derivatives, demethoxycurcumin [1-(4-hydroxy phenyl), 7-(4-hydroxy, 3-methoxy phenyl) hepta-1, 6-diene-3, 5-dione] and bisdemethoxycurcumin [1, 7-bis-(4-hydroxy phenyl) hepta-1, 6-diene-3, 5-dione]. Curcumin with its two methoxy groups has a reddish orange colour, whereas demethoxycurcumin with one methoxy group is orange-yellow, and bis-demethoxy curcumin without methoxy groups is yellow (Madsen et al., 2003). Other minor components are also present. The structure of these three curcuminoids viz., curcumin, demethoxycurcumin and bisdemethoxycurcumin is shown in Fig 1.4.
The curcuminoids can be collectively isolated from the extract of the spice by crystallisation. *Curcuma longa* is the richest and cheapest source of these diferuloyl methane derivatives (Balakrishnan, 2007). The relative proportion of these curcuminoids varies with the cultivar (Govindarajan and Stahl, 1980). Turmeric curcuminoids are important natural pigments. However, they are inherently lipid and water insoluble and are sensitive to light, pH, solvent system, and oxygen (Price and Buescher, 1996). Curcuminoids shows a variety of physiological and pharmacological properties. Several studies indicate curcumin to be anti-carcinogenic, anti-inflammatory, anti-venom, anti-viral and anti-microbial activities. Curcumin is reported to be a powerful antioxidant to restore both oxidative and reductive damage caused (Kapoor and Priyadarsini, 2001).

1.6.6.4. Use of turmeric

Turmeric is one of the important widely used. Turmeric and its extractives have diverse applications. Turmeric is a unique and versatile natural plant produce combining the properties of a spice, food colourant, cosmetic, and drug. In ethnic cuisine, turmeric is a common flavour ingredient. It is one of the principal ingredients
in curry powder due to its colour and aromatic flavour. Turmeric has proven antioxidative, anti-inflammatory, anti-carcinogenic, anti-mutagenic, anti-microbial, anti-viral, and anti-parasitic properties and is a known skin care and health food ingredient capable of preventing or retarding a number of illnesses (Balakrishnan, 2007). It has long been used in both Ayurvedic and Chinese medicines as an anti-inflammatory substance, to treat digestive disorders and in liver problems, and for the treatment of skin diseases and wound healing. Epidemiological observations suggest that turmeric consumption may reduce certain forms of cancer and render other protective biological effects in humans, which are attributed to its constituent-curcumin (Radha et al., 2006). The unique properties of the spice are attributable to the essential oil and curcuminoid components present therein.

In Asian countries, dry or fresh turmeric, as well as ground turmeric, are used for vegetable and meat dishes and soup-like preparations. In all cases, it is used mainly as a colouring agent, replacing synthetic colours, e.g. tartrazine, which are used formerly. In the food industry, turmeric powder is used in mustard paste, curry powder, etc. Curcumin or curcuminoids concentrate for food colour use is not a regular article of commerce because turmeric oleoresin is cheaper and satisfactory for most of the uses. However, in some food products, oleoresin is incompatible. Example includes ice creams, gelatins, lemonades, and liqueurs (Govindarajan and Stahl, 1980). Curcumin is included in the list of permitted colours with a restricted use because it is allotted a low ADI (acceptable daily intake) of 0-3 mg/kg body weight/day.

1.6.7. Role of starch in agglomeration and structure

In general, starch powders are semi-crystalline in nature. Its structure composes of amorphous and crystalline region in which glass transition and melting or gelatinisation may occur when the particles are in a high temperature condition such as in the drying process (Hoover, 2001). The particle size of starch grains varies widely, depending on the source. Chemically, starch is a carbohydrate and is a mixture of two polymers: α-amylose and amylopeptin. On heating starch in excess water, in the temperature range 55-75°C, starch undergoes the irreversible process of gelatinisation, in which it swells and partially dissolves. The amylopeptin absorbs water and swells and the amylose forms a clear viscous gel (Knight, 2001). Hence,
food powders with a high amount of starch help in the formation of agglomerates due to the process of gelatinisation. Liquid bridge and solid bridge may occur among the starch particles to form agglomerates. This is true in case of agglomeration of food powders that occurs during the drying process due to the formation of either liquid bridge or solid bridge (Tomas, 2007; Foster, Bronlund and Pasterson, 2006; Boonyai, Bhandari and Howes, 2004; Adhikari et al., 2003). Liquid bridge is generated in amorphous powder when it is at the temperature higher than its glass transition temperature. Its surface changes from a solid-like glassy phase to a liquid-like rubbery phase and becomes sticky. When neighbouring powder particles collide, the particles undergo the agglomeration process (Truong et al., 2004). Solid bridge mechanism occurs in solid or crystalline powder at the temperature higher than its melting temperature. The solid or crystalline portion in the powder particles melts and forms a bridge at the contact points resulting in the particle agglomeration (Tomas, 2007; Viguie et al., 2007; Nijdam and Langrish, 2006). Aichayawanich et al. (2011) have investigated the mechanism of agglomeration of cassava starch during pneumatic conveyor drying. It has been found that the phase transition correlates with starch agglomeration during drying. When the starch phase is in the rubbery phase, the agglomeration of the starch particles increases. However, the agglomeration of the starch decreases when the starch phase is in the glassy phase. This indicates that the agglomeration mechanism of the starch is the result of the liquid bridge formation.

1.7. Conclusions

Properties of food powder and their conversion to agglomerated products are important areas that directly affect the selection of process equipment, storage ability and product formulation. The area of understanding the behaviour of food powder is still at an infant stage though there is considerable progress in other non-food areas like ceramic, mining/metallurgy and pharmaceutical technology. Scope exists to study the properties of food powder with an emphasis in developing different food formulations. The specific areas that require attention are characterisation and understanding of food powders (e.g., turmeric) along with functional behaviour. It is also desirable that raw materials from different sources are also considered for research investigations to improve our existing knowledge on food powders.