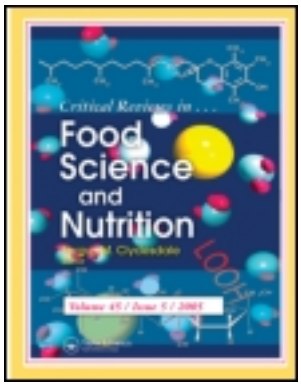

Critical Reviews in Food Science and Nutrition
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/bfsn20

Hydrocolloid Gel Particles: Formation, Characterization, and Application

P. Burey [a] , B. R. Bhandari [b] , T. Howes [c] & M. J. Gidley [a]

[a] Centre for Nutrition and Food Sciences , The University of Queensland , Brisbane, QLD 4072, Australia

[b] School of Land, Crop, and Food Sciences , The University of Queensland , Brisbane, QLD 4072, Australia

[c] School of Engineering , The University of Queensland , Brisbane, QLD 4072, Australia

Published online: 02 May 2008.

To cite this article: P. Burey , B. R. Bhandari , T. Howes & M. J. Gidley (2008) Hydrocolloid Gel Particles: Formation, Characterization, and Application, Critical Reviews in Food Science and Nutrition, 48:5, 361-377, DOI: 10.1080/10408390701347801

To link to this article: http://dx.doi.org/10.1080/10408390701347801

Critical Reviews in Food Science and Nutrition, 48:361–377 (2008)

ISSN: 1040-8398
DOI: 10.1080/10408390701347801

Taylor & Francis
Taylor & Francis Group

Hydrocolloid Gel Particles: Formation, Characterization, and Application

P. BUREY,[1] B. R. BHANDARI,[2] T. HOWES,[3] and M. J. GIDLEY[1]

[1]Centre for Nutrition and Food Sciences, The University of Queensland, Brisbane, QLD 4072, Australia
[2]School of Land, Crop, and Food Sciences, The University of Queensland, Brisbane, QLD 4072, Australia
[3]School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

Hydrocolloid gel particles of micron and sub-micron size are particularly attractive for use in many applications in the food, agricultural, pharmaceutical, and chemical industries, due to their biocompatibility, perception as "natural" materials, and soft-solid texture. Industrial applications for such particles include uses as texturizers in confectionery and cosmetic products, slow-release encapsulation agents for flavors, nutrients, and pharmaceutical products, and thickeners in soups and sauces. Properties such as particle size, hardness, shape, texture, and molecular release rates can be important for individual applications. In addition, product formats will determine specific needs for physical form (e.g. dry or wet) and compatibility with other components. The diverse range of potential applications for hydrocolloid gel particles provide a driver for understanding-led tailoring of raw material and process conditions. This review introduces some of the materials that are used to form hydrocolloid gel particles and the corresponding gel formation mechanisms. One issue of importance in the production of hydrocolloid gel particles is the control of particle properties, such as release profiles, strength, and detectability within products. An alternative technique to traditional methods of hydrocolloid gel particle production is evaluated and a model for control of particle size, and subsequently other particle properties, is proposed. Key properties of hydrocolloid gel particles are identified and characterization methods for evaluating these properties are described.

Keywords hydrocolloid, polysaccharide, gel particle, gelation, spray drying

INTRODUCTION

Hydrocolloids are hydrophilic polymers which generally contain many hydroxyl groups and may be polyelectrolytes. They are derived from vegetable, animal, microbial, or synthetic origins and are naturally present in foodstuffs or added to control the functional properties of such materials (Glicksman, 1983a; Hoefler, 2004). In most practical applications of hydrocolloids, they are primarily polysaccharides, although some proteins may be used. Hydrocolloids are used to modify many food properties including rheology (in the form of thickening and gelling) and water binding as well as emulsion stabilization, prevention of ice recryztallization and enhancement of organoleptic properties (Hoefler, 2004; Nussinovitch, 1997). Additional applications include adhesion, suspension, flocculation, foam stabilization, and film formation.

Address correspondence to Paulomi (Polly) Burey, Centre for Nutrition and Food Sciences, Hartley Teakle Building 83, University of Queensland, Brisbane, QLD 4072, Australia, E-mail: p.burey@uq.edu.au; polly.burey@ihug.com.au

One particular use of hydrocolloid materials, which is of growing interest, is in the form of gel particles for encapsulation or texture control within food, pharmaceutical, probiotic, medical, and cosmetic products (Gidley and Hedges, 1994; Hunik and Tramper, 1993; Juang et al., 2002; King, 1995; Klokk and Melvik, 2002; Krasaekoopt et al., 2003; Lapitsky and Kaler, 2004; Malone and Appelqvist, 2003; Mukai-Correa et al., 2004; Ocio et al., 1997; Sriamornsak and Nuthanid, 1998; Sugiura et al., 2005; Vogelsang et al., 2000; Wandrey et al., 2003; Wong et al., 2002; Zimmerman et al., 2005). Particulate forms of gelled systems are prized for their "short" texture, their ability to be processed in a flowable form, and the opportunity to tailor molecular release properties based on particle size, shape, and material characteristics. Hydrocolloids are particularly attractive for these applications as they are biocompatible and often from natural sources.

This paper reviews current work related to the formation and application of hydrocolloid gel particles. The need for studying these systems further is addressed. Network formation mechanisms of some gelling hydrocolloids are introduced and then

specific hydrocolloids which could be attractive for use in gel particle formation are described. The mechanisms which control gel particle formation are described and their effects on gel particle size are illustrated. Several gel particle formation techniques are evaluated and opportunities for further research in the area are outlined.

FIELDS OF APPLICATION

Hydrocolloids provide a renewable source of structuring and controlled release agents for a variety of potential uses, and are commonly encountered in food, pharmaceutical, agricultural, and other applications that require bio-compatibility.

Swollen particulate forms of gelled hydrocolloids are particularly useful as they combine macroscopic structure formation with an ability to flow and often have an attractive soft solid texture, which is especially sought in food applications, all at high water contents (>95%).

Hydrocolloid gel particles have many useful applications of which the most commonly encountered are:

- Structuring agents for use in food products
- Dispersed phases for strength and texturizing applications in food materials
- Controlled release agents for use in pharmaceutical, food and agricultural applications

Many consumer products are based on a soft-solid texture, or have soft-solid inclusions. There are often two distinct routes to achieving these features. One involves lipid-based structures such as emulsions or crystalline phases. Alternatively, structures based on particulate hydrocolloid systems can be used.

Many examples exist of the use of particulate hydrocolloids, with one motivation being the replacement of soft-solid textures traditionally achieved through structured fats. Specific examples of uses include particulate phases in confectionery and other soft-solid foods often involving gelatin inclusions, texturizers in cosmetic creams, encapsulation agents for flavors and nutrients, slow release watering agents for plants, drug delivery agents for pharmaceutical products, thickeners in soups and sauces, and absorbent agents.

In food applications, the most commonly encountered particulate structuring agent is starch. On cooking of starches, granules swell to produce a microstructure of swollen granules in a continuous phase of solubilized polymers. Swollen granule "ghosts" are often fragile, being largely broken down through processing, especially at high shear (Gotlieb and Capelle, 2005). Chemical cross-linking of starches is used to reinforce granules and provide a limit to gelatinization-driven swelling by tethering polysaccharide chains together (van de Velde et al., 2002). After cooking, these swollen granules are sufficiently robust to survive even the harshest of food processing regimes such as retorting (Paterson et al., 1997; van de Velde et al., 2002).

There are numerous application areas for chemically cross-linked starches, mostly based on their particulate character. However, for some applications, a non-chemical route would be preferred. There is a potential opportunity for particulate hydrocolloid systems to replace chemically cross-linked starches based on appropriate structuring, processing, and molecular release properties without the need for chemical treatment.

The characteristics of gel particles, and the application for which they are used, will depend on the type of hydrocolloid, the network formation mechanism and the processing method used for particle formation. Whilst there is a plethora of information available on bulk gel formation and gel properties, little research on the control of discrete gel particle properties has been reported. This review aims to introduce some of the concepts which are relevant to the control of gel particle properties and suggest ways in which this control may be achieved.

NETWORK FORMATION MECHANISMS

Hydrocolloid gel networks form through entwining and cross-linking of polymer chains to form a three-dimensional network. The mechanism by which this interchain linking occurs can vary and other reviews have covered this in great detail (Burchard and Ross-Murphy, 1990; Djabourov, 1991). However, for gelation of hydrocolloids there are three main mechanisms, namely: Ionotropic Gelation, Cold-Set Gelation, and Heat-Set Gelation, which will be outlined here. Other gelling or network mechanisms already built into the raw material (e.g. starches and plant cell walls) are outside the scope of this review. Hydrocolloid gelation can involve a hierarchy of structures, the most common of which is the aggregation of primary interchain linkages into "junction zones" which form the basis for the three-dimensional network characteristic of a gel (Fig. 1).

Various parameters such as temperature, the presence of ions, and the inherent structure of the hydrocolloid can affect the physical arrangement of junction zones within the network.

Ionotropic Gelation

Ionotropic gelation occurs via cross-linking of hydrocolloid chains with ions, typically cation-mediated gelation of negatively charged polysaccharides (Glicksman, 1983c; Hoefler, 2004). Without the presence of specific ions at appropriate concentrations, the hydrocolloid will typically have less valuable thickener properties. Examples of such systems are alginate, carrageenan, and pectin (Christensen, 1983; Draget, 2000; Imeson, 2000; King, 1983; May, 2000) There are two main techniques by which ionotropic gelation can be carried out, namely diffusion setting and internal gelation.

Diffusion Setting

Diffusion setting involves the introduction of a hydrocolloid solution to an ionic solution, with gelation occurring via diffusion of ions into the hydrocolloid solution (Glicksman, 1983a;

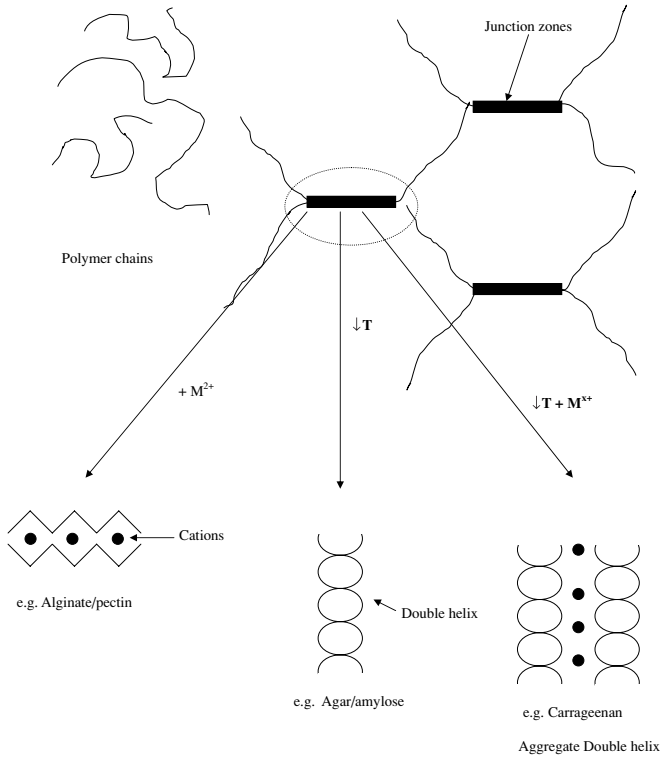

Figure 1 Illustration of cross-linking in hydrocolloid gels.

Hoefler, 2004; Nussinovitch, 1997). The disadvantage of this technique is that it can often cause inhomogeneous gelation of gel particles due to the diffusion mechanism. Surface gelation often occurs prior to core gelation and can inhibit core gelation, leading to gel particles with firm outer surfaces and soft cores. However, where this is the desired microstructure, this may be the preferred route.

Internal Gelation

Internal gelation overcomes the main disadvantage of diffusion setting as it requires the dispersion of ions prior to their activation in order to cause gelation of hydrocolloid particles. This usually involves the addition of an inactive form of the ion that will cause crosslinking of the hydrocolloid, which is then activated by a change in e.g. pH after sufficient dispersion of the ion is complete (Glicksman, 1983a; Hoefler, 2004). This is particularly useful in alginate systems which can gel rapidly and may become inhomogeneous if gelation occurs before adequate ion dispersion has occurred.

Cold-Set Gelation

Networks may form from hydrocolloid solutions that are cooled from elevated temperatures. Typically a solution is made by dissolving a hydrocolloid in powder form in water at high temperature or at boiling point and then cooling to room temperature. As the solution cools, enthalpically-stabilized interchain helices may form from segments of individual chains, leading to a three-dimensional network. Examples of such systems are gelatin and agar (Glicksman, 1983a; Hazen, 2004; Hoefler, 2004).

Heat-Set Gelation

Heat-set gels require the application of heat to gel (e.g. curdlan, methyl cellulose, starch). Heat setting is the least common technique used for forming gel particles and is usually only used where heat setting is required in foods (e.g. the use of starch in sauces). Heat setting mechanisms occur by unfolding/expansion of native structures (e.g. starch and native proteins) and their subsequent rearrangement into a network (Djabourov, 1991). One interesting feature of starch granules is that they are already particulate in their native form.

TYPES OF HYDROCOLLOID GELS

There are many industrially important gelling hydrocolloids from diverse origins (Table 1).

Some of the materials shown in Table 1 are of particular interest for use in the production of gel particles and are described below.

Agar

Agar, or agarose, is derived primarily from the Gelidium and Gracilaria species of seaweed and was first produced and developed in Japan (Glicksman, 1983b; Hoefler, 2004; Williams and Phillips, 2000). Agar is a complex mixture of polysaccharides which all have the same backbone structure but are substituted to a variable degree with charged groups. The backbone structure is termed agarose and is essentially sulphate-free and consists of chains of alternate β-1,3-linked-D-galactose and α-1,4-linked 3,6-anhydro-L-galactose (Glicksman, 1983b) (Fig. 2).

Agarose molecular weights are typically at least 100,000 Daltons (Armisen and Galatas, 2000). Agar gels via a cold-set mechanism and the gelling ability of agar is due to the formation of

Table 1 Sources of industrially important natural gelling hydrocolloids (modified from Williams and Phillips (2000))

Source	Specific Source	Hydrocolloids	Primary Use
Botanical	Plants	Starch, pectin, cellulose	Thickener and/or gelling agent
Algal	Red seaweeds	Agar, carrageenan	Gelling agent
	Brown seaweeds	Alginate	Gelling agent
Microbial		Curdlan	Thickener and/or gelling agent
Animal		Gelatin	Thickener and/or gelling agent

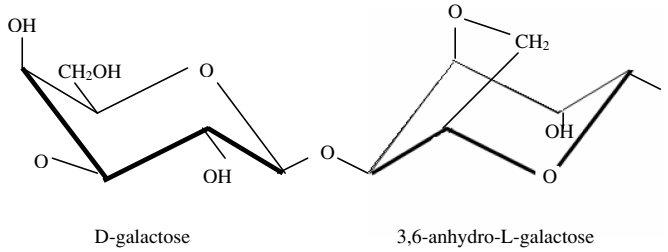

Figure 2 Agar structure.

double helices involving two polymer chains, driven in part by the rigidity of 3,6-anhydro-L-galactose residues. The anhydro bridges together with limited conformational flexibility around glycosidic bonds constrain the molecule, promoting the formation of a regular helix; subsequent aggregation of helices results in the formation of a gel. Agar gels can be formed in dilute solutions with concentrations lower than 1 w/w% (Glicksman, 1983b; Hoefler, 2004; Williams and Phillips, 2000). The gels that are formed tend to be rigid, brittle, have well-defined shapes, and distinct melting and setting points. The gels also demonstrate both syneresis and hysteresis with agar gelation occurring at temperatures far below the melting temperature. A 1.5 w/w% agar solution forms a gel on cooling to about 32–39°C but does not melt below 85°C (Glicksman, 1983b; Hoefler, 2004; Williams and Phillips, 2000).

Alginate

Alginates or algin is a generic term for the salts and derivatives of alginic acid which are derived primarily from brown seaweed (Phaeophyceae) (King, 1983). Alginates are linear unbranched polymers containing β-(1→4)-linked D-mannuronic acid (M) and α-(1→4)-linked L-guluronic acid (G) residues (Fig. 3). The proportion of M and G residues is dependent on the seaweed species from which the alginic acid is isolated. The sequence of M and G residues varies between species and probably within single polymer chains, based on the types of sequences shown in Fig. 4.

Alginates are commercially available as sodium, potassium, or ammonium salts and are produced in a range of mesh sizes,

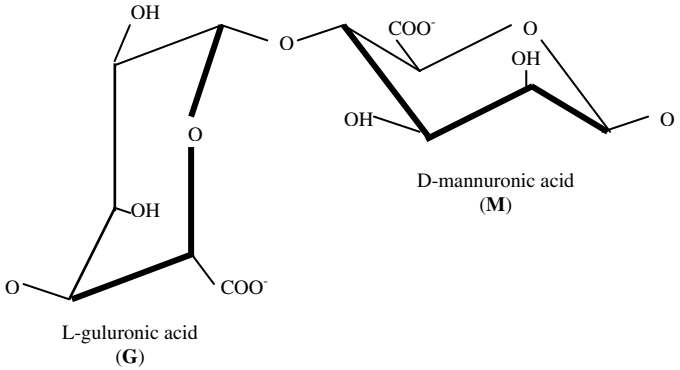

Figure 3 Alginate structure.

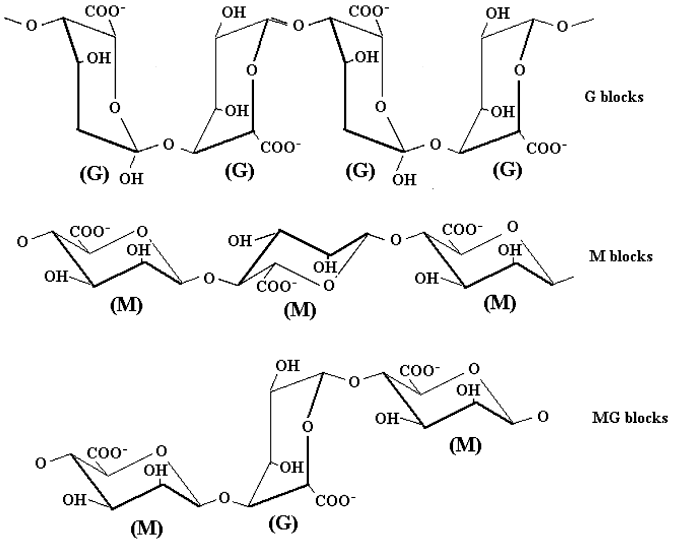

Figure 4 Block types in alginate. (Modified from Nussinovitch (1997)).

viscosity grades, and calcium levels to provide specific functionalities. Alginates can be prepared with a large range of molecular weights—60,000–700,000 Daltons depending on the application (Draget et al., 1994).

Alginate forms gels via an ionotropic mechanism and gels particularly well in the presence of divalent cations such as calcium (Biswal and Singh, 2004), although barium and strontium also show excellent gelling properties with alginate (Draget, 2000). Gelation occurs by interaction between the cations and the guluronic acid residues (Douglas and Tabrizian, 2005; Glicksman, 1983a). The kinetics of alginate gelation can be affected by the temperature at which gelation occurs, as well as alginate concentration and ion concentration (Draget, 2000). Alginate can gel rapidly in the presence of non-sequestered calcium ions and hence the ability to control introduction of these cross-linking ions is important. As a result, the internal setting method may be more attractive unless a rigid particle core and fluid center is desired (Draget, 2000; Glicksman, 1983b; Hoefler, 2004). Typically used gelling concentrations for alginate are from 1–2 w/w% (Blandino et al., 1999; Liu et al., 2003).

Carrageenan

Carrageenans are extracted from red seaweeds of the class Rhodophyceae, in which it is involved in the maintenance of structure as a major component of the cell wall. Carrageenan does not have a single molecular structure but consists of a family of structures, a group of linear galactan polysaccharides that have an ester sulfate content of 15–40% (w/w) and contain alternating (1→3)- and (1→4)-β-D-glycosidic linkages (Imeson, 2000, Nussinovitch, 1997).

The three types of commercially available carrageenans are known as κ, ι, and λ (Fig. 5). They do not exist in isolation in the natural world and commercial carrageenans are either mixtures of these types, with one type predominating, or they are hybrid

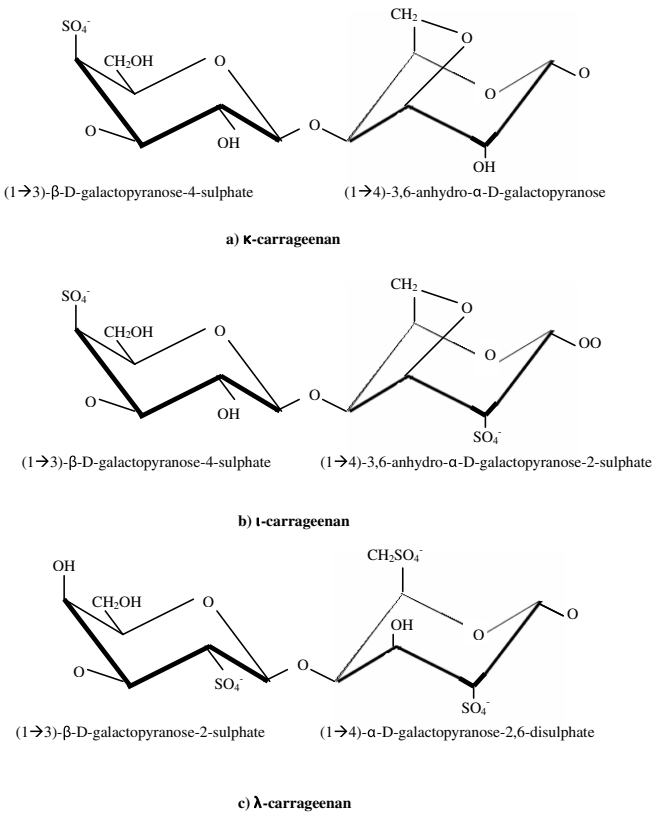

Figure 5 Carrageenan structural types.

molecules containing structural components of more than one type (Hoefler, 2004).

The calcium and potassium salts require heating to 60°C to completely hydrate (Hoefler, 2004; Imeson, 2000) prior to gelation. Carrageenan gels form via an ionotropic gelation mechanism coupled with a cold-set mechanism (Belton et al., 1984). Gel formation in κ- and ι-carrageenans involves helix formation on cooling from a hot solution together with the gel-inducing K^+ or Ca^{2+} cations respectively, which not only aid helix formation but subsequently support aggregating linkages between the helices so forming the junction zones (Imeson, 2000; Rochas and Rinaudo, 1984). The addition of extra ions to a gelling system increases the stability of the helix and promotes helix aggregation which is important for the gelation process via the so-called domain model (Morris, et al., 1980).

The cations that can be used to form kappa carrageenan gels can be divided into three categories with respect to helix-promoting abilities:

- Non, specific, monovalent–Li^+, Na^+, $(CH_3)_4N^+$
- Divalent–Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}
- Specific monovalent ions–K^+, NH_4^+, Cs^+

The specific monovalent cations bind to the helix of κ-carrageenan based on their ionic size; smaller (Li^+, Na^+) and larger ($(CH_3)_4N^+$) monovalent ions are both excluded (Morris et al., 1980; Rochas and Rinaudo, 1984). κ-carrageenan typically forms a rigid, brittle gel.

ι-carrageenan shows strong helix stabilization with divalent ions, such as calcium. No site-specific binding seems to be involved, with the effect being due to the higher charge density of both ι-carrageenan and the multivalent cation. ι-carrageenan gels are typically softer, shear reversible, elastic, and cohesive. λ-carrageenan does not appear to gel but has some use as a thickener.

The three types of carrageenan gels have very different textures, due to the differences in their sulfate groups and anhydro bridges (Imeson, 2000). The sodium salts of all three are cold water soluble and do not gel until sufficient potassium (for κ-carrageenan) or calcium (for ι-carrageenan) ions are introduced into the system. Typical gelling concentrations used are 0.5–3% (Nussinovitch, 1997).

Pectin

Pectin is found in virtually all land-based plants and is a structural polymer, the intercellular "glue" that helps to reinforce the basic cellulose structure of plant cell walls (Glicksman, 1983c; May, 2000). Commercial pectin is extracted under mildly acidic conditions from citrus peel or apple pomace (dried pulp) and sometimes from sugar beet residues or sunflower heads (Hoefler, 2004; May, 2000).

The chemical structure of pectin consists of a linear chain of galacturonic acid units with molecular weights of approximately 110,000–150,000 (Christensen, 1983; Hoefler, 2004; May, 2000). While still in the fruit there is, on average, one free acid group to between three and four methyl esters of galacturonic acid, although there is no repeating sequence within the polymer chain. This corresponds to a degree of esterification (DE) of 70–80%. Esterification can be controlled during the extraction process so that the DE of the final pectin product can range from 0–75%. It is the DE and the arrangement of methyl esters along the pectin molecule that controls how the pectin behaves as a gelling agent or protein-stabilizing agent (Hoefler, 2004).

In the plant cell wall, pectin includes regions known as rhamnogalacturonan I and II that have complex molecular structures. However, commercial pectin is extracted from sources which have relatively low amounts of these structural features which are further reduced by the extraction conditions used in commercial pectin production. From the point of view of gelling properties, the structure shown in Fig. 6 represents all of the important features.

Pectin that has a DE of less than 50% is referred to as low ester (LE) pectin. Generally LE pectins gel via an ionotropic gelation mechanism with divalent ions (e.g. calcium) while high ester (HE) pectins gel at high soluble solids and low pH (Hoefler, 2004) as encountered in jam preparation (Nussinovitch, 1997). Sugars play a role in the formation of the HE pectin gel network by changing the solvent structure such that pectin chains are forced together, thereby forming a network structure based on hydrophobic interactions (Nussinovitch, 1997).

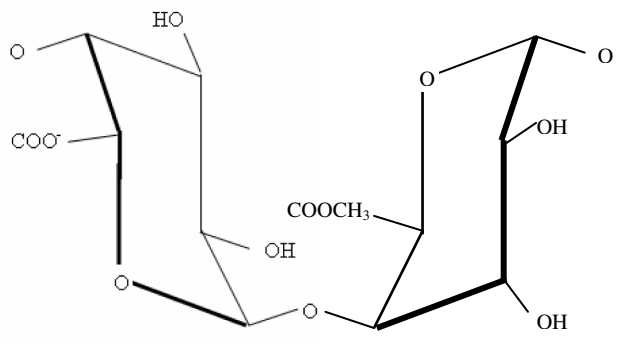

Figure 6 Pectin structure.

For low-ester pectins an "egg-box" model of network formation has been suggested for the primary junction zones in the gel network (Rees, 1982) which is similar to the network structure formed in alginate gels. The basis of the network is pectin chains cross-linked by calcium ions through chelation by carboxyl and hydroxyl groups (Rees, 1982).

Pectin can be in acid or metal salt form. It is water-soluble in all forms and can achieve high solubility in water at room temperature with sufficient shear, although for complete hydration it is necessary to heat to about 60°C (Hoefler, 2004). Typical gel concentrations range from 2–4 w/w% for HE pectins and 0.1–4 w/w% for LE pectins (Glicksman, 1983c; May, 2000). Similar to alginate, the gel properties of LE pectin gels are affected by hydrocolloid concentration, ion concentration, and the method of preparation.

Gelatin

Gelatin differs from the hydrocolloids discussed above in that it is derived from an animal protein, collagen, via controlled acid or alkaline hydrolysis. Collagen may come from hide, bone, or other collagenous material (Belitz and Grosch, 1999). Commonly the collagen used is of bovine (cow), porcine (pig), or piscine (fish) origins (Johnston-Banks, 1990). The properties of gelatins are affected by the source, age, and type of collagen (Rix, 1990).

A typical gelatin consists of 14% moisture, 84% protein, and 2% ash (Rix, 1990). The protein consists of a mixture of amino acids of which glycine, proline, and hydroxyproline are present in the most abundance (Cuppo et al., 2001; Johnston-Banks, 1990). Gelatin molecules contain repeating sequences of glycine-X-Y triplets, where X and Y are frequently proline and hydroxyproline amino acids (Fig. 7).

These repeating sequences occur over extended regions of the polymer chain. This regularity is necessary in order to form the characteristic triple helical structure in gelatin and other collagen family proteins and the subsequent ability to form gels in which triple helical segments form the basis for cross-linking and three-dimensional network formation (Clark and Ross-Murphy, 1990).

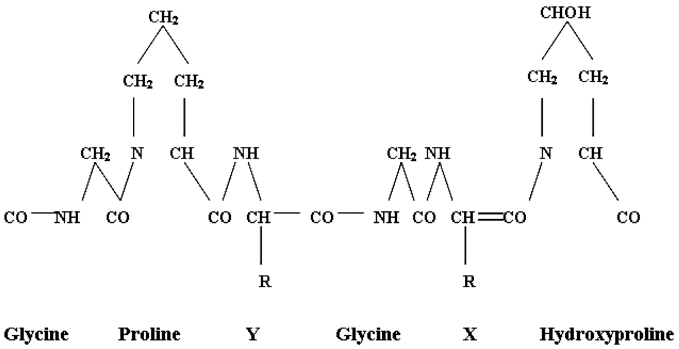

Figure 7 Repeating structure in gelatin responsible for triple helix structure.

Gelatin forms a thermoreversible gel through a cold-setting mechanism in aqueous solvents (Djabourov, 1991). Above 40°C gelatin in solution behaves like a typical synthetic polymer with the individual macromolecules each assuming random-coil configurations (Finer et al., 1975) with typical molecular weights of 2×10^5 Daltons (Bohidar and Jena, 1993). These random coils consist of single polypeptide chains, termed α-chains that may be entangled. Upon cooling these coils undergo a coil-to helix transition, leading to gelation (Fig. 8) (Finer et al., 1975).

Gelatin gels are typically made from higher concentrations than gels formed with agar, alginate, carrageenan, and pectin. Typical gelatin gel concentrations used in food products are 1–5 w/w% (Tosh et al., 2003; Williams, 1964). Gel properties are typically affected by gelatin concentration, cooling rate used during gelation, pH, and temperature at which the particular source of gelatin will gel. Gelation temperatures for gelatin are typically just above room temperature; this is one of the factors leading to the relatively slow gel setting kinetics for gelatin.

HYDROCOLLOID GEL PARTICLES–IN-USE PROPERTIES

Hydrocolloid gel particles can be characterized in many different ways in relation to their use in structured materials.

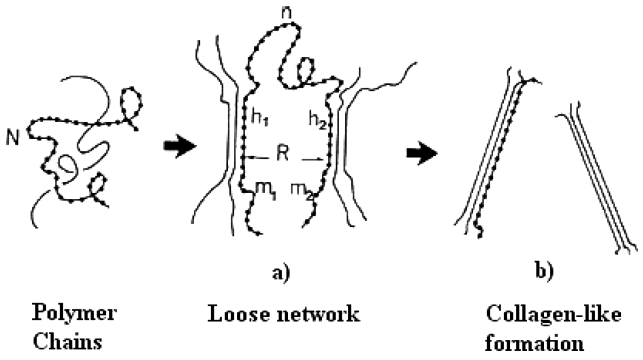

Figure 8 Schematic of gelatin gelation. Two steps are involved A) formation of a loose network and B) renaturation to a collagen assembly (modified from Djabourov 1991).

Two aspects will be discussed here—size/shape, and in-mouth detectability.

Size and Shape Definition

As a broad dictionary definition, a particle is defined as "a minute fragment or quantity of matter or the smallest perceptible or discernible part of an aggregation or mass." Using modern analytical techniques, particles can now be detected on the nanometer scale; however, particles may not be discernible by human senses (sight in visible light, touch/mouthfeel) when incorporated into materials until the micron or millimeter scale. Techniques for assessing the size and shape of the microgel particles will be addressed in a subsequent section.

In-Mouth Detectability and Factors Affecting Sensorial Detection

Acceptance of hydrocolloid gel particles in food products may be based on (lack of) detectability in the mouth. Particle detectability in foodstuffs can depend on the particle characteristics as well as features of the medium in which they reside, including such characteristics as water absorption, sedimentation rate of particles, size, shape, and deformation resistance (Imai et al., 1999).

Visual acceptability of a product containing particles may be based on whether it is desirable to observe particles in visible light. In some applications, the use of suspended particles will give food products a cloudy appearance which may not be ideal for consumer acceptance. Visibility of gel particles will depend on size; very small particles may be minute enough that they cannot be observed in visible light, whilst very large expanded gel particles may also be invisible due to their refractive index approaching that of their surrounding medium.

When particles are detected sensorially by the mouth, the materials are often described as "grainy" or "gritty." Harder particles have been shown to be detected at smaller sizes through detection of a gritty texture (Utz, 1986). (Engelen et al., 2005) found that large, hard, sharp particles in a low viscosity medium produce a more rough, gritty, and unpleasant sensation than small, soft, and smooth particles in a higher viscosity medium.

An example of size of particles combined with their medium having an effect on detectability comes from the fact that sugar particles $\geq$25 μm in chocolate can be detected by the roof of the mouth (Rostagno, 1969), although they cannot be detected in a softer product such as fondant (Woodruff and Gilder, 1931). In smoother, creamier products such as margarine and ice cream, particle detection can vary, with 22 μm particles the minimum size detected in margarine by the mouth, and 55 μm the minimum size detectable in ice cream (Imai et al., 1999). Hard particles, such as alumina, can be detected at smaller sizes of 10 μm.

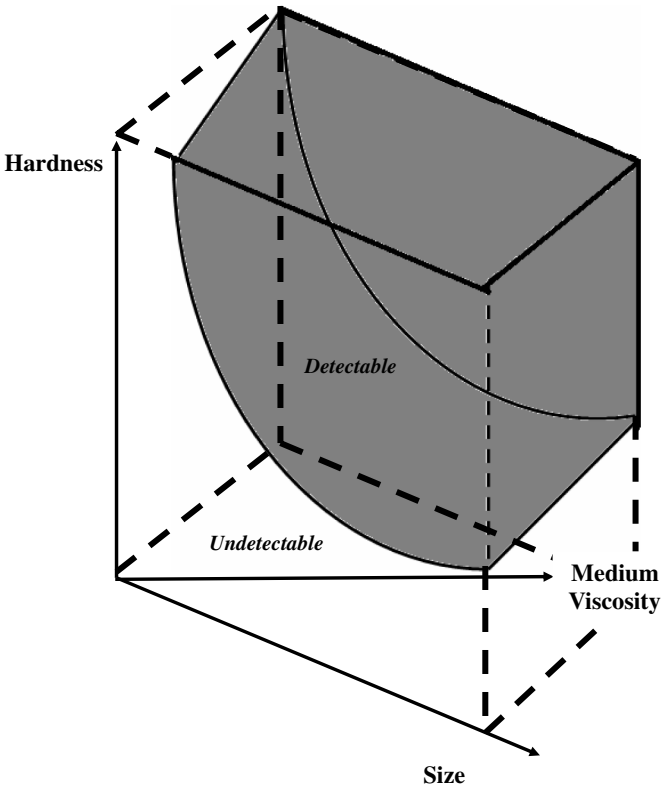

Figure 9 Particle detectability as a function of hardness, size, and suspension medium viscosity.

Therefore the combination of particle characteristics that determine the level of particle detection are: particle size, particle hardness, and medium viscosity (Fig. 9). Hence if the objective is to prevent or reduce the detection of particles within a food material, it is preferable to use soft uniform particles in a high viscosity medium. The use of hydrocolloid gel particles may achieve this aim.

HYDROCOLLOID GEL PARTICLES: FORMATION PRINCIPLES

There are many techniques available for the production of hydrocolloid gel particles, the use of which can be dependent on whether the hydrocolloid may gel in water without additives, as in the case of agar and gelatin, or whether ions are required to aid gelation, as in the case of alginate, carrageenan, and low methoxy pectin. The main purpose of most of these techniques is to cause droplet breakup during a process of gelling the polymer phase. The combination of particle/droplet formation and the gelation driving force will determine final particle characteristics, such as the size and the strength.

There are two main mechanisms for gel particle formation; continuous phase formation and dispersed phase formation (Fig. 10). The methods differ in the order of process steps, which can lead to different gel particle properties. Continuous phase

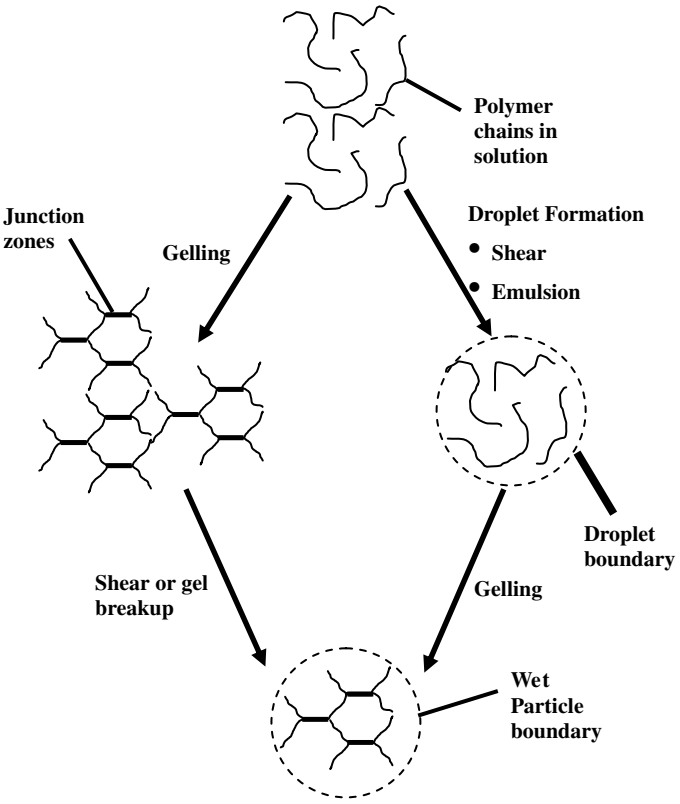

Figure 10 Schematic of gel particle formation mechanisms.

formation occurs when the gel is formed first and then broken up into smaller pieces; whereas dispersed phase formation occurs when droplets are formed first, which are then transformed into gel particles.

HYDROCOLLOID GEL PARTICLE PRODUCTION METHODS

Continuous Phase Formation

Continuous phase formation of gel particles consists of forming the gel or pregel first and then breaking up the gel/pregel to form discrete gel particles. Coacervation and shear processes are most frequently used.

Coacervation

Coacervation typically involves the separation of a colloidal system into two liquid phases. The phase more concentrated in the colloid component is the coacervate, and the other phase is the equilibrium solution (Gander et al., 2002). Polymer coacervation is a well-established technique which is often used for reversible gelation and encapsulation of biological materials, molecules or cells (Gander et al., 2002; Gouin, 2004; Thomasin et al., 1998). In simple coacervation, the polymer is separated out by the use of electrolytes or desolvated by the addition of a water miscible nonsolvent, or by a change in temperature.

Complex coacervation is essentially driven by the attractive forces of oppositely charged polymers (Gander et al., 2002), but can also be be controlled by changes in pH, temperature, and time (Burgess and Carless, 1984; Chilvers et al., 1988). Gelatin is an excellent example of a hydrocolloid that can form gel systems via a coacervation pathway and is known to form particle systems, using this technique, often with gum arabic (de Jong and Lens, 1932; Gouin, 2004; Malone and Appelqvist, 2003; Mohanty et al., 2004; Mohanty and Bohidar, 2006). Particle sizes on the order of 150–400 μm have been formed (Malone and Appelqvist, 2003), although particle sizes as small as 50–400 nm can also be achieved(Mohanty et al., 2004). Particles formed from the coacervation technique are often produced in mixed hydrocolloid systems (de Kruif et al., 2004; Joseph and Venkataram, 1995; Lucinda-Silva and Evangelista, 2003).

Shear Gels

Breakup of a hydrocolloid solution or gel using shear, to form discrete regions (that subsequently gel) or particles of gel material is frequently used. This approach works particularly well for multiphase systems (Wolf et al., 2001a; Wolf et al., 2001b). The most common approach is for a hydrocolloid solution to be brought close to gelation and then sheared to encourage the breakup of the incipient gel into smaller particles.

In multiphase systems, if the ratio of viscosities of the mixed hydrocolloids is controlled, then particles of many shapes and sizes can be formed. To obtain small particles the continuous medium must have low viscosity, while the discrete phase has high viscosity, and vice versa to obtain large particles. Studies of shear gel particles have shown that the particle size and shape are dependent on the viscosity ratio of mixed phase systems, shear stress, shear rate, and type of shear (Wolf et al., 2001a; Wolf et al., 2001b). Oscillatory shear tends to promote small spherical particles, while steady shear causes the formation of larger elongated particles. This has been shown in various studies of deforming droplets of hydrocolloids such as carrageenan, pectin, and gelatin (Hamberg et al., 2003; Lofgren et al., 2002; Walkenström and Hermansson, 1998). One of the most important factors controlling the size and shape of the hydrocolloid droplets are the competing mechanisms of droplet gelation and dissolution or spreading of the droplets. Typical gel particle sizes obtained using this technique are 4–100 μm (Wolf et al., 2001b).

Dispersed Phase Formation

Dispersed phase formation involves formation of a droplet prior to gelation; the droplet then becomes a discrete gel particle after gelation has occurred. This technique is particularly useful for systems which gel via ionotropic gelation as droplets of the hydrocolloid solution can be formed prior to the introduction of ions to aid gelation. Examples of gel particle formation techniques which use this mechanism include extrusion and variations thereof, and emulsion formation.

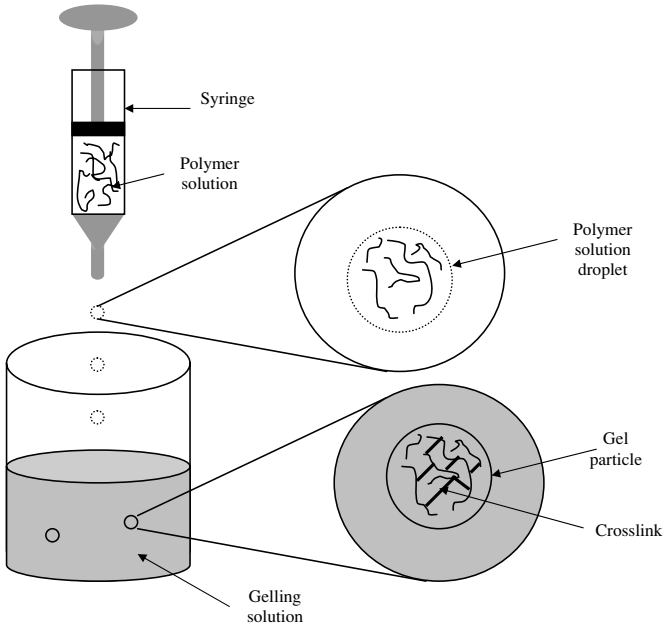

Figure 11 Extrusion formation of gel particles.

Extrusion

Extrusion is a commonly used technique for the formation of gel particles. On a small scale this may involve the use of a syringe needle (Blandino et al., 1999; Cheng and Lim, 2004; Hills et al., 2000; Hunik and Tramper, 1993). A hydrocolloid solution is loaded in a syringe and then extruded through a needle, to form solution droplets which then gel based on the conditions that the solution is extruded into (Fig. 11). The size of the droplets, and thus the subsequent gel particles, depends upon the diameter of the needle, the flow rate of the solution, and the viscosity of the solution.

This technique may be applicable to fast gelling hydrocolloids that do not require ions for gelation, but can also be used to extrude droplets into a hardening bath containing ions to promote gelation of the solution. If the gel is ionotropic, then the concentration of the ionic solution in the hardening bath will also affect final gel particle size. Typical gel particle sizes using this technique are 0.5–6 mm using conventional dropping methods (Blandino et al., 1999; Murakata et al., 2001; Ouwerx et al., 1998) and on the scale of hundreds of microns if modified techniques are used to atomize the hydrocolloid solution (Murakata et al., 2001). On an industrial scale commercial extruders and scraped-surface heat exchangers may be used to form gel particles (Brown et al., 2004; Peng et al., 2006).

Electrostatic

The electrostatic technique is a modified version of the small-scale extrusion technique where the syringe and the solution have opposite charges, which can affect gel particle size (Goosen, 2003; Klokk and Melvik, 2002; Zvitov and Nussinovitch, 2001; Zvitov and Nussinovitch, 2003). The rate at which the droplets form, and droplet size, is needle diameter, charge arrangement (electrode geometry and spacing), and strength of electric field (Bugarski et al., 1994), although hydrocolloid solution and hardening solution (if present) properties can also have an effect. The most effective electrode and charge arrangement for producing small droplets is a positively charged needle and a grounded plate. Two other arrangements are also possible; positively charged plate attached to needle, and a positively charged collecting solution (Goosen, 2003). If a positive charge is always on the needle, this ensures that the smallest gel particle size is produced at the lowest applied potential (Goosen, 2003). Particle sizes ranging from 40–2500 μm can be achieved using this method (Bugarski et al., 1994; Goosen, 2003; Zvitov and Nussinovitch, 2003).

Ultrasonic

This technique is also a modified version of the extrusion method in which ultrasonic breakup of a polymer solution stream is used. Liquid is pushed from a reservoir to a nozzle, which is forced to vibrate at ultrasonic frequencies. The liquid is broken into homogeneous droplets that gel when dropped into a hardening bath (Cellesi et al., 2004; Hunik and Tramper, 1993). Droplet, and subsequently gel particle size, is controlled by the flow rate of solution and the ultrasonic frequency at which the droplets are vibrated. Gel particles can range in size from hundreds of microns (Cellesi et al., 2004) up to 1–5 mm (Hunik and Tramper, 1993) using this technique.

Emulsion

The emulsion technique uses media other than water to aid gel particle formation. In food applications, the hydrocolloid solution is often suspended in vegetable oil and then introduced to the appropriate ionic solution to promote gelation (Lamprecht et al., 2000, Sugiura et al., 2005). The hydrocolloid and ionic solution droplets collide with each other in the stream of oil, and the reaction between the hydrocolloid and ions proceeds when successful coalescence of the droplets takes place (Fig. 12) (Campbell et al., 2004; Liu et al., 2003; Malone and Appelqvist, 2003).

The size of the gel particles formed using this method is dependent on the viscosity of the suspending oil, ratio of oil to hydrocolloid solution, emulsifier type, and amount of energy used to create the oil-hydrocolloid emulsion (Reis et al., 2006). Hydrocolloid solution droplet sizes can range from 0.2–80 μm (Huang et al., 2001), although they can be as large as 5000 μm (Malone and Appelqvist, 2003). Gel particle sizes can range from as low as 10 μm up to 3 mm (Liu et al., 2003; Malone and Appelqvist, 2003). There is a difficulty with this technique if aqueous gel particles are required as adequate removal of the oil phase from the droplets can prove difficult or messy, and adds another separation step to the process.

AN ALTERNATIVE APPROACH: FORMATION OF GEL PARTICLES FROM A DRIED INTERMEDIATE

There are several limitations of the techniques described above. These may include:

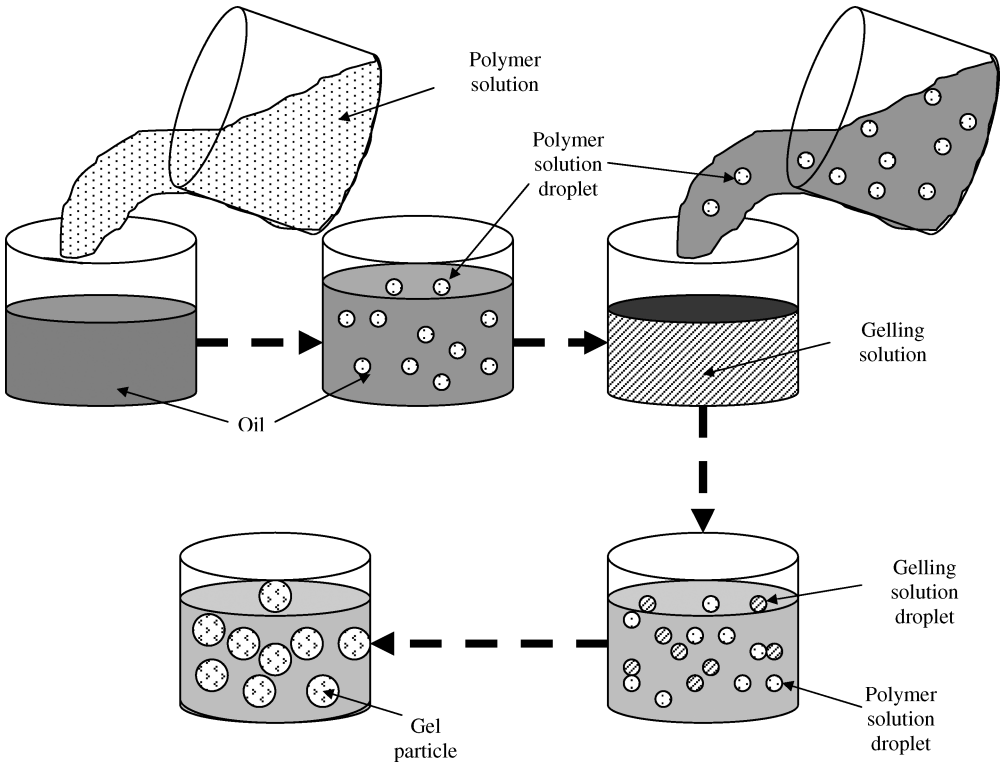

Figure 12 Emulsion formation of gel particles.

- The requirement for sophisticated equipment
- Difficulties in scaling up
- Expensive storage and transport costs due to the high level of water

The extrusion method may find widespread use for the production of gel particles within complex food products such as reduced fat spreads and frozen desserts, but is likely to be less useful for the preparation of discrete micron scale gel particles. In order to broaden application opportunities, additional approaches are required for the large-scale production of hydrocolloid gel particles. A dried intermediate is attractive in many cases, as transport and storage costs are minimized, and products can be made at the time and place that they are desired. Spray drying could be used to produce intermediate particles prior to gelation via hydration in an appropriate liquid medium.

This gel particle formation process therefore consists of two major steps: 1. Spray drying of a hydrocolloid solution; 2. Hydration of spray dried particles in an appropriate medium to form gel particles.

Dried Intermediate Formation–Spray Drying

A spray dried intermediate minimizes volume/mass, and hence storage and transport requirements are much less than for hydrated gel particles. Spray drying has already been proven to scale up well and has been used for large scale operations (e.g. milk powder, fruit juices etc) (Bhandari, 2005; Deis, 1997; Masters, 1991). Spray drying technology has been used for many years and is a very simple process, requiring standard equipment. It is suitable for both lab-scale and industrial scale particle formation and has been used with excellent results for microencapsulation of flavors, probiotics, and drug delivery (Krasaekoopt et al., 2003).

Spray drying involves atomization of a liquid feed and application of heat to dry the atomised solution (Bhandari, 2005; Masters, 1991) (Fig. 13). The objective is to produce a spray of high surface-to-volume ratio droplets (ideally of equal size), then to uniformly and quickly evaporate the water. Droplet, and ultimately dry particle size, can be controlled by flow rate, solution concentration, temperature, pressure, feed-to-air ratio, and the atomization method (Elversson and Millqvist-Fureby, 2005; Masters, 1991). Atomization is an important operation in spray drying, which controls droplet formation, with the two most common techniques being nozzle atomization and rotating disk atomization.

Nozzle

The use of a single fluid nozzle is common in spray drying. the solution is passed through a nozzle of a certain orifice size and under high pressure (Fig. 14). The liquid leaves the nozzle in a thin film at the orifice edges, but disintegrates rapidly into droplets. Droplet size can be controlled by all the parameters mentioned previously, as well as by nozzle diameter. This atomization technique may be prone to clogging at the nozzle and hence may encounter problems if gelling or highly viscous

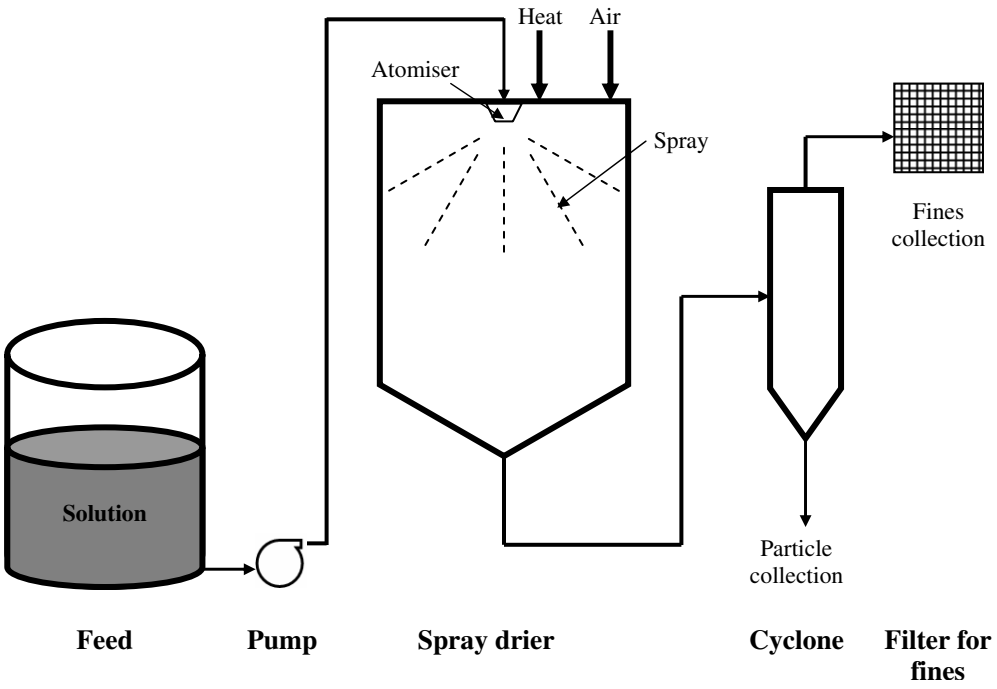

Figure 13 Schematic of the spray drying process.

solutions are used. The size of droplets formed using a nozzle atomizer range from 10–600 μm (Bhandari, 2005; Masters, 1991; Oakley, 2004). Particle size distributions are typically at the larger end of this scale, but have a narrow range of diameters (Bhandari, 2005). The mean particle size of spray dried particles can range from 30–80 μm, although particles as small as 1–2 μm can be formed, if there is a large difference between initial and final solids content.

Rotating Disk

This is the most commonly used atomizer in the food industry (Masters, 1991). The solution is dropped onto the rotating disk which then spreads into a thin film at the disk edge (Fig. 14). The rotation of the disk and friction with the surrounding air causes the film to disintegrate into droplets. A wide range of particle sizes can be formed and can be controlled by manipulating disk rotational speed, as well as other parameters mentioned previously. Clogging rarely occurs as there are no small orifices to get blocked. Usage of a rotating disk atomizer causes formation of droplets ranging in size from 10–600 μm (Bhandari, 2005; Masters, 1991; Oakley, 2004). Particle size distributions are typically very broad, with particles of diameters as small as a few microns, ranging up to hundreds of microns. The mean particle size of spray dried particles can range from 30–80 μm and size distribution is dependent on the initial solids content and desired final solids content.

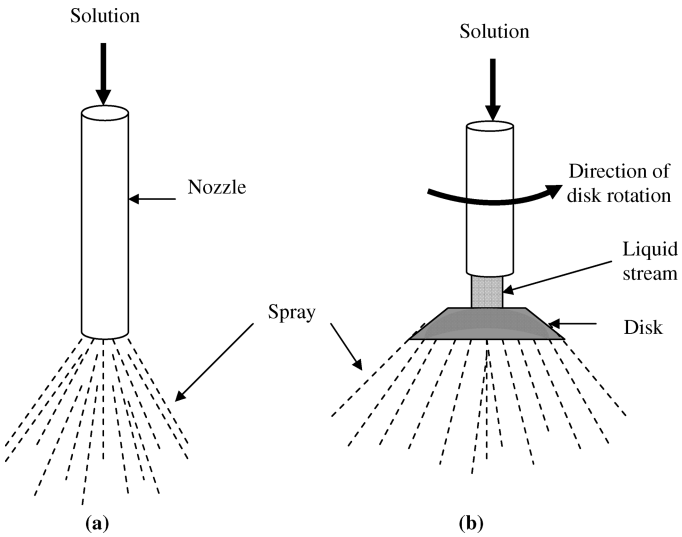

Figure 14 Schematic of a) nozzle atomization; b) disk atomization.

Gel Particle Formation–Hydration

The use of a spray-dried intermediate allows ease of control of particle properties via manipulation of particle gelation and expansion kinetics (Fig. 15). By controlling gelation and expansion in tandem, it is possible to create a range of particle sizes from a spray dried intermediate ranging from 2–30 times the size of the dried particle, typically 5–400 μm (Gidley and Hedges, 1994).

Figure 15 depicts various hydration regimes, which can lead to several different gel products, ranging from low-swelling particles (Type I), through to medium (Type II) and large swelling particles (Type III) to dissolved polymer chains (Type IV), to continuous gel networks (Type V).

Type I particles are formed when gelation kinetics are very fast compared with hydration-driven expansion of the dried

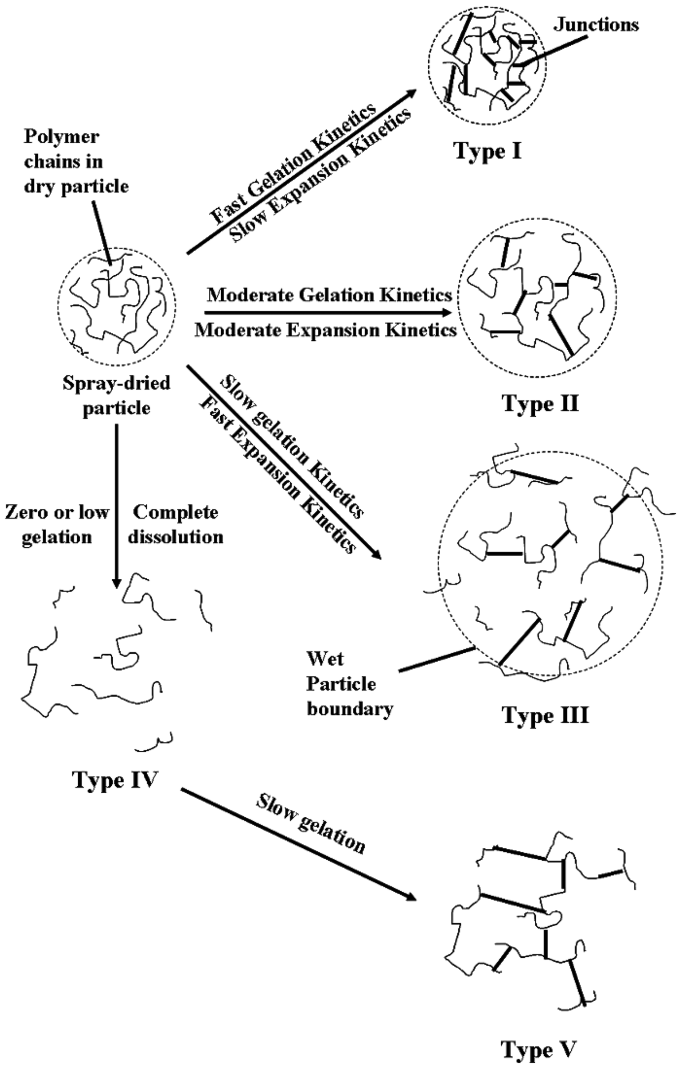

Figure 15 Formation of gel particles and gels from a dried intermediate.

hydrocolloid particle, such that polymer chains crosslink so rapidly that there is no time for significant particle expansion to occur. Type II and III particles form when gelation and particle expansion kinetics are competitive. Relatively small particles (Type II) are formed when gelation kinetics result in limited particle expansion. Larger particles (Type III) are formed when expansion is fast compared with gelation kinetics. In the limit of slow gelation and fast expansion, polymer chains dissolve from expanded particles (Type IV). If there is a gelation driving force, hydrocolloid chains may not remain in solution but subsequently form a continuous gel (Type V).

Factors which may affect gelation and expansion kinetics include hydrocolloid source (Wandrey et al., 2003), hydrocolloid concentration (Blandino et al., 1999), the presence of ions (Bajpai and Sharma, 2004; Ramakrishnan and Prud'homme, 2000), temperature (Lootens et al., 2003; Marcotte et al., 2001), and pH (Lootens et al., 2003). By selection of hydrocolloid type and rehydration conditions, this approach offers a way in which to control particle size and ultimately other particle properties such as strength, solubility, and release kinetics of encapsulated material.

EXAMPLES OF APPLICATIONS

Gel particles have many applications and find use in food, pharmaceutical, agricultural, and cosmetic industries. Two common types of applications for gel particles are in texturing or structuring applications and for encapsulation. Many applications make use of the combination of flow in suspension coupled with rheological or release properties of particles. Examples of non-food applications include coatings, bioencapsulation, enhanced oil recovery, inks, controlled drug delivery, and cream formulations in personal care products (Adams et al., 2004; Gidley and Hedges, 1994). The same application benefits are of value to the food industry, but the range of polymer materials available is limited by the requirement for regulatory approval. Hydrocolloid gel particles from natural polymers are of particular interest to the food industry as they can lead to rheological and release properties that would otherwise require chemically-modified or synthetic polymers.

Textural Applications

Gel particles may be used to provide texture and structure to a wide range of foods and drinks, as well as non-food products. Hydrocolloids play an important role in the overall acceptability of food products by controlling the physical stability of foods and overall mouth-feel properties (Marcotte et al., 2001). Applications are diverse and include restructured food particles in materials such as apple puree and carrot products (Marcotte et al., 2000; Ocio et al., 1997) and the control of the shape of a dispersed gel phase within an emulsion to create structured systems with novel rheological and sensorial properties (Simeone et al., 2005; Wolf et al., 2001b).

Encapsulation and Release

Microparticles formed from hydrocolloids are widely used for encapsulation applications (Hegenbart, 1993), particularly in drug delivery and nutrient encapsulation for food. It is necessary to use appropriate techologies for encapsulation, so that encapsulant release occurs at an acceptable rate and concentration. The use of encapsulation by hydrocolloid materials is particularly attractive as it can help in situations where the encapsulated material has poor solubility, requires slow release into its surroundings, or when delayed release until placed in appropriate conditions is desired. In some applications the particles are used in a dry form; however, a gel form has advantages where it can be used in hydrated media without breakdown which may be undesirable. For example, gel particles have been extensively investigated as a means of encapsulating "healthy" bacteria to improve survival under gastric conditions to maximize delivery

to the colon (Nussinovitch et al., 1997; Zvitov and Nussinovitch, 2003). Other uses for such particles are the encapsulation of insulin or drugs in pectin particles (Cheng and Lim, 2004; Sriamornsak and Nuthanid, 1998). Some examples of food applications include the use of alginate gel particles to encapsulate vitamin C (Desai et al., 2005) and hydrocolloid particles for the encapsulation of flavors (Malone and Appelqvist, 2003).

GEL PARTICLE CHARACTERISATION TECHNIQUES

Many gel particle characteristics are directly related to end product perception by consumers, and hence success in application. Some of the major properties of gel particles and the techniques used for characterizing them are described below.

Particle Size, Shape, and Structure

Particle morphology is important as it can directly impact on consumer perception (Engelen et al., 2005; Imai et al., 1999) as well as influence other properties. Therefore it is important to understand particle morphology and use appropriate techniques for studying particle properties. Two commonly used techniques for evaluating particle size and morphology are laser diffraction analysis and microscopy (Gavini et al., 2005; Klokk and Melvik, 2002; Kortesuo et al., 2000; Rosinski et al., 2002). Nuclear Magnetic Resonance (NMR) can also be used for examining porosity of gel particles as well as observing the gelation process (Dobies et al., 2005; Duez et al., 2000; Hills et al., 2000).

Laser Diffraction

Particle size distributions can be determined by the use of laser diffraction analysis, which is based on the diffraction of light at the surface of particles. Two factors are important for effectively obtaining particle size distributions, namely the laser wavelength coupled with machine optics and the presence of sufficient contrast between a particle surface and the suspending fluid to define the surface location. Standard measurement devices such as the Malvern Mastersizer use different optical attachments to detect particles in different size ranges, which can be as wide as 0.02–2000 μm.

Particle size distributions of hard particles have been determined using laser diffraction for many years (Pike, 1979) and now gel particle size distributions can also be obtained. Hydrocolloid gel particle systems have recently been studied using laser diffraction analysis with alginate being the most commonly studied material (Gavini et al., 2005; Klokk and Melvik, 2002; Liu et al., 2003; Rosinski et al., 2002). Particle sizes on the scale of μm are typically described. Light scattering may also provide information about structure on a mesoscopic scale, typically 100–1000 nm (Poon and Haw, 1997). It is important to realize that some difficulties may arise in using laser diffraction for highly swollen particles, where the concentration of hydrocolloid is low, resulting in limited optical contrast between the medium and the gel particles.

Microscopy

Particle size can also be determined via microscopy techniques, such as light microscopy (LM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM); in addition, microscopy techniques can also provide information about the shape and the topological features of particles.

Bright field and fluorescence LM are frequently used because they allow selective staining of different chemical components. LM may be useful in observing microscopic gel particles, but it does not have the resolution of SEM or TEM. It is however, a quick and simple method to characterize particle preparations before more complex methods are utilized. Provided contrast between particles and a suspending fluid can be achieved (e.g. through the use of selective stains), image analysis software can be used to provide descriptions of particle population properties such as size distributions and shape factors.

SEM is useful for examining the surface of microstructural components (Egerton, 2005). Samples are typically frozen, fractured, and coated with a metal compound in order to examine macromolecular organization within particles (Bhatnagar and Hanna, 1997). Environmental scanning electron microscopy (ESEM) allows viewing of the surface of a hydrated sample without the need for coating. This is possible by observing the samples under a partial vacuum (Egerton, 2005). Although resolution is not as high as for SEM, the milder preparation process provides more confidence that artefactual structure modification is avoided.

TEM is a method that may be used to view the microstructure of a thin sample by passing electrons through it. In the case of food gels, the section must be fixed and stained with a heavy metal compound to provide contrast between the various components (Kaláb et al., 1995).

There are some difficulties with sample preparation techniques for both SEM and TEM. Cryo-sectioning involves freezing and ice crystals may damage the structure. Plastic embedding involves dehydration and can cause shrinkage. Confocal scanning laser microscopy (CSLM) offers some advantages in that there is minimal sample processing, and three-dimensional images can be obtained, however, resolution is similar to LM, so electron microscopy is still required to investigate fine details (Autio and Laurikainen, 1997).

Previous studies of hydrocolloid gel particles have mostly used LM to observe the particles and have provided useful information on particle shape and size (Cellesi et al., 2004; Lamprecht et al., 2000; Liu et al., 2003; Sriamornsak and Nuthanid, 1998; Sriamornsak et al., 2004; Wong et al., 2002; Zvitov and Nussinovitch, 2003). The limitation of LM is that it mostly produces only two-dimensional images and does not have enough resolution to observe sub-micron structural features on or within the particles.

Several recent studies have used SEM to observe gel particle features more closely. The use of SEM has allowed observation of fiber and pore structures, as well as surface topology (Ouwerx et al., 1998; Sriamornsak et al., 2004; Velings and Mestdagh, 1995; Zvitov and Nussinovitch, 2003). Conventional SEM requires drying of samples so there is some loss of structure due to the removal of water, but it has proved useful for observing the internal structure of the hydrocolloid network within bead particles. TEM has also been used to observe network structure (Adams et al., 2004), but again would have the same difficulties associated with dehydration.

Traditionally AFM has been used to observe surface structures of materials, and is an attractive technique to utilize for this purpose as it has the ability of performing three-dimensional measurements with a resolution on the order of nanometres (Bonell, 1993). Another advantage of this technique is the very simple sample preparation, hence avoiding damaging or altering the sample prior to measurement (Starostina and West, 2006), and also the ability to observe samples in air or under solution. The use of AFM for observing nanoscale particles has developed only in the last few years and hence the capabilities are still being explored. Interest in the use of AFM for observing soft particles has grown in recent times, particularly in the medical field (Starostina and West, 2006), and has great potential for use in observing hydrocolloid gel particles. AFM also has the capability of carrying out mechanical measurements, providing further information on sample characteristics.

Image analysis is used to determine properties of microscopic features from micrographs and can be used in conjunction with images from any of the microscopy techniques mentioned above. Characterization of both particle shape and size can be carried out, providing detailed information about particle size distributions as well as individual particle properties (Langton and Hermansson, 1993; Russ, 2005). Simple measurements of particle characteristics (e.g diameter, shape factor) can be quickly measured. It has been used to analyse such systems as biopolymer particle suspensions (Wolf et al., 2001b) and shear gel systems (Adams et al., 2004), providing quantitative measures of images.

NMR techniques have more recently been used to study internal gel particle structure as well as gelation of gel particles (Dobies et al., 2005; Duez et al., 2000; Grant et al., 2005; Hills et al., 2000). In these studies, water proton relaxation time distributions are obtained, to complement the information on the hydrocolloid architecture observable from SEM or TEM.

Mechanical Characteristics–Rheology/Texture/Mouthfeel

There are many techniques available for evaluating the mechanical behavior of macroscopic particles; however, there can be difficulties associated with analyzing the sub-micron and micron-sized particles of interest in food applications, requiring more specialized techniques. Some techniques that have been used include nano-indentation and AFM for the study of individual particles, and rheometry and texture analysis for bulk dispersions of particles. These analysis techniques are more commonly used for the study of hard particles, and so whilst potentially useful for the study of soft gel particles, there may be practical difficulties that need to be addressed.

Nanoindentation

Nanoindentation testing is used to determine elastic modulus and hardness data of samples from load-displacement measurements. In a typical test, a measure of the residual impression left by an indenter is carried out (Fischer-Cripps, 2004). The impression is measured as a function of indenter load. As the impression that is left is so small, it is not possible to view the impression by simple optical means (LM), hence the depth of penetration is measured, and the impression size is determined from known indenter geometry and the measured penetration depth (Fischer-Cripps, 2004). There have been very few studies of nanoindentation of soft gel particles, as the technique is typically used for hard particles or surfaces.

Rheometry

Rheometry is traditionally an extremely useful technique for measuring deformation and flow of both synthetic polymer and biopolymer materials. Shear rheometry is commonly used on liquid or semi-solid materials, while extensional or compressive rheometry may be used on semi-solid or solid materials.

Rheometry can be useful for evaluating the deformation and flow behavior of particle suspensions and has been used successfully to characterize agar gel microparticles (Adams et al., 2004) and alginate particles encapsulating biocatalysts (Vogelsang et al., 2000). Information about the rheological behavior of gel particles can be useful in determining both static (small deformation) and yield/flow behavior of particles in different media which can then be related to sensorial properties in products such as food materials or cosmetic products. The measurements may also relate back to in-mouth particle detectability, a key quality determinant in food applications.

Texture Analysis

Texture profile analysis involves large deformation testing of samples so it is often limited to measurements on macroscale samples. It was developed in the early 1960s to imitate deformation of food samples by the jaw, by observing the behavior that would correspond to the first two bites of a sample (Borde et al., 2002; Friedman et al., 1963). The test involves a two-cycle penetration test into the food sample, with the force developed observed over time. The output obtained shows a two peak force curve, and gives an indication of recovery behavior after deformation. Calculations are carried out to determine the magnitude of textural parameters (Bourne, 2002). These parameters are dependent on testing geometries, so it is important to be consistent with the sample size when testing materials. The technique could be useful for testing bulk samples of hydrocolloid gel particles or for testing products that contain such particles.

Molecular Release–Food/Pharmaceuticals

Hydrocolloid gel particles have potential applications in encapsulation of materials such as flavors, nutrients, probiotics, and drugs. The gel particles can release the encapsulated material slowly or the hydrocolloid "shell" can break down under appropriate conditions to facilitate release of the material. The rate at which material is released is one of the most important factors for application success and can be influenced by characteristics such as particle size and particle membrane diffusivity. The characterization of release profiles together with particle morphology allows the development of understanding of mechanisms involved in determining release rates. The ability to withstand different environments of pH, temperature, and ionic strength may also be an issue depending upon the application (Nussinovitch et al., 1997; Velings and Mestdagh, 1995).

Studies of pectin as an encapsulation material for drug delivery have shown that the dissolution medium affects drug release from pectin microspheres by modifying the drug solubility and integrity of the pectin matrix (Sriamornsak and Nuthanid, 1998). A comprehensive study of various hydrocolloids for use in encapsulation of flavors was carried out by Malone and Appelqvist (2003), where it was found that particle composition and structure both had an effect on the rate of release. The particles were tested for release under various conditions of mechanical failure, temperature, and alpha-amylase susceptibility in order to mimic the breakdown conditions within the human body. It was concluded that the control of these parameters could control the release profile of the encapsulated flavor.

OPPORTUNITIES FOR FURTHER RESEARCH

The application opportunities for hydrocolloid gel particles in foods are widespread and also linked to current trends in food innovation such as the controlled delivery of functional actives and the development of lower calorie equivalents of traditional foods. These drivers ensure that gel particles will be further investigated and applied in the food sector. Three areas of specific opportunity for future R&D are:

- Translation of findings related to drug delivery to bioactive delivery from foods
- Understanding the role of mechanical and thermal processing operations on the formation and stability of gel particles in finished foods.
- Exploitation of dried intermediates as a convenient route to gel particles of controllable size and properties produced when needed. This area is currently under investigation by the authors.

REFERENCES

Adams, S., Frith, W. J., and Stokes, J. R. (2004). Influence of particle modulus on the rheological properties of agar microgel suspensions. *J Rheol*., **48**:1195–1213.

Armisen, R., and Galatas, F. (2000). Agar. **In**: Handbook of Hydrocolloids. pp. 21–40. Phillips, G. O. and Williams, P. A., Eds., CRC Press, Boca Raton.

Autio, K., and Laurikainen, T. (1997). Relationships between flour/dough microstructure and dough handling and baking properties. *Trends Food Sci. Technol*., **8**:181–185.

Bajpai, S. K., and Sharma, S. (2004). Investigation of swelling/degradation behaviour of alginate beads crosslinked with Ca^{2+} and Ba^{2+} ions. *React Funct Polym*., **59**:129–140.

Belitz, H.-D. and Grosch, W. (1999). Food Chemistry. Springer Verlag, Berlin.

Belton, P. S., Chilvers, G. R., Morris, V. J., and Tanner, S. F. (1984). Effects of group I cations on the gelation of iota carrageenan. *Int J Biol Macromol*., **6**:303–308.

Bhandari, B. (2005). Spray Drying and Powder Properties. **In**:Handbook of Food Science, Technology and Engineering. In press. Hui, Y. H. and Sherkat, F., Eds., Taylor and Francis, Boca Raton.

Bhatnagar, S., and Hanna, M. A. (1997). Modification of microstructure of starch extruded with selected lipids. *Starch*., **49**:12–20.

Biswal, D. R., and Singh, R. P. (2004). The flocculation and rheological characteristics of hydrolyzed and unhydrolyzed grafted sodium alginate in aqueous solutions. *J Appl Polym Sci*., **94**:1480–1488.

Blandino, A., Macias, M., and Cantero, D. (1999). Formation of calcium alginate gel capsules: Influence of sodium alginate and $CaCl_2$ concentration on gelation kinetics. *J Biosci Bioeng*., **88**:686–689.

Bohidar, H. B., and Jena, S. S. (1993). Kinetics of sol-gel transition in thermoreversible gelation of gelatin. *J Chem Phys*., **98**:8970–8977.

Borde, B., Bizot, H., Vigier, G., and Buleon, A. (2002). Calorimetric analysis of the structural relaxation in partially hydrated amorphous polysaccharides. *Carbohyd Polym*., **48**:111–123.

Bourne, M. C. (2002). Food Texture and Viscosity: Concept and Measurement. Academic Press Inc., New York.

Brown, C. R. T., Fairley, P., and Lam, S. (2004). Hair treatment compositions. US Patent no. 6719967.

Bugarski, B., Li, Q. L., Goosen, M. F. A., Poncelet, D., Neufeld, R. J., and Vunjakg (1994). Electrostatic droplet generation–mechanism of polymer droplet formation. *AICHE J*., **40**:1026–1031.

Burchard, W., and Ross-Murphy, S. B. (1990). Physical Networks–Polymers and Gels. Elsevier Science, Essex.

Burgess, D. J., and Carless, J. E. (1984). Microelectrophoretic studies of gelatin and acacia for the prediction of complex coacervation. *J Colloid Interf Sci*., **98**:1–8.

Campbell, A., Taylor, P., Cayre, O. J., and Paunov, V. N. (2004). Preparation of aqueous gel beads coated by lipid bilayers. *Chem Commun*., **21**:2378–2379.

Cellesi, F., Weber, W., Fussenegger, M., Hubbell, J. A., and Tirelli, N. (2004). Towards a fully synthetic substitute of alginate: optimization of a thermal gelation/chemical cross-linking scheme ("tandem" gelation) for the production of beads and liquid-core capsules. *Biotechnol Bioeng*., **88**:740–749.

Cheng, K., and Lim, L.-Y. (2004). Insulin-loaded calcium pectinate nanoparticles: Effects of pectin molecular weight and formula pH. *Drug Dev Ind Pharm*., **30**:359–367.

Chilvers, G. R., Gunning, A. P., and Morris, V. J. (1988). Coacervation of gelatin-xm6 mixtures and their use in microencapsulation. *Carbohyd Polym*., **8**:55–61.

Christensen, S. H. (1983). Pectins. **In**:Food Hydrocolloids. pp. 205–229. Glicksman, M., Eds., CRC Press Inc., Boca Raton

Clark, A. H., and Ross-Murphy, S. B. (1990). Shear Modulus–Concentration Relationships for Biopolymer Gels. Comparison of Independent and Cooperative Crosslink Descriptions. **In**:Physical Networks–Polymers and Gels. pp. 209–230. Burchard, W., and Ross-Murphy, S. B., Eds., Elsevier Science, London.

Cuppo, F., Venuti, M., and Cesaro, A. (2001). Kinetics of gelatin transitions with phase separation: T-jump and step-wise DSC study. *Int J Biol Macromol*., **28**:331–341.

de Jong, H. G. B., and Lens, J. (1932). Coacervation (separation) in mixtures concentrated gum arabic and gelatine sol. *Kolloid Z Z Polym*., **58**:209–214.

de Kruif, C. G., Weinbreck, F., and de Vries, R. (2004). Complex coacervation of proteins and anionic polysaccharides. *Curr Opin Colloid In*., **9**:340–349.

Deis, R. C. (1997). Spray Drying–Innovative Use of an Old Process. Food Product Design. Available from: http://www.foodproductdesign.com/archive/1997/0597DE.html [Accessed 12 Dec 2005]

Desai, K. G. H., Liu, C., and Park, H. J. (2005). Characteristics of vitamin C immobilized particles and sodium alginate beads containing immobilized particles. *J Microencapsul*., **22**:363–376.

Djabourov, M. (1991). Gelation–A Review. *Polym Int*., **25**:135–143.

Dobies, M., Kusmia, S., and Jurga, S. (2005). ^{1}H NMR and rheological studies of the calcium induced gelation process in aqueous low methoxyl pectin solutions. *Acta Phys Pol A*., **108**:33–46.

Douglas, K. L., and Tabrizian, M. (2005). Effect of experimental parameters on the formation of alginate-chitosan nanoparticles and evaluation for their potential application as DNA carrier. *J Biomat Sci-Polym E*., **16**:43–56.

Draget, K. I. (2000). Alginates. **In**: Handbook of Hydrocolloids. pp. 379–395. Phillips, G. O., and Williams, P. A., Eds., CRC Press, Boca Raton.

Draget, K. I., Skjak Braek, G., and Smidsrod, O. (1994). Alginic acid gels: the effect of alginate chemical composition and molecular weight. *Carbohyd Polym*., **25**:31–38.

Duez, J.-M., Mestdagh, M., Demeure, R., Goudemant, J.-F., Hills, B. P., and Godward, J. (2000). NMR studies of calcium-induced alginate gelation. Part I–MRI tests of gelation models. *Magn Reson Chem*., **38**:324–330.

Egerton, R. F. (2005). Physical principles of electron microscopy: An introduction to TEM, SEM, and AEM Springer, New York.

Elversson, J., and Millqvist-Fureby, A. (2005). Particle size and density in spray drying–effects of carbohydrate properties *J. Pharm. Sci*., **94**:2049–2060.

Engelen, L., van der Bilt, A., Schipper, M., and Bosman, F. (2005). Oral size perception of particles: effect of size, type, viscosity and method. *J Texture Stud*., **36**:373–386.

Finer, E. G., Franks, F., Phillips, M. C., and Sugget, A. (1975). Gel formation from solutions of single chain gelatin. *Biopolymers*., **14**:1995–2005.

Fischer-Cripps, A. C. (2004). Nanoindentation. Springer-Verlag, New York.

Friedman, H. H., Whitney, J. E., and Sczczesniak, A. S. (1963). The texturometer–a new instrument for objective texture measurement. *J Food Sci*., **28**:390–396.

Gander, B., Blanco-Príeto, M. J., Thomasin, C., Wandrey, C., and Hunkeler, D. (2002). Coacervation of Phase Separation. **In**: Encyclopedia of Pharmaceutical Technology. pp. 481–496. Swarbrick, J., Eds.

Gavini, E., Rassu, G., Sanna, V., Cossu, M., and Giunchedi, P. (2005). Mucoadhesive microspheres for nasal administration of an antiemetic drug, metoclopramide: in-vitro/ex-vivo studies. *J Pharm Pharmacol*., **57**:287–294.

Gidley, M. J., and Hedges, N. D. (1994). Suspensions of gelled biopolymers. US Patent No. 5738897.

Glicksman, M. (1983a). Food Hydrocolloids–Volume 1. CRC Press Inc, Boca Raton.

Glicksman, M. (1983b). Food Hydrocolloids–Volume 2. CRC Press Inc., Boca Raton.

Glicksman, M. (1983c). Food Hydrocolloids–Volume 3. CRC Press Inc., Boca Raton.

Goosen, M. F. A. (2003). Experimental and modeling studies of mass transfer in microencapsulated cell systems. *Trop J Pharm Res*., **1**:3–14.

Gotlieb, K. F., and Capelle, A. (2005). Starch derivatization : fascinating and unique industrial opportunities Wageningen Academic Publishers, Wageningen.

Gouin, S. (2004). Microencapsulation: industrial appraisal of existing technologies and trends. *Trends Food Sci Tech*., **15**:330–347.

Grant, S. C., Celper, S., Gauffin-Holmberg, I., Simpson, N. E., Blackband, S. J., and Constantinidis, I. (2005). Alginate assessment by NMR microscopy. *J Mater Sci-Mater M*., **16**:511–514.

Hamberg, L., Wohlwend, M., Walkenstrom, P., and Hermansson, A.-M. (2003). Shapes and shaping of biopolymer drops in hyperbolic flow. *Food Hydrocolloid*., **17**:641–652.

Hazen, C. (2004). Hydrocolloid Handbook. Food Product Design. Available from: http://www.foodproductdesign.com/archive/2004/1004CS.html [Accessed 06 May 2005]

Hegenbart, S. (1993). Encapsulated Ingredients: Keep Problems Covered. Food Product Design. Available from: http://www.foodproductdesign.com/archive/1993/0493CS.html [Accessed 28 Jun 2005]

Hills, B. P., Godward, J., Debatty, M., Barras, L., Saturio, C. P., and Ouwerx, C. (2000). NMR studies of calcium induced alginate gelation. Part II. The internal bead structure. *Magn Reson Chem*., **38**:719–728.

Hoefler, A. C. (2004). Hydrocolloids. Eagen Press, Minnesota.

Huang, X., Kakuda, Y., and Cui, W. (2001). Hydrocolloids in emulsions: particle size distribution and interfacial activity. *Food Hydrocolloid*., **15**:533–542.

Hunik, J. H., and Tramper, J. (1993). Large-scale production of k-carrageenan droplets for gel-bead production: theoretical and practical limitations of size and production rate, *Biotechnol Progr.*, **9**:186–192.

Imai, E., Saito, K., Hatakeyama, A., Hatae, K., and Shimada, A. (1999). Effect of physical properties of food particles on the degree of graininess perceived in the mouth. *J Texture Stud*., **30**:59–88.

Imeson, A. P. (2000). Carrageenan. **In**: Handbook of Hydrocolloids. pp. 87–102. Phillips, G. O., and Williams, P. A., Eds., CRC Press, Boca Raton.

Johnston-Banks, F. A. (1990). Gelatine. **In**: Food Gels. pp. 233–269. Harris, P., Elsevier Science Publishers Ltd., New York.

Joseph, I., and Venkataram, S. (1995). Indomethacin sustained release from alginate-gelatin or pectin-gelatin coacervates. *Int J Pharm*., **126**:161–168.

Juang, R.-S., Wu, F.-C., and Tseng, R.-L. (2002). Use of chemically modified chitosan beads for sorption and enzyme immobilisation. *Adv Environ Res*., **6**:171–177.

Kaláb, M., Allan-Wojtas, P., and Miller, S. S. (1995). Microscopy and other imaging techniques in food structure analysis. *Trends Food Sci. Technol*., **6**:177–186.

King, A. H. (1983). Brown Seaweed Extracts (Alginates). **In**: Food Hydrocollids. pp. 115–182. Glicksman, M., Eds., CRC Press, Boca Raton.

King, A. H. (1995). Encapsulation of Food Ingredients: A Review of Available Technology, Focusing on Hydrocolloids. **In**: Encapsulation and Controlled Release of Food Ingredients. pp. 26–39. Risch, S. J., and Reineccius, G. A., Eds., American Chemical Society, Washington.

Klokk, T. E., and Melvik, J. E. (2002). Controlling the size of alginate gel beads by use of high electrostatic potential. *J Microencapsul*., **19**:415–424.

Kortesuo, P., Ahola, M., Kangas, M., Kangasniemi, I., Yli-Urpo, A., and Kiesvaara, J. (2000). In vitro evaluation of sol-gel processed spray dried silica gel microspheres as carrier in controlled drug delivery. *Int J Pharm*., **200**:223–229.

Krasaekoopt, W., Bhandari, B., and Deeth, H. (2003). Evaluation of encapsulation techniques of probiotics for yoghurt. *Int Dairy J*., **13**:3–13.

Lamprecht, A., Schäfer, U., and Lehr, C.-M. (2000). Structural Analysis of Microparticles by Confocal Laser Scanning Microscopy. AAPS PharmSciTech. **1**. Available from: http://aapspharmscitech.org/articles/pt0103/pt010317/pt010317.pdf [Accessed 28 Jun 2005]

Langton, M., and Hermansson, A. M. (1993). Image-analysis determination of particle-size distribution. *Food Hydrocolloid*., **7**:11–22.

Lapitsky, Y., and Kaler, E. W. (2004). Formation of surfactant and polyelectrolyte gel particles in aqueous solutions. *Colloid Surface A*., **250**:179–187.

Liu, X. D., Bao, D. C., Xue, W. M., Xiong, Y., Yu, W. T., Yu, X. J., Ma, X. J., and Yuan, Q. (2003). Preparation of uniform calcium alginate gel beads by membrane emulsification coupled with internal gelation. *J App Polym Sci*., **87**:848–852.

Lofgren, C., Walkenstrom, P., and Hermansson, A.-M. (2002). Microstructure and rheological behavior of pure and mixed pectin gels. *Biomacromolecules*., **3**:1144–1153.

Lootens, D., Capel, F., Durand, D., Nicolai, T., Boulenguer, P., and Langendorff, V. (2003). Influence of pH, Ca concentration, temperature and amidation on the gelation of low methoxyl pectin. *Food Hydrocolloid*., **17**:237–244.

Lucinda-Silva, R. M., and Evangelista, R. C. (2003). Microspheres of alginate-chitosan containing isoniazid. *J Microencapsul*., **20**:145–152.

Malone, M., and Appelqvist, I. A. M. (2003). Gelled emulsion particles for the controlled release of lipophilic volatiles during eating. *J Control Release*., **90**:227–241.

Marcotte, M., Hoshahili, A. R. T., and Ramaswamy, H. S. (2001). Rheological properties of selected hydrocolloids as a function of concentration and temperature. *Food Res Int*., **34**:695–703.

Marcotte, M., Taherian, A. R., and Ramaswamy, H. S. (2000). Physical properties of reconstituted carrot/alginate particles stable for aseptic processing. *J Food Process Eng*., **23**:463–480.

Masters, K. (1991). Spray Drying Handbook. Longman and Scientific Technical, New York.

May, C. D. (2000). Pectins. **In**: Handbook of Hydrocolloids. pp. 169–188. Phillips, G. O., and Williams, P. A., Eds., CRC Press, Boca Raton.

Mohanty, B., Aswal, V. K., Goyal, P. S., and Bohidar, H. B. (2004). Small-angle neutron and dynamic light scattering study of gelatin coacervates. *Pramana-J Phys.*, **63**:271–276.

Mohanty, B., and Bohidar, H. B. (2006). Microscopic structure of gelatin coacervates. *Int. J. Biol. Macromol.*, **3**:39–46.

Morris, E. R., Rees, D. A., and Robinson, G. (1980). Cation-specific aggregation of carrageenan helices: domain model of polymer gel structure. *J. Mol. Biol.*, **138**:349–362.

Mukai-Correa, R., Prata, A. S., Alvim, I. D., and Grosso, C. R. F. (2004). Controlled release of protein from hydrocolloid gel microbeads before and after drying. *Curr Drug Del.*, **1**:265–273.

Murakata, T., Honma, H., Nakazato, S., Kuroda, C., and Sato, S. (2001). Control of particle size of calcium alginate gel bead by application of electric field to interface between aqueous and organic phases. *J Chem Eng Jpn.*, **34**:299–305.

Nussinovitch, A. (1997). Hydrocolloid Applications. Chapman and Hall, London.

Nussinovitch, A., Gershon, Z., and Nussinovitch, M. (1997). Temperature stable liquid core hydrocolloid capsules. *Food Hydrocolloid.*, **11**:209–215.

Oakley, D. E. (2004). Spray dryer modeling in theory and practice. *Dry. Technol.*, **22**:1371–1402.

Ocio, M. J., Fiszman, S. M., Gasque, F., Rodrigo, M., and Martinez, A. (1997). Development of a restructured alginate food particle suitable for high temperature-short time process validation. *Food Hydrocolloid.*, **11**:423–427.

Ouwerx, C., Velings, N., Mestdagh, M. M., and Axelos, M. A. V. (1998). Physico-chemical properties and rheology of alginate gel beads formed with various divalent cations. *Polym Gels Netw.*, **6**:393–408.

Paterson, L. A., Hill, S. E., Mitchell, J. R., and Blanshard, J. M. V. (1997). Sulphite and oxidative-reductive depolymerization reactions. *Food Chem.*, **60**:143–147.

Peng, H., Martineau, L., and Shek, P. (2006). Method of producing layered polymeric articles. US Patent No. 20060061005.

Pike, E. R. (1979). The Malvern correlator. *Phys Technol.*, **10**:104–109.

Poon, W. C. K., and Haw, M. D. (1997). Mesoscopic structure formation in colloidal aggregation and gelation. *Adv Colloid Interfac.*, **73**:71–126.

Ramakrishnan, S., and Prud'homme, R. K. (2000). Effect of solvent quality and ions on the rheology and gelation of kappa-carrageenan. *J Rheol.*, **44**:885–896.

Rees, D. A. (1982). Polysaccharide conformation in solutions and gels–recent results on pectins. *Carbohyd Polym.*, **2**:254–263.

Reis, C. P., Neufeld, R. J., Vilela, S., Ribeiro, A. J., and Veiga, F. (2006). Review and current status of emulsion/dispersion technology using an internal gelation process for the design of alginate particles. *J Microencapsul.*, **23**:245–257.

Rix, A. (1990). Gelling and Whipping Agents. **In**: Sugar Confectionery Manufacture. pp. 57–76. Jackson, E. B., Eds., Van Nostrand Reinhold, Glasgow.

Rochas, C., and Rinaudo, M. (1984). Mechanism of gel formation in κ-carrageenan. *Biopolymers.*, **23**:735–745.

Rosinski, S., Grigorescu, G., Lewinska, D., Ritzen, L. G., Viernstein, H., Teunou, E., Poncelet, D., Zhang, Z., Fan, Z., D., S., Marison, I., and Hunkeler, D. (2002). Characterisation of microcapsules: Recommended methods based on round-robin testing. *J Microencapsul.*, **19**:641–659.

Rostagno, W. (1969). Chocolate particle size and its organoleptic influence. *Manuf Conf.*, **49**:81–85.

Russ, J. C. (2005). Image analysis of food microstructures. CRC Press, Boca Raton.

Simeone, M., Tassieri, M., Sibillo, V., and Guido, S. (2005). Effect of sol-gel transition on shear-induced drop deformation in aqueous mixtures of gellan and κ-carrageenan. *J Colloid Interf Sci.*, **281**:488–494.

Sriamornsak, P., and Nuthanid, J. (1998). Calcium pectinate gel beads for controlled release drug delivery: I. Preparation and in vitro release studies. *Int J Pharm.*, **160**:207–212.

Sriamornsak, P., Thirawong, N., and Puttipipatkhachorn, S. (2004). Morphology and Buoyancy of Oil-entrapped Calcium Pectinate Gel Beads. The American Association of Pharmaceutical Scientists Journal. **6**. Available from: http://www.aapsj.org/articles/aapsj0603/aapsj060324/aapsj060324.pdf [Accessed 09 Aug 2005]

Sugiura, S., Odo, T., Izumida, Y., Aoyagi, Y., Satake, M., Ochiai, A., Ohkohchi, N., and Nakajima, M. (2005). Size control of calcium alginate beads containing living cells using micro-nozzle array. *Biomaterials.*, **26**:3327–3331.

Thomasin, C., Merkle, H. P., and Gander, B. (1998). Drug microencapsulation by PLA/PLGA coacervation in the light of thermodynamics. 2. Parameters determining microsphere formation. *J Pharm Sci.*, **87**:269–275.

Tosh, S., Marangoni, A., Hallet, F., and Britt, I. (2003). Aging dynamics in gelatin gel microstructure. *Food Hydrocolloid.*, **17**:503–513.

Utz, K.-H. (1986). The interocclusal tactile fine sensitivity of the natural teeth as studied by aluminium oxide particles. *Deut Zahnaerztl Z.*, **41**:313–315.

van de Velde, F., van Riel, J., and Tromp, R. H. (2002). Visualisation of starch granule morphologies using confocal scanning laser microscopy (CSLM). *J Food Sci Agr.*, **82**:1528–1536.

Velings, N. M., and Mestdagh, M. M. (1995). Physico-Chemical Properties of Alginate Gel Beads. *Polym Gels Netw.*, **3**:311–330.

Vogelsang, C., Wijffels, R. H., and Ostgaard, K. (2000). Rheological properties and mechanical stability of new gel-entrapment systems applied in bioreactors. *Biotechnol Bioeng.*, **70**:247–253.

Walkenström, P., and Hermansson, A.-M. (1998). Effects of shear on pure and mixed gels of gelatin and particulate whey protein. *Food Hydrocolloid.*, **12**:77–87.

Wandrey, C., Espinosa, D., Rehor, A., and Hunkeler, D. (2003). Influence of alginate characteristics on the properties of multi-component microcapsules. *J Microencapsul.*, **20**:591–611.

Williams, C. T. (1964). Chocolate and Confectionery. Leonard Hill, London.

Williams, P. A., and Phillips, G. O. (2000). Introduction to Food Hydrocolloids. **In**: Handbook of Hydrocolloids. pp. 1–19. Phillips, G. O., and Williams, P. A., Eds., CRC Press, Boca Raton.

Wolf, B., Frith, W. J., and Norton, I. T. (2001a). Influence of gelation on particle shape in sheared biopolymer blends. *J Rheol.*, **45**:1141–1157.

Wolf, B., Frith, W. J., Singleton, S., Tassieri, M., and Norton, I. T. (2001b). Shear behaviour of biopolymer suspensions with spheroidal and cylindrical particles. *Rheol Acta.*, **40**:238–247.

Wong, T. W., Lee, H. Y., Chan, L. W., and Heng, P. W. S. (2002). Drug release properties of pectinate microspheres prepared by emulsification method. *Int J Pharm.*, **242**:233–237.

Woodruff, S., and Gilder, H. V. (1931). Photomicrographic studies of sucrose crystals. *J Phys Chem.*, **35**:1355–1367.

Zimmerman, H., Zimmerman, D., Reuss, R., Feilen, P. J., Manz, B., Katsen, A., Weber, M., Ihmig, F. R., Ehrhart, F., Gebner, P., Behringer, M., Steinbach, A., Wegner, L. H., Sukhorukov, V. L., Vasquez, J. A., Schneider, S., Weber, M. M., Volke, F., Wolf, R., and Zimmerman, U. (2005). Towards a medically approved technology for alginate-based microcapsules allowing long-term immunoisolated transplantation. *J Mater Sci-Mater M.*, **16**:491–501.

Zvitov, R., and Nussinovitch, A. (2001). Weight, mechanical and structural changes induced in alginate beads by DC electrical field. *Food Hydrocolloid.*, **15**:33–42.

Zvitov, R., and Nussinovitch, A. (2003). Changes induced by DC electrical field in agar, agarose, alginate and gellan gel beads. *Food Hydrocolloid.*, **17**:255–263.