4 Designed Food Structures Based on Hydrocolloids

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4.1 INTRODUCTION

This chapter aims to provide an overview of the fundamentals and technological tools to exploit hydrocolloid technology on a particulate level for influencing food structure.

Hydrocolloids, and more often mixtures thereof, are commonly added to foods and other products (pharmaceuticals, paints, personal care) to impart specific flow properties, textures, appearance and, where required, tactile and oral properties. Hydrocolloids are water soluble gums and tend therefore to be applied to foods with an aqueous-based continuous product phase. Similarly, designed food structures based on hydrocolloids are typically applied in water-continuous products. Meanwhile, hydrocolloids are increasingly applied to structure aqueous product phases such as the most inner phase in a water-in-oil-in-water emulsion (Sapei *et al*., 2012). Wassen *et al*. (2012) have recently shown phase separation of hydrocolloids occurring in such water droplets.

This chapter is concerned with the design of hydrocolloid food particles on the micrometre scale, corresponding to the size range of droplets in classical food emulsions. Design principles based on solutions of single hydrocolloids and further opportunities for formulation of food particles from hydrocolloid mixtures are outlined. A requirement is that at least one component in the system has the ability to form a gel, for example, via thermal transition or ion-induced gelation. Introducing particulate food hydrocolloids widens the product design space based on what is a low energy density ingredient. It should be noted that, in addition to the approaches discussed in this chapter, native starches represent a *natural* particulate food thickener and their superior properties with regard to tastant release compared with molecular-based hydrocolloid thickeners has been discussed (Ferry *et al*., 2006).

Formulation Engineering of Foods, First Edition. Edited by Jennifer E. Norton, Peter J. Fryer, and Ian T. Norton.

Extrusion-processed particulate forms of the hydrocolloid xanthan gum have been developed for this same reason (Farhat *et al*., 2006; Sereno *et al*., 2007). Burey *et al*. (2008) have published a review paper on the formation, characterisation and application of hydrocolloid gel particles.

Section 4.2 of this chapter introduces the fundamentals of the phase behaviour of hydrocolloid mixtures and lists some common food hydrocolloid mixtures. Technology based on solutions of single hydrocolloids known as *sheared gel* or *fluid gel technology* was first introduced in 1990 (Brown *et al*., 1990) and is the subject of Section 4.3. Fluid gel technology has also been applied to hydrocolloid mixtures (Brown *et al*., 1995; Foster *et al*., 1996). Applying the principle of flow structuring to hydrocolloid mixtures, but in well-defined flow fields, is then introduced in Section 4.4. It requires the mixed system to phase separate into two-phase aqueous mixtures, also widely referred to as *water-in-water* emulsions. The flow behaviour of such systems is governed by the same physical principles, including the rules for droplet break-up and coalescence, as conventional emulsions, and can be treated as such both theoretically and practically. Consequently, application of well-controlled flow fields combined with kinetic trapping of the flow-induced structures allows manufacture of “shape-controlled” hydrocolloid food particles. Water-in-oil emulsions with a gelling hydrocolloid-based water phase have been processed in the same fashion to manufacture shaped food particles (Section 4.5). These may be directly applied in lipid-based food products. The recent upsurge in microfluidics has also been exploited in food particle structuring. A brief overview is provided in Section 4.6. High- pressure treatments have also been investigated as a tool to structure food particles from liquid hydrocolloid mixtures, and references are included (Section 4.6).

4.2 HYDROCOLLOID MIXTURES

Phase separation in hydrocolloid mixtures is a common phenomenon and is due to the high molecular weight of the hydrocolloids. This results in relatively low entropy of mixing and the interactions between different segments of the hydrocolloid determine the free energy of mixing. In the case of overall repulsive interaction, phase separation is observed above certain hydrocolloid concentrations. In two-component hydrocolloid mixtures each will collect predominantly in one of the two resulting aqueous phases (Albertsson, 1995). A water-in-water emulsion has formed. For attractive interactions between the hydrocolloid segments, phase separation will lead to a concentrated phase enriched in both hydrocolloids contained in the mixture (complex coacervation) and a hydrocolloid-depleted phase (Turgeon *et al*., 2003). This type of behaviour is, for example, observed for mixtures of two oppositely charged hydrocolloids. The hydrocolloid concentration required to induce phase separation depends on the level of interaction and many phase diagrams have been published in the literature. However, it is worth stressing that phase diagrams are based on equilibrium conditions and their usefulness in the design of dynamic processes is therefore somewhat limited. Full miscibility between two hydrocolloids in aqueous solution requires the molecules to have very similar properties (Albertsson, 1995).

4.2.1 Water-in-water emulsions

Water-in-water emulsions form as a result of the presence of two incompatible hydrocolloids in aqueous solution, and this microstructure is frequently observed for polysaccharide–polysaccharide mixtures and polysaccharide–protein mixtures. Fig. 4.1 shows a schematic which includes the idea of separating the two hydrocolloid-rich phases. This is of interest for bioseparation processes (Tolstoguzov, 1988), or indeed for designing food structures. Separating the equilibrium phases and recombining at a different phase ratio may be beneficial for the food structuring process. Turgeon *et al*. (2003) published a more extensive schematic showing the possible food microstructures that could be developed from incompatible hydrocolloid mixtures, see Fig. 4.2.

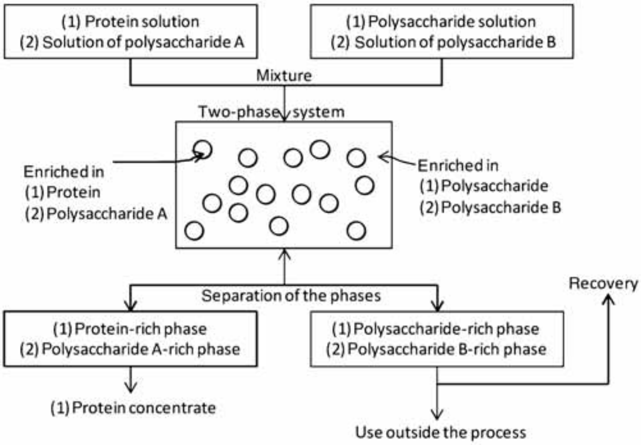


Fig. 4.1 Schematic of phase separation in aqueous mixtures of two incompatible biopolymers leading to the formation of a water-in-water emulsion. (1) Depicts an incompatible protein–polysaccharide mixture with schematic for bioseparation or membraneless osmosis process; (2) shows the situation for a two-component polysaccharide mixture. Reproduced with permission from Tolstoguzov (1988). Concentration and purification of proteins by means of two-phase systems: membraneless osmosis process. *Food Hydrocolloids* 2(3), 195–207. Elsevier.

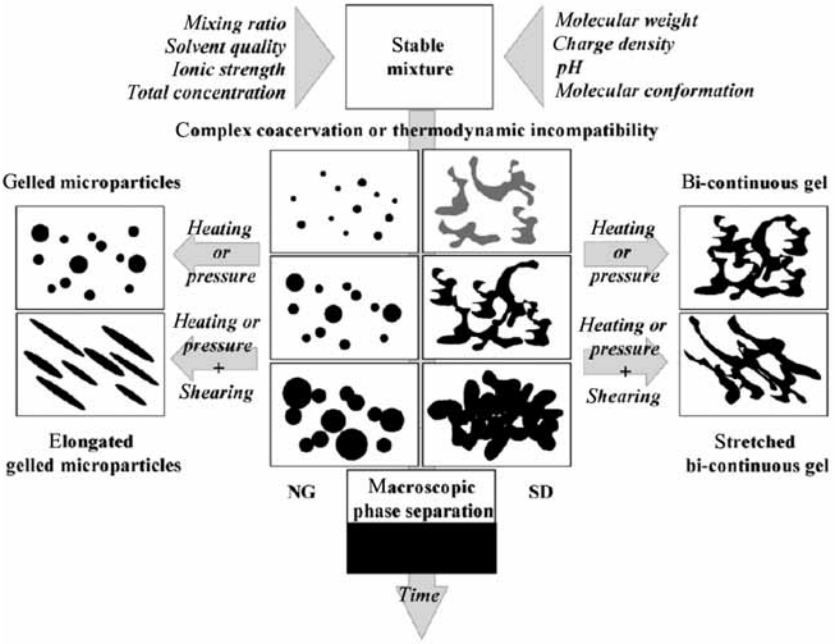


Fig. 4.2 Schematic representation of factors affecting phase separation in protein–polysaccharide mixtures. NG and SD refer to nucleation and growth and spinodal decomposition respectively, see text. Reproduced with permission from Turgeon *et al.*, (2003). Protein-polysaccharide interactions: phase-ordering kinetics, thermodynamic and structural aspects. *Current Opinion in Colloid & Interface Science* 8(4–5), 401–414. Elsevier.

Micrographs of water-in-water emulsions are shown in Fig. 4.3, including a microstructure (4.3d) featuring hierarchical or droplet-in-droplet structures resulting from secondary phase separation which may occur as a result of further cooling.

Phase equilibrium behaviour is described by phase diagrams; see Fig. 4.4 for the two common representations. The solid line represents the binodal separating the one-phase region from the two-phase region. The equilibrium phase concentrations can be read off the respective axes following the tie line. Phase behaviour and thus location of the binodal and tie lines depend not only on the hydrocolloid characteristics but also on pH, ion concentration and temperature, see Fig. 4.5. Phase separation may be via the nucleation and growth (NG) mechanism or the spinodal decomposition (SD) mechanism, depending on where a mixture is quenched to in the phase diagram. NG leads to random formation of droplets, similar to those shown in Fig. 4.6. SD occurs as a result of deeper quenches and results in bicontinuous morphology or droplet morphology with characteristic length scale. Butler (2002) conducted a systematic investigation into these two mechanisms, using the same hydrocolloid mixture (gelatin–maltodextrin). In a further study

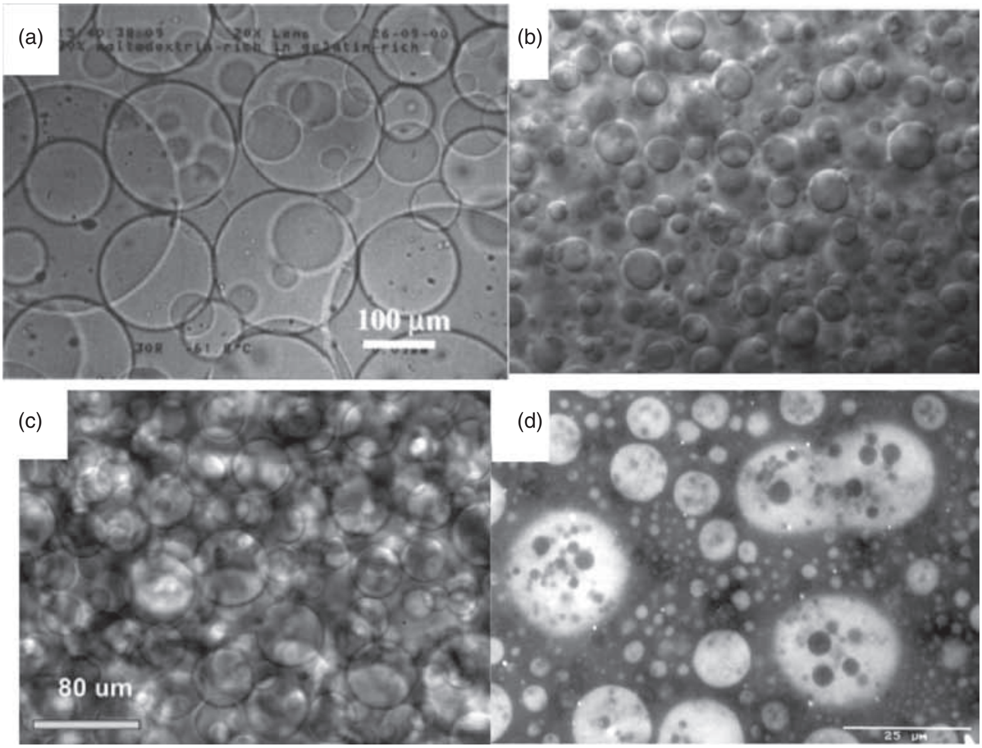


Fig. 4.3 (a) Maltodextrin–gelatin; (b): alginate–caseinate; (c) gelatin–dextran; (d) phenomenon of secondary phase separation in a gelatin–maltodextrin mixture. (a) Reproduced with permission from Stokes *et al.*, (2001). Phase-separated biopolymer mixture rheology: Prediction using a viscoelastic emulsion model. *Journal of Rheology* 45(5), 1173–1191. AIP. (b) Reproduced with permission from Antonov and Moldenaers (2011). Structure formation and phase-separation behaviour of aqueous casein-alginate emulsions in the presence of strong polyelectrolyte. *Food Hydrocolloids* 25(3), 350–360. Elsevier. (c) Reproduced with permission from Antonov and Moldenaers (2012). Strong polyelectrolyte – Induced mixing in concentrated biopolymer aqueous emulsions. *Food Hydrocolloids* 28(1), 213–223. Elsevier. (d) Reproduced with permission from Norton and Frith (2001). Microstructure design in mixed biopolymer composites. *Food Hydrocolloids* 15(4–6), 543–553. Elsevier.

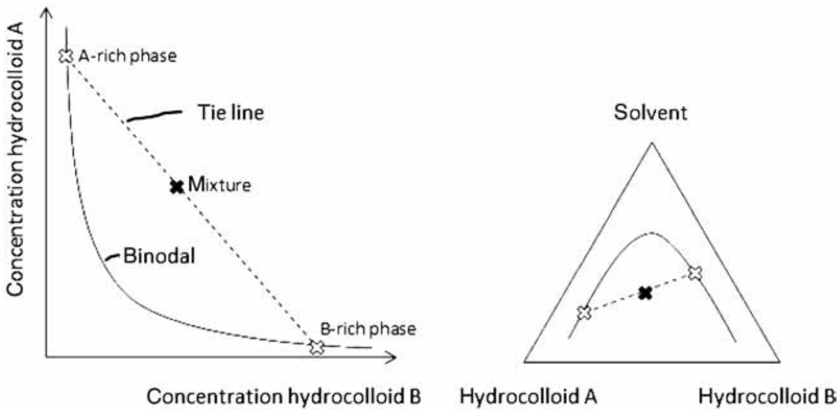


Fig. 4.4 Phase diagram for phase separating hydrocolloid mixtures. Left: Binary representation. Right: Ternary phase diagram.

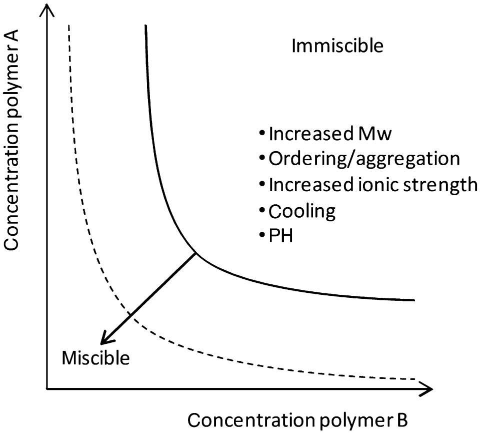


Fig. 4.5 Conditions influencing the position of the bimodal. Reproduced with permission from Lundin *et al.*, (2003). *Phase separation in foods. Texture in food.* M. McKenna. Cambridge, Woodhead Publishing Ltd. 1, 63–85. Woodhead Publishing.

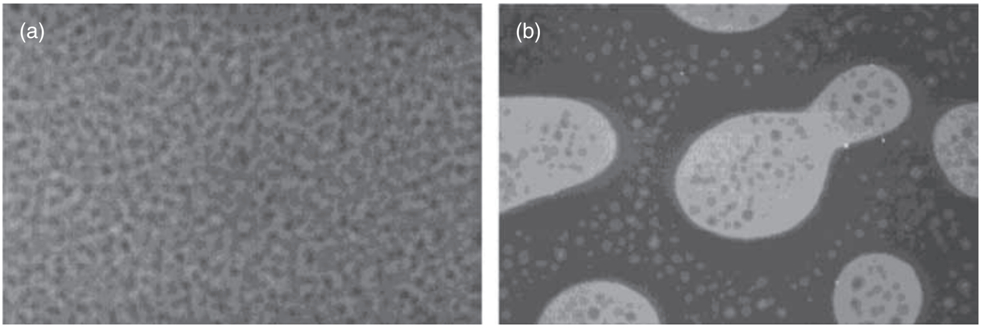


Fig. 4.6 (a) Micrograph showing a trapped bicontinuous microstructure of gelatin–maltodextrin at 20 °C developed through SD. Image width 718 μm. (b) Close up of secondary phase separation with dextran-rich droplets developing inside the dispersed gelatin-rich droplets. Image width 72 μm. Reproduced with permission from Butler and Heppenstall-Butler (2003). "Delayed" phase separation in a gelatin/dextran mixture studied by small-angle light scattering, turbidity, confocal laser scanning microscopy, and polarimetry. *Biomacromolecules* 4(4), 928–936. ACS.

on the same system (Butler and Heppenstall-Butler, 2003), secondary phase separation was recorded (see Figs. 4.3 and 4.6).

Methods on how to obtain a phase diagram vary depending on the hydrocolloids involved and a large number of phase separating hydrocolloid mixtures and their phase diagrams have been described in literature. Techniques such as image analysis (Gaaloul *et al.*, 2010), confocal laser scanning microscopy (Butler and Heppenstall-Butler, 2003; Fang *et al.*, 2006), small-angle light scattering (Butler and Heppenstall-Butler, 2003; Loret *et al.*, 2005), Fourier transform infrared (FTIR) spectroscopy (Loret *et al.*, 2005; De Giacomo *et al.*, 2008),

Table 4.1 Examples for phase separating hydrocolloid mixtures with at least one gelling component.

Mixture	References
Gelatin–maltodextrin	Aymard *et al.*, 2000; Stokes *et al.*, 2001; Butler, 2002; Leisner *et al.*, 2002; Lundell *et al.*, 2004; Loret *et al.*, 2005; De Giacomo *et al.*, 2008; Fransson *et al.*, 2009, 2010
Oat β-glucan–whey protein isolate	Kontogiorgos *et al.*, 2009
Gelatin–k-carrageenan	Fang *et al.*, 2006
Maltodextrin–agarose	Loret *et al.*, 2005
Whey protein–pectin	Turgeon and Beaulieu, 2004
Agar–gelatin	Clark *et al.*, 1983; Guido *et al.*, 2002; Simeone *et al.*, 2004
Agarose–gelatin	Zasypkin *et al.*, 1997
Gelatin–methylcellulose	Zasypkin *et al.*, 1997
Gelatin–sodium alginate	Zasypkin *et al.*, 1997
Casein–alginate	Antonov and Moldenaers, 2011

Raman spectroscopy (Pudney *et al.*, 2003), turbidity (Aymard *et al.*, 2000; Butler and Heppenstall-Butler, 2003) and polarimetry (Butler and Heppenstall-Butler, 2003) have been used. Bulk phase separation is often accelerated through centrifugation; however, attention needs to be paid to possible fractionation of molecular weight (Loret *et al.*, 2005). Phase behaviour can be influenced not just by thermodynamic conditions, but also by geometric confinement (Fransson *et al.*, 2009, 2010).

Table 4.1 lists hydrocolloid mixtures that are relevant to application in microstructure design in foods (containing at least one gelling component). Fig. 4.7 shows the phase diagram obtained for a mixture of gelatin and maltodextrin and the evolution of the phase boundary at 0.1M total ionic strength with temperature. This system has been studied by many researchers (see references in Table 4.1) and has been applied in the formulation of low fat spreads (Norton *et al.*, 2008).

4.2.2 Emulsion behaviour of water-in-water emulsions

Prior to gelation, the material behaviour of water-in-water emulsions is akin to conventional emulsions based on two immiscible liquids such as food oil and water. Emulsions are commonly processed in flow fields. Efficiency in terms of resulting droplet size distribution depends largely on the flow stresses acting at the droplets surfaces and the viscosity (behaviour) of the oil and water phase, as well as the interfacial tension. It is worth noting that the interfacial tension in emulsions based on two aqueous-based phases is about two to three

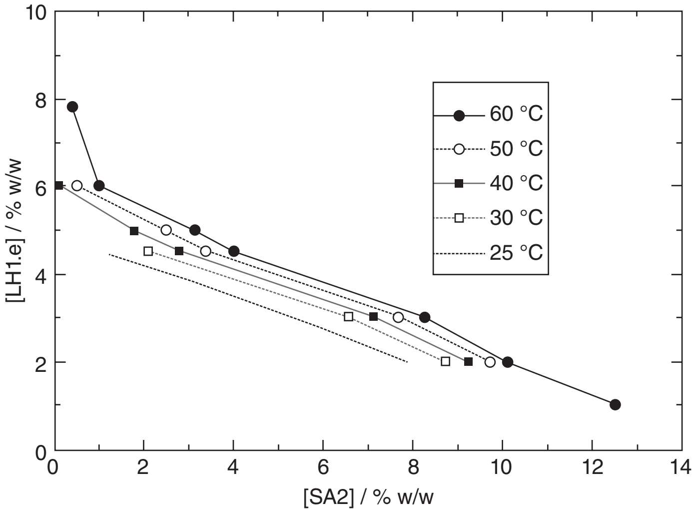
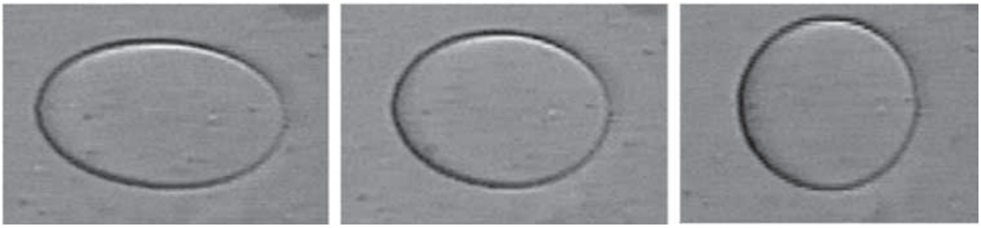


Fig. 4.7 Evolution of the phase boundary for gelatin–maltodextrin mixtures at 0.1M total ionic strength with temperature. Reproduced with permission from Aymard *et al.*, (2000). A turbidimetric study of phase separating biopolymer mixtures during thermal ramping. *Langmuir* 16(19), 7383–7391. ACS.



t = 0 s, *D* = 0.24 *t* = 0.5 s, *D* = 0.15 *t* = 2.0 s, *D* = 0

Fig. 4.8 Single droplet deformation/relaxation studied in shear flow of a gelatin-rich droplet in pullulan-rich continuous phase. From left to right: Fully deformed droplet at equilibrium in steady shear. The extent of droplet deformation depends on flow stresses, interfacial tension and phase viscosities. At zero time the flow is stopped causing the ellipsoidal deformed droplet to relax back to a sphere. Analysis of the change in droplet shape with time is an alternative method to obtain the interfacial tension. Reproduced with permission from Ding *et al.*, (2005). The effect of temperature and composition on the interfacial tension and rheology of separated phases in gelatin/pullulan mixtures. *Food Hydrocolloids* 19(3), 567–574. Elsevier.

orders of magnitude lower than what is encountered in conventional food emulsions, notwithstanding adsorbed food emulsifiers. The low interfacial tension presents a challenge in its quantification; methods based on analysing the deformation behaviour of single droplets of one of the two hydrocolloid-rich phases immersed in the second hydrocolloid-rich phase (see Fig. 4.8) have been applied successfully (Wolf *et al.*, 2000; Scholten *et al.*, 2002; Simeone *et al.*, 2004), including the effect of temperature and position in the phase diagram

(Ding *et al*., 2005). Another method includes rheo-optics (Van Puyvelde *et al*., 2002).

Attempts have been made to design emulsifiers for water-in-water emulsions analogous to the use of emulsifiers in conventional oil–water-based food emulsions. These have been largely unsuccessful when based on natural materials, due to unsuitable molecular shape (Butler, pers. comm.). Routes tested include surface-active particles and polysaccharide–protein conjugates. Recently, successful trapping of protein (and latex) particles at the droplet interfaces in water-in-water emulsions has been reported (Balakrishnan *et al*., 2012) and promises further developments in these systems.

4.3 FLUID GEL TECHNOLOGY

Fluid gel particles can be obtained through the mechanical disruption of network-forming gel clusters, mechanical break up of an already formed gel or through spinodal decomposition following a trigger mechanism such as temperature quench, or the addition of salt to bring the solution out from a one-phase equilibrium situation. Understanding of the underlying scientific principles has been developed over the years from an early paper (Norton *et al*., 1999) to recent new insights (Gabriele *et al*., 2009, 2010; Le Reverend *et al*., 2010; Gabriele, 2011).

In brief, preparation of fluid gels involves preparation of the hydrocolloid-containing feed solution, which is then submitted to shear while controlling temperature. Shear devices that have been applied include jacketed vessels fitted with an overhead stirrer that may or may not be wall scraping (Brown *et al*., 1995; Norton *et al*., 1999) and well-defined shear flow in the cone-and-plate geometry of a rotational shear rheometer, as well as the more complex coaxial flow as with a concentric cylinder device (Norton *et al*., 1999) and flow-through pin stirrer heat exchangers (Gabriele, 2011).

Depending on the processing conditions and properties of the hydrocolloid solution (type and concentration of hydrocolloid, solvent quality), the shape of fluid gel particles has been described as irregular-shaped large (Gabriele, 2011), nearly spherical (Gabriele, 2011) and hairy (Norton *et al*., 1999).

Processing a phase separating hydrocolloid mixture composed of gelatin and oxidised starch under shear, while cooling to impart gelation of the gelatin phase has been shown to lead to gelatin-included gelled particle suspensions. Applying the same temperature history in the absence of shear showed a range of phase behaviours (Foster *et al*., 1996; see Fig. 4.9). Thus, in the design of a flow process involving

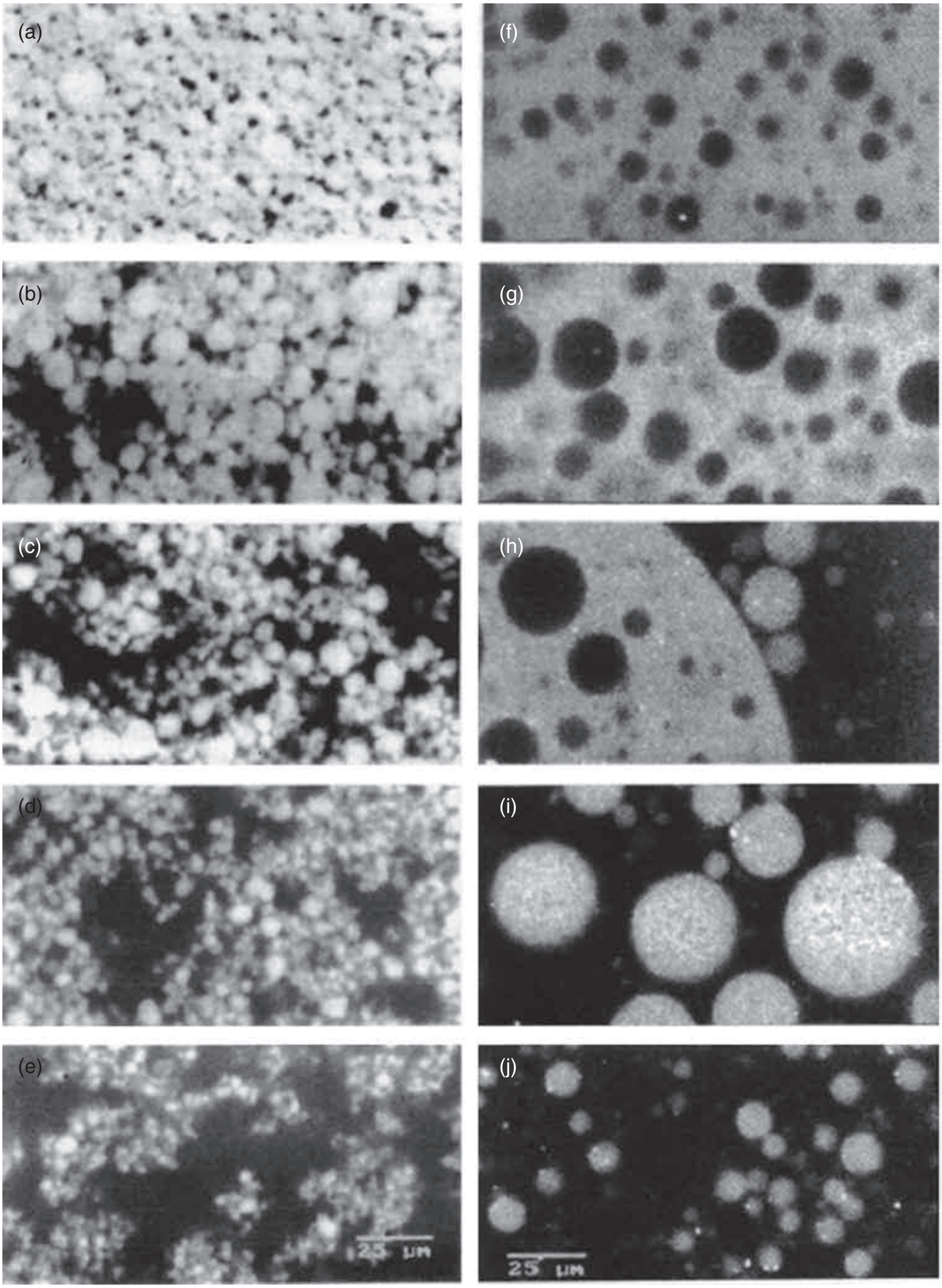


Fig. 4.9 Confocal micrographs of shear cooled (micrographs on the left) and corresponding quiescently cooled (micrographs on the right) mixtures of gelatin–oxidised starch at different phase volumes. Reproduced with permission from Foster *et al.*, (1996) Phase inversion of water-in-water emulsions. In: Phillips et al., editors. *Gums and Stabilisers for the Food Industry* 8, 301, Figure 4. Oxford University Press.

hydrocolloid mixtures, attention needs to be paid to the effect of shear on the phase behaviour.

4.4 STRUCTURING OF WATER-IN-WATER EMULSIONS

Phase separating hydrocolloid mixtures prepared from two hydrocolloids of which only one is gelling can be processed into gel particle suspensions, or filled gels. Composite gels will form if both hydrocolloids are gelling and these are not further discussed in this book chapter (consult the extensive literature published by Tolstoguzov).

Spherical particles and non-spherical particles can be fabricated through gelation under quiescent conditions and during flow respectively. Quiescent phase separation has been discussed in Section 4.2.1 and the effect of shear on phase behaviour has been stressed. Choosing appropriate hydrocolloids and process parameters, including solution conditions, allows manufacture of spherical food gel particles. Quiescent design options include non-spherical shapes by trapping phase separation during spinodal decomposition and internal structures through secondary phase separation (see Section 4.2.1).

It is a well-known phenomenon that emulsion droplets subjected to fluid flow undergo deformation, break-up and coalescence. The extent to which they deform depends on the flow stresses and material properties of the two phases and the interface. Break-up occurs when the flow stresses overcome the deformation resisting capillary pressure (Δp_k), the magnitude of which depends on the droplet diameter (x) and the interfacial tension (γ); $\Delta p_k = 4\gamma/x$ for a spherical droplet. There are also dynamic effects and break-up can occur on relaxation. The reader is referred to textbooks covering processing of food emulsions (Friberg *et al.*, 2004; McClements, 2005) and a review article on microstructure evolution in polymer blends (Tucker and Moldenaers, 2002). Structure equilibrium in steady flow is characterised by a balance between break-up and coalescence. However, the shape of the gelled particle almost certainly deviates from any prediction based on equilibrium droplet deformation in steady flow, as gelation brings the system out of equilibrium and the interfacial properties as well as the rheology of the droplet and matrix phase alter.

The simplest flow processing device that has been used to obtain non-spherical gel particle suspensions is the stirred pot device (Brown *et al.*, 1989, 1995). It has been widely used to produce fluid gels introduced in Section 4.3. The particle structures depend significantly on the rotational speed of the stirrer, temperature profile and gelation treatment, and are generally irregular. The irregularity of and the limited control over particle shape based on fluid gel technology generated a resurgance in research activity on flow-induced structuring of hydrocolloid gel-based particles using well-defined flow fields. The generation of anisotropic gel structures including fibres, capillary structures and gels with fibres was pioneered by Tolstoguzov and co-workers (Tolstoguzov *et al.*, 1973; Tolstoguzov, 1974; Antonov *et al.*, 1980). They used flow devices employing some sort of orifice flow, termed spinneretless spinning. More recently, microfluidics orifice flow and other microfluidics geometries have been successfully used to structure spherical and deformed gel particle structures (see Section 4.6). Flow processing of hydrocolloid solutions in oil represents a further method (see Section 4.5). Simple shear flow generated in rotational devices or pipe flow has also been exploited for the engineering of regularly shaped hydrocolloid gel particles (Wolf *et al.*, 2000; Frith *et al.*, 2003). The principle of all these processes is to initiate gelation while the deforming flow stresses act at the droplet interface, thus trapping the flow-induced morphology. Depending on the hydrocolloid, chemical- or temperature-induced gelation is appropriate. Temperature-induced gelation may be easier to be put in place for practical application. The dynamic nature of these processes means that the phase behaviour of the hydrocolloid mixture is not readily described by a phase diagram. Also, predictive models for flow-induced deformation of emulsion droplets need to be applied with caution as the material properties of both emulsion phases as well as the interface change upon gelation (Wolf *et al.*, 2001a). In the liquid–liquid state, formulae built on original equations by Taylor (1934) can be successfully applied. To induce significant droplet deformation in shear flow, a suitable viscosity ratio between the droplet phase and the continuous phase is required (Grace, 1982). However, a suitable choice of phase viscosities becomes difficult and new mixtures need to be trialled because the changes in viscosity behaviour, especially close to gelation, are considerable. Concomitantly, at least the gelling phase becomes somewhat viscoelastic. Similarly, the interfacial properties change and attempts have been made to apply simple emulsion models through the droplet gelation phase in water-in-water emulsions (Wolf *et al.*, 2001a).

Three hydrocolloid mixtures suitable for generating anisotropic gel particles in steady shear flow are gelatin–guar, gellan–κ-carrageenan and gellan–sodium alginate (the first hydrocolloid in these pairs is the hydrocolloid enriched in the droplet–gel particle phase); see Fig. 4.10 for microstructures obtained at one selected concentration and flow shear stress for each of these three systems. These microstructures were processed in a cone-and-plate gap of a dynamic stress rheometer while shear stress was kept constant (Wolf *et al.*, 2000). A typical processing graph is reproduced in Fig. 4.11 showing the temperature profile and the viscosity response of the mixed system to the processing regime.

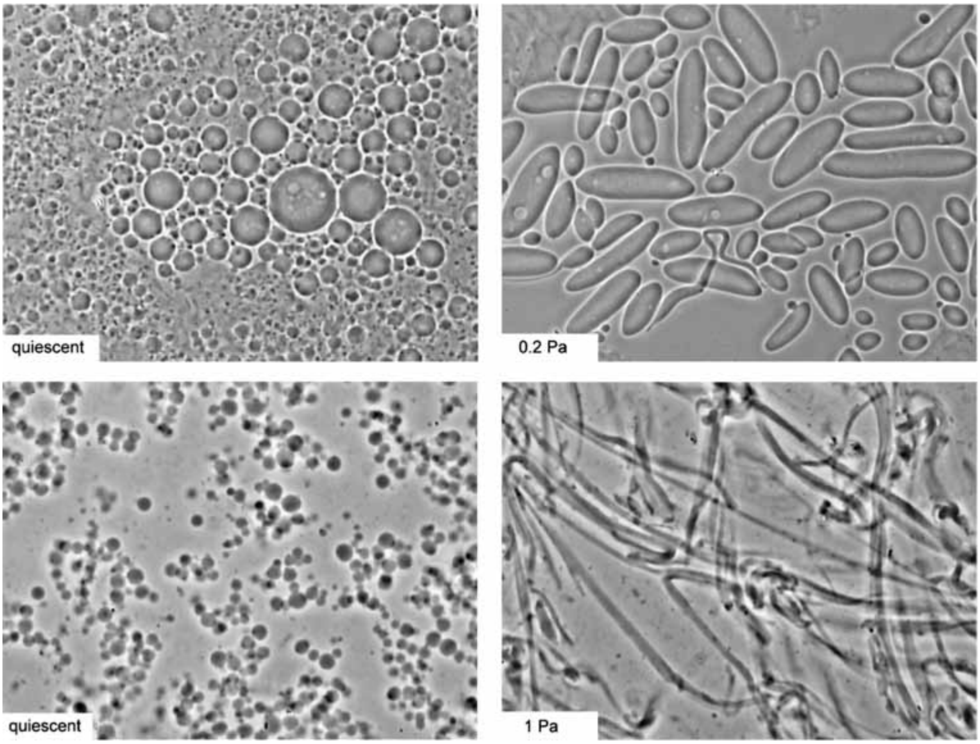


Fig. 4.10 Food gel particles obtained through laminar flow processing at constant low shear stress indicated on the micrographs, while cooling the samples at roughly 1 °C/min from 60 °sC through the gelation point of the included phase. Top: 2% gellan–2% κ-carrageenan. Bottom: 0.75% gelatin–1% guar. Reproduced with permission from Wolf *et al.*, (2000). Shear-induced anisotropic microstructure in phase-separated biopolymer mixtures. *Food Hydrocolloids* 14(3), 217–225. Elsevier.

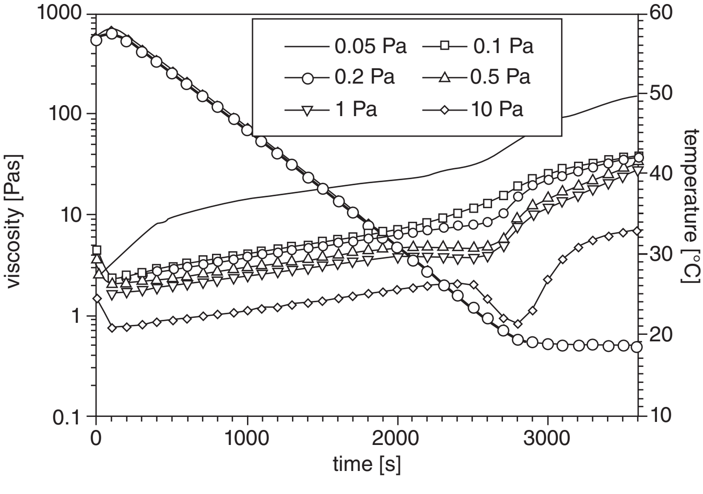


Fig. 4.11 Viscosity data for stress controlled cooled gelatin-guar mixtures. Reproduced with permission from Wolf *et al.*, (2000). Shear-induced anisotropic microstructure in phase-separated biopolymer mixtures. *Food Hydrocolloids* 14(3), 217–225. Elsevier.

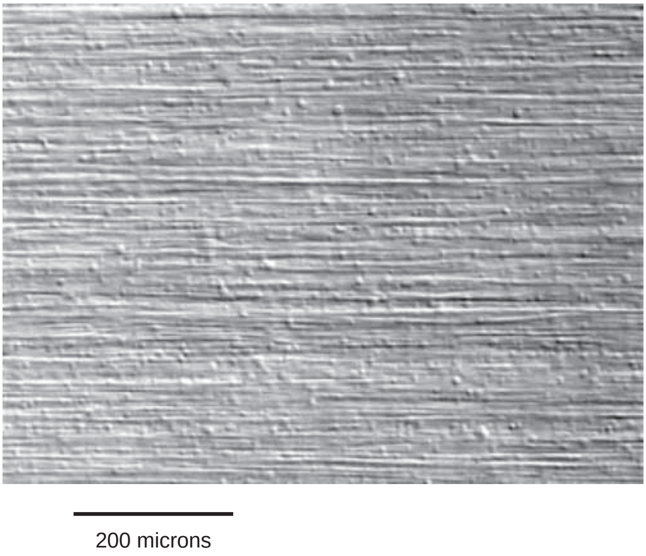


Fig. 4.12 Aligned gellan-rich fibres embedded in carrageenan-rich matrix, as structured by shear cooling in Couette flow. Reproduced with permission from Wolf *et al.*, (2001). Shear behaviour of biopolymer suspensions with spheroidal and cylindrical particles. *Rheologica Acta* 40(3), 238–247. Elsevier.

Deviation from the monotonic increase in mixture viscosity due to cooling indicates onset of gelation of the internal phase.

The shape of the particles can be described as ellipsoidal, becoming increasingly cylindrical with increasing flow stresses. Depending on the material properties of the hydrocolloids used, cylindrically shaped gelled particles, referred to as gelled fibres, can indeed be trapped. As rheology modifiers, gelled fibres lead to the largest differences in behaviour compared with gelled spheres. However, it is important to bear in mind that gelled fibres are flexible. It has been observed that long gelled fibres, once brought out of alignment in the direction of shear flow, remain somewhat entangled. Alignment is present immediately after their manufacture, as shown in Fig. 4.12. Acquisition of viscosity curves for processed gelled particles that have not previously been removed from the shear gap leads to classical differences in suspension flow behaviour, from spherical particle through to highly anisotropic cylindrical particles or fibres (see Fig. 4.13). Once entangled, viscosity at high shear stress or shear rate is higher than for a comparable system with spherical gel particles, due to the bigger dimensions of the fibre ball and the entrapped continuous phase fluid. Corresponding data for agar fibre suspensions, which, when produced at low enough aspect ratios, behave like rigid fibres, can be found in (Wolf *et al.*, 2007).

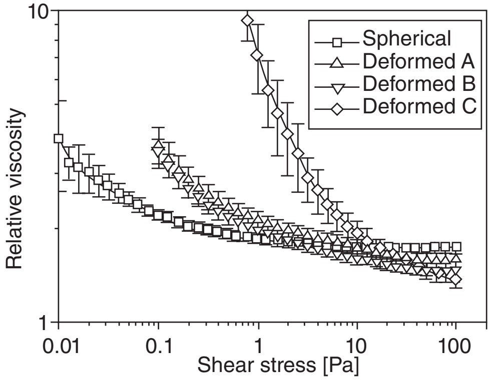


Fig. 4.13 Shear viscosity behaviour represented as relative viscosity (ratio of suspension viscosity over suspending medium viscosity) for gellan–carrageenan mixtures with included gellan-rich particles of increasing anisotropy whereby deformed C refers to fibres. Reproduced with permission from Wolf *et al.*, (2001b). Shear behaviour of biopolymer suspensions with spheroidal and cylindrical particles. *Rheologica Acta* 40(3), 238–247.

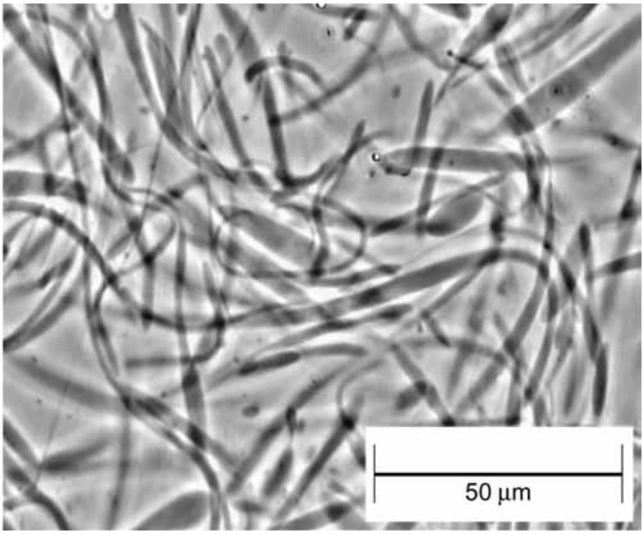


Fig. 4.14 Carrageenan-rich fibres processed in guar gum solution using a tubular heat exchanger. Reproduced from Frith *et al.*, (2003). Fibre containing composition. EPO, Unilever. EP1285588.

Continuous processing of gel fibres has been successfully demonstrated using a tubular heat exchanger configuration (Frith *et al.*, 2003) allowing production of structures shown in Fig. 4.14.

Laminar flow fields with a stretching flow component have also been investigated for manufacture of gel particles based on water-in-oil emulsions, see Section 4.5. Superimposition of stretching flow allows broadening of the spectrum of obtainable particle shapes.

4.5 HYDROCOLLOID PARTICLES FROM WATER-IN-OIL EMULSIONS

Processing of shaped hydrocolloid particles from water-in-oil emulsions presents different challenges. Compared with water-in-water emulsions, the interfacial tension is two to three orders of magnitude higher, and to generate elongated particles pure shear flow is not very efficient. Devices combining shear and elongational flow such as a four-roll mill have been developed (Walther *et al*., 2002; see Fig. 4.15). Depending on the relative importance of shear and extensional stresses, and the cooling regime to impart gelation of the included hydrcolloid phase, different shapes were produced; the first examples published were based on silicon oil as the continuous phase shown in Fig. 4.16. Later, the researchers succesfully used vegetable oil containing a suitable emulsifier and a broad range of hydrocolloid solutions as the internal phase (Walther *et al*., 2004) and also developed a co-flowing system that shows potential for scale-up (Walther *et al*., 2005).

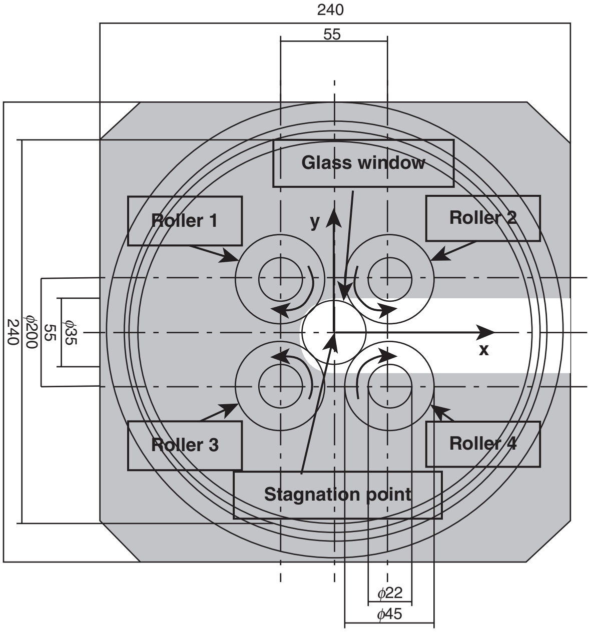


Fig. 4.15 Research four-roll mill with dimensions (mm) to fit a microscope stage for observation of structuring process. Reproduced with permission from Walther *et al.*, (2002). Flow processing and gel formation – a promising combination for the design of the shape of gelatin drops. *Food Hydrocolloids* 16(6), 633–643. Elsevier.

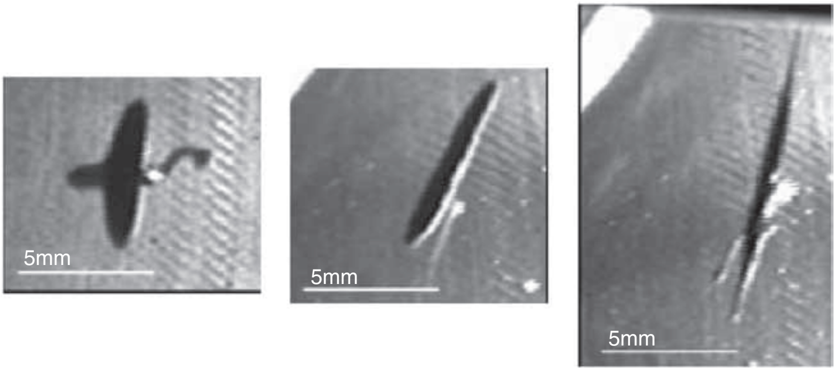


Fig. 4.16 Shaped gelatin drops produced by processing in silicon oil in a four-roll mill. Note the large size of the gelled particles. Reproduced with permission from Walther *et al.*, (2002) Flow processing and gel formation – a promising combination for the design of the shape of gelatin drops. *Food Hydrocolloids* 16(6), 633–643. Elsevier.

4.6 MICROFLUIDICS: HIGH-PRESSURE PROCESSING

Microfluidics deals with the behaviour, precise control and manipulation of fluids that are geometrically constrained to a small, typically sub-millimetre, scale. It is a relatively young discipline and an introduction to microfluidics can be found, for example, by Tabeling (2006). Application of microfluidics to medium- or large-scale food manufacture is still somewhat in its infancy and may never really take off, as scale-up presents a multitude of challenges including hygiene and process control. However, rotating membrane processing (Schadler and Windhab, 2006; Vladisavljevic and Williams, 2006; Hancocks, 2011; Pawlik and Norton, 2012a,b) presents an alternative and scalable route to achieving good levels of control over microstructure.

In recent years the use of microfluidics for fabrication of controlled microstructures has become increasingly popular. It allows manufacture of monodisperse gel particles of controlled material properties through solidification of droplets generated through microfluidic templating (Fig. 4.17). One of the most cited early papers originates from the Weitz group outlining the fabrication of monodisperse gel shells and functional microgels (Kim *et al.*, 2007). In terms of food-grade gelling hydrocolloids, the use of alginate (Amici *et al.*, 2008; Seiffert and Weitz, 2010; Ogonczyk *et al.*, 2011; Seiffert, 2011) and pectin (Ogonczyk *et al.*, 2011) appears to be most popular. Review articles in this field include Engl *et al.* (2008), Seiffert (2011) and Wang *et al.* (2011). The microfluidics approach can also be exploited to manufacture anisotropic gel particles (Zhang *et al.*, 2011) or microfibers (Hong *et al.*, 2007) (Fig. 4.18).

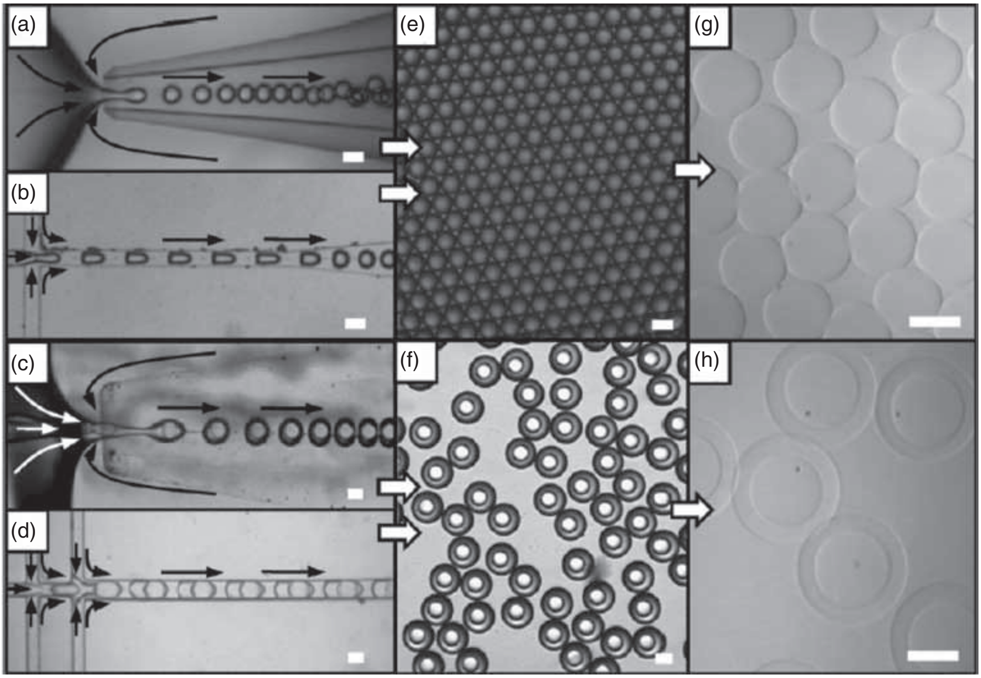


Fig. 4.17 Droplet-based microfluidic templating of microgel particles as shown in (Seiffert, 2011). (a) Glass microcapillary and (b) PDMS elastomer-based microfluidic devices producing single emulsion droplets. (c) Glass microcapillary and (d) PDMS elastomer-based microfluidic devices producing double emulsion droplets-in-droplets. (e, f) Monodisperse single and double emulsion droplets as obtained by these processes. (g) Monodisperse spherical microgels resulting from the single emulsion templates in Panel (e). (h) Monodisperse microshells resulting from the double emulsion templates in Panel (f). All scale bars denote 50 μm. Arrows indicate the direction of flow. Reproduced with permission from Seiffert (2011) Functional Microgels Tailored by Droplet-Based Microfluidics. *Macromolecular Rapid Communications* 32(20), 1600–1609. John Wiley & Sons.

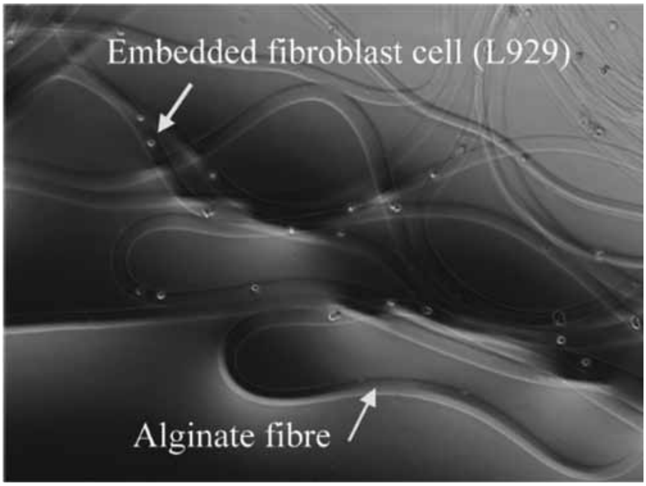


Fig. 4.18 Alginate fibres produced in a microfluidics device. Fibre width is ~20 μm and set-up was developed to encapsulate cells. Reproduced with permission from Hong *et al.*, (2007) Spherical and cylindrical microencapsulation of living cells using microfluidic devices. *Korea-Australia Rheology Journal* 19(3), 157–164. Springer-Verlag Berlin/Heidelberg.

In addition to the material properties and geometry of the microfluidic channel and the suspending fluid, the rheological character of the hydrocolloid solution forming the droplet affects the structure output of microfluidics devices (Harvie *et al.*, 2006, 2007, 2008; Hong and Cooper-White, 2009).

High-pressure processing presents another method that has been applied to texturisation of hydrocolloids and hydrocolloid mixtures, in particular in the presence of dairy proteins (Michel *et al.*, 2001; Rademacher *et al.*, 2003; Keim and Hinrichs, 2004; Kresic *et al.*, 2006; Lopez-Fandino, 2006; Johnston and Gray, 2008); the cited references do not include references focusing on the change of emulsifying capacity through high-pressure processing.

4.7 CONCLUSIONS

As this review has demonstrated, a raft of methods/techniques have been explored in order to manufacture designed hydrocolloid particles at the same scale as food emulsion droplets, for developing healthier foods. Additionally, the opportunity of employing gelation to kinetically trap non-spherical particles has opened the formulation window, and offers ways to impart novel product properties, physical material properties and sensory properties. In view of the ever increasing drive for healthier foods, and the existing knowledge base in the scientific literature, in the near future one would imagine an increase in the up-scale development and application by food manufacturers of the processes reviewed here.

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