Handbook of Industrial Water Soluble Polymers

Edited by

Peter A. Williams
Director
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North East Wales Institute, UK

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Chapter 1
Introduction

Peter A. Williams

Water soluble polymers are widely used in a broad range of industrial products and processes including, foods, pharmaceuticals, cosmetics, personal care products, paints and other coatings, inks, pigments, construction materials, adhesives, paper making, paper coating, water clarification, effluent treatment, etc. The polymers may be natural or synthetic with an array of molecular chemistries, structures and sizes. Although often present at very low concentrations they have a very significant influence on the overall properties of products and on product processing.

They have a number of key functionalities, including their ability to:

- increase the viscosity of solutions;
- form physical gels;
- stabilise dispersions and emulsions by adsorbing onto particles/droplets and inhibiting aggregation;
- induce particle aggregation to facilitate solid–liquid separation;
- modify surface properties to control wetting properties and inhibit deposition;
- solubilise hydrophobic compounds by complexation;
- facilitate the controlled release and delivery of active compounds.

This introductory chapter gives a brief overview of the key functional characteristics of water soluble polymers which are considered in more detail within the various chapters in this book.

1.1 Rheological behaviour

Water soluble polymers are able to form viscous solutions at concentrations of 1% or less and are widely used as thickeners in a broad range of products [1–7]. The viscosity of polymer solutions shows a marked increase at a critical polymer concentration commonly referred to as C^* which corresponds to the transition from the so-called 'dilute region', where the polymer molecules are free to move independently in solution without touching, to the 'semi-dilute region' where molecular crowding gives rise to the overlap of polymer coils and entanglement occurs. In the case of solid particles, the viscosity of spheres increases exponentially above a critical volume fraction of ~0.6, while for plate-like and rod-like particles the critical volume fraction is much lower. For polymer coils the viscosity only increases above a volume fraction of 1.0. The viscosity of polymer solutions is influenced significantly by the hydrodynamic volume of the polymer chains and hence is a function of shape, molecular mass, chain rigidity and electrostatic charge density. As will be discussed in

Chapters 2 and 3, polymer solutions normally exhibit Newtonian behaviour at concentrations well below C*, i.e. their viscosity is not dependent on the rate of shear, however, above C* non-Newtonian behaviour is usually observed. For most polymer-thickened systems, the viscosity–shear rate plot displays a high viscosity Newtonian plateau at low shear (typically at shear rates $< 1/s$), a shear-thinning region (at shear rates ~ 1–$10^2/s$) and a low viscosity plateau at high shear ($>10^2/s$). The magnitude of the viscosity at low shear determines the suspending properties. For example, xanthan gum has a very high low-shear viscosity and is now widely used in a variety of industries (e.g. food, pharmaceutical, agrochemicals, construction, etc.) to inhibit particle sedimentation and droplet creaming. Its other key feature is that it is highly shear thinning and so on stirring/pumping, etc. the viscosity decreases significantly enabling the product to flow. A classic example of its use is in the Food Industry in salad dressings. Even at very low concentrations the viscosity at low shear is such that xanthan can suspend herbs/spices but after shaking the bottle the dressing flows from the bottle. There are a range of polymer thickeners available commercially which include a number of natural polymers and their derivatives together with a range of synthetic polymers, largely acrylic based copolymers. The latter commonly have varying degrees of crosslinking and co-monomer types in order to control the viscosity–shear rate profile and solubility characteristics. For example, low degrees of crosslinking have the effect of increasing the molecular mass (and hence hydrodynamic volume) and consequently improve the thickening power. At high degrees of crosslinking the molecules are in the form of swellable microgels and the viscosity–volume fraction profiles are more similar to hard spheres rather than polymer coils. Copolymerisation of acrylics with surfactant monomers gives rise to so-called 'associative thickeners'. The long alkyl chains incorporated into the polymer backbone or at the end of the polymer chains tend to associate through hydrophobic bonding in aqueous solution giving rise to the formation of weak three-dimensional networks which have a high low-shear viscosity but which are highly shear thinning.

As is discussed in Chapter 4 a number of water soluble polymers (mainly natural polymers) are able to form three dimensional gel structures, at very low concentrations ($<1\%$), by physical association of their polymer chains [2–6, 8]. This results in the formation of stable junction zones through, for example, hydrogen bonding (e.g. starch), hydrophobic association (e.g. high methoxy pectin), cation mediated crosslinking (e.g. pectin and alginate with calcium ions, guar gum and polyvinyl alcohol with borate ions), etc. In addition depending on the polymer, the gelation process may be triggered by increasing temperature (e.g. methylcellulose, hydroxypropylmethyl cellulose, polyethylene (PEO)–polypropylene (PPO) triblock copolymers) or decreasing temperature (e.g. agarose, carrageenan, gellan gum, gelatine). Gel formation only occurs above a critical minimum concentration, C_0, which is specific for each polymer. Below C_0 precipitation may result. C_0 is not the same as the critical overlap concentration, C^*, noted above. The properties of individual hydrocolloid gels vary considerably in strength and elasticity due to differences in the flexibility of the polymer chains, the number and nature of the junction zones and the degree of chain aggregation.

1.2 Polymer adsorption and colloid stability

Polymers will readily adsorb onto the surface of particles or droplets and are commonly used to control the stability and rheology of particulate dispersions and emulsions [9–12].

At low polymer additions the polymer molecules can rearrange at the surface and adsorb with a flat configuration with most of the segments in trains in contact or close to the surface. At higher polymer additions, where there is competition for surface sites, polymers adsorb with some of their segments in 'trains' and with some segments in 'loops' or 'tails' protruding away from the surface into solution (Figure 1.1). The proportion of trains to loops/tails depends on the energy of adsorption. Non-ionic polymers tend to adsorb with a significant proportion of their segments in loops and tails while polyelectrolytes can adsorb onto certain surfaces (through electrostatic interaction) with the majority of their segments in trains. Since polymers adsorb through many points of contact, the process is usually irreversible to dilution with the same solvent. The kinetics of adsorption is controlled by the rate of diffusion of the polymer molecules to the surface i.e., smaller molecules will adsorb initially. If the energy of adsorption is weak, namely through van der Waals forces (typical for adsorption of non-ionic polymers), molecular rearrangements can occur on the surface and the smaller molecules may be displaced by higher molecular mass molecules. If the energy of adsorption is strong, notably through electrostatic interaction (typical for polyelectrolytes) the small molecules cannot be displaced.

For charged polymers adsorbing onto particles of the same charge, the adsorbed polymer can increase the particle surface charge and hence inhibit particle aggregation by charge repulsions (electrostatic stabilisation) [9–13]. For example, low molecular mass sodium polyacrylate is commonly used to disperse clay and calcium carbonate used for coating high quality paper. Lower molecular mass polymers are preferred so that the viscosity of the dispersion does not increase significantly due to unadsorbed polymer in the continuous phase [14]. For certain applications, sulphonated polymers such as lignosulphonate are used as dispersants since unlike carboxyl- or phosphate-containing polymers they are not precipitated by the high concentrations of dissolved calcium ions.

In the case of polymers adsorbing onto particles of opposite charge, low additions of a relatively low molecular mass polymer may cause the particles to aggregate by reducing the net charge on the particles. In the case of very high molecular mass polymers (both non-ionic polymers and polyelectrolytes) particle aggregation can occur by the polymer adsorbing onto more than one particle simultaneously, so-called bridging flocculation. For example, polyacrylamides, (anionic, neutral or cationic) are commonly used in the treatment of industrial wastewater or sewage, where usually low (≤1%) volume fractions of solids need to be removed from water streams. The synthesis and properties of a range of polymeric flocculants are discussed in detail in Chapter 6.

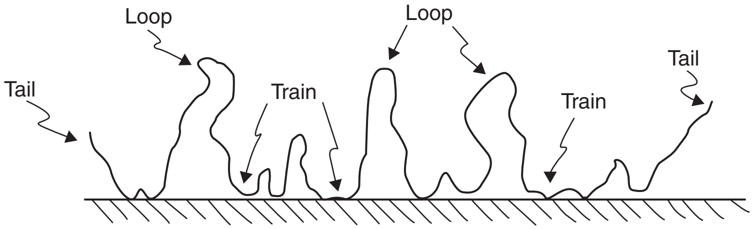

Figure 1.1 Schematic illustration showing the adsorption of a polymer molecule onto a surface with varying proportions of segments in trains, loops and tails.

When the surfaces of particles are fully covered by polymer molecules, the extending layers can prevent aggregation by 'steric stabilisation' [9–13]. This arises from the increase in osmotic pressure (enthalpic contribution) and configurational constraints (entropic contribution) experienced by the segments when the adsorbed polymer layers overlap. Steric stabilisation will occur under good solvent conditions if the polymer layer extends out to a sufficient distance to prevent association through short range van der Waals attractive forces (Figure 1.2).

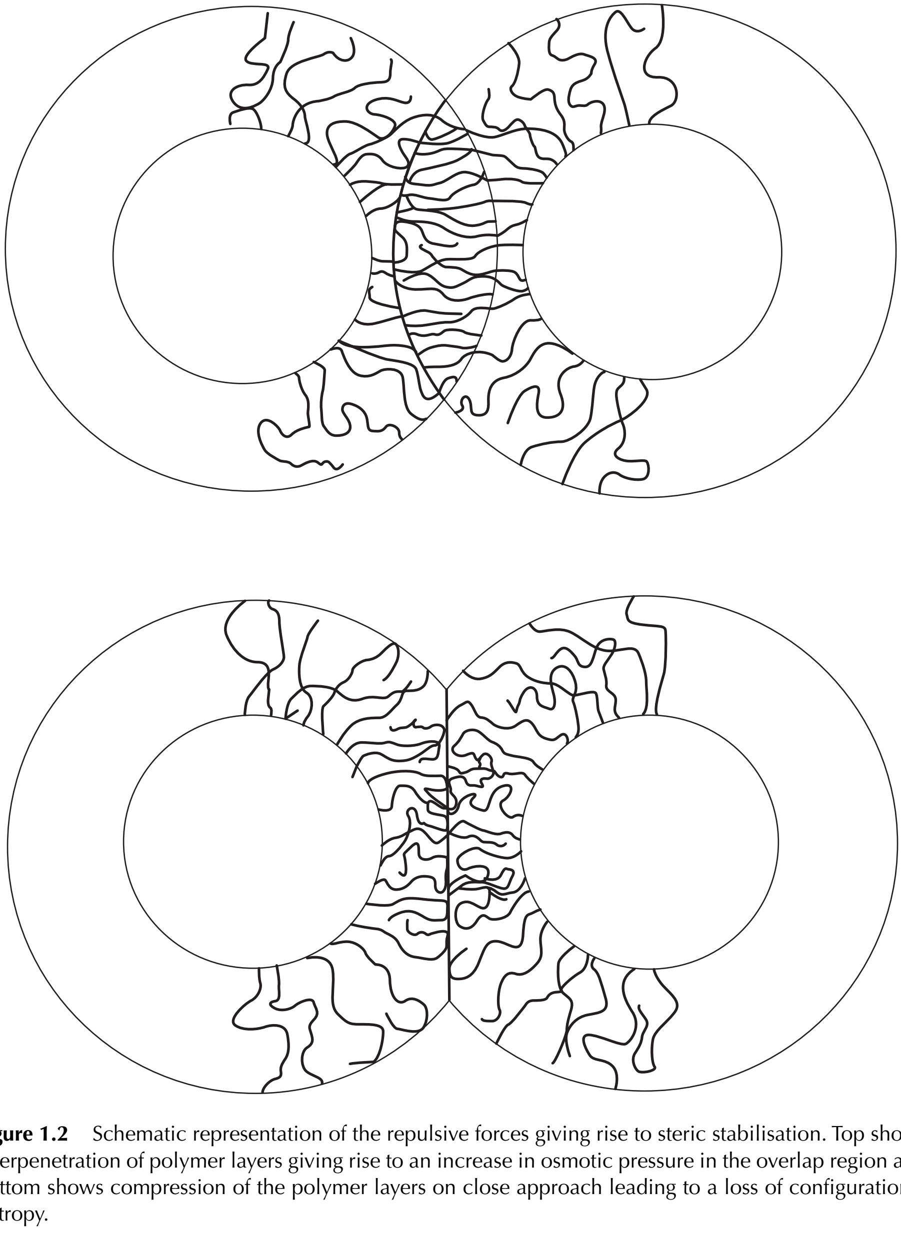

Figure 1.2 Schematic representation of the repulsive forces giving rise to steric stabilisation. Top shows interpenetration of polymer layers giving rise to an increase in osmotic pressure in the overlap region and bottom shows compression of the polymer layers on close approach leading to a loss of configurational entropy.

A range of polymers with varying molecular architectures are nowadays used to confer steric stabilisation. Typical examples include graft (comb-like) and AB block copolymers (Figure 1.3). One of the components of the copolymer anchors the polymer chains to the surface while the other extends out into solution to provide a steric barrier. The chemical nature of each of the components can be selected to suit the particular need. Chapter 7 reviews the synthesis and solution properties of block and graft copolymers.

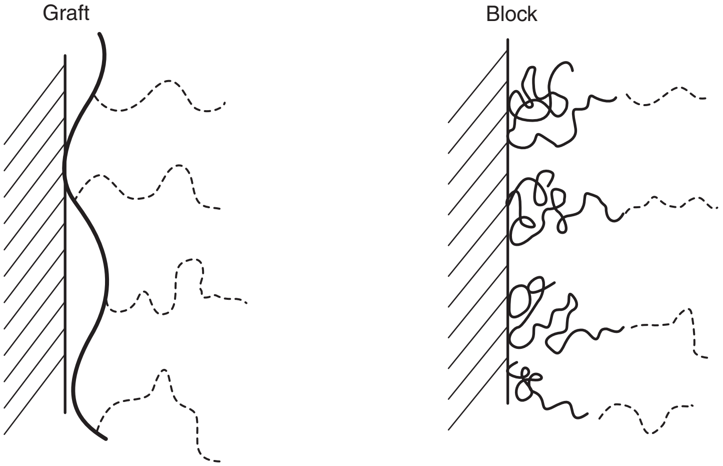

Figure 1.3 Schematic representation of graft and block copolymers adsorbed on a surface.

In the Food Industry the choice of stabiliser is restricted by legislation but there are a wide range of natural 'copolymers' to choose from, notably proteins and also certain polysaccharides such as gum Arabic. The latter consists of three molecular fractions, one of which has a 'wattle-blossom' type structure in which branched carbohydrate blocks are linked to a common polypeptide chain (Figure 1.4) [15]. Gum Arabic is widely used to stabilise concentrated flavour oils for application in beverages and it has been argued that the polypeptide anchors the molecules to the surface of the oil droplets while the carbohydrate blocks protrude out into solution and confer stability through electrostatic and steric mechanisms. There is considerable interest nowadays in forming polysaccharide–protein complexes to

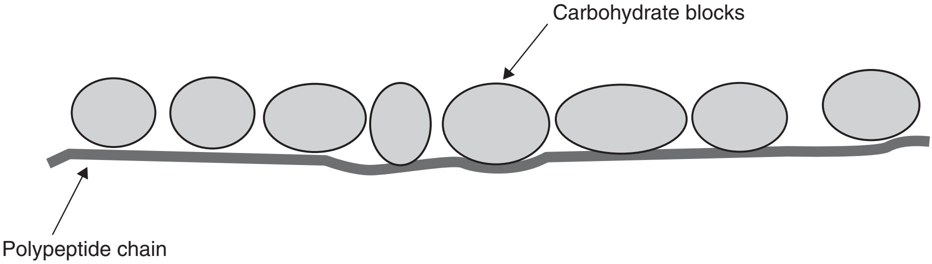

Figure 1.4 Schematic representation of the 'wattle-blossom structure' of one of the components of gum Arabic, which is responsible for its emulsification properties.

match the performance of gum Arabic. The role of proteins and polysaccharides in encapsulation and their influence in conferring emulsion stability is reviewed in Chapter 5.

The presence of non-adsorbed polymer in the continuous phase of particulate dispersions and emulsions can lead to weak particle/droplet aggregation by a volume restriction mechanism commonly referred to as depletion flocculation [10, 11, 13]. For example it has been shown that the addition of hydroxyethyl cellulose (0.08%) can lead to the aggregation of latex particles in paint formulations [16] and that the presence of xanthan gum at levels as low as 0.01% can induce the flocculation of emulsion droplets in mayonnaise and dressing formulations [17]. Depletion flocculation arises due to polymer molecules being excluded from the space between particles at short separations. This results in an osmotic pressure differential between the excluded region and the continuous phase leading to a net attractive force between particles (Figure 1.5). If the depletion force is greater than the sum of the electrostatic and steric repulsive forces, aggregation will occur.

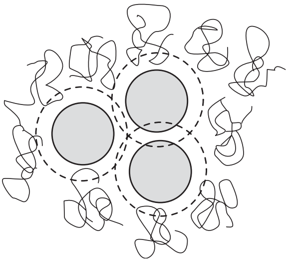

Figure 1.5 Schematic representation of the situation giving rise to depletion flocculation. Polymer molecules are excluded from the space between particles causing an osmotic pressure differential between the excluded region and the continuous phase and giving rise to a net attractive depletion force.

1.3 Surface modification

As polymers adsorb strongly to surfaces they can be used to change the surface energy and wetting characteristics. An example of this can be seen with the drainage of glass and crockery. After washing with surfactants and then rinsing in water the contact angle will be close to zero and a thin film of water will adhere to the plate. The film of water will evaporate with time leaving spots due to dust or salts present in the water. By adsorbing monolayers of hydrophilic polymers to the plate surface, the contact angle can be increased. With polymers that are slightly hydrophobic, the contact angle can be brought to about 30° and will facilitate the draining of the water film in a single sheet down the plate.

Polymers can also be used to prevent the adsorption of proteins to surfaces. For example, polyvinylpyrrolidone can prevent protein adsorbing onto a variety of surfaces and it can also displace adsorbed protein [18]. This has led, for example, to its application in the coating of filtration membranes in order to reduce biofouling. Polymers are also used to inhibit the adhesion of bacteria or water-borne micro-organisms onto surfaces [19, 20]. Bacteria are usually surrounded by exocellular polysaccharides that can aid adhesion to clean surfaces. Thus prosthetic devices and vascular implants carrying blood suffer from the build up of biofilms, leading to blockages and infection. This build up can be markedly reduced by adsorbing a water soluble polymer on the surface. Typical polymers include polyethylene glycol (PEG) or PEG copolymers (e.g. PEG-acrylate). There is currently also much interest in using ‘biocompatible polymers’ such as hyaluronan to coat the surface of biomaterials [21]. As the micro-organism approaches the polymer-coated surface, segments of the exocellular polysaccharide and the surface-attached polymer overlap resulting in steric repulsion, thus inhibiting adsorption.

1.4 Complexation and controlled release

Many drugs, pesticides, dyes, etc. are hydrophobic in nature and hence are water insoluble. It has been shown that complexation or encapsulation of such active compounds with specific water soluble polymers can render them water soluble. A typical example is that of the complexation of hydrophobic compounds with polyvinylpyrrolidone. This polymer has a strong dipole, with a significant positive potential on one side of the polymer chain due to the amide nitrogen and a significant negative potential on the other due to the amide oxygen. The nitrogen is surrounded by hydrophobic methylene and methine groups while the oxygen is available to interact with solvent molecules [22]. Unlike other water soluble polymers, polyvinylpyrrolidone has the ability to dissolve in both water and organic solvents such as chloroform. Complexes between polyvinylpyrrolidone and water insoluble compounds can be produced by dissolving both the polymer and compound in chloroform and then removing the solvent by evaporation. The solid complex obtained can be instantly dissolved in water and this is illustrated in Figure 1.6 which shows the solubility of a hydrophobic dye, sudan red, alone and in the form of a complex with polyvinylpyrrolidone in water. At low polymer dye ratios (1:20) the dye is still completely insoluble. As the ratio increases (up to 2:1) some solubility is conferred but above this ratio the dye complex is completely soluble yielding optically clear solutions.

Further examples of polymers used to solubilise hydrophobic compounds are polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO-PPO-PEO) triblock-type copolymers. Such polymers form micelles in solution with the more hydrophobic PPO chains forming the inner core and the more hydrophilic PEO chains the outer shell. Hydrophobic materials are able to dissolve within the core of the micelles and such systems are finding increasing

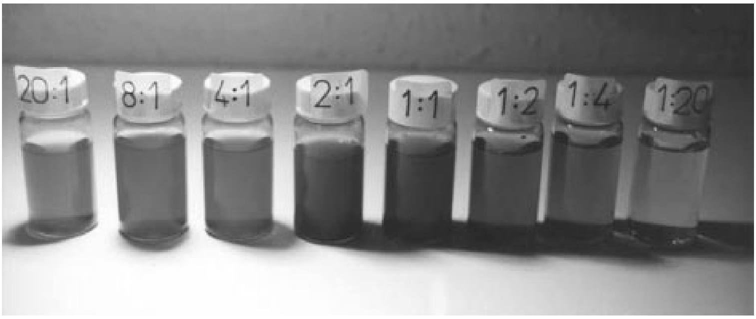

Figure 1.6 Photograph showing the solubility of complexes formed between Sudan red and polyvinylpyrrolidone in water at varying polymer:dye ratios. The dye is insoluble in water at polymer:dye ratios of <2:1 but is soluble at ratios of >4:1.

use in drug delivery. These are discussed in more detail in Chapter 7. Other polymeric systems, notably dendrimers, can also be used to solubilise compounds for drug delivery and other applications and their synthesis, properties are fully reviewed in Chapters 8. Another means of delivering active compounds is by encapsulating them within highly crosslinked polymer microgels. The microgels can be produced with a range of chemistries which enables them swell and contract by changing the solvent conditions (e.g. pH, ionic strength) and temperature. Active compounds within the matrix of the microgel are retained when the microgel is in its swollen state but are released when the microgel contracts. The synthesis, properties and applications of microgels are reviewed in Chapter 9.

1.5 Packaging

Water soluble polymers are also now finding application in the area of packaging. For example polyvinyl alcohol pouches are used to dispense liquid detergent formulations. The pouch is placed in the washing machine and the polyvinyl alcohol slowly dissolves to release the liquid. The emphasis nowadays is to use natural polymers, both polysaccharides and proteins, as packing materials because of their ability to biodegrade and recent advances in this area are covered in Chapter 10.

References

1. Barnes, H.A. (ed.) (2000) *A Handbook of Elementary Rheology Institute of Non-Newtonian Fluid Mechanics.* University of Wales, Publishers, Aberystwyth.
2. Lapasin, R. and Pricl, S. (eds) (1995) *Rheology of Industrial Polysaccharides: Theory and Application.* Blackie Academic and Professional, Glasgow.
3. Phillips, G.O. and Williams, P.A. (eds) (2000) *Handbook of Hydrocolloids.* Woodhead Publishing Ltd., Cambridge.
4. Stephen, A.M., Phillips, G.O. and Williams, P.A. (eds) (2006) *Food Polysaccharides and Their Applications*, 2nd edn. Taylor and Francis, Boca Raton, FL.
5. Whister, R.L. and BeMiller, J.N. (eds) (1993) *Industrial Gums: Polysaccharides and Their Derivatives*, 3rd edn. Academic Press, London, UK.
6. Imeson, A. (ed) (1992) *Thickeners and Gelling Agents for Food.* Blackie Academic and Professional, Glasgow.
7. American Chemical Society (1989) *Polymers in Aqueous Media; Performance Through Association, Advances in Chemistry Series 223.* American Chemical Society Publishers.
8. Harris, P. (ed.) (1990) *Food Gels.* Elsevier Science Publishers, London, UK.
9. Tadros, Th.F. (ed.) (1987) *Solid/Liquid Dispersions.* Academic Press Publishers, London.
10. Fennel Evans, D. and Wennerstrom, H. (eds) (1999) *The Colloidal Domain: Where Physics, Chemistry and Biology Meet*, 2nd edn. Wiley-VCH Weinheim, New York.
11. Fleer, G.J., Cohen Stuart, M.A., Scheutjens, J.M.H.M., Cosgrove, T. and Vincent, B. (eds) (1993) *Polymers at Interfaces.* Chapman and Hall, London.
12. Cosgrove, T.C. (ed.) (2005) *Colloid Science: Principles, Methods and Applications.* Blackwell Publishing Ltd, Oxford.
13. Hunter, R.J. (ed.) (1993) *Introduction to Modern Colloidal Chemistry.* Oxford University Press, Oxford.
14. Williams, P.A., Harrop, R. and Robb, I.D. (1985) *J. Chem. Soc. Farad. Trans. I*, **81**, 3635.

15. Williams, P.A. and Phillips, G.O. (2006) Gums and mucilages. In A.M. Stephen, G.O. Phillips and P.A. Williams (eds), *Food Polysaccharides and Their Applications*, 2nd edn. Taylor and Francis, Boca Raton, Florida, pp. 455.
16. Sperry, P.R., Hopfenberg, H.B. and Thomas, N.L. (1981) *J. Colloid Interface Sci.*, **82**, 62.
17. Velez, G., Fernandez, M.A., Munoz, J., Williams, P.A. and English, R.J. (2003) *J. Agric. Food Chem.*, **51**, 265.
18. Robinson, S. and Williams, P.A. (2003) *Langmuir*, **19**, 559.
19. Lee, H.J., Park, K.D., Park, H.D., Lee, W.K., Han, D.K., Kim, S.H. and Kim, Y.H. (2000) *Colloid. Surf. B –Biointerf.*, **18**, 355.
20. Vacheethasanee, K. and Marchant, R.E. (2000) *J. Biomed. Mat. Res.*, **50**, 302.
21. Kennedy, J.F., Phillips, G.O., Williams, P.A. and Hascall, V.C. (eds) (2002) *Hyaluronan*, Vol. 2. Woodhead Publishing Ltd, Cambridge.
22. Smith, J.N., Meadows, J. and Williams, P.A. (1996) *Langmuir*, **12**, 3773.

Chapter 2
Natural Thickeners

Graham Sworn

2.1 Introduction

Natural thickeners can be defined as products obtained from natural sources such as plants, seeds, seaweeds and microorganisms. These products are high molecular weight polymers composed of polysaccharides and are often referred to as hydrocolloids. Production processes vary from simple collection of tree exudates and milling in the case of gum arabic to more complex production by fermentation as in the case of xanthan gum. A number of these natural thickeners are also derivatised in order to modify their properties. Table 2.1 provides a simple classification of these products by source. Tables 2.2–2.4 provide an overview of the main natural thickening agents and their applications. A brief description of each class of hydrocolloids is given below but for more detailed information on each of the hydrocolloids there are a number of publications available [1–3].

2.1.1 Marine polysaccharides

This group includes the carrageenans, a group of sulphated galactans, which are extracted from red seaweed (Rhodophyceae) species such as *Eucheuma cotonii*, *Eucheuma spinosum*, *Chondrus crispus* and *Gigartina* species. The carrageenans are split into three main types according to their ester sulphate content. These are lambda, iota and kappa in the order of decreasing ester sulphate content. The carrageenan type varies according to the weed source. Lambda carrageenan is a non-gelling thickener whereas iota and kappa types are gelling.

Table 2.1 Classification of polysaccharides

Marine	Botanical	Microbial	Chemically modified
Carrageenans	Guar gum	Xanthan gum	Cellulose gums
Agar–agar	Locust bean gum	Gellan gum	Modified starches
Alginates	Gum tragacanth	Pullulan	Propylene glycol alginate
	Konjac glucomannan	Curdlan	Modified guar gum
	Tara gum	Dextran	
	Cassia gum	Welan gum	
	Gum arabic	Rhamsan	
	Pectin	Succinoglycan	
	Starches		

Table 2.2 Summary of natural thickeners

Product	E number	Origin	Source	Region	Constituent sugars	Applications
Guar gum	E 412	Seed	*Cyamopsis tetragonolobus*	India, Pakistan	L-mannose, D-galactose	Drinks, sauces, soups, ketchups, dressings, flour additive
Locust bean gum (LBG, Carob)	E 410	Seed	*Ceratonia siliqua*	Spain, Morocco, Portugal	L-mannose, D-galactose	Ice cream, hot prepared sauces, soups, ketchups, dressings
Tara gum	E 417	Seed	*Caesalpinia spinosa*	Peru, Equador	Galactomannan	Sauces, soups, ketchups, dressings
Cassia gum	E 499	Seed	*Cassia tora, Cassia obtusiflolia*	Sub-tropical	Galactomannan	Pet foods
Karaya	E 416	Plant exudate	*Sterculia urens*	India, Senegal, Mali	D-galacturonic acid, L-rhamnose, D-galactose, D-glucuronic acid	Brown sauce, coatings, fillings, toppings, chewing gum
Gum Tragacanth	E 413	Plant exudate	*Astragulus* species	Iran, Turkey	L-arabinose, D-galactose, D-galacturonic acid, L-rhamnose	Confectionery icings, dressings, flavour oil emulsions
Gum Arabic (Acacia gum)	E 414	Tree exudate	*Acacia senegal, sayal*	Sudan	D-galactose, D-glucuronic acid, L-rhamnose/L-arabinose	Drinks, confectionery gums, adhesives
Konjac	E 425i–ii	Tuber	*Amorphophallus konjac*	Far East	D-mannose, D-glucose	Desserts, aspics, surimi, frozen desserts, sauces, batters
Xanthan gum	E 415	Microbial	*Xanthomonas campestris*	USA, Europe, China	D-glucose, mannose, glucuronic acid	Sauces, dressings, drinks, fruit preparations, cakes, desserts, meat products, cosmetics, cleaners, oil drilling
Succinoglycan	Not permitted in food (except Japan)	Microbial	*Agrobacterium tumefaciens*	Europe, Japan	Galactose, Glucose	Acidic cleaners, Food products (Japan only)
Welan gum	Not permitted in food	Microbial	*Alcaligenes* species	USA	D-glucose, glucuronic acid, L-rhamnose, mannose	Tyre sealants, de-icing fluids, pigment suspensions for concrete
Rhamsan gum	Not permitted in food	Microbial	*Alcaligenes* species	USA	D-glucose, glucuronic acid, L-rhamnose	Cleaners
Sodium alginate	E 401–E 404	Brown seaweeds	*Laminaria, Macrocystis, Ecklonia, Lessonia* species	North/South America, Europe, Australia, Africa	Mannuronic acid, guluronic acid	Sauces, salad dressings, desserts, fruit preparations, ice cream, water ices, onion rings, low fat spreads, bakery filling creams, fruit pies, textile printing, paper industry
Pectin (high and low ester)	E 440	Fruit	Citrus, apple, sugar beet, sunflower	North/South America, Europe	Galacturonic acid, rhamnose, galactose, arabinose	Jams, confectionery, bakery fillings, toppings, fruit preparations, glazes, sauces, water ices, sorbets, yogurt drinks

Table 2.3 Summary of derivatives of natural thickeners

Product	E number	Base material	Reactant	Applications
Carboxymethyl guar	Not permitted in food	Guar gum	Sodium monochloroacetate	Printing pastes (reactive dyestuffs)
Hydroxypropyl guar	Not permitted in food	Guar gum	Propylene oxide	Cosmetics, textile finishing
Phosphated guar	Not permitted in food	Guar gum	Sodium dihydrogen phosphate	Paper products
Cationic guar	Not permitted in food	Guar gum	2′3′-epoxypropyl-trimethyl ammonium chloride	Hair and skin care products, paper manufacture, waste water clarification
Propylene glycol alginate (PGA, propane 1,2-diol alginate)	E405	Alginic acid	Propylene oxide	Salad dressings, meringues, ice cream, noodles, fermented milk drinks, dairy desserts, beer
Carboxyl methyl cellulose (CMC)	E 466	Cellulose	Monochloroacetic acid	Drinks, dairy drinks, powdered drinks, sauces, dressings, ice cream, water ices, bakery products, low pH dairy products, cosmetics, paper, textiles, oil drilling, adhesives
Hydroxypropyl cellulose (HPC)	E 463	Cellulose	Chloromethane and propylene oxide	Aerated toppings
Hydroxypropylmethyl cellulose (HPMC)	E 464	Cellulose	Propylene oxide	Soya burgers, sausages, onion rings, potato croquettes, waffles, batters, coatings, doughnuts, gluten free bakery products, shampoo, lotions
Methyl cellulose	E 461	Cellulose	Chloromethane	Soya burgers, sausages, onion rings, potato croquettes, waffles, batters, coatings, doughnuts, gluten free bakery products, building materials
Methyl ethyl cellulose (MEC)	E 465	Cellulose	Chloromethane and chloroethane	Non-dairy creams, toppings, aerated desserts, mousses, meringues, mallows, batters
Ammidated pectin	E 440ii	High ester pectin	Ammonia	Jams, confectionery, bakery fillings, toppings, fruit preparations, glazes, sauces, water ices, sorbets, yogurt drinks

Table 2.4 Summary of starch derivatives

Product	E Number	Applications
Oxidised starch	E 1404	Confectionery, dairy products, batters and breadings, coatings
Monostarch phosphate	E 1410	Frozen gravies, pie fillings, dressings
Distarch phosphate	E 1412	Sauces, dressings, dry mix puddings, baked goods
Phosphated distarch phosphate	E 1413	Sauces, frozen gravies, pie fillings
Acetylated distarch phosphate	E 1414	Soups, sauces, dairy products, fruit fillings, pet foods, chilled and frozen meals
Acetylated starch	E 1420	Batters, breadings, snacks, cereals, confectionery
Acetylated distarch adipate	E 1422	Gravies, sauces, dressings, sweet and savoury fillings, fruit preparations, dairy products, chilled and frozen meals
Hydroxypropyl starch	E 1440	Meat, beverages, low-fat and low-calorie foods
Hydroxypropyl distarch phosphate	E 1442	Gravies, soups, sauces, dressings, sweet and savoury fillings, fruit preparations, dairy products, chilled and frozen meals, meat
Starch sodium octenylsuccinate	E 1450	Spray dried flavours, beverage emulsions, emulsified sauces, dressings

Iota forms soft, thixotropic gels in the presence of calcium whereas kappa forms firm, brittle gels in the presence of potassium or to a lesser extent calcium.

Alginates are extracted from brown seaweed (Phaeophyceae) species such as *Macrocystis pyrifera*, *Laminaria hyperborea* and *Ascophylum nodosum*. Alginates are block copolymers composed of manuronic acid (M) and guluronic acid (G) residues. The ratio of these substituents, the M/G ratio is dependent on the weed source and the part of the weed used. M/G ratio also governs the properties of the alginate. Sodium salts of alginate are soluble in water and are used as thickeners and gelling agents. Gelation occurs through addition of calcium. Alginates rich in manuronic acid residues (high M) form softer more flexible gels with little or no syneresis compared to their guluronic-acid-rich (high G) counterparts.

Agar is a collective term for a complex mixture of polysaccharides which are extracted from *Gelidium* and *Gracilaria* species of red seaweed. Agarose, a neutral polymer, and agaropectin, a charged sulphated polymer, are the two major fractions. Agar typically forms firm, brittle gels on cooling and show thermal hysteresis. It is used extensively in microbiological media and confectionery products.

2.1.2 Botanical polysaccharides

This is perhaps the most diverse group of polysaccharides. Many of these materials have been known to man for centuries. Guar gum, locust bean gum (LBG), tara and cassia gum are composed of a $(1 \rightarrow 4)$ linked mannose backbone with single galactose substituents and are therefore referred to as galactomannans. They differ in the degree of galactose substitution, guar typically containing one galactose per every two mannose residues whereas LBG typically has only one galactose every four to five residues. All the galactomannans are thickeners and their properties, such as solubility and interaction with xanthan or carrageenan, are governed by the galactose content. For example, guar is soluble in cold water whereas LBG must be heated to ~90°C to hydrate. LBG, under certain conditions, will form soft flexible gels with xanthan whereas guar only shows a synergistic increase in viscosity. Tara and cassia gum have properties intermediate to those of guar and LBG.

Pectins are extracted from a variety of sources including apples and citrus fruits. They are composed of galacturonic acid residues with occasional rhamnose interruptions. They are usually classified in terms of their degree of methyl esterification. Low ester ($<50\%$) pectins gel in a similar way to alginates through reaction with calcium. High ester ($>50\%$) pectins require low pH and high soluble solids ($>\sim55\%$) to gel. Under these conditions intermolecular electrostatic repulsions are reduced. The type of solids has an effect on the gels. For example, sucrose is more effective at promoting gelation than corn syrup. This class of polysaccharides also includes the starches and gum arabic.

2.1.3 Microbial polysaccharides

There have been many microbial polysaccharides produced by fermentation including, dextran, welan, rhamsan, pullulan, curdlan and scleroglucan that have caught the imagination of the academics and industrialist alike. However, very few have found widespread use industrially. The notable exception to this is xanthan gum. It is produced during fermentation by the organism *Xanthomonas campestris*. Its primary structure is a linear $(1 \rightarrow 4)$ linked β-D-glucose backbone (as in cellulose) with a trisaccharide side chain on every other glucose, containing a glucuronic acid residue linked $(1 \rightarrow 4)$ to a terminal mannose unit and $(1 \rightarrow 2)$ to a second mannose that connects to the backbone. The terminal mannose is pyruvylated and the non-terminal residue carries an acetyl group. Xanthan gum is soluble in cold water and is an extremely effective thickener. It also interacts synergistically with the galactomannans.

2.1.4 Chemically modified polysaccharides

This group includes the chemically modified cellulose products such as carboxymethyl cellulose (CMC), hydroxypropylmethyl cellulose (HPMC) and hydroxyethyl cellulose (HEC). The purpose of these modifications is primarily to render the basic cellulose backbone soluble. In this way a range of cellulose-based products are produced with a variety of functions from thickening in the case of CMC to thermogelation in HPMC. Similarly, there are a wide variety of chemically modified starches available including hydroxyethyl and hydroxypropyl. These modifications to the native starch improve stability to heat and to acid, improve processing and reduce the tendency to retrogradation. Alginates are also modified by esterification with propylene glycol to produce propane 1,2-diol alginate (PGA). This modification makes the alginates less sensitive to precipitation by acid and calcium which enables the PGA to remain in solution below pH 4.0. Chemically modified guar gums are also available commercially for non-food applications. Modifications include carboxymethylation to improve alkali compatibility, hydroxyalkylation to improve solubility and compatibility

Table 2.5 Functionality of natural thickeners

Function	Example
Adhesive	Glazes, icings, frostings, wall paper paste
Binding agent	Pet foods
Bodying agent	Dietetic beverages
Crystallisation inhibitor	Ice cream, sugar syrups, frozen foods
Clarifying agent (fining)	Beer, wine
Cloud agent	Fruit drinks, beverages
Coating agent	Confectionery, fabricated onion rings
Dietary fibre	Cereals, bread
Emulsifier	Salad dressings
Encapsulating agent	Powdered flavours
Film former	Sausage casings, protective coatings, paper sizing
Flocculating agent	Wine
Foam stabiliser	Whipped toppings, beer
Gelling agent	Puddings, desserts, confectionery
Moulding	Gum drops, jelly candies
Protective colloid	Flavour emulsions
Stabiliser	Salad dressings, ice cream, cosmetics
Suspending agent	Chocolate milk, drilling fluids
Swelling agent	Processed meat products
Syneresis inhibitor	Cheese, frozen foods
Thickening agent	Jams, pie fillings, sauces, toilet cleaners, cosmetics
Whipping agent	Toppings, marshmallows

with electrolytes, phosphatisation to cross-link the guar and improve the film-forming properties and cationisation to create a cationic guar gum for use in conditioning shampoos and cosmetic preparations.

Natural thickeners and their derivatives are used in many different industries including food, oil drilling, paper coating, pesticides, textile and carpet printing, cosmetics, personal care and pharmaceuticals. A casual glance at the labels in any supermarket will very quickly reveal the diversity of products containing these versatile thickeners. They are found in salad dressings, ice cream, confectionery, soups and sauces, toilet cleaners, and shampoo for example. Technical literature on hydrocolloids from suppliers and academics alike also testify to the wide range of functional properties they bring to an application (Table 2.5) [1]. It is also evident that most of these functional properties have at one time or another been associated with all of the commercial hydrocolloids. There is a great deal of overlap between different hydrocolloids in terms of functionality and application but it is also true that each of the hydrocolloids tends to excel in a few specific areas. Much of the functionality associated with natural thickeners can be related to the rheological behaviour.

2.2 Introduction to rheology

Rheology is the science of flow and deformation of matter and is considered a branch of physics. The flow of materials has been a concern since the earliest times. Lucretius, a

Roman poet and philosopher born at the beginning of the 1st century BC, wrote in his poem *De Rerum Natura* (*On the nature of things*):

> For water moves and flows with so very small a moving power because it is made of small rolling shapes. But on the other hand, the nature of honey has more cohesion, its fluid is more sluggish, and its movement more tardy, for the whole mass of its matter coheres more closely assuredly because it is not made of bodies so smooth or so delicate and round.

The modern science of rheology can be traced back to the formation of the Society of Rheology and the founding of the *Journal of Rheology* in 1928. This was initiated by Prof. E.C. Bingham. In fact, Prof. Bingham is referred to as the 'Founder of Modern Rheology' in Scott Blairs book of 1938, *An Introduction to Industrial Rheology*, which constitutes the first comprehensive British text on the subject [4].

The science of rheology encompasses the behaviour of both solid and liquid materials. This extends from a perfectly elastic solid, defined by Robert Hooke in 1678, to a perfectly viscous liquid, defined by Newton in 1687, and to the myriad of viscoelastic materials in between. The rheology of natural thickeners is primarily concerned with viscosity and viscoelasticity.

2.2.1 Measurement of viscosity

The viscosity of a fluid is a measure of the frictional resistance it offers to an applied shearing force. Figure 2.1 shows two parallel planes in a fluid, separated by a distance (dx) and having velocities of flow differing by (dv). According to Newton's law of viscous flow, the frictional force (F), resisting the relative motion of two adjacent layers in the liquid, is proportional to the area (A) and the velocity gradient (dv/dx):

$$F = \eta A(\mathrm{d}v/\mathrm{d}x) \tag{2.1}$$

The proportionality constant (η) is known as the coefficient of viscosity or simply as viscosity.

This equation is more typically in the form:

$$\sigma = \eta\dot{\gamma} \tag{2.2}$$

where the shear stress (σ) is equivalent to the force per unit area (F/A) and the shear rate ($\dot{\gamma}$) is the velocity gradient (dv/dx). In other words, the viscosity is equal to the shear stress divided by the shear rate.

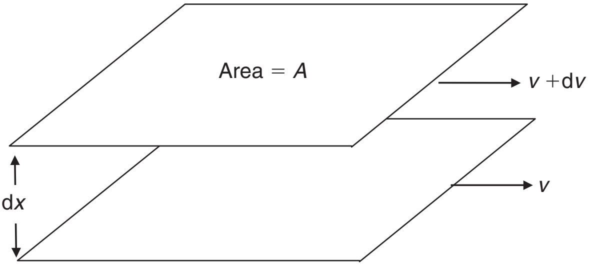

Figure 2.1 The definition of the coefficient of viscosity (η). Two parallel layers of fluid, of area A, are separated by a distance dx, and the difference in their velocities is dv.