Hydrocolloids: Structure-Function Relationships

Saphwan Al-Assaf and Glyn O. Phillips review the factors influencing the functionality of acacia gum and other hydrocolloids of interest to the food industry

Sources and properties of hydrocolloids

The hydrocolloids associated with polysaccharides originate from plant (e.g. plant cell walls, tree exudates, seeds, tuber/roots, seaweeds) or animal sources (hyaluronan, chitin, chondroitin sulphate). Additionally, certain types of bacteria (or fungi) can also produce hydrocolloids (xanthan, gellan, wellan). They are made up of monosaccharides (sugar units) glycosidically linked, through water elimination, to yield mixtures of similar but not identical molecules of differing molecular dimensions, with the distribution often dependent on the source, method of extraction and subsequently processing conditions. Their composition can be derived either from the same sugar unit (cellulose and starch), two different monomers (alginate, hyaluronan) or often a number of different monosaccharides, as in gum arabic (galactose, arabinose, rhamnose and uronic acid).

Their good solubility in water is due to the presence of many hydroxyl groups, but is influenced by the nature of the monosaccharides present. Neutral hydrocolloids are less soluble than those which contain uronic acids, which are often in the polyelectrolyte form (charged or ionic). When dissolved in water, hydrocolloids can adopt various conformations (spherical, random coil or rod-like) depending on the nature of the monosaccharides, the inter-sugar linkage (α or β) and their ability to associate by intra and intermolecular interactions. These in turn will determine the characteristics of the solution flow behaviour.

Functionality in a given commercial application is controlled by a number of factors, the most important of which are the structure and conformation in aqueous solutions and the way these are influenced by specific or non-specific interactions with other ingredients. The degree of polymerisation and size (molecular weight and dimensions) are other factors that determine their physical properties. Hence, considerable efforts to achieve accurate characterisation are necessary to determine the structure-function relationships.

In the food industry, their ability to emulsify oil droplets, modify flow properties, gelling ability, stabilisation, prevent sugar crystallisation, impart texture and mouth feel of aqueous foodstuffs are often utilised. Figure 1 shows an example of how various hydrocolloids gums, from various sources, can modify the flow properties as measured by a controlled stress rheometer.

The viscosity of a given hydrocolloid is influenced by the concentration, molecular weight and structure (linear, branched or slightly branched). At a given molecular weight, linear structures are capable of producing entanglements between polymeric chains at much lower concentration compared to branched structures. This is clearly illustrated in the highly branched structure of gum arabic which shows the lowest viscosity compared to all other hydrocolloids shown in Fig. 1.

Here, we will initially describe, in more detail compared to other hydrocolloids (Fig. 1), the structure-function relationship of acacia gums. Our objectives are to summarise work carried out in our laboratory and to outline recent opportunities and research in this field (Table 1).

Acacia gum

Acacia gum is the exudate from the Acacia tree, which is one of the most ubiquitous genera in the plant kingdom (1). Gum nodule formation occurs in the cambial region of the stems or branches. Gummosis is promoted when the tree is subjected to stress conditions such as heat, drought, and insect attack. The tapping process is the systematic wounding of the tree by farmers during the dry season in November/December in order to regulate the production. The timing and intensity of tapping have been reported to influence the gum yield. The gum will start to collect in the wound within 4-6 weeks depending on the weather condition. The gums are secreted as sticky fluid and grow up to 1.5-7.5 cm in diameter, and gradually dry and harden on exposure to the atmosphere. Collectors harvest the partially dried gum, and multiple collections up to three times at three-week intervals from the same tree are possible. A yield of 0.5-2 kg is obtained per tree annually. The quality of product collected from the various collection intervals is the subject of current investigation with the view of establishing a method to reduce the

Figure 1. Shear flow viscosity of various hydrocolloid gums plotted as a function of shear rate. Measurements were carried out in distilled water at 25°C.
natural highs in variation which has been widely acknowledged. Acacia species are distributed throughout tropical and warm temperate areas of the world, with the largest concentrations occurring in Australia (955 species), with also high numbers in the Americas (ca. 185 species), Africa (144 species) and Asia (89 species). Across Sub-Saharan Africa they form the so-called ‘gum belt’. There are more than 50 Acacia species in Sudan which is currently the largest producer in the world. *Acacia senegal* and *Acacia seyal* remain the most commercially exploited species of the whole Acacia resource.

The current WHO/ECFA Specification (1998), which is internationally accepted, has also been approved by Codex Alimentarius. *Acacia arabica* (A. seyal), *Acacia gum*; *Acacia seyal*; arabic gum; INS No. 414. 

**Definition:** Gum arabic is a dried exudate obtained from the stems and branches of *Acacia seyal* (L.) Willd. or *Acacia senegal* (fam. Leguminosae).

The European Specification (E 414) is slightly broader and defines Acacia gum as a dried exudate obtained from the stems and branches of the natural strains of *Acacia seyal* (L.) Willd. or closely related species of Acacia (fam. Leguminosae).

Recent EC legislation has approved gum arabic as an ingredient which can be labelled as a food dietary fibre. This recent change has created an opportunity and demand for *A. seyal* due to its lower viscosity, which can be used at higher concentration compared to *A. senegal*. The low viscosity, as mentioned above, is due to its highly branched structure and therefore can be dissolved up to 50% w/v to produce a solution of moderate viscosity. In ancient Egypt, gum acacia was used as a binder in cosmetics and inks, and as an agent in the mumification process. It was introduced to Europe through various Arabian ports and came to be called ‘Gum Arabic’ after its place of origin or port of export (2).

Gum arabic (*A. seyal*) is predominately carbohydrate made up of approximately galactose (44%), rhamnose (13%), arabinose (27%), glucuronic acid and 4-O-methyl glucuronic acid (16%). It also contains 2-3% peptide moieties as an integral part of the structure.

Various fractionation techniques have demonstrated the heterogeneous complex nature of this polysaccharide by the presence of three main fractions. These fractions are: arabinogalactan protein complex (AGP), arabinogalactan (AG) and glucoprotein (GP). Each fraction contains a range of different molecular weight components with different protein contents (4). The AGP fraction is composed of hydrophilic carbohydrate blocks linked to a protein chain and has been reported to have a wattle blossom-type structure due to being readily degraded by proteolytic enzyme - see Fig. 2 (5). There are other alternative models proposed for the structure of gum arabic such as the twist hairy rope, extensim, AGP-GPI lipid anchor, and revised wattle blossom model which were recently reported (6).

Treatment of gum arabic with protease results in a complete loss of its extensibility properties (7) and interfibrillar elasticity (8). It is now widely accepted that gum arabic’s role as an emulsifier is achieved as a consequence of its amphiphilic character due to the presence of protein and polysaccharide moieties. It works by reducing the oil-water interfacial tension, thereby facilitating the disruption of emulsion droplets during homogenisation. The peptides are hydrophobic and strongly adsorbs on to the surface of oil droplets, whilst the polysaccharide chains are hydrophilic and extend out into the solution, preventing droplet flocculation and coalescence through electrostatic and steric repulsion forces, which can be summarised by the term electrostatic (2) (see Fig. 2).

The interfacial membrane formed around the oil droplets prevents them from aggregating (flocculating and/or coalescing). Recent study of the interfacial rheology of acacia gums has shown that *A. senegal* produces an elastic interfacial film at liquid/liquid and liquid/air interfaces. The elasticity and viscosity increase with increasing the concentration and the % of the AGP component (8,9) and there is a direct relationship between the proportion of the AGP component and emulsifying stability. We have proposed that the proportion of the AGP and molecular weight parameters can be readily determined by gel permeation chromatography coupled on line to multi-angle laser light scattering, refractive index and UV detectors (GPC-MALLS).

Consequently, the molecular weight parameters of good and poor emulsifiers can be readily identified (10) and have currently been used by a number of users and suppliers as a standard method for quality control system. The technique has been also applied to investigate the molecular weight distribution for a wide range of commercial samples of *A. seyal*.

**Xanthan**

Xanthan is the name given to extra-fibrillar polysaccharide secreted by a wide range of bacteria belonging to the genus Xanthomonas. It is an anionic hydrocolloid with a cellulose backbone (β-(1-4)-D-glucose substituted at C3 on alternate glucose residues with a trisaccharide side chain (11)). The non-carbohydrate substituents include O-acetate on the inner mannose residue and pyruvate on the terminal mannose residue. Different strains or fermentation conditions give rise to differing degrees of acetylation of the pyruvylate, which moderate the functionality. In Fig. 1, xanthan at 1% shows a very high viscosity at low shear rate (deformation) and thus provides excellent emulsion stability for dispersed solids or emulsion, while its high shear thinning behaviour gives low viscosity on solid bridging to mixing or pouring. It is relatively unaffected by ionic strength, pH (1,1-3), and therefore found use in products such as salad dressings. Xanthan in its natural state has been proposed to be bimolecular antiparallel double helices. It may form a still intra molecular (single molecule hairpin) double stranded helical conformation by the annealing of the less stiff 'natural' denatured elongated single stranded chains. The glucan backbone is protected by the side chains, which make it hardly stable to acid, alkalis and enzymes (particularly cellulase).

**Carboxymethyl cellulose**

Carboxymethyl cellulose (CMC) is chemically modified cellulose. Its structure is based on cellulose (β-(1-4)-D-glucopyranose polymer of cellulose. Cellulose is insoluble in water and when it is modified by regeneration (amide) or by crosslinking with carboxymethyl group. This is how the insoluble cellulose can be made water,

provided by a range of suppliers in the three different forms (killed, spray-dried and instant soluble) and has provided valuable information about the state of the material and its effect, processing of adulteration and identification of Acacia species other than *Acacia seyal*.

**Application**

- Coating of an oil droplet by the high molecular weight fraction (AGP).
- Direct correlation between the proportion and molecular weight of the AGP and the emulsification performance and stability due to the elasticity of film formed at the interface. Heat induced hydrophobic associations in the solid state result in the highest performance due to increasing the proportion of the AGP. This is the basis of enhanced gums commercially available under the trade name Supergum®.

**Emulsification in beverages**

- Emulsifier for the paste base.
- Thickening properties (viscosity) and film forming are required as a glaze in candy products. Binding agent for the paste base.

**Texture and flavour modification in confectionery**

- Preventing sugar crystallisation and emulsifying fat to ensure even distribution throughout the product. Long-term emulsion stability is not required particularly for products with high sugar and low moisture contents such as jujubes, pastilles, caramel and toffees.

**Confectionery**

- Free flowing, adhesion properties, control the water absorption and to impart smoothness.

- Interact and bind water; to thicken as a gel. Gel formation with enhanced water absorption. High proportion of AGP.

- “Lace curtain” effect on beer. Maximise content of high molecular weight component rich in protein which responsible for producing the foams. Other products include marshmallows and whipping creams.

**Wine**

- Emulsifier and stabilizer for colour particularly in red wine by forming a protective film layer to prevent precipitation; reduce perception of acidity and tannin harshness; provide sensory impacts that include nose, palate and mouth feel modifications. Best performance achieved with high proportion of AGP to give long-term emulsion stability.

**Dietary fibre**

- Dairy products, processed fruits, bakery items, frozen desserts, meat products and food for diabetics. Need ability to fermentation in colon to give short-chain fatty acids, with bulking ability. *A. seyal* is typically used due to its low viscosity compared to *A. senegal*.

**Note:**

- *Acacia arabica* is the gum arabic (ACG) from which most commercial ACG is obtained.
- ACG contains 2% arabinogalactan protein (AGP).

**Table 1. Summary of gum arabic applications in various food products.**

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<thead>
<tr>
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<th>Necessary functionality and features needed for best performance</th>
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**Figure 2.** (a) Schematic representation of the ‘wattle blossom’ structure of the arabinogalactan protein fraction in *A. seyal*. (b) Coating of the oil droplets by the AGP fraction.
Hyaluronan is an example of animal polysaccharides and is type AB polymer. It is made up of repeating disaccharide units of β-(1→4)-D-glucuronic acid and β-(1→3)-N-acetyl D-glucosamine. It is found naturally in vitreous humour, synovial fluid and umbilical cord and in many animal tissues in smaller concentrations. Hyaluronan can also be produced from certain strains of Streptococcus bacteria by fermentation, extraction and subsequent purification from the broth. This hyaluronidase traditionally has been used in a wide variety of areas such as joint diseases supplement, eye surgery, ear surgery, tear substitution, wound healing, skin care, as a component of artificial matrices and in bioengineering for tissue scaffolding. Recent advances have resulted in reducing the cost of production significantly, which made it possible to produce food grade preparations. In solution, it adopts a random coil conformation and has unique rheological properties resulting from its large molecular volume and from extensive interaction and entanglement of the molecular coils. 

Pectin

Pectin is widely used in the food industry as an emulsifier, stabiliser and a gelling agent. It is extracted from plant cell walls such as those of citrus, tomato, sugar beet and apple. Pectin is composed of (1→4)-linked α-D-galacturonic acid residues in either the free acid (salt) or methyl ester form. This homogalacturonan region is referred to as the ‘smooth region’. The homogalacturonan backbone is occasionally interrupted by α-(1→2)-linked α-L-rhamnopyranose residues, referred to as the ‘hairy region’. Neutral sugar side chains are connected through O-4 or O-3 to the rhamnose units. Pectins are frequently classified in two categories, namely, the high methoxyl pectins with a degree of methylation DM > 50% and the low methoxyl (LM) pectins with DM < 50%. Low methoxyl (LM) pectin gels form as a result of interactions with calcium over a wide range of soluble solids and pH values. On the other hand, high methoxyl (HM) pectin forms gel at low pH (pH 3.5) and in the presence of sugar. The principle use of pectin to date has been in the making of jams and jellies. However, it has more recently been employed as a stabiliser in juice beverages and acid dairy drinks.

References


A full list of the references used in compiling this paper is available from the author.*

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