POLYSACCHARIDES AT FLUID INTERFACES OF FOOD SYSTEMS

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Abstract

Fabrication of next generation polysaccharides with interfacial properties is driven by the need to create high performance surfactants that operate at extreme environments, as for example in complex food formulations or in the gastrointestinal tract. The present review examines the behaviour of polysaccharides at fluid food interfaces focusing on their performance in the absence of any other intentionally added interfacially active components. Relevant theoretical principles of colloidal stabilisation using concepts that have been developed for synthetic polymers at interfaces are firstly introduced. The role of protein that in most cases is present in polysaccharide preparations either as contaminant or as integral part of the structure is also discussed. Critical assessment of the literature reveals that although protein may contribute to emulsion formation mostly as an anchor for polysaccharides to attach, it is not the determinant factor for the long-term emulsion stability, irrespectively of polysaccharide structure. Interfacial performance of key polysaccharides is also assessed revealing shared characteristics in their modes of adsorption. Conformation of polysaccharides, as affected by the composition of the aqueous solvent needs to be closely controlled, as it seems to be the underlying fundamental cause of stabilisation events and appears to be more important than the constituent polysaccharide sugar-monomers. Finally, polysaccharide adsorption is better understood by regarding them as copolymers, as this approach may assist to better control their properties with the aim to create the next generation biosurfactants.

Keywords: polysaccharide; interface; emulsion; copolymer; food

Contents

1. Introduction

Polysaccharides are biopolymers that are formed *via* condensation of the hemiacetal hydroxyl group of one sugar and a hydroxyl group of another sugar unit thus forming an *O*-glycosidic linkage. These reactions are commonly carried out *in vivo* through biosynthetic pathways naturally occurring in living organisms. Although there has been progress in carbohydrate polymerisation, the development of efficient pathways to obtain structurally complex synthetic polysaccharides is still challenging [1]. Such a synthetic route would allow fabrication of polysaccharides with reproducible and well-defined properties. As a result of the absence of readily available synthetic routes, the majority of polysaccharides have to be obtained from natural sources using suitable extraction methodologies that target the polysaccharide of interest. When further tailoring of the properties is required, chemical or physical modification may improve the functionality of the extracted material. Typical examples include modified starches or cellulose derivatives where functionalisation of certain groups or grafting of chains brings about remarkable changes to functionality [2-4].

Polysaccharides are routinely used in food and pharmaceutical industries, mostly as thickeners, dispersion stabilisers or water structuring agents. These functional properties are employed to create structures with reproducible physical properties [5]. In recent years, however, the need to create advanced formulations that bypass gastric environment, delay lipid digestion to prolong satiety, and deliver bioactives in the gastrointestinal tract at the site of interest has boosted the research on the fundamental properties of polysaccharides at interfaces [6, 7]. The main reason is that polysaccharide-based structures may resist attack from proteases as well as the acidic environment of stomach that frequently impair the performance of protein and surfactant-based formulations [8]. Nevertheless, once at the interface, polysaccharides present difficulties with adsorption strength that arises not only from their hydrophilic character but also from their complex macromolecular conformations and, quite frequently, structure.

The objective of this review is to bring to light shared characteristics of interfacially active polysaccharides with diverse fine structures and colloid-stabilisation properties by examining findings in the literature and identifying commonalities in their behaviour. The present work focuses on the functionality of polysaccharides at the oil-water interface, as they are the most industrially important colloidal food systems although air-water interfaces are also discussed. To that end, theoretical considerations of polymer adsorption are first introduced followed by a discussion on the role of protein that is usually found either as a contaminant or as integral part of the structure. Subsequently, a description of the interfacial behaviour and a discussion of the factors that control performance of key polysaccharides is presented. Finally, information that at times seems to be unrelated is synthesized to identify common functionality characteristics thus allowing an escape from empiricism and to proceed to rational design of surface active polysaccharides and advanced colloidal systems.

2. Theoretical considerations

The functionality of polysaccharides at interfaces is primarily influenced by their bulk solution properties that are described thermodynamically by the changes in the free energy of mixing (ΔG_{mix}) of the pure polymer-solvent system (i.e., polysaccharide-aqueous solvent system). Description of solution properties are important, as they dictate the fate of the biopolymer at the interface once it interacts with, most frequently, an aqueous solvent. For instance, when the interactions between polysaccharide chains and solvent are favourable then its arrangement at a hydrophobic liquid interface becomes problematic. On the contrary, when the solvent is not appropriate for chain solvation it may lead to either self-association or interfacial anchoring [9, 10]. To this end, Flory-Huggins theory [11] employs the second law of thermodynamics and distinguishes two contributions to ΔG_{mix}, that is the enthalpy (ΔH_{mix}) and the entropy of mixing (ΔS_{mix}):

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

148 The entropy of mixing ΔS_{mix} is given by:

149 $$\Delta S_{mix} = -k[n_1 \ln\varphi_1 + n_2 \ln\varphi_2] \quad (2)$$

150 where k is the Boltzmann constant and n_1 and n_2 is the number of solvent or polysaccharide
151 molecules with a volume fraction φ_1 or φ_2, respectively, whereas the enthalpy of mixing is
152 given by:

153 $$\Delta H_{mix} = n_1 \varphi_2 \chi kT \quad (3)$$

154 where χ is the dimensionless Flory–Huggins interaction parameter that describes the
155 polysaccharide-solvent interactions. Combination of equations (1) and (3) results in an
156 expression for the free energy of mixing where parameter χ plays decisive role, as it is discussed
157 below:

158 $$\Delta G_{mix} = kT[n_1 \ln\varphi_1 + n_2 \ln\varphi_2 + \chi n_1 \varphi_2] \quad (4)$$

159 In addition to the above, the osmotic pressure, π, that is created upon mixing a polysaccharide
160 with a solvent may be expressed as a function of its concentration c_2 as:

161 $$\frac{\pi}{c_2} = RT[\frac{1}{M_2} + B_2 + \ldots] \quad (5)$$

162 with M_2 being the molecular mass of the polysaccharide and B_2 the second virial coefficient,
163 which reflects the energy of interactions between solvent and polysaccharide segments.
164 Combining information from equations 4 and 5 it emerges that a solvent will be appropriate to
165 dissolve the polysaccharide depending on the values of χ and B_2. These two parameters are
166 powerful tools to describe the suitability of the aqueous solvent for a particular solvent-
167 polysaccharide system. In the limiting case, when $B_2 = 0$ and $\chi = 0.5$ the polysaccharide attains
168 ideal chain conformations when is mixed with the solvent i.e., no excluded volume effects are
169 present and the chains neither repel nor attract each other. At these conditions the solvent is
170 termed θ-solvent and the temperature that this condition occurs is termed θ-temperature. For
171 instance, Huggins constants obtained for okra pectin at 20 ^{o}C dispersed in aqueous solvent in
172 the presence of salt at pH 7.0 suggest that these are θ-conditions for this specific polysaccharide

with chains adopting their unperturbed dimensions [12]. Deviation from this temperature results in departure from θ-conditions and changes in chain conformations depending on the specific pectin architecture [13]. When $\chi > 0.5$ and $B_2 < 0$ the solvent is *poor* i.e., it does not have the capacity to dissolve the polysaccharide whereas when $\chi < 0.5$ and $B_2 > 0$ the solvent is termed *good* and the chains readily expand and swell in the solvent. An ideal adsorbing polysaccharide needs to have strong tendency to anchor at the interface and requires the aqueous solvent to have $\chi > 0.5$ for the hydrophobic segments. At the same time, to confer good stabilisation it needs to be soluble in that same solvent that necessitates $\chi < 0.5$. Biopolymers that successfully resolve this conflict are proteins that under appropriate solvent conditions, for example, away from their isoelectric point, they arrange at the oil-water interface and stabilise the dispersion. This is because proteins, as heteropolymers, contain both hydrophobic and hydrophilic amino acids, the balance of which, dictate their interfacial behaviour. In addition, changes in solvent quality (e.g., pH or salts) influence protein hydrophobicity [14] and interactions between different protein species [15], a hallmark of the dynamic relationship between solvent-polymer interactions and interfacial functionality. On the contrary, homo-polysaccharides (e.g., amylose) are not the most suitable for stabilisation of dispersions, as multiple hydroxyl groups confer high solubility in aqueous environments and poor adsorption at the interface. This deficiency is rectified by introducing "short blocks" on the chains that are water-insoluble and have strong affinity for the interface [16]. Typical examples, as it is discussed below, are modified starches or cellulose derivatives where various hydrophobic groups are covalently attached (methyl, hydroxypropyl, etc.) to enhance hydrophobicity and interfacial adsorption. It becomes evident that solubility of polysaccharides in the appropriate environment is crucial for its interfacial functionality, as it can be tuned with changes in salt, pH, presence of multivalent cations or temperature depending on its monomer composition. In addition, polysaccharides may carry branches or side groups with their

198 solubility being different than that of the backbone. For instance, octenyl branches of octenyl
199 succinic anhydride modified-starch (OSA-starch) or rhamnogalacturonan-I blocks (RG-I) in
200 pectins may have different solubility in the aqueous environment than the other segments of
201 the polysaccharide chain. The solubility of polysaccharide constituent parts becomes even
202 more important when considering the particularly diverse and complex food environment that
203 they need to operate. For example, solubility of a hydrophobic side chain, and as a result its
204 functionality, may differ substantially when the dispersed phase is a triglyceride (e.g., in a salad
205 dressing) or a terpene (e.g., in a fruit-flavoured beverage). Understanding, therefore, the
206 interactions of polysaccharide chains with the aqueous solvent seems to be the first step
207 towards rational design of functional polysaccharides with advanced interfacial properties.
208 The theoretical treatment of adsorption of polymers at interfaces that may also be
209 employed for polysaccharides has been advanced by Scheutjens and Fleer (SF theory) [17, 18].
210 The theory predicts that the configuration of the chains at the interface depends on the
211 adsorption energy of the chains, the configurational entropy of mixing, and the Flory–Huggins
212 interaction parameter, χ [16, 19]. Depending on the specific chemical structure of the chain,
213 polysaccharides adsorb spontaneously when the interactions between polysaccharide and the
214 interface is more favourable than that of the solvent and the interface. It should be noted that
215 adsorption is sensitive to the type of surface and its structure with most realistic scenarios for
216 food systems being “soft” interfaces (i.e., oil-water in emulsions or air-water in foams) rather
217 than solid impenetrable surfaces. SF theory uses statistical mechanics to describe the polymer
218 configuration at the interface as trains, loops, or tails interacting to a different degree with the
219 interfacial layer and has been found to be suitable to describe the adsorption modes of
220 polysaccharides [20]. Loops are regions located between two points of contact with the
221 interface, tails are those between the free end of the chain and the nearest contact point to the
222 surface, while trains are sections that are strongly adsorbed at the interface carrying most of

223 the hydrophobic groups (Figure 1a). This would be common mode of adsorption in
224 polysaccharides that have alternating functionalised sugar residues, as for example in
225 chemically modified celluloses or starches. It should be noted that chemical modification of
226 polysaccharides generates random rather than strictly alternating functionalisation patterns and
227 as a result these may be described as random copolymers. Another common mode of adsorption
228 that is relevant to polysaccharides is that of di-block copolymers (Figure 1b). This type of
229 polysaccharides consist of two regions (blocks) with distinct sugar residues and/or
230 functionalisation (e.g., pectin). In that case, the most hydrophobic block adsorbs at the interface
231 whereas the other block, frequently termed "buoy", forms a lateral layer toward the solvent.
232 Multiple blocks may be also envisaged that might also be present in naturally extracted
233 polysaccharides and in that case adsorption would be an extension of the di-block mechanism.
234 Fluid interfaces in food systems are usually stabilised by a combination of electrostatic
235 and steric mechanisms [21]. Assuming that two droplets have been sufficiently covered with a
236 polysaccharide layer of thickness δ and approach each other to a distance $h < 2\delta$ then the
237 polysaccharide layers will interact with each other (Figure 2). Two cases may be distinguished
238 in this scenario: (i) the chains overlap and interpenetrate or (ii) the layers compress each other
239 thus increasing the local biopolymer concentration in the overlapping zone [22]. Both of these
240 interactions affect the conformation of the adsorbed polysaccharide resulting in changes on the
241 fraction of segments directly in contact with the interface (i.e., on the interfacial tension) and
242 also on the thickness of the adsorbed layer [23]. For a colloidal system stabilised with
243 polymeric surfactants the total free energy of interaction (G_{total}) is given by:

244 $$G_{total} = G_{mix} + G_{elastic} + G_{vdW} + G_{electr} \quad (6)$$

245 where G_{mix} is the mixing interaction between chains and aqueous solvent, $G_{elastic}$ is due to the
246 loss of configurational entropy of the chains, G_{vdW} is the free energy due to van der Waals
247 attraction and G_{electr} is the free energy due to electrostatic interactions. When chains that belong

to different particles interact the configurational entropy of the chains ($G_{elastic}$) is reduced, as they now have less space to move freely due to volume reduction in the overlapping zone. $G_{elastic}$ as well as G_{electr} are always positive indicating repulsion. G_{electr} is zero for polysaccharides that do not carry charges but when considering polyelectrolytes (e.g., pectin) the presence of electrostatic interactions complicates the landscape, as charge density, ionic strength, and pH need to be taken into account since electrostatic stabilisation also contributes along with steric effects [19]. van der Waals free energy (G_{vdW}) is always negative (i.e., attraction), however, the free energy of steric stabilisation ($G_{steric} = G_{\mathrm{mix}} + G_{elastic}$) depends on the values of Flory-Huggins parameter. When the mixing of polysaccharide segments with the solvent is favourable (i.e., $\chi < 0.5$) then $G_{mix} > 0$ creating a repulsion, whereas when $\chi > 0.5$ (i.e. the chains are in poor solvent) $G_{mix} < 0$ and the mixing interaction becomes attractive [16, 24]. The above description of events using equilibrium thermodynamics leads to the conclusion that careful tailoring of the aqueous solvent properties and polysaccharide molecular weight may be one of the routes for efficient colloidal stabilisation using polysaccharides. This is not easy to be realised as food systems are quite complex, frequently with simultaneous presence of various chemical species at the interface [25]. One of the macromolecules that are frequently present at the interface of polysaccharide-stabilised emulsions is protein. The presence of protein and its role on the interfacial functionality of polysaccharides, is discussed in the next section.

3. The role of protein

Protein-polysaccharide interactions have been used extensively as a vehicle to form and stabilise emulsions [6, 21]. Typical structures include polysaccharide-protein electrostatic complexes, naturally occurring complexes where the protein moiety is found grafted on the polysaccharide backbone, or Maillard-conjugates where protein is covalently attached on the polysaccharide backbone through Maillard reaction. In the latter systems, the fraction of

protein is particularly high (1:1 or higher) and plays crucial role in the overall interfacial functionality of the conjugate [26]. The present discussion is focused only on systems where the protein is naturally covalently grafted or is found as contaminant during the isolation process, that is, no protein has been intentionally added in the system.

Interfacially active polysaccharides isolated in the laboratory or industry quite frequently carry a protein component that is usually in the range of 10 % with industrial preparations being somewhat purer [27]. It is important to note that the term "protein" when it refers to polysaccharide preparations it is rather generic and poorly biochemically defined. Apart from the protein fraction in gum Arabic [28] and some sporadic biochemical analysis of proteins in pectins [29, 30] or soy soluble polysaccharides [31] there is very little understanding of these fractions with regard to their amino acid composition, folding patterns, or physicochemical properties. This lack of information becomes even more important in the case of contaminants, as proteins may present batch-to-batch variations depending on the source, extraction methodology or even harvest season and maturity of the raw material and, as a result, control of the functionality and reproducibility of the protein fraction may be problematic. In the literature, however, it becomes increasingly evident that the protein component of polysaccharide preparations, although it contributes to the emulsion formation, it is not the dominant biopolymer that provides long-term dispersion stability. For instance, both early and recent studies consistently fail to find a straightforward relationship between emulsion stability and protein concentration in emulsions stabilised using only polysaccharides [27, 32-35]. For example, in pectin-stabilised emulsions protein is not the dominant biopolymer at the interface and depending on pectin structure its interfacial concentration is up to nine times higher than that of protein [35-37]. These observations suggest that although protein structure may be essential for anchoring the polysaccharide to the interface it is difficult to find a straightforward relationship between protein load and stability.

In recent years, attention has been shifted to the role of interfacial rheological properties in a bid to account for the stability of emulsions and foams of complex biopolymer systems. The overarching finding is that there is a strong link between interfacial microstructure and its nonlinear response to applied deformations [25, 38-44]. Consequently, the strength of the interfacial film to resist rupture, which essentially depends on macromolecular interactions and conformational changes, needs to be considered [25, 45]. This approach appears to be more suitable to explain differences between polysaccharide-stabilised emulsions in contrast to relying only on composition analysis of interfaces (e.g., interfacial protein concentration). Despite the fact that there is plenty of work on the interfacial rheology of protein or protein-polysaccharide fluid interfaces there is very little devoted to the study of polysaccharide-laden systems [35, 42, 43, 46, 47]. In these seemingly disparate studies a common trend emerges, that the conformational behaviour, as evidenced by the use of polysaccharides with different architectures, is key for the elasticity and strength of polysaccharide-laden interfacial films. A relatively recent approach that provides in-depth information on the interfacial rheology of such systems is the use of Lissajous plots [44, 48]. The curve shape gives valuable information on the interfacial behaviour upon extension or compression and may be linked to dispersion stability and interaction strength between the components that reside at the interface. Asymmetrical Lissajous plots indicate that surfaces behave differently on compression than on extension stemming from complexities in the interfacial microstructure (Figure 3b). Specifically, upon compression polysaccharide dominated interfaces display strain-hardening behaviour in contrast to extension where strain-softening is observed [35, 41, 47, 49]. In that regard, on extension (e.g., droplet break up or Ostwald ripening) the continuity of the polysaccharide interfacial film may be disrupted exposing the underlying dispersed phase (Figure 3a) thus making the emulsion prone to bridging flocculation or further coarsening. On the contrary, when the interface is sufficiently covered with polysaccharide (Figure 3c) it

exhibits strain-hardening indicating strong interactions between polysaccharide chains. As a result, when the polysaccharide is sufficiently capable to create small droplets it provides efficient long-term steric stabilisation. At this juncture, it seems necessary to propose that additional research should be directed towards the interfacial rheology of polysaccharide-laden systems, as it may be beneficial for in-depth understanding of their mechanism of action.

4. Performance of polysaccharides at the oil/water interface

4.1 Modified starch

Starch is the storage carbohydrate polymer of higher plants consisting solely of glucose making it particularly hydrophilic thus posing constraints in its functionality as emulsifier. On this account, it requires hydrophobic functionalisation to become surface active. Starch can be modified with esterification of various hydrophobic groups [50], including dodecenyl succinic anhydride (DDSA) [51], propionate [52] or most commonly octenyl succinic anhydride (OSA) [53, 54]. The latter starch-derivative is approved by the Food and Drug Administration and European Union for food uses including replacing gum Arabic in beverage formulations and could be also used in a wide range of food systems with industrial significance [53, 55]. OSA-starch is made by the reaction of starch and anhydrous octenyl succinic acid under alkaline conditions [56]. The reaction not only imparts hydrophobicity to the chains but also weak negative charge, as only one of the two carboxyl groups of succinic acid is esterified. Surface activity of OSA-starches is comparable to that of whey proteins and because dispersion stability is not influenced by pH they may be used in acidic formulations near the isoelectric point of proteins [57]. Generally, OSA-starches form thick interfacial layers that are mainly due to jamming at the interface that is caused by chain orientation [58]. Chains of high molecular mass adsorb preferentially at the interface during emulsification with steric hindrance being the main stabilisation mechanism [57, 59]. Emulsions prepared using amorphous OSA-starches exhibit greater stability than those prepared with granular OSA-starches. This is attributed to the increased rate of adsorption and formation of thick interfacial

layers, as well as to compact packing on the surface resulting from the flexible assembly behaviour of amorphous starch chains [60]. In addition, OSA-starch has the ability to adsorb at cationically charged droplets (e.g., presence of chitosan) with the thickness of the steric barrier being charge-density dependant. Accordingly, when the charge density of the interface decreases, the surface load also decreases resulting in thinner steric barrier [61]. Apart from charge density, degree of substitution (DS) and its pattern ("blockiness") also play important role for its functionality. Degree of blockiness (i.e., the presence of contiguous blocks with hydrophobic grafting) has been found to play important role [61] while adsorption kinetics and emulsion stability depend on the hydrodynamic radius and DS of starch and the chemical nature of the dispersed phase [62, 63]. Finally, gastrointestinal fate of emulsions prepared with OSA-starches depends on their fine structure, as increase in the DS contributes to higher emulsion stability in the gastric fluid (i.e., changes in ionic strength, pH, and enzymes) and a greater extent of lipid digestion [64], a behaviour that may be linked to changes in the digestibility of OSA-starches with different DS [65].

4.2 Cellulose derivatives

Cellulose, the structural polysaccharide of higher plants, is insoluble in water and as a result it cannot be used in aqueous systems without prior chemical functionalisation. Derivatisation of cellulose proceeds with introduction of functional groups at the free hydroxyls of the cellulose backbone. Common cellulose derivatives of industrial importance include carboxymethyl cellulose (CMC), methyl-cellulose (MC), and hydroxypropylmethyl cellulose (HPMC). HPMC is surface active with hydrophobic (methyl) and hydrophilic (hydroxypropyl) groups being distributed along the cellulose backbone and is able to be adsorbed at both air-water [66] and oil-water interfaces [67-70]. The interfacial behaviour of HPMC is strongly influenced by the chemical nature of the dispersed phase and its functionality is more similar to proteins than to other surface active polysaccharides [68]. In addition, it is frequently more surface active than proteins, and at high concentrations tends to dominate the

interfacial properties and displace proteins from the interface usually through competitive adsorption [71]. Adsorption at the air–water surface usually proceeds in three stages commencing with diffusion and penetration of HPMC to the surface, followed by conformational changes of the adsorbed chains to a state of minimum free energy that depend on its molecular characteristics (e.g., degree of substitution, methoxyl/hydroxypropyl ratio etc.) [66]. Its anchoring mechanism at the oil-water interface is similar to that of random copolymers (train-loop-tail model, Figure 1a) with the hydrophobic segments along the polysaccharide chain attaching at the interface forming trains, which are separated by hydrophilic loops and tails that extend into the aqueous phase. Once at the liquid-liquid interface only a few segments are adsorbed forming a closely packed layer [72]. In addition, hydrophobic interactions can be modulated by changes in pH thus influencing long term emulsion stability and their performance at the oil-water interface [67, 69].

Early studies on methylcellulose revealed that they exhibit interfacial activity and facilitate emulsion formation enhancing their stability [73, 74] by forming protective layers around the droplet [70]. Interfacial tension generally decreases with increase in total degree of methoxyl substitution and is facilitated by the uniform distribution of the substituent groups along the cellulose backbone [75]. In addition, the most efficient stabilization of liquid interfaces is obtained with the lower molar mass methylcelluloses [76]. Methylcellulose-based emulsions can be used to delay lipid digestion to enhance satiety or protect bioactives from the gastric environment. The physical properties of the interfacial layer play crucial role to this and, generally, the more resistant is the layer the more resilient is against digestive enzymes or low pH [77]. High methoxyl contents are associated with high viscoelasticity (before and after digestion) and the lowest fat bio-accessibility [78, 79]. In addition, bile salts have been found to bind to cellulose derivatives with the strength and extent of interaction depending on the molecular characteristics of the chains. As a result, they may control lipid digestion by means

of competing with bile salts for the oil–water interface even at conditions that are physiologically relevant within the duodenum (e.g., high bile salt concentrations) [80]. Finally, another potential route to prolong lipid digestion would be through interfacial gelation with cellulose derivatives that are tailored to gel at temperatures as low as body-temperature [81].

4.3 Pectin

Pectin is another important constituent of plant cell walls that is rich in galacturonic acid with particularly complex structure. Interfacial activity of pectin depends on its type and stems from the presence of methyl and acetyl groups, the macromolecular characteristics of the chains (e.g., molecular weight, branching etc.) and the presence of protein and/or ferulic acids [82, 83]. Although protein contributes to interfacial activity of pectin, growing evidence in the literature suggests that it is not the only determinant factor for its emulsification capacity and long-term stability of emulsions [36, 84-87]. For example, it has been shown for sugar beet pectin that about 3 % protein is optimum for interfacial activity [86] with its removal resulting in loss of functionality [88]. On the contrary, sugar beet pectin with variable amounts of protein results in formation of emulsions of comparable droplet sizes and stability [89] with the long-term stability being attributed to the presence of neutral sugar side-chains [84]. Further reports also have not identified a direct relationship between the protein content and stability [35, 85] whereas ferulic acids may also be involved [90, 91] indicating that protein is not the sole determinant of functionality. Acetyl groups, similarly to ferulic, could enhance interfacial activity of pectin resulting in smaller droplets during emulsification [92-95]. A minimum of 10 % acetylation is needed to improve the emulsifying properties of pectin, particularly at low protein contents [90, 96]. In addition to acetylation, a direct relationship between degree of methylesterification and emulsifying capacity of citrus pectin has been recently demonstrated [96] in contrast to earlier studies that found that the content of methyl esters is of minor importance [92]. Finally, chemical modifications of pectin, as for example in alkylated citrus

pectins with different alkyl chain length and degree of alkyl substitution, may result in improved emulsification properties [97].

The accessibility of protein, methyl and acetyl groups, and ferulic acids to the interface may depend on the molecular weight of pectin, however, the results are inconsistent. Early reports suggested that low molecular weight favours emulsifying activity possibly due to the better accessibility of surface-active groups to the interface. However, very low molecular weight pectin creates coarse emulsions due to their inability to provide effective steric stabilisation [85, 89, 92, 94, 98]. On the contrary, recent studies did not demonstrate a direct relationship between molar mass of citrus pectin and its emulsifying capacity [96]. There is some evidence in the literature that increase of molecular mass of sugar beet pectin after cross-linking of chains *via* di-ferulic bridges may create smaller droplets resulting in improved long-term stability compared to those stabilized with non-cross-linked pectin [99]. It has been also shown that pectin fractions adsorbed at the oil-water interface are enriched in neutral sugars (e.g., arabinose and galactose) suggesting that rhamnogalacturonan-I (RG-I) containing pectin could have improved emulsifying properties, as opposed to pectins with linear backbone [95]. These results were further supported by the side-chain enzymatic degradation of sugar beet pectin revealing a decrease of interfacial activity and stabilising properties of enzymatically modified pectin in comparison to non-modified counterparts [100]. The impact of side-chains on emulsion-forming properties of pectin could be attributed to the interfacial activity of protein and ferulic acid that most frequently are attached to the side-chains acting as anchors. In addition, the presence of neutral sugar side-chains contributes to the long-term emulsion stability due to the formation of thick interfacial layers thus providing effective steric stabilisation that impedes coalescence [84]. It has been shown that okra and sugar beet pectin stabilise emulsions at low pH values, where chains adopt compact conformations resulting in the formation of thick interfacial layers thus providing a combination of steric and electrostatic

stabilisation [35, 46]. The ability of pectin to stabilise sterically oil droplets is attributed to the RG-I domains, whereas electrostatic stabilisation originates from HG-domains due to the ionisation of carboxylic groups. Specifically, the prevalence of RG-I segments and the length of their branches have been shown to influence emulsion stability. In particular, branches of intermediate length exhibit optimum emulsification capacity whereas short or long branches do not favour emulsification. Furthermore, low amounts of RG-I segments improve long term stability of emulsions in contrast to those containing high amounts of RG-I [101]. RG-I-driven steric stabilisation has been also found to play important role in delaying lipid digestion by modulating lipase activity and free fatty acid release from oil droplets [102, 103].

4.4 Gum Arabic

Gum Arabic is the archetypal emulsifying polysaccharide that is obtained as the exudate of the Acacia tree species (*A. senegal* or *A. seyal*) and is most commonly used to stabilise essential oils and flavours in food beverage emulsions but also in delivery systems to protect sensitive bioactives from environmental stress (e.g., oxidation) [104, 105]. Gum Arabic is a highly branched anionic polyelectrolyte of low charge density with the carbohydrate segments of the structure covalently linked to polypeptide chains [106-108]. Three fractions are generally distinguished, namely, the arabinogalactan-peptide (AGp), making up the major fraction of gum Arabic, the arabinogalactan-protein complex (AGP), and a minor fraction referred to as glycoproteins (GP) [108, 109]. There is a large number of studies devoted to the emulsification and interfacial properties of gum Arabic probing various sets of conditions and operation environments. The consensus is that the AGP component is the fraction mostly responsible for its interfacial properties with the rest of the fractions playing variable roles depending on the conditions [108] while removal of protein after treatment with proteolytic enzymes results in loss of emulsification capacity [110, 111]. It should be noted that the emulsifying properties of gum Arabic are inconsistent and depend on *Acacia* species, growing conditions, age of tree and other botanical characteristics making the choice of raw material

(e.g., region, batch etc.) of paramount importance for the consistency and reproducibility of its functional properties [112]. This behaviour stems from the differences in chain configurations and intermolecular interactions as well as protein content that control their interfacial properties and stabilisation mechanisms [42]. As mentioned above, control of interfacial activity of hydrocolloids is facilitated by the accessibility of the hydrophobic moieties to the interface, which is usually restricted by polysaccharide chains present in the bulk, and the net surface charge of adsorbing molecules. It has been shown that the presence of aggregates in gum Arabic solution improves interfacial activity by enhancing the accessibility of protein to the interface [46, 113]. This also leads to high interfacial loads that are much higher than those corresponding to monolayer adsorption [114]. In addition, the thickness of the adsorbed layer increases over time due to the formation of multilayers, which occurs as a consequence of electrostatic interactions [115]. In a similar manner to pectin emulsification, the protein content alone cannot be used to as the only predictor of emulsification performance of gum Arabic, as samples with similar protein content differ in emulsifying capacity and emulsion stability [108]. This behaviour confirms the view that the nature and distribution of the proteinaceous component along the polysaccharide chains and not just its overall amount also play important role. Finally, gum Arabic may be modified either by chemical [116] or physical methods [117] enhancing the overall hydrophobicity of the chains thus improving the emulsification properties of the natural counterpart.

4.5 Other polysaccharides

Research to identify natural carbohydrate polymers with interfacial activity continues unabated and there is a rich profusion of polysaccharide sources with different structures that may stabilise food liquid interfaces [33, 118-120]. Chitosan is obtained after alkaline treatment of chitin from the shells of crustaceans, is insoluble in water and positively charged, in contrast to most charged polysaccharides used in foods [121, 122]. Chitosan is not particularly active at the air-water interface but it adsorbs readily at the oil-water interface stabilising emulsions

503 by both steric and electrostatic mechanisms [123]. Chitosan emulsifies oils without any
504 additional surfactant and the emulsification properties are strongly linked to the amount of
505 hydrophobic acetyl groups with higher the acetyl content resulting in better emulsion stability
506 [124-126]. Corn fiber gum is an arabinoxylan that is obtained *via* alkaline extraction from
507 agricultural wastes of the corn industry and exhibits high water solubility and low viscosity.
508 Corn fibre gum has been touted as a potential replacement of gum Arabic [127] because of its
509 excellent emulsification properties that are linked to the presence of phenolic acids, and protein
510 in addition to its high molecular weight and branching [128-130]. Acidic polysaccharides
511 extracted from co-products of soy protein isolation processes, known as soybean soluble
512 polysaccharides (SSPS), also contain a protein moiety in the structure. SSPS have high water
513 solubility producing low viscosity solutions with the stability of emulsions formed with SSPS
514 not affected by pH or ionic strength [131-133]. This can be attributed to the fact that solution
515 conformation of SSPS is not affected by pH [134] further strengthening the link between
516 conformation and functionality. The protein fraction present in SSPS participate in emulsion
517 formation acting as anchor for the polysaccharide chains to attach that in turn stabilise the
518 droplets against aggregation by steric interactions in a similar manner to the other
519 polysaccharides that were described above. However, once more, a lack of correlation between
520 protein content and stability has been shown revealing that protein alone is not solely capable
521 to provide optimum functionality [31, 132].

522 It becomes apparent, that the view holding protein responsible for the interfacial
523 properties of polysaccharides and emulsion stability, is outdated. Although protein may
524 contribute during emulsification and formation of interfacial structures it does not seem to be
525 capable to provide long-term stability of dispersions emulsified solely using polysaccharide
526 preparations. Common characteristics in the mechanisms of their functionality that emerge
527 from the above assessment of literature are discussed in the next section.

5. Concluding remarks and future outlook

Critical assessment of literature findings leads us to the observation that efficient functionality of polysaccharide chains requires a certain degree of repetitive structure similar to that of copolymers. This may include structures that resemble random, block or graft co-polymers, as all types can be found depending on the polysaccharide, although strictly alternating copolymers are rather difficult to be established with natural polysaccharides. Accordingly, theories that have been developed for copolymer adsorption at interfaces would be better suited to theoretically analyse and treat experimental data [19]. In this context, three modes of polysaccharide adsorption are distinguished based on their chain architecture (Figure 4). Polysaccharides that are more likely to have a random copolymer structure, as for instance cellulose derivatives, adsorb through their hydrophobic moieties at the oil-water interface. Because of the random nature of the hydrophobic patches distribution, it is more likely that this type of polysaccharides have multiple anchoring points that spread out along the interface but do not have prominent lateral chains protruding to the aqueous phase. Consequently, steric stabilisation efficiency may be limited. This is in contrast to the polysaccharides with di-block (e.g., blocky pectin) or graft copolymer (e.g. gum Arabic) architectures where the lateral chains protrude to the aqueous phase providing efficient steric stabilisation. In reality, natural polysaccharides would fall into an intermediate situation, as it is rather difficult with the current state of knowledge to establish structural purity, as in the case of synthetic polymers. For example, pectin is a typical block co-polymer that depending on the source may be di-block, triblock, or grafted [135, 136]. Another example that illustrates the importance of chain architecture comes from numerical simulations on the effect of side chain of graft copolymers on the efficiency for steric stabilisation. As the size of the side chains increases, the attractive forces between two droplets decrease indicating more efficient steric stabilisation [137]. These findings have been shown to be consistent with recent experimental work on okra pectin-stabilised emulsions, which can be considered as a graft co-polymer, as samples with long

554 branches generally exhibit greater long-term stability than their counterparts with shorter
555 branches [101]. In addition, brush-like polysaccharides inspired by synthetic polymers [138-
556 140] could provide an alternative pathway toward interfacial stability as polysaccharides with
557 such structures have recently started being described in the literature [141, 142]. This could be
558 achieved not only after isolation of polysaccharides but also with chemical (e.g., chemical
559 grafting of chains) or enzymatic modifications to provide man-made structures that are more
560 suitable for stabilisation of colloidal dispersions by enhancing the extent of the repulsive steric
561 forces.

562 Once the mode has been established, the fate of polysaccharide at the interface and
563 ultimately the stability of the dispersion depends on its molecular characteristics and aqueous
564 solvent-polysaccharide interactions. The latter, influence polysaccharide conformation that in
565 food systems are usually controlled by pH, ionic strength (e.g., NaCl or $CaCl_2$), sweetener (e.g.,
566 sucrose, glucose), chemical nature of the dispersed phase (e.g., triglyceride, terpene) or
567 temperature. For instance, progressive increase in temperature changes drastically pectin
568 conformation in solution creating structures with inefficient space filling capacity ("open"
569 structures) [13] that may indicate poor steric stabilisation ability. Such a behaviour may be
570 problematic during processing (e.g., pasteurisation) where temperature is increased
571 progressively or on storage at sub-optimal conditions (e.g., ~30 ^{o}C) thus resulting in losses of
572 functionality and dispersion stability. A route to better predict the behaviour of polysaccharides
573 before venturing to applications would be through fundamental understanding of
574 conformations throughout their relevant operational conditions by construction of
575 "conformational maps". Such an effort would provide knowledge on how chains in contact
576 with the solvent behave so as to predict steric stabilisation capacity by creating a "selective"
577 solvent environment [143, 144]. Accordingly, emulsification ability of polysaccharides should
578 not only be discussed in terms of "structure *vs.* function" but also in terms of "conformation

vs. function". In conclusion, rather than proceeding with heuristic approaches to optimise polysaccharide functionality, deeper integration of theories from synthetic polymer science within the hydrocolloid field must be sought. This would provide a much needed mechanistic view to describe the complex formation and stabilisation of liquid interfaces with polysaccharides by establishing relationships between the nature and strength of interactions and their contribution to stability.

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968 **Figure captions**

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970 **Figure 1**: Idealised polysaccharide configuration at interfaces. Black spheres represent
971 hydrophobic units that adsorb at the oil-water interface whereas red spheres are hydrophilic
972 units that exhibit propensity for the aqueous phase. (a) Train-loop-tail mode of adsorption that
973 is common in polysaccharides with randomly functionalised sugar residues, and (b) mode of
974 adsorption that is relevant to polysaccharides resembling di-block copolymers. The "anchor"
975 (hydrophobic block) adsorbs at the interface whereas the "buoy" (hydrophilic block) forms
976 lateral layers towards the aqueous phase.

977

978 **Figure 2:** Polysaccharide-laden (red spheres) oil droplets (yellow spheres) forming interfacial
979 layers of thickness δ. When two droplets approach each other at distance $h < 2\delta$ then (a) the
980 chains overlap and interpenetrate, or (b) the layers compress each other. The total interaction
981 energy dictates if the dispersion is sterically stabilised or aggregates [24].

982

983 **Figure 3:** Surfaces behave differently on extension than on compression resulting in
984 asymmetrical Lissajous plots (b). On extension, strain-softening is observed as the
985 intermolecular forces are not strong enough to hold the interface together ((b), light shaded
986 area of the plot). This may result in exposed areas on the droplets ((a), white arrows over the
987 green fluorescent droplet) that are prone to bridging flocculation or coalescence. On
988 compression the surfaces display strain hardening ((b), densely shaded area of the plot) and
989 the droplets are fully covered with a polysaccharide layer ((c), green fluorescent droplet).
990 Images show pectin-stabilised droplets with data from [35].

991

Figure 4: Modes of polysaccharide adsorption based on chain architecture. Polysaccharides with random co-polymer structure adsorb at the oil-water interface with multiple hydrophobic anchoring points that spread out along the interface. The limited lateral chain protrusion to the aqueous phase results in little steric stabilisation efficiency. In polysaccharides with graft co-polymer architectures the lateral chains protrude to the aqueous phase providing efficient steric stabilisation. In di-block or multiblock copolymers the hydrophilic "buoys" provide prominent steric stabilisation.

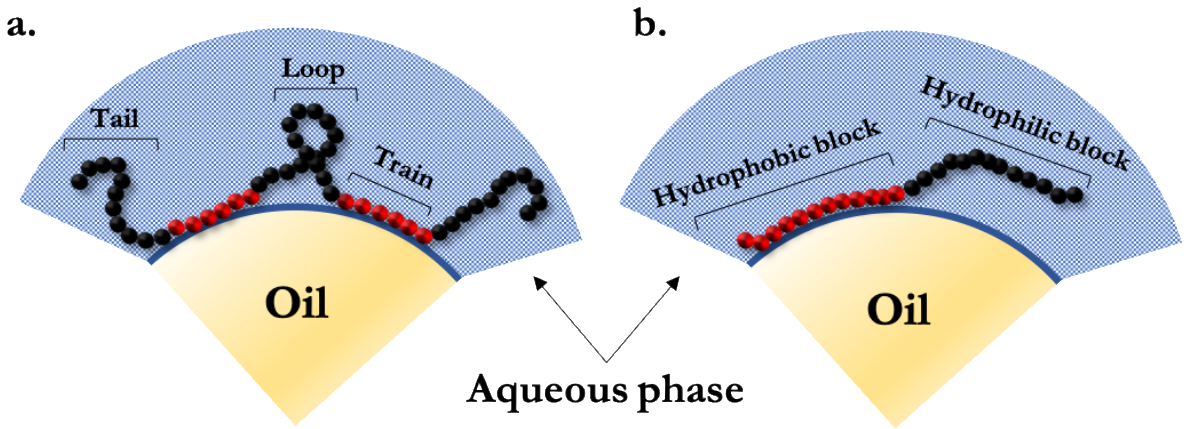
a.
Loop
Tail
Train
Oil
b.
Hydrophilic block
Hydrophobic block
Oil
Aqueous phase

Figure 1

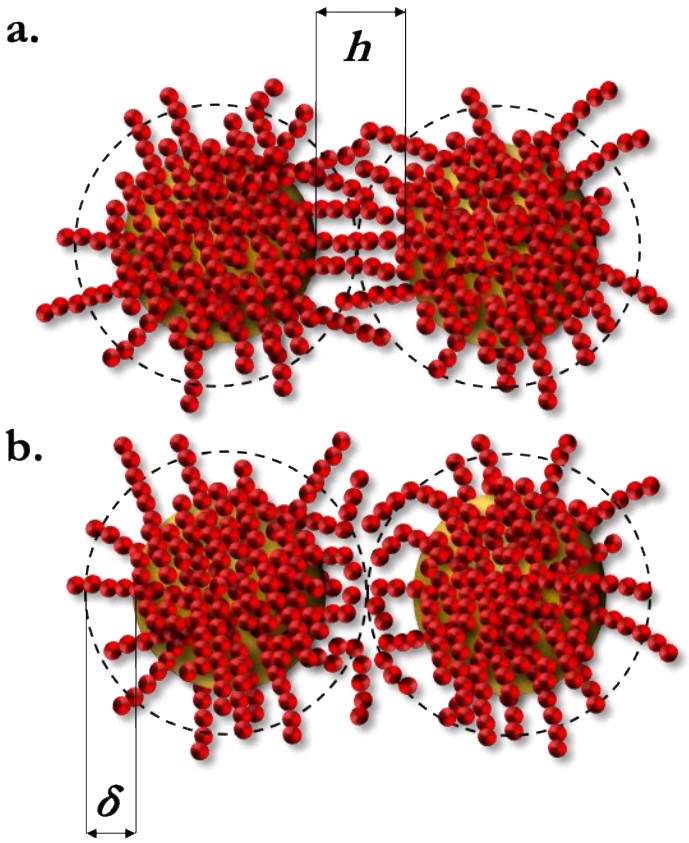

Figure 2

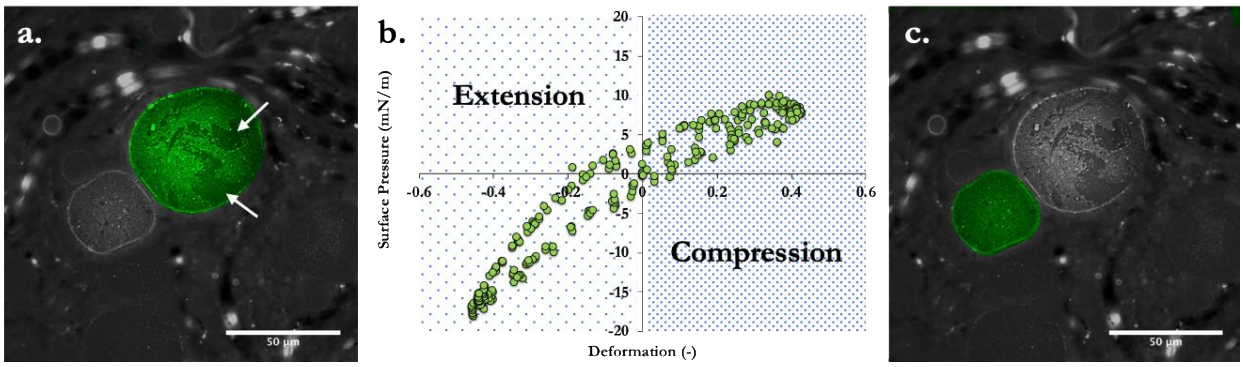
a.
50 µm
b.
Extension
Compression
Surface Pressure (mN/m)
Deformation (-)
20
15
10
5
0
-5
-10
-15
-20
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
c.
50 µm

Figure 3

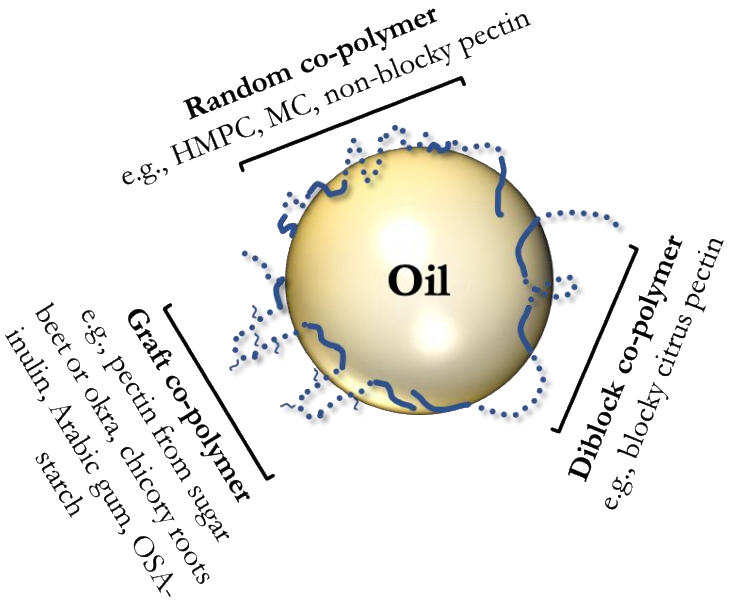
Random co-polymer
e.g., HMPC, MC, non-blocky pectin
Oil
Graft co-polymer
e.g., pectin from sugar beet or okra, chicory roots inulin, Arabic gum, OSA-starch
Diblock co-polymer
e.g., blocky citrus pectin

Figure 4