Eur. Phys. J. Special Topics **222**, 73–81 (2013)

DOI: 10.1140/epjst/e2013-01827-x

THE EUROPEAN PHYSICAL JOURNAL SPECIAL TOPICS

Review

Rheology of interfacial protein-polysaccharide composites

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Received 16 April 2013 / Received in final form 23 April 2013
Published online 17 June 2013

Abstract. The morphology and mechanical properties of protein adsorption layers can significantly be altered by the presence of surfactants, lipids, particles, other proteins, and polysaccharides. In food emulsions, polysaccharides are primarily considered as bulk thickener but can under appropriate environmental conditions stabilize or destabilize the protein adsorption layer and, thus, the entire emulsion system. Despite their ubiquitous usage as stabilization agent, relatively few investigations focus on the interfacial rheology of composite protein/polysaccharide adsorption layers. The manuscript provides a brief review on both main stabilization mechanisms, thermodynamic phase separation and electrostatic interaction and discusses the rheological response in light of the environmental conditions such as ionic strength and pH.

1 Protein/polysaccharide mixtures and interfacial aggregation of proteins

The phase separation of protein/polysaccharide mixtures (also called biopolymer mixtures) is based on depletion and coacervation as described already for colloidal particle/polymer mixtures by Bungenberg De Jong [1]: the one-phase mixture of water soluble protein and polysaccharide separates into two phases with different composition [2–9]. During depletion (thermodynamic incompartibility, seggregation) both phases are composed primarily out of one ingredient with traces of the other ingredient. As a consequence, there will be a polysaccharide rich phase with small amounts of proteins present and a protein rich phase with little amounts of polysaccharides solved. The solubility limit of the biopolymer mixture depends on the protein/polysaccharide composition but seldom surpasses more than a few percent. On the other hand, during coacervation (complexation, precipitation, association) a protein/polysaccharide precipitate and a supernatant is formed. The supernatant contains traces of protein and polysaccharide at the solubility limit. In food system depletion flocculation and coacervation are used to stabilize milk products, spreads, dressings as well as creating water-in-water emulsion for calorie reduced foods [10–14]. Electrostatic charges

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in protein/polysaccharide mixtures can out-rule depletion and coacervation and significantly influence the phase separation. Same charge on both biopolymers promotes depletion (positive free energy of interaction), while coacervation is observed when the two biopolymers have opposite net charge. Mixture of charged and uncharged biopolymers in the absence of salt tend not to phase separate (entropy of mixing term favors distribution of counter ions across whole system), while the excess of salt and changes of pH promotes immiscibility e.g. the salting out of proteins (creation of polyelectrolyte rich phase without a gross imbalance of counter ions). Electrostatic interactions are mainly carried by charged polysaccharides such as pectin, xanthan, carrageenans, or chemically modified polysaccharides and starches upon hydration [15].

The interfacial activity and the ability to form a protein adsorption layer is governed by the significant entropical gain upon adsorption and denaturation of the protein at interfaces [16]. The degree of unfolding/denaturing strongly depends on the protein's stability, which is given by the internal secondary and tertiary structure and the resulting interactions within the folded protein. The interfacial concentration of protein is not governed by an adsorption isotherm but by the adsorption time and the denaturing of the protein at the interface. This means that over time a protein adsorption layer can be formed at the interface regardless the originally protein concentration in the bulk. Assuming that the protein bulk concentration is below the solubility limit for phase separation, the solubility limit can be surpassed at the interface when a sufficient amount of proteins have accumulated. As a consequence, a protein/polysaccharide mixture that is compatible in the bulk may phase separate at the interface due to elevated protein concentration. Such two-dimensional phase separation can take place at the air/liquid or liquid/liquid interface and influences the mechanical stability of the protein/polysaccharide adsorption layer. Since polysaccharides are generally not surface active [17], the composite adsorption layer is anchored by the amphiphilic protein at the interfaces. A few exceptions are naturally occurring protein-polysaccharide complexes such as gum acacia, hydrophobically modified biopolymers (cellulose, starch), acetylated and depolymerized pectin. To form a protein/polysaccharide composite, similar to bulk systems, such adsorption layer can be additionally stabilized by electrostatic charges. In particular, denatured proteins at the interface may expose polar and charged amino acid residues, which interact electrostatically with acidic polysaccharides: the negatively charged carboxyl groups of the polysaccharide interact with the positively charged α-amino, ϵ-amino, imidazole, and guannidinium groups of the protein [2,18]. Reduction of the pH increases the interaction strength between proteins and anionic polysaccharides until the isoelectric point of the complex is reached and precipitation occurs.

The mechanical stability of adsorption layers is extensively studied by interfacial rheology, which is commonly divided into the areas of shear and dilatational rheometry. Shear experiments give access to interaction forces lateral to the adsorption layer while dilatational interfacial properties provide information on the elongational properties of the adsorption layer. Overviews on the interfacial rheology of protein adsorption layers and their engineering aspects in stabilizing emulsions and foams are given by a number of authors [19–28].

2 Protein composite adsorption layers

Composite adsorption layers can generally be formed by protein/small molecular weight surfactants, protein/lipid, protein/particles, protein/protein, and protein/polysaccharide mixtures (for examples of investigated adsorption layers see Tables III, IV, and VI in Sagis [27]). The morphological and rheological properties of protein/small molecular weight surfactant and protein/lipid systems are subject of

several outstanding reviews (see e.g. [2,26,29,30]). The interfacial rheology of protein-particle adsorption layers is studied less extensively and can be considered as emerging field.

2.1 Protein-protein adsorption layers

Protein-protein adsorption layers can be formed from any combination of globular and random-coil proteins. For protein mixtures of globular proteins ("hard" proteins), the adsorption, denaturing, and surface rearrangement hardly will reach equilibrium. In competition with random coil proteins ("soft" proteins), which have larger surface affinity due to their open native structure and are more exchangeable, globular proteins can stand their place at the interface for two reasons: (i) "first come – first serve", the fastest adsorbing protein will set the adsorption layer properties, and (ii) denaturing renders desorption of globular protein into the bulk phase thermodynamically unfavorable (Dickinson Rules of Thumb [31]. The competitive adsorption of α_{s1}-casein and β-casein at the liquid/liquid interface (n-tetradecane) show the "First come-first serve" concept [32]. Hunter et al. [33] showed that in sequential adsorption of β-casein and lysozyme at the air/liquid interface neither has the chance to displace the first-comer from the interface.

In case, both competing proteins are present in equal concentration in the bulk phase, the fastest adsorbing and denaturing protein will be dominant at the interface. As an example, the competitive adsorption of β-casein and lysozyme is discussed by Xu and Damodaran [34]: the interfacial composition for any bulk concentration ratio is governed by the arrival rate and available area (again an adsorption process that is not thermodynamically controlled). Preconditioning of globular proteins, e.g. by heat treatment or pH change or just using "technical grade" instead of purified proteins will generally increase their chance to adsorb at interfaces faster (shown for β-lactoglobumin [35] and α-lactoglobumin [36]).

The phase separation of binary mixtures of two proteins at the air/liquid interfaces was reported for bovine serum albumin and α-lactalbumin in combination with β-casein [37,38], a result in contrast to other observations for mixed β-lactoglobulin/β-casein films [39]. Brownian dynamics simulation showed that phase separation is possible for proteins with no or small exchange between bulk and interfacial regions, i.e. for adsorbed and denatured proteins [40]. As driving force the authors identified the ability of denatured proteins to form hydrogen and disulfide bridges: strong and irreversible bonds will trap phase separation in an early stage and give a homogeneous layer while weaker bonds allow more time for phase separation. In this respect, β-lactoglobulin will form a homogenous layer due to the exposure of disulfide bridges, while more hard proteins such as bovine serum albumin will give raise to phase separation.

2.2 Protein-polysaccharide adsorption layers

Polysaccharides (hydrocolloids) are generally not surface active but can carry charges. Therefore it is advisable to carefully check the intrinsic properties of the used polysaccharide: a number of publications claiming the reduction of the interfacial tension by the addition of polysaccharids rather measure impurities such as protein and lipid fractions originating from the biopolymer source and conclude with the misleading statement that biopolymers are surface active [41]. When polysaccharides do not adsorb on their own to interfaces, they can do so in the presence of proteins by either forming a phase separated interfacial layer or an electrostatically stabilized interfacial layer. In the first case, the adsorption process can be roughly summarized by

Table 1. Overview of protein-polysaccharide compositions used to stabilize emulsions and foams (Asterix identifying the manuscripts where the influence of bulk phase separation were explicitly discussed, CMC = carboxymethyl cellulose).

Protein	Polysaccharide	Author
Emulsions (liquid/liquid interface)		
Casein	Gelatin	Dickinson & Murray [42]
Casein	Pectin	Dickinson [41], de Bont et al. [43]
Sodium Casein	Xanthan	Cao et al. [44], Moschakis et al. [45], Liu et al. [46]
Sodium Casein	CMC	Cao et al. [44]
β-Lactoglobulin	Gelatin	Gu et al. [47]
β-Lactoglobulin	ι-Carrageenan	Gu et al. [47–50]
β-Lactoglobulin	Dextran	Dickinson [41]
β-Lactoglobulin	Gum Arabic	Bouyer et al. [51]*
β-Lactoglobulin	Pectin	Ganzevles et al. [52]*
Whey Protein	Amylopectin	Ye et al. [53]
Whey Protein	Chitosan	Laplante et al. [54]
Whey Protein	Flaxseed Gums	Khalloufi et al. [55]
Whey Protein	λ-Carrageenan	Weinbeck et al. [56]
Bovine Serum Albumin	Dextran	Dickinson & Semenova [57]
Bovine Serum Albumin	Alginate	Ward-Smith et al. [58]
Bovine Serum Albumin	Methyl Cellulose	Sarker et al. [59]
Bovine Serum Albumin	κ-Carrageenan	Dickinson & Pawlowsky [60,61]
Methemoglobin	CMC	Ward-Smith et al. [58]
Gum Arabic	Pectin	Nakauma et al. [62]
Foams (air/liquid interface)		
Whey Protein	Alginate	Perez et al. [63]
Whey Protein	ι-Carrageenan	Perez et al. [63]
β-Lactoglobulin	Gum Arabic	Schmitt et al. [12]
β-Lactoglobulin	κ-Carrageenan	Carp et al. [64]
Egg Albumin	κ-Carrageenan	Miquelim et al. [65]
Egg Albumin	Xanthan	Miquelim et al. [65]
Egg Albumin	Guar	Miquelim et al. [65]

following two steps: the protein adsorbs and denatures at the interface providing environmental conditions for the polysaccharides in contact with the protein to form a phase separated two-dimensional adsorption layer. Electrostatic interaction stabilizing a protein-polysaccharide layer are hydrogen bonds, hydrophobic bonds, and ion-crosslinks. It is generally assumed that charged polysaccharides such as pectin or carrageenan contribute more to the interfacial stabilization than pure thermodynamical phase separation. The "first come – first serve" rule of thumb also applies to protein-polysaccharide adsorption layer. However, a closer look to the solubility limit in bulk can avoid surprises: solutions above the solubility limit will deplete already in the bulk and will reduce the amount of free protein forming an adsorption layer, while successive addition of polysaccharides after the formation of the protein adsorption layer will lead to a sterically and electrostatically stable layer [26].

In a vast number of publications, the stabilizing effect of protein-polysaccharide adsorption layers was mainly investigated indirectly by the increased stability of emulsions and foams, i.e. the enhanced stability towards coalescence, creaming, film rupture, and drainage [19,41]. Table 1 gives a glance on the investigated protein-polysaccharide combinations. Since it cannot be excluded that the claimed emulsion and foam stability originates at least partly from bulk depletion and coacervation, this studies do not replace direct rheological investigations of the adsorption layer.

When it comes to the direct investigation of the mechanical properties of the protein-polysaccharide adsorption layer only a limited number of publication is available, which are summarized in Table 2. The influence of non-charged/charged and non-interfacial active/interfacial active polysaccharides on the interfacial tension and dilatational rheological properties of soy protein adsorption layers was studied by Martinez et al. [66]. While the interfacial tension was, as expected, not effected by locust bean gum, both ι-carrageenan (charged, non-interfacial active) and hydroxypropylmethyl cellulose (HPMC, interfacial active) decrease the interfacial tension. For ι-carrageenan this is somehow unusual but could be related to impurities present in the raw material and/or insufficient electrostatic grounding of the Langmuir balance/Wilhelmy plate. The dilatational storage modulus E_s' of the soy protein/HPMC composite shows marginal changes in comparison to pure protein layer suggesting a competitive adsorption between protein and polysaccharide weakens the adsorption layer. The soy protein/locust bean gum layer shows a moderate increase of the storage modulus, while the soy protein/ι-carrageenan composite almost triples the elasticity values of the pure protein film. For locust bean gum a thermodynamically driven phase separation could reasoning the increase of E_s' but for the charged ι-carrageenan electrostatic interactions stabilize the composite adsorption layer. In a similar investigation, the same research group investigated the interfacial tension and dilatational rheology of β-lactoglobulin/polysaccharide adsorption layers [67]. Two charged polysaccharides (xanthan and λ-carrageenan) are compared with surface active propylene glycol alginate (PGA) with different degrees of esterification. Again the charged but non-interfacial active polysaccharides showed the highest increase in E_s' of the adsorption layer with xanthan being most effective (five to six times increase of E_s' in comparison to the pure protein layer). The surface active PGA is in comparison to HPMC (see Martinez et al. [66]) increasing the dilatational storage modulus but only up to twice of the value of the β-lactoglobulin layer. An influence of the different degree of esterification was observed for the decrease in interfacial tension (higher for high degree of esterification) but not for the interfacial rheological response.

The rheology of soy protein isolates/high methoxyl pectin adsorption layers at the air/liquid interface showed that pure soy protein interfacial layers are weakly cross-linked polymer networks with a small regime of linear viscoelasticity response. Highly hydrophilic polysaccharides that do not adsorb by their own at the interface show a cooperative behavior with protein that promotes a significant increase of surface pressure of adsorbed films: the rheological behavior of composite soy protein isolates/high methoxyl pectin layers shows that the pectin addition increases the elastic interfacial modulus [76]. Similar to Martinez et al. [66] and Baeza et al. [67,72], the authors suggest that pectin promotes the complexation of the protein by the added polysaccharide and neglect electrostatic interactions introduced by the hydrated pectin. The influence of charge density was studied for high methoxyl pectin and low methoxyl pectin on the β-lactoglobulin/polysaccharide adsorption layers [70] but again discussed only in the framework of thermodynamical phase separation assuming a neutral pH situation.

An outstanding contribution to clarify the electrostatic interaction and stabilization of protein/polysaccharide complexes at air-liquid interfaces was presented by Ganzevles et al. [52,68,71]. The β-lactoglobulin/pectin and β-lactoglobulin/pullulan interface was studied by interfacial rheology, neutron reflectivity, and time resolved fluorescence anisotropy. Varying the ratio of β-lactoglobulin/pectin, i.e. the charges exposed to the protein adsorption layer, the interfacial tension was increased and E_s' decreased (see Figures 2 and 4 of Ganzevles et al. [52]). The decrease of the dilatational storage modulus is in the first instance somehow contradictory to the increase of the modulus as discussed previously for charged systems. Considering the influence of the ionic strength, Ganzevles et al. [52] could show that this parameter can render

Table 2. Overview of protein-polysaccharide composition studies by interfacial rheology (G'_s & G''_s = interfacial shear storage and loss modulus, E'_s & E''_s = interfacial dilatational storage and loss modulus, HPMC = hydroxypropylmethyl cellulose, PGA = Propylene Glycol Alginate).

Protein	**Polysaccharide**	**Property**	**Author**
Protein - non-charged, non-interfacial active Polysaccharide			
Soy Protein	Locust Bean Gum	E'_s, E''_s	Martinez et al. [66]
Egg Albumin	Guar	E'_s, E''_s, G'_s, G''_s	Miquelim et al. [65]
Protein - charged, non-interfacial active Polysaccharide			
β-Lactoglobulin	Pectin	E'_s, E''_s, G'_s, G''_s	Ganzevles et al. [52,68], Sperber et al. [69], Perez et al. [70]
β-Lactoglobulin	Pullulan	E'_s, E''_s, G'_s, G''_s	Ganzevles et al. [71]
β-Lactoglobulin	Xanthan	E'_s, E''_s	Baeza et al. [67,72]
β-Lactoglobulin	λ-Carrageenan	E'_s, E''_s	Baeza et al. [67,72]
Whey Protein	λ-Carrageenan	E'_s, E''_s	Perez et al. [73]
Whey Protein	Sodium Alginate	E'_s, E''_s	Perez et al. [73]
Whey Protein	Pectin	E'_s, E''_s	Perez et al. [70]
Whey Protein	Dextran	E'_s, E''_s	Wooster & Augustin [74]
Sodium Caseinate	Dextran Sulfate	E'_s, E''_s, G'_s, G''_s	Jourdain et al. [75]
Soy Protein Isolate	Pectin	E'_s, E''_s, G'_s, G''_s	Piazza et al. [76]
Soy Protein	ι-Carrageenan	E'_s, E''_s	Martinez et al. [66]
Egg Albumin	κ-Carrageenan	E'_s, E''_s, G'_s, G''_s	Miquelim et al. [65]
Egg Albumin	Xanthan	E'_s, E''_s, G'_s, G''_s	Miquelim et al. [65]
Protein - interfacial active Polysaccharide			
Soy Protein	HPMC	E'_s, E''_s	Martinez et al. [66]
Whey Protein	HPMC	E'_s, E''_s	Perez et al. [73]
β-Casein	HPMC	G'_s, G''_s	Arboleya & Wilde [77]
β-Lactoglobulin	HPMC	G'_s, G''_s	Arboleya & Wilde [77]
β-Lactoglobulin	PGA	E'_s, E''_s	Baeza et al. [67,72]
Protein - Polysaccharide complexes (acacia gum)			
Acacia Gum	-	E'_s, E''_s, G'_s, G''_s	Erni et al. [78]
Acacia Gum	β-Casein	-	Damodaran & Razumovsky [79]
Acacia Gum	α-Gliadin	E'_s, E''_s	Ducel et al. [80]
Acacia Gum	Pea Globulin	E'_s, E''_s	Ducel et al. [80]
Acacia Gum	-	G'_s, G''_s	Elmanan et al. [81]
Mesquite Gum	-	G'_s, G''_s	Roman-Guerrero et al. [82]

the rheological response to both a stronger or a weaker layer. Therefore, revisiting the interfacial rheology of protein/charged polysaccharide layers investigated before seems advisable. In addition, the authors could also show that different charge densities of the pullulan polysaccharide could suppress the formation of an adsorption layer and hence the decrease of interfacial rheological response (see Figs. 1 and 3 of Ganzevles et al. [68]). A follow-up work by Sperber et al. [69] could confirm the observation for β-lactoglobulin/pectin adsorption layers: the reduced electrostatic repulsion of different methyl ester groups along the pectin chain and the protein increases the interfacial rheological moduli.

The naturally occurring protein/polysaccharide complexes (arabinogalactan-protein complex (AGP) or proteoglycans) such as acacia gums (Gum Arabic), bree tree gums, or coffee beans are used for the stabilization of beverage emulsion for encapsulation [80,83,84]. Interfacial rheological data on this complexes are relatively scarce [78,80–82], but show strong viscoelastic properties in both shear and dilatational experiments indicating the formation of a network and/or a two-dimensional soft glass at the interface.

3 Conclusion

Interfacial tension, interfacial rheology, and layer thickness investigations (e.g. neutron reflectivity and time resolved fluorescence anisotropy) on protein/polysaccharide adsorption layers suggest that electrostatic interaction between proteins and polysaccharides is the governing parameter to control both aggregation and mechanical properties. Thermodynamical phase separation in the adsorption layer can be considered under neutral charge conditions but plays a minor role in charged systems and in the presence of interfacial active polysaccharides. For the time being, interfacial rheology on protein/polysaccharide adsorption layers focus only on a limited number of systems (mainly β-lactoglobulin, caseins, and soy protein) and environmental conditions. Beside other systems as summarized in Table 2 also more extreme environmental conditions (e.g. present in the intestine) as well as the influence of slightly modified protein structures on the layer's rheology should be addressed in future [85].

This manuscript is based on a presentation given at the Lorentz Center Workshop on "Dynamics of Complex Fluid-Fluid Interfaces" during September 2011 [86]. Nathalie Scheuble is acknowledged for the critical reading on the manuscript. Anne-Kris and Jörg Fell are kindly acknowledged for lending their cabin at the Norwegian coast where most of the manuscript was prepared.

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