Food Hydrocolloids 70 (2017) 329–344

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

A comparison of corn fiber gum, hydrophobically modified starch, gum arabic and soybean soluble polysaccharide: Interfacial dynamics, viscoelastic response at oil/water interfaces and emulsion stabilization mechanisms

Qiangwei Jin [a], Xiaobei Li [b], Zhixiang Cai [a], Fei Zhang [c], Madhav P. Yadav [d], Hongbin Zhang [a, *]

[a] Advanced Rheology Institute, Department of Polymer Science and Engineering, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Nutrition & Health, DuPont, Shanghai 200335, China
[c] Corporate R&D Division, Materials Science Department, Firmenich Aromatics (China) Co. Ltd., Shanghai 201108, China
[d] Eastern Regional Research Center, Agricultural Research Service, US Department of Agricultural, Wydmoor, PA 19038, USA

ARTICLE INFO

Article history:
Received 13 November 2016
Received in revised form
17 February 2017
Accepted 2 March 2017
Available online 26 April 2017

Keywords:
Interfacial rheology
Branched polysaccharide
Emulsification
Emulsion stability
Double wall-ring

ABSTRACT

The interfacial rheology of polysaccharide adsorption layers of corn fiber gum (CFG), octenyl succinate anhydride-modified starch (OSA-s), gum arabic (GA) and soybean soluble polysaccharides (SSPS) at the oil/water interface and their emulsifying properties in oil-in-water (O/W) emulsions were compared. All four amphiphilic polymers contain different amounts of protein and they are of high molecular weight with highly branched structure. Based on the obtained interfacial shear rheological information such as a number of influence factor dependence (time, concentration, temperature, strain dependency) of interfacial dynamic moduli, creep or relaxation response, and steady/dynamic flow behavior of the interfacial layers, we found pronounced differences in the viscoelastic response of the four hybrid polyelectrolytes in shear flow. The adsorbed film of CFG is unique because it exhibits a predominantly viscous showing an apparently increasing storage modulus throughout the whole test without a saturated value whereas OSA-s produces a pure viscous layer at interface with a very low viscosity and quick forming kinetics; in contrast, both GA and SSPS form more rigid, solid–like layers. Models to describe the distinct interfacial dynamics and stabilizing mechanism of the four emulsifiers involving steric repulsion and electrostatic repulsion are proposed. Emulsifying properties of the four polymers are evaluated in terms of the emulsion physical properties, droplet-size distribution and optical microscopy observation. The effect of concentration and storage temperature on the interfacial viscoelastic response and the corresponding emulsion stability of each biopolymer are also compared.

1. Introduction

There are three broad types of emulsifying agents used in food – small molecule surfactants, macromolecule proteins and polysaccharides. The former are efficient in emulsification (Lobo & Svereika, 2003; Pelan, Watts, Campbell, & Lips, 1997), while less effective in conferring long-term stability than the latter two of biopolymers (Dickinson, 2003; Lucassen-Reynders, 1994). Proteins are not commonly classified as emulsifiers for traditional and marketing reasons, though they do function as such during food manufacture (Dickinson, 2003). Their application are more susceptible to the change of environmental conditions (Chanamai & McClements, 2002; Padala, Williams, & Phillips, 2009). Many polysaccharides are used as functional ingredients in food industry to provide nutrition and control flavor, texture and shelf-life (Dickinson, 2009a, 2009b). Emulsification and the control of emulsion stability are important functional roles of some food polysaccharides. However, although most of these polysaccharides can act as stabilizing agents of emulsions, only a few of them can be used as emulsifying agents. It has been pointed out that an effective

* Corresponding author.
E-mail address: hbzhang@sjtu.edu.cn (H. Zhang).

http://dx.doi.org/10.1016/j.foodhyd.2017.03.005
0268-005X/

biopolymer in stabilizing emulsion should possess the characteristics of strong adsorption, complete surface coverage, and forming a thick steric stabilizing layer or/and a charged stabilizing layer (Dickinson, 2003). Therefore, such a polysaccharide must contain numerous and sufficient hydrophobic groups that are able to quickly adsorb to and spread out at the interface. Besides, steric hindrance (provided by carbohydrate moiety) combined with electrostatic repulsion must build an energy barrier for long-term stability at the interface (Dickinson, 1992).

One of the most commonly recognized biopolymer surfactants in stabilizing flavor oil-in-water emulsions is gum arabic (GA, also called Acacia gum), a natural branched complex heteropolysaccharide containing ~2% of a polypeptide (Randall, Phillips, & Williams, 1988). This natural exudate from acacia trees has three main components including major fraction of arabinogalactan (AG), minor fraction of glycoprotein (GP) and the complex fraction, arabinogalactan protein (AGP). The AGP component with a 'wattle blossom' type structure has been established as effective component for emulsification properties (Randall, Phillips, & Williams, 1989; Renard, Lavenant-Gourgeon, Ralet, & Sanchez, 2006). Octenyl succinate anhydride-modified starch (OSA-s) has been identified as the most promising alternative to GA (Chanamai & McClements, 2002; Prochaska, Kędziora, Le Thanh, & Lewandowicz, 2007) since it can be gained in a sufficient supply and at a relatively low cost compared to GA. The OSA-s (Purity Gum Ultra, PGU) used in this study is derived from waxy maize starch that is made up of amylopectin, on which both lipophilic and anionic traits are introduced. Soybean soluble polysaccharides (SSPS), an acidic biopolymer extracted from the byproduct of soy protein isolate production, containing a negatively charged highly branched backbone mainly composed of rhamnogalacturonan and neutral branched chains with a protein fraction at the end of the molecules, has been shown capable of stabilizing oil-in-water emulsions at a lower concentration compared with GA and modified starch, and its emulsion stability is not affected by pH or ionic strength (Buffo, Reineccius, & Oehlert, 2001; Chivero, Gohtani, Yoshii, & Nakamura, 2016; Nakamura, Takahashi, Yoshida, Maeda, & Corredig, 2004).

Corn fiber gum (CFG) is extracted from low-value byproduct of corn dry or wet milling processes using alkaline hydrogen peroxide method. It has received increasing attention because of the potential use as a novel and functional industrial emulsifiers (Yadav, Cooke, Johnston, & Hicks, 2010; Yadav, Johnston, & Hicks, 2009; Yadav, Johnston, Hotchkiss Jr, & Hicks, 2007). CFG consists of a backbone of β (1, 4) linked xylopyranose residues with branches consisting of arabinofuranose, also contains small amounts of protein, lipid and so on (Yadav et al., 2010).

The above mentioned four polysaccharides have the same features of highly branched structures, high molecular weights, high water solubility and low viscosities over a wide range of concentrations. Their surface activities have their own molecular origin in both i) the compact hydrophilic carbohydrate backbones and ii) the presence of protein component linked covalently to the polysaccharides or short, non-polar substituent groups introduced by chemical modification.

Emulsions are thermodynamically unstable systems containing at least two immiscible fluids. The stability of emulsions is related to droplet size, zeta-potential, interfacial and bulk rheological properties, creaming behavior and so on (Dokić, Krstonošić, & Nikolić, 2012; Taherian, Fustier, Britten, & Ramaswamy, 2008). Among characterization methods of emulsions, interfacial rheology is particularly useful for product design and development, sensory evaluation and the long-term stability estimation (Sharma, Jaishankar, Wang, & McKinley, 2011). Interfacial fluid elements in two-phase flows are normally subjected to both dilation and shear deformation (Edwards, Brenner, & Wasan, 1991). The interfacial shear technique is very sensitive to the structure and composition of the adsorbed layer and the intermolecular interactions in the formed film (Bos & Vliet, 2001). It is quite suitable for macromolecular surface-active species that display substantial interfacial viscoelastic behavior. While most of the interfacial shear studies have been focused on proteins (Freer, Yim, Fuller, & Radke, 2004; Krägel, Derkatch, & Miller, 2008; Li et al., 2016; Roth, Murray, & Dickinson, 2000) and small molecule surfactants (Erni, Fischer, & Windhab, 2005; Golemanov, Tcholakova, Denkov, Pelan, & Stoyanov, 2012), studies on the interfacial viscoelasticity induced by polysaccharides have also attracted much attention since the first report on GA by Warburton (1966). Quite a lot of work has been done mainly using the hybrid polyelectrolyte of GA as a model polymer emulsifier. Recently, Bouyer et al. (2011) compared the difference in stabilization mechanisms of the emulsions induced by GA, β-lactoglobulin and their complexes by interfacial dilational rheology. Al-Assaf et al. (Elmanan, Al-Assaf, Phillips, & Williams, 2008) performed a detailed shear rheological study on the air/liquid (A/L) and liquid/liquid (L/L) interfaces covered with two kinds of gum arabic (*Acacia senegal* and *Acacia seyal*) and discussed the influences of aging, enzymatic degradation and sources of the gum. Especially, Erni et al. (2007) compared interfacial shear and dilation rheological response of GA and OSA starch (Purity Gum BE) at oil/water interface. Interfacial viscoelasticity involving another hybrid polyelectrolyte of pectin has also been reported (Tamm & Drusch, 2017).

However, despite recent advances in more detailed interfacial rheological characterization of GA, a comprehensive interfacial rheological study of CFG is still missing. Furthermore, no overall comparison has yet been made among the interfacial rheology of the four highly branched macromolecular emulsifiers of CFG, OSA-s, GA and SSPS. In our previous study, we have investigated the bulk rheological properties of the aqueous solutions of the above mentioned four kinds of biopolymers and compared their interfacial activities at A/L interfaces as well as their chain structural morphology (Jin, Cai, Li, Yadav, & Zhang, 2017). While the efficiency of interfacial tension reduction has been confirmed for all of the four polysaccharides (Jin et al., 2017), interfacial rheological characterization at A/L interface allows a better understanding of the possible emulsification and the stabilizing mechanism of these emulsifiers. This successive article focuses on the interfacial dynamics of the four polymers at L/L interface, their interfacial stabilized mechanism and emulsifying ability. The purposes are i) to reveal and compare the distinguishing interfacial rheological properties of the four biopolymer emulsifiers at L/L interfaces with a focused attention to CFG, ii) to give insights into the differences of interfacial adsorption and stabilization mechanism of these emulsifiers, thus drawing sketches to interpret the viscoelastic properties of the polymer adsorption layers at L/L interface, which should be of special importance in their technological applications, and iii) to investigate the emulsion stabilities induced by the four gums and compare them to interfacial rheological properties. The effects of bulk concentration and temperature on the interfacial properties and emulsion stabilities, as well as various interfacial rheological tests including dynamic shear at variable deformation amplitudes and frequencies, transient shear under creep and stress relaxation, and steady shear in a wide range of shear rates have also been considered and discussed.

2. Materials and methods

2.1. Materials and characterization

CFG was isolated from corn fiber using an alkaline extraction method following previously published method (Yadav et al., 2010).