Journal of Food Engineering xxx (2017) 1–11

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Impact of polysaccharide molecular characteristics on viscosity enhancement and depletion flocculation

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ARTICLE INFO

Article history:
Received 21 February 2017
Received in revised form
14 March 2017
Accepted 21 March 2017
Available online xxx

Keywords:
Gum arabic
Corn fiber gum
Beet pectin
Natural emulsifiers
Molecular characteristics

ABSTRACT

The molecular characteristics (molar mass, hydrodynamic radius, and electrical potential) of gum arabic, corn fiber gum, and beet pectin dissolved in aqueous solutions were measured using size-exclusion chromatography and electrophoresis. Corn fiber gum and beet pectin had extended molecular structures that entrained large quantities of water, whereas gum arabic had a more compact structure. The effectiveness of the polysaccharides at increasing solution viscosity and promoting depletion flocculation decreased in the following manner: beet pectin > corn fiber gum > gum arabic. Mathematical models were used to relate differences in the molar mass and hydrodynamic radius of the polysaccharides to their ability to thicken solutions and promote depletion flocculation. There was good qualitative agreement between the models and experiments, but relatively poor quantitative agreement. The information obtained in this study may be useful for selecting appropriate natural emulsifiers to utilize in emulsion-based products.

1. Introduction

Polysaccharides are widely utilized in the food industry as functional ingredients for their physicochemical and physiological attributes (Stephen et al., 2006). Many of the polysaccharides isolated from food sources are hydrophilic or amphiphilic polymers that have extended flexible structures (Cui, 2005). As a result, they have good water-solubility and are capable of thickening aqueous solutions, forming hydrogels, or stabilizing oil-in-water emulsions. Moreover, indigestible polysaccharides (“dietary fibers”) have beneficial health effects, such as reducing constipation, diabetes, heart disease, and cancer (Grundy et al., 2016). The functional attributes of polysaccharides are ultimately determined by their molecular characteristics, such as molecular weight, conformation, hydrophobicity, and electrical charge (Stephen et al., 2006). There is therefore considerable interest in understanding the relationship between the functional and molecular characteristics of specific polysaccharides.

In this study, we focus on the properties of three surface-active polysaccharides that can be used to form and stabilize oil-in-water emulsions: gum arabic, corn fiber, and beet pectin. Gum arabic is an amphiphilic biopolymer typically isolated from the *Acacia senegal* tree located primarily in Western Africa (Williams and Phillips, 2009). It is a complex substance that consists of three major biopolymer fractions that consist primarily of polysaccharides and glycoproteins (Williams and Phillips, 2009). Gum arabic is currently the most widely used natural amphiphilic polysaccharide used in the food industry, where it is commonly utilized to form and stabilize beverage emulsions, such as soft drinks (Piorkowski and McClements, 2014). Beet pectin is another amphiphilic biopolymer that is typically isolated from sugar beet (Christiaens et al., 2016; Ngouemazong et al., 2015; Siew et al., 2008). Unlike many other forms of pectin, sugar beet pectin has a strong tendency to adsorb to oil-water interfaces because it has appreciable quantities of non-polar phenolic groups and proteins covalently attached to the polar polysaccharide chain (Leroux et al., 2003; Nakauma et al., 2008). Consequently, beet pectin has the ability to adsorb to the surfaces of oil droplets and protect them from aggregation (Chen et al., 2016; Gülseren and Corredig, 2014; Zhang et al., 2015). An important potential commercial benefit of using

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http://dx.doi.org/10.1016/j.jfoodeng.2017.03.021
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Please cite this article in press as: Bai, L., et al., Impact of polysaccharide molecular characteristics on viscosity enhancement and depletion flocculation, Journal of Food Engineering (2017), http://dx.doi.org/10.1016/j.jfoodeng.2017.03.021

beet pectin is that lower amounts can be used to form and stabilize emulsions than gum arabic (Burapapadh et al., 2010; Funami et al., 2011). Corn fiber gum is an amphiphilic biopolymer that is a byproduct obtained during the milling of corn (Yadav et al., 2007b; Yadav et al., 2010). Like beet pectin, corn fiber gum mainly consists of a polar polysaccharide chain with a number of non-polar groups covalently attached, such as phenolic groups, lipids, and proteins (Kokubun et al., 2014; Yadav et al., 2007a; Yadav et al., 2008). The ability of corn fiber gum to form and stabilize oil-in-water emulsions has been evaluated in a number of studies (Cirre et al., 2014; Lehtonen et al., 2016; Mikkonen et al., 2016; Yadav et al., 2009; Yadav et al., 2007b). For convenience, the gum arabic, corn fiber gum and beet pectin ingredients used in our study are referred to as “polysaccharides”, but in practice it should be stressed that they all contain a small amount of protein that plays an important role in determining their surface activity.

Surface-active polysaccharides are often used to facilitate the formation and stability of oil-in-water emulsions (Dickinson, 2003; McClements and Gumus, 2016). During homogenization, they adsorb to the oil droplet surfaces with the non-polar groups protruding into the oil phase and the polar groups protruding into the surrounding aqueous phase. As a result, they facilitate further droplet disruption by reducing the oil-water interfacial tension and Laplace pressure. In addition, they enhance the stability of the emulsions to aggregation by generating a strong steric and electrostatic repulsion between the polysaccharide-coated droplets (McClements and Gumus, 2016). An important feature of emulsions stabilized by polysaccharides is that they are usually highly resistant to changes in pH, ionic strength, or temperature because of the strong long-range steric repulsion acting between the droplets. Nevertheless, there are some drawbacks to utilizing amphiphilic polysaccharides as emulsifiers. Firstly, they form highly viscous solutions when used at sufficiently high levels, which can limit the total amount of oil that can be successfully homogenized. Secondly, they can promote emulsion instability when used above a certain level due to a depletion flocculation mechanism, which can reduce the long-term stability of some products. It is therefore important to understand the relationship between the molecular features of specific polysaccharides and their tendency to enhance viscosity or induce depletion flocculation (McClements, 2000).

2. Relationship of molecular properties of polysaccharides to their functional attributes

The following simple relationships have been developed to relate the molecular characteristics of biopolymers in aqueous solutions to their ability to increase viscosity and promote depletion flocculation (McClements, 2000).

2.1. Viscosity enhancement

To a first approximation, the ability of a biopolymer to increase the viscosity of an aqueous solution can be described by the following equation:

$$\frac{\eta}{\eta_1} = \left(1 - \frac{\varphi_E}{\varphi_C}\right)^{-2} \qquad (1)$$

Here, η is the shear viscosity of the biopolymer solution, η_1 is the viscosity of the solvent (water), ϕ_E is the effective volume fraction of the biopolymer molecules in solution, and ϕ_C is the critical packing fraction (around 0.57). The critical packing fraction is related to the biopolymer level where the hydrated biopolymer molecules become closely packed, which leads to a steep increase in solution viscosity. The effective volume fraction of the hydrated biopolymer molecules in solution can be approximated by the following expression:

$$\varphi_E = \frac{4}{3}\pi r_H^3\left(\frac{cN_A}{M}\right) \qquad (2)$$

Here, r_H is the hydrodynamic radius of the biopolymer molecules in solution (m), c is the concentration of the biopolymers in solution (kg m^{-3}), N_A is Avogadro’s number (mol^{-1}), and M is the molar mass of the biopolymer (kg mol^{-1}). The above equations predict that the viscosity of a biopolymer solution increases as the biopolymer concentration increases, and as the hydrodynamic radius increases. This equation assumes the biopolymers are monodisperse (*i.e.,* they all have the same molar mass), but in practice they are polydisperse, and so the equation would have to be modified to take this effect into account.

Equations (1) and (2) can be used to calculate a critical viscosity concentration (CVC), *i.e.,* the biopolymer concentration where the shear viscosity reaches a high value.

$$CVC = \frac{3\varphi_E^* M}{4\pi r_H^3 N_A} \qquad (3)$$

For the sake of simplicity, it is arbitrarily assumed that the CVC occurs when the viscosity of the biopolymer solution is hundred times that of the pure solvent ($\eta/\eta_1 = 100$). A hundred-fold increase in viscosity would be expected to greatly retard creaming in an emulsion. Inserting this value and $\phi_C = 0.57$ into Equation (1) gives: $\phi^*_E \approx 0.53$. The lower the value of CVC, the more effective a biopolymer is as a thickening agent. Equation (3) indicates that CVC decreases as the biopolymer molecular weight decreases or hydrodynamic radius increases. Theoretical predictions of the impact of biopolymer characteristics on the CVC are presented in Fig. 1. These calculations show that for a fixed molecular weight, the CVC

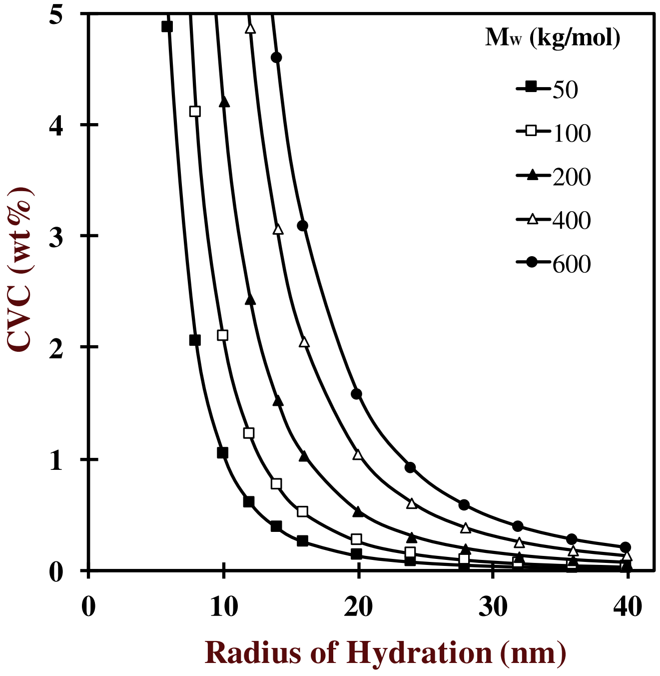

Fig. 1. Theoretical prediction of the dependence of the critical viscosity concentration (CVC), which is the biopolymer level where a biopolymer solution has a very high viscosity, on biopolymer molecular characteristics (hydrodynamic radius and molecular weight).

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