Food Hydrocolloids xxx (2016) 1–8

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Pectin at the oil-water interface: Relationship of molecular composition and structure to functionality

K. Alba, V. Kontogiorgos*

School of Applied Sciences, Department of Biological Sciences, University of Huddersfield, HD1 3DH, UK

ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form
10 July 2016
Accepted 24 July 2016
Available online xxx

Keywords:
Pectin
Emulsions
Interface
Extraction
Isolation

ABSTRACT

The present review examines how macromolecular structure and functional groups of pectin affect its functionality with particular focus on its interfacial activity. We venture into a description of the particularly complex pectin structure and describe the major building blocks and their properties. In the following section, the role of each structural parameter is discussed with particular attention to protein, degree of acetylation and methylation, molecular weight, and branching. Finally, we discuss how modification of the extraction conditions could be tailored to obtain pectin with the desired emulsification properties. It is proposed that pectin with protein content in the range of 3%, with degree of acetylation greater than 10%, molecular weight between 100 and 200 $\times$ 10^3 g mol^{-1} and enriched in RG-I segments is more likely to perform well as an emulsifier. To tailor such a structure, an aqueous extraction protocol with low pH values (between 2.5 and 3.5) with a strong monoprotic acid (e.g., HCl) and one-step solvent precipitation should be selected. The proposed set of extraction conditions could be used as a first step towards rational design of pectin with desirable interfacial functionality.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Current food and pharmaceutical processes focus on several critical formulation aspects with the overall aim to improve human health (e.g., functional foods that lower cholesterol) or produce products with consumer-tailored specifications (e.g., products for vegetarians). The challenges arise from the increasing public interest in the availability of "natural" food ingredients where only naturally available materials such as carbohydrates or proteins should be used. For instance, replacement of gelatin or synthetic surfactants (e.g., Tweens) that have been utilized for structuring of foods or hard-shelled capsules are some examples of these demands. Therefore, the investigation of novel structures and sources that could replace existing ingredients is ongoing.

The technological performance as emulsifier of various polysaccharides is usually controlled by its molecular properties (e.g., conformation, polyelectrolyte nature, surface charge density, molecular weight etc.) and its intra- and inter-chain interactions. Several hydrocolloids (e.g., carrageenan, xanthan, Arabic gum) can be used as emulsifiers as they have the ability to rapidly adsorb to the interface, reduce the interfacial tension to facilitate droplet disruption and impede droplet aggregation. This is typically attributed to the presence of hydrophobic elements in biopolymer structure such as protein, ferulic acids, or acetyl groups (Bouyer, Mekhloufi, Rosilio, Grossiord, & Agnely, 2012; McClements & Gumus, 2016; Petri, 2015). Pectin is a polysaccharide that is widely utilized across food and pharmaceutical industries as a gelling material, stabilizer or delivery agent. The structural diversity of pectin results in a multitude of functional properties and is considered as a potential multifunctional food and pharmaceutical ingredient. The aims of the present review are to embark on an exploration of how structure of pectin influences its interfacial properties and how we can manipulate its structure with tailored extraction protocols to achieve optimum functionality.

2. Structural characteristics of pectin

Pectin belongs to family of covalently linked galacturonic acid-rich plant cell wall polysaccharides. They are found in primary cell walls of dicots and non-graminaceous monocots (~35%), in grasses and other commelinids (~2–10%), and in woody tissues (~5%) (Ridley, O'Neill, & Mohnen, 2001). Some pectin molecules are covalently bonded or tightly associated with other types of cell wall polysaccharides, such as hemicelluloses and cellulose (McCann &

* Corresponding author.
E-mail address: v.kontogiorgos@hud.ac.uk (V. Kontogiorgos).

http://dx.doi.org/10.1016/j.foodhyd.2016.07.026
0268-005X/© 2016 Elsevier Ltd. All rights reserved.

Please cite this article in press as: Alba, K., & Kontogiorgos, V., Pectin at the oil-water interface: Relationship of molecular composition and structure to functionality, *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.07.026

Roberts, 1991; Mohnen, 2008; Peng & She, 2014). The entire cellulose-hemicellulose network is embedded in a matrix of pectic polysaccharides, which form a hydrated and cross-linked three-dimensional network (Zandleven et al., 2007). Early work on carbohydrate chemistry of plant cells used the umbrella term "pectic substances", which included pectin and other highly viscous polysaccharides such as xyloglucans (Sinnott, 2007). Current usage confines the word "pectin" to a group of heteropolysaccharides with backbone mainly composed of D-galacturonic acid units (D-Gal*p*A, ~65%) bonded with α-(1 → 4) glycosidic linkages. The diversity of pectin structures (e.g., length of neutral side chains, molecular weight, degree of polymerization, methyl- and acetyl-esterification, and branching of side chains) depends on the botanical source, plant ripening state and applied extraction conditions (Bagherian, Zokaee Ashtiani, Fouladitajar, & Mohtashamy, 2011; Guo et al., 2014; Müller-Maatsch et al., 2016; Ng et al., 2013; Paniagua et al., 2014).

In its simplest ideal description, pectin macromolecule is a diblock copolymer of two major structural classes. Homogalacturonan (HG) and rhamnogalacturonan I (RG-I), are found in most pectin assemblies and the intra- and inter-molecular interactions between these two segments control their functional properties. In the majority of the cases, other regions can be also distinguished depending on the source, namely, rhamnogalacturonan II (RG-II), xylogalacturonan (XGA), apiogalacturonan (AGA), arabinogalactan (AG-I, AG-II) and arabinan (Fig. 1). Branches with distinct structure from the main backbone originate from the RG-I, RG-II and AG-I ("hairy" regions) making pectin essentially a graft copolymer of HG and RG-I. It should be stressed that extracted pectin is usually polydisperse consisting of complex mixtures of the previously mentioned segments.

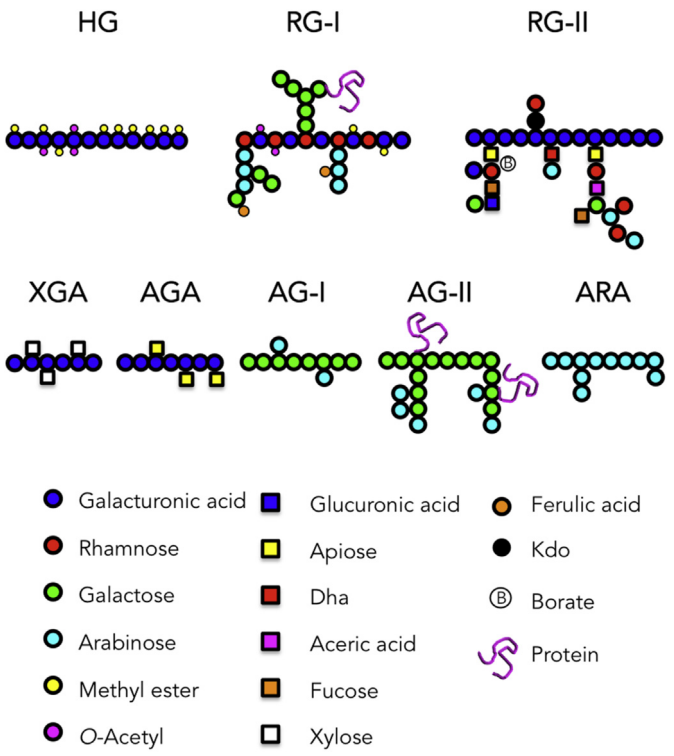

Fig. 1. Schematic of the major building blocks encountered in pectin from various botanical sources. HG: homogalacturonan, RG-I: rhamnogalacturonan-I, RG-II: rhamnogalacturonan-II, XGA: xylogalacturonan, AGA: apiogalacturonan, AG-I: arabinogalacturonan-I, AG-II: arabinogalacturonan-II, and ARA: arabinan. Protein can be found on RG-I and AG-II and contribute to interfacial activity.

Homogalacturonan is the most abundant polymeric segment of pectin, and plant cell walls consist of about 65% HG (Mohnen, 2008) (Fig. 1). HG is composed of long chains of linear 1 → 4 linked α-D-Gal*p*A residues (~200 units) and some of the carboxyl groups are methyl-esterified at C-6 position and/or acetyl-esterified at *O*-2 and/or *O*-3 positions of Gal*p*A depending on plant species (Sinnott, 2007). *O*-Acetyl rich homogalacturonans have been also isolated from sugar beet, cacao pod husks and spinach (Perrone et al., 2002; Ralet et al., 2005; Vriesmann, Teófilo, & Petkowicz, 2011). Conventionally, HGs with greater than 50% methyl-esterification of Gal*p*A residues are described as high methyl-esterified (HM) and those with lower than 50% are defined as low methyl-esterified (LM). The methyl esterification of linear HG units determines the industrial applicability of pectin (e.g., gelation), which depends not only on the amount of methyl-esterification, but also on distribution of methyl groups on the HG backbone (Dominiak et al., 2014).

Rhamnogalacturonan I (RG-I) represents around 20–35% of pectin in plant cell wall (Obro, Harholt, Scheller, & Orfila, 2004). Its backbone is composed of the repeating disaccharide galacturonic acid and rhamnose [α-(1 → 2)-D-Gal*p*A–α-(1 → 4)-L-Rha*p*]$_n$ where *n* can be greater than 100 (Fig. 1). The RG-I backbone is partially substituted at *O*-4 and/or *O*-3 positions of α-L-Rha*p* residues with polymeric side-chains predominantly composed of α-(1 → 5)-L-arabinans and β-(1 → 4)-D-galactans, arabinogalactans-I (AG-I), arabinogalactans-II (AG-II) and galacto-arabinans (Mohnen, 2008) (Fig. 1). The side-chains can be a single unit such as β-D-Gal*p*-(1 → 4), but also polymeric, such as arabinan and arabinogalactan-I (AG-I). The galactan and arabinan side-chains of RG-I are the most flexible parts of the pectin molecule with the higher degree of conformational freedom exhibited by arabinan (Sinnott, 2007). AG-I is composed of α-1→4 linked β-D-Gal*p* backbone and α-L-Ara*f* are attached to the *O*-3 position of galactosyl residues (Ridley et al., 2001). The galactan chain of AG-I may have branches of one or more Ara*f* residues or a single terminal Ara*p* residue. Arabinogalactans-II (AG-II) are predominantly associated with proteins (arabinogalactan proteins or AGPs) (Vincken, 2003) (Fig. 1). The proportion and distribution of branched Rha*p* residues typically varies in the range of 20–80% depending on the source of polysaccharide (Visser & Voragen, 1996). This also results in a heterogeneous structure of RG-I arabinan and galactan side-chains from source to source, something that has been observed for pectic polysaccharides from the walls of apple, sugar beet, soybean, persimmon, and potato (Duan, Wang, Dong, Fang, & Li, 2003; Huisman et al., 2001; Obro et al., 2004; Sakamoto & Sakai, 1995; Schols & Voragen, 1996). However, unbranched RG-I molecules have been also reported in seed mucilages (Western et al., 2004). The RG-I backbone can be acetylated at *O*-2 and/or *O*-3 positions of Gal*p*A or at *O*-3 position of Rha*p* residues depending on the plant species (Sengkhamparn et al., 2009; Vincken, 2003; Voragen, Coenen, Verhoef, & Schols, 2009). Typically, carboxyl groups of α-D-Gal*p*A residue are not methyl-esterified in RG-I, however, methylated RG-I fractions has been reported in pectin isolates from apple, citrus peels, kidney beans and flax hypocotyls (Ridley et al., 2001; Rihouey et al., 1995).

Rhamnogalacturonan II (RG-II) is a minor (~10%) pectic component of plant cell walls and represents about 0.5–8% in dicots, non-graminaceous, monocots, and gymnosperms, and less than 0.1% in primary walls of commelinid monocots (Jackson et al., 2007; Matsunaga et al., 2004). RG-II has been detected in the cell walls of many tissues of edible plants including apple, kiwi, carrot, tomato, grape and pumpkin (Buffetto et al., 2014; Cui, 2005; Ishii, Matsunaga, & Hayashi, 2001). RG-II is typically described as a stretch of HG backbone, approximately seven to nine 1 → 4 linked α-D-Gal*p*A residues with four heteropolymeric side-chains attached (Caffall & Mohnen, 2009). The structure of RG-II is highly complex with twelve different types of sugars and over twenty different

Please cite this article in press as: Alba, K., & Kontogiorgos, V., Pectin at the oil-water interface: Relationship of molecular composition and structure to functionality, *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.07.026

Download English Version:

https://daneshyari.com/en/article/4984025

Download Persian Version:

https://daneshyari.com/article/4984025

Daneshyari.com