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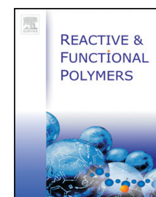

Physicochemical characterisation of hawthorn pectins and their performing in stabilising oil-in-water emulsions

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ABSTRACT

The physicochemical characteristics, intrinsic viscosity, adsorption dynamics and emulsifying properties of two hawthorn accessions pectins (HP50 and HP55) were evaluated and compared to those obtained for commercial citrus pectin (CP). Mark-Houwink-Kuhn-Sakurada coefficients, $a_{MHKS} = 0.71 \pm 0.02$ and $k_{MHKS} = 5.08 \times 10^{-3} \pm 2 \times 10^{-4}$ g dL^{-1} were obtained from intrinsic viscosity data. The diffusion (K_{diff}), penetration (K_1) and the rearrangement (K_2) constants were determined from adsorption dynamics data of the pectins at the canola oil-water interface. K_{diff} was higher and K_1 was lower for HP50 than for HP55 and for CP. These results had bearing on the stability of oil-in-water emulsions. Higher K_{diff} produced smaller initial droplet sizes, due to the faster diffusion of molecules to the interface, while lower K_1 produced longer-term stability, as a more consolidated and stronger interfacial film was formed faster, making arduous the penetration of newly arriving molecules through the monolayer. The rate of creaming was lower the smaller was the initial droplet size and the higher the apparent viscosity of the emulsions.

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1. Introduction

Pectin is used in a number of foods as a gelling agent, thickener, texturizer, emulsifier and stabilizer [1]. The backbone of pectin molecules is composed of poly-α-(1 → 4)-D-galacturonic acid with carboxyl groups in the methyl ester form [2]. Although pectin can be found in many plant tissues, its main commercial production is conventionally based on apple pomace and citrus peel [3]. New sources of pectin are recommendable to explore in order to seek new technological functionalities and for contributing to the social and economic development of local producers. Hawthorn (*Crataegus* spp.) is a genus of fruit-bearing trees or shrubs distributed in North America, East Asia, Central Asia, and Europe, belonging to the Rosaceae family, which contains high amounts of pectin [4,5]. In the last decades, more effort has been put into exploring the properties of pectins from different sources since the consumer demand for natural food ingredients and emulsifiers has increased. The functional properties of pectins depend on the molecular weight (MW), degree of esterification, acetyl-esterification, source, and extraction method [6,7]. Thus, for pinpointing their potential applications, it is necessary to characterise their physicochemical properties. To our knowledge, studies on hawthorn pectins have been limited to elucidating their partial structural features and viscosity of the cold-water extracts [4]; the viscoelastic and textural properties of gels [8]; the soluble protopectin and pectin levels from hawthorn fruits at different ripening stages [9]; and the extraction optimisation and some physicochemical properties [5]. However, there are no studies regarding the interfacial adsorption of hawthorn pectins at the oil-water interface, and their ability to stabilise oil-in-water emulsions. When pectins, independently of their source, are destined to be used in emulsion stabilisation, it must be established if they possess surface activity, the ability to produce small oil droplet sizes and stabilise them against flocculation, coalescence and gravitational separation [10]. The application of pectins as emulsifiers is limited due to scant knowledge about their surface-active-molecular features [11]. It has been reported that citrus peel and apple pomace pectins are not effective emulsifying agents irrespective of their degree of esterification (DE) [12]. Other authors have reported that beet and citrus pectin were capable of stabilising oil-in-water emulsions, and that the small amount of protein associated to pectin played a key role [13]. The proteinaceous material adsorbs at the oil-water interface, and the oil droplets are sterically stabilised by the hydrophilic polysaccharide moieties protruding into the aqueous phase [14]. Additionally, acetyl within the galacturonic backbone and phenolic esters in the side chains have been shown to cause additional anchoring at the interface [15]. Depolymerised citrus pectin, with the MW of 70,000 Da and 70% DE, was capable to produce stable fine rapeseed oil-in-water emulsions. Only a small pectin fraction (25%) became associated with the oil droplets, and this contained most of the protein fraction present in the polysaccharide [16]. As only a small fraction of the pectin molecules adsorb at the interface, the remaining pectin

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molecules increase the continuous phase viscosity, and the tendency of the dispersed oil droplets to approach each other and coalesce is deterred [10]. Research about the interfacial characteristics of pectins, in our case of hawthorn pectins, in terms of molecular diffusion, penetration and configurational rearrangement of their adsorbed segments at oil-water interfaces and their relationship with their physicochemical properties may provide useful knowledge for the design of stable food grade emulsions. In this sense, it is important to compare the hawthorn pectin properties with those of commercial pectins such as citrus pectin, even when their physicochemical features are obviously different, in order to evaluate their commercial and technological potential [17]. In this regard, there are no systematic researches on the physicochemical characterisation of pectins from different hawthorn accessions and the relationship with emulsions stability.

The objectives of this work were to determine for two hawthorn pectin accessions the: (1) physicochemical properties and molecular weight; (2) rheological properties of aqueous solutions; (3) adsorption dynamics at the oil-water interface; (4) capability to form and stabilise oil-in-water emulsions; and (5) to compare the results with those obtained for a commercial citrus pectin.

2. Materials and methods

2.1. Materials

Hawthorn fruits (*Crataegus* spp.) of the accessions 50 (HP50) and 55 (HP55) were obtained from the Hawthorn germplasm bank of the Universidad Autonoma Chapingo (Texcoco, State of Mexico, Mexico). Pectin from citrus peel (CP; P9135 product number) was purchased from Sigma-Aldrich Mexico (Toluca, State of Mexico, Mexico). Canola oil (Alimentos Capullo, Mexico City, Mexico) was purified with Florisil (60–100 mesh, product number 46385, Sigma-Aldrich Mexico) and used as the oil phase of the emulsions. All the reagents used were analytical grade. The water used for all the experiments was double distilled and deionised.

2.2. Pectin extraction and purification

The pectin was extracted as follows: 100 g of hawthorn fruit pulp (75.4% moisture) were blended with 1 L of citric acid (4% w/v). The extraction was carried out at 85 °C for 60 min in a shaking water bath. The resulting extract was cooled to room temperature (20 ± 2 °C) and filtered through a Whatman No. 1 filter paper using a Buchner funnel which was connected to a vacuum pump. The filtrate was added with 96% ethanol in a 1:1 volume ratio, kept for 24 h at 5 °C, to allow pectin precipitation and to reach the equilibrium state [18]. The pectin was then separated by filtration through a Whatman No. 1 filter paper and washed twice with 70% ethanol in a 1:1 volume ratio for eliminating impurities. The mixture was centrifuged at 3300 ×g for 20 min at 20 °C using a Sorvall RC-5B centrifuge (GMI, Inc., Ramsay, MN, USA), and the supernatant was discarded. The pellet was dialysed in tubing having a pore size of 12,000 nominal MW cut-off (Spectra/Por 6 Dialysis Membrane, Spectrum Laboratories, Rancho Dominguez, CA, USA), against distilled water at 5 °C for 96 h, with changing of dialysing water twice a day [19]. The material remaining within the dialysis tubing was dried in an air-circulating oven (Memmert, Wisconsin Oven Distributors, Eagle, WI, USA) at 35 °C during 24 h. The dried pectin was ground with a pestle and mortar in order to obtain a fine powder. The fresh (Y_f) and dry basis (Y) pectin yields were calculated using Eqs. (1) and (2), respectively [18]:

$$Y_f(\%) = 100 \langle weight\ of\ dried\ pectin\ (g) | weight\ of\ fresh\ haw\ pulp\ (g) \rangle \tag{1}$$

$$Y(\%) = 100 \frac{Y_f}{(100 - moisture\ content\ of\ fresh\ haw\ pulp)}. \tag{2}$$

2.3. Pectin physicochemical characterisation

2.3.1. Analytical methods

The percentage of nitrogen in the pectin was determined by the Kjeldahl method using a Büchi system (Scrubber 412, Digestion unit 426 and Distillation unit K-314; Büchi Labortechnik AG, Flawil, Switzerland). The protein content was calculated using a conversion factor of 6.25. The moisture content was estimated by heating at 105 °C until constant weight was achieved. Ash content was estimated by heating (muffle furnace) at 550 °C until constant weight was achieved [20]. Galacturonic acid content was determined by the sulfamate/3-phenylphenol colourimetric assay [21], using D-galacturonic acid as standard (Sigma-Aldrich Mexico, Toluca, State of Mexico, Mexico). Phenolic content was analysed using Folin-Ciocalteu's reagent [22] and gallic acid as the standard (Sigma-Aldrich Mexico, Toluca, State of Mexico, Mexico). The content of total phenolics was expressed in μg gallic acid equivalents (GAE)/mg pectin.

2.3.2. Degree of esterification of the pectin

DE of the pectin was determined by a titrimetric method of Singthong et al. [23] with slight modifications. Pectin powder (500 mg) was moistened with 2 mL of ethanol and dissolved in 100 mL of carbon dioxide-free water. After the sample was completely dissolved, 5 drops of phenolphthalein were added, the sample was titrated with 0.5 M sodium hydroxide and the result was recorded as the initial titre. Then, 10 mL of 0.5 M sodium hydroxide were added, the sample was shaken vigorously, and allowed to stand for 15 min; 10 mL of 0.5 M hydrochloric acid were added and the sample was shaken until the pink colour disappeared. Phenolphthalein (5 drops) was added and the solution was titrated with 0.5 M sodium hydroxide to a faint pink colour that persisted after vigorous shaking (end-point). This volume of titration was recorded as the final titre. The DE was calculated from the following formula:

$$\%DE = [final\ titre/(initial\ titre + final\ titre)]\ x\ 100 \tag{3}$$

2.3.3. Methoxyl percentage

The methoxyl percentage (MeO%) was determined according to Zouambia et al. [24]. Since the amount of methoxyl in 100% of esterified pectin is 16.32%, the methoxyl percentage was calculated from the following equation:

$$MeO\% = \frac{16.32}{100}\ x\ DE \tag{4}$$

2.3.4. Average molecular weight of pectin

The average molecular weight of pectin (MW_{GPC}) was determined by gel permeation chromatography (GPC) procedure of Román-Guerrero et al. [25] with slight modifications. Pectin solutions (20 mg mL^{-1}, 0.15 M NaCl) were solubilised under magnetic stirring during 30 min at room temperature (20 ± 2 °C), let to stand for 24 h for achieving complete hydration, then filtered through a 0.45 μm membrane filter (Millipore Co., Milford, NH, USA), and manually injected (5 mL) through a packed column with gel Sephacryl S-500-HR (Amersham Pharmacia Biotech, Piscataway, NJ, USA) with an inner diameter of 2.54 cm and 88.5 cm length, coupled to a low-pressure liquid chromatography system (Biologic LP, Bio-Rad, Hercules, CA, USA). For eluent 0.15 M NaCl at a flow rate of 0.57 mL min^{-1} was used. Elution was monitored by UV absorption at 280 nm. The calibration curve was made using the following standards: blue dextran (2000 kDa), bovine thyroglobulin (669 kDa), bovine γ-globulin (158 kDa), chicken ovalbumin (44 kDa), horse myoglobin (17 kDa) and vitamin B12 (1.35 kDa) (Bio-Rad, Hercules, CA, USA).

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