



Rheological surface properties of commercial citrus pectins at different pH and concentration

Noemi Baldino, Olga Mileti, Francesca R. Lupi, Domenico Gabriele*

Department of Information, Modeling, Electronics and System Engineering, (D.I.M.E.S.) University of Calabria, Via P. Bucci, Cubo 39C, I-87036, Rende, CS, Italy

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ABSTRACT

The interfacial activity of commercial low-methoxy (LM) and high-methoxy (HM) pectins from citrus peel was investigated at air-water interfaces by focusing on the role of their molecular weight (MW) and degree of methoxylation (DM). A pendant drop tensiometer was used to carry out transient interfacial tension measurements and small amplitude oscillations. Different pectin concentrations (ranging between 0.00001 g/100 g and 5 g/100 g) and pH conditions (4 and 6) were used during the tests. It was observed that citrus pectins are characterised by interesting surface properties that could allow potential practical uses. Experimental results evidenced that MW affects the diffusion of molecules towards the interface, whereas other investigated parameters (i.e. surface tension, adsorption rate, dynamic moduli) seem more dependent on DM and a clear dependence on MW was not observed. pH conditions modify intermolecular interactions in the bulk and surface layer, even if their effects are related to the fraction and distribution of carboxylic groups along the chain. As a consequence, a complex dependence on investigated parameters was observed and no clear relationship was obtained. Nevertheless, among tested commercial samples LM pectins exhibited the most interesting properties and this behaviour seems related to the intermolecular interactions occurring among them.

1. Introduction

Pectin is a complex mixture of polysaccharides that consist mainly of galacturonic acid (GalA) (at least 65% according to the definition of “pectin” given by the Joint FAO/WHO Expert Committee on Food Additives (JECFA, 2009)) even if the fine structure of the single components can be significantly different (Willats, Knox, & Mikkelsen, 2006). Three main pectic polysaccharide domains are identified (Willats et al., 2006): Homogalacturonan (HG), where GalA units are covalently α (1 \rightarrow 4) linked to form a linear backbone; Rhamnogalacturonan I (RGI) consisting of the repeating disaccharide [\rightarrow 4]- α -D-GalA-(1 \rightarrow 2)- α -L-Rha-(1 \rightarrow) to which glycan units are connected to rhamnose component; Rhamnogalacturonan II (RGII) having a HG backbone where complex side chains are connected to GalA units.

The GalA units of the pectin chain are variously methylesterified and this significantly affects the structural properties of this biopolymer. As a consequence, the degree of methoxylation (or methylesterification, DM) is used to classify pectin into high-methoxyl (HM) pectins, containing more than 50% esterified carboxyl groups (DM > 50), and low-methoxyl (LM) pectins, with < 50% esterified carboxyl groups (DM < 50) (May, 1990).

Pectin is produced, at industrial level, by extraction from apple

pomace and citrus peels, even though other sources are available such as sugar beet and sunflowers head residues, cocoa husks, potato pulp, soy hull, etc. (Thakur, Singh, & Handa, 1997; Yancheva, Markova, Murdzheva, Vasileva, & Slavov, 2016).

It is mainly used for its gelling ability in the food industry in jams, fruit preparations, desserts and confectionery, and as a viscosity enhancer and stabilizer in beverages and, moreover, as a stabilizer of acid milk drinks and in dairy products (Dickinson, Semenova, Antipova, & Pelan, 1998; May, 1990; Schmidt, Schütz, & Schuchmann, 2017; Yancheva et al., 2016).

In fact, HM pectin can form a three-dimensional network through hydrogen bonds and hydrophobic interactions between the methyl-ester groups whereas LM pectin gelation occurs mainly thanks to ionic linkages with divalent ions (typically calcium ions) (de Cindio, Gabriele, & Lupi, 2016).

It is considered as a “safe” food ingredient, therefore there is no maximum acceptable daily intake and it is only recommended to use it at a level not higher than the necessary amount, according to good manufacturing practice (de Cindio et al., 2016). Moreover, pectin is a source of dietary fibre and therefore can be considered a healthy ingredient due to the ability to lower cholesterol as well as having several beneficial effects on the colon (Willats et al., 2006).

* Corresponding author.

E-mail address: domenico.gabriele@unical.it (D. Gabriele).

Even if the food use is probably the most important, it is worth noticing the growing use of this biopolymer also in different areas, such as pharmaceutical, cosmetic or biomedical products (de Cindio et al., 2016). Pectin was used as structuring agent of aqueous phase in emulgels and bigels for cosmetic use (Lupi et al., 2015, 2016); in nasal drug carriers as mucoadhesive polymer owing to hydrogen bonding with mucin; in oral drug delivery owing to its ability to be resistant to enzymes in the gastrointestinal tract and to be degraded by the intestinal microflora; in gels to be used as wound healing patches, etc. (for further detail see Munarin, Tanzi, and Petrini (2012)).

In addition to the “bulk” properties, recently, pectin interfacial properties has been studied with the aim of investigating their potential ability to modify the structure of interfacial layers (air/water or oil/water) and to be used as natural emulsifier (Alba & Kontogiorgos, 2017). It was observed that pectin displays emulsifying properties (Leroux, Langendorff, Schick, Vaishnav, & Mazoyer, 2003; Ngouémazong, Christiaens, Shpigelman, Van Loey, & Hendrickx, 2015; Schmidt et al., 2015) in addition to the well-known thickening effect of the dispersing water phase (which improves emulsion stability). Literature results evidenced interesting interfacial properties in sugar beet pectin (Leroux et al., 2003; Yapo, Robert, Etienne, Wathelet, & Paquot, 2007) and, more recently, in citrus pectin (Schmidt et al., 2015, 2017).

The origin of these properties is not very clear and it was attributed to different structural factors such as the acetyl content and protein fraction (particularly high in sugar beet pectin) (Leroux et al., 2003), low molecular weight (Akhtar, Dickinson, Mazoyer, & Langendorff, 2002; Yapo et al., 2007), degree of esterification (Akhtar et al., 2002), internal charge distribution (Lutz, Aserin, Wicker, & Garti, 2009), ferulic acid content (Alba & Kontogiorgos, 2017) etc.

It is worth noticing that also contradictory results have been obtained in a recent study by Schmidt et al. (2015). In fact, they did not observe a direct relationship between low molecular weight and emulsifying activities whereas they found a relevant influence of DM contradicting the findings of Akhtar et al. (2002) who observed only minor effects of this parameter.

Although further studies seem still necessary to better understand these effects, the oil/water interfacial effects of pectin have been widely investigated in recent years; on the contrary, few studies are available on the foaming ability and air/water interfacial properties of these polysaccharides.

Foam is a dispersion of a gaseous phase in a solid or liquid dispersing medium (Sadahira, Lopes, Rodrigues, & Netto, 2014). In the food industry, owing to the peculiar characteristics (mainly related to texture) given by aeration, foams are widely used; beer, bread, whipped cream, confectionery products, sorbets, are just a few examples of aerated foods from different areas (Campbell & Mougeot, 1999). Surface-active agents are necessary to make easier the aeration step and to improve foam stability (Rodríguez Patino et al., 2008). Among them, a mixture of proteins and polysaccharides are frequently adopted, although only few polysaccharides have proven to have a real (even if often limited) surface activity whereas often they only modify the protein surface layer properties (Baeza, Pilosof, Sanchez, & Rodríguez Patino, 2006; Rodríguez Patino et al., 2008).

According to recent studies (Gromer, Kirby, Gunning, & Morris, 2009; Liu et al., 2016; Perez, Sanchez, Patino, Rubiolo, & Santiago, 2011; Yancheva et al., 2016), it seems that pectin from different sources (sugar beet, soya hull, waste rose petals, citrus peels and apple pomace) exhibit interesting surface properties. Nevertheless, few data describing surface rheological properties are available, and less information is available when commercial products (i.e. not specifically modified) are considered (see for instance Perez et al. (2011)).

Although a quantitative correlation between interfacial properties and foam macroscopic characteristics is still not clear, it is known, at least from a qualitative point of view, that layer microstructure affects foam production and stability (Maldonado-Valderrama & Patino, 2010; Martin, Grolle, Bos, Stuart, & van Vliet, 2002). Starting from these

Table 1

Sample identification, degree of methylation (DM), molecular weight (MW), protein content, equilibrium surface pressure (π_{eq}) at pH 4 and pH 6 of pectins used. The same letters, for each parameter, identify the absence of statistically significant differences.

Pectin ID	DM (%)	MW (kDa)	Protein (g/100 g)	π_{eq} at pH 4 (mN·m)	π_{eq} at pH 6 (mN·m)
HM104	65.3	104	1.70 ± 0.1	23.4 ± 0.3 ^a	24.7 ± 0.5 ^d
HM145	65.1	145	1.50 ± 0.1	19.4 ± 0.5 ^b	25.1 ± 0.7 ^d
LM96	41	96	1.80 ± 0.1	28.0 ± 0.2 ^c	29.6 ± 0.1 ^e
LM123	42.9	123	1.90 ± 0.1	23.0 ± 0.8 ^a	26.2 ± 0.3 ^f

considerations, in the present work, four commercial citrus pectins, with different DM and molecular weight, were investigated at air/water interface using different pH and concentration with the aim of exploring their potential ability to build a viscoelastic layer.

2. Materials and methods

2.1. Materials

Four commercial citrus pectins (kindly supplied by Silvateam Food Ingredients srl, Italy) at high and low methylation degree are used in this work (Table 1).

Pectins were characterised through their degree of methoxylation and molecular weight.

DM was determined by the pectin producer (i.e. Silvateam Food Ingredients srl) according to the titration procedure recommended by JECFA (2009) and described in detail in Migliori, Gabriele, Checchetti, Facciolo, and Battipede (2011). The average viscometric molecular weight (MW) was determined using a viscometric method based on the relationship between MW and the intrinsic viscosity that, in turn, was estimated by measuring the viscosity of pectin solutions at different dilution rates; the procedure is described in detail by Lupi et al. (2015).

With the aim of investigating the potential effects of degree of methylesterification and molecular weight on interfacial behaviour, two HM samples (HM145 and HM104) with similar DM (65.1 and 65.3, respectively) and different average molecular weights were chosen. In the same way, two LM samples (LM123 and LM96) with similar DM (42.9 and 41, respectively) and molecular weights close to those of HM samples were used. It is worth noticing that commercial products were used in this work, therefore it was not possible to have an accurate control on molecular weight and only samples with “similar” values were individuated.

Pectin solutions were prepared by dissolving the proper amount of polysaccharide in a citrate buffer at the investigated pH (4 and 6), keeping constant the ionic strength (I) at 100 mM. These pH values were chosen because they are within the typical range of a number of food foams (e.g. mousses, ice creams, whipped creams, meringues, different types of dairy-based systems, etc.) where pectin could be used, alone or in combination with other agents such as protein.

The buffer was prepared with a twice-distilled water obtained from a Milli-Q purification system (Millipore, USA), and it was checked for contaminants before each experiment, measuring the surface tension of the buffer solution at the air/water interface at room temperature. All the reagents used were purchased from Sigma Aldrich.

Pectins were dispersed in the buffer solution at room temperature (22 ± 1 °C) stirring for 12 h by using a heating magnetic stirrer (AREX, Velp scientific, Italy), to promote the complete solubilisation of the polysaccharide in buffer. Afterwards the interfacial measurements were performed.

2.2. Total protein content in pectin

In order to assess the presence of protein residues, resulting from the extraction step of the pectin from the raw materials, a Bradford protein

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