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Emulsion stabilizing properties of citrus pectin and its interactions with conventional emulsifiers in oil-in-water emulsions

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ABSTRACT

The present work focused on the *(i)* physical characterization of the emulsion stabilizing potential of citrus pectin (CP) with different degree of methylesterification (DM; CP82, CP38 and CP10) and *(ii)* evaluation of interactions that occur between CP and conventional emulsifiers (Tween80 and phosphatidylcholine) used for emulsion stabilization.

Firstly, the emulsifying properties of different samples were studied by evaluating the electrical charge, hydrodynamic radius, adsorbed layer thickness and change in interfacial tension. The results showed that the pectin charge was strongly dependent on its DM and pH of the aqueous phase. For example, the hydrodynamic volume and adsorbed layer thickness of CP10 were larger compared to CP38 and CP82 at neutral pH due to the presence of more chargeable carboxylic groups. Moreover, it was quantitatively shown that CP is capable of reducing the interfacial tension of an oil droplet regardless its DM, evidencing its adsorption at the oil-water interfaces and surface active properties.

Secondly, the physicochemical stability of oil-in-water emulsions was evaluated during short-term storage at 4 °C. All pectin-emulsions showed the formation of a cream layer after one day. However, the nature and extent of this layer depended on the emulsion composition. All pectin single-emulsifier stabilized emulsions presented a cream layer most likely caused by bridging flocculation induced by the pectin structures. Contrastingly, depletion flocculation was observed in case of the multiple-emulsifier stabilized emulsions. In all cases, the destabilization phenomena observed were reversible as the particle size did not dramatically change over storage time, showing that CP has emulsion stabilizing potential.

1. Introduction

Oil-in-water (o/w) emulsions are interesting delivery systems of lipophilic bioactive compounds, such as vitamins and antioxidants (McClements, 2010). These emulsions are thermodynamically unstable systems, consisting of dispersed oil droplets in a continuous, aqueous phase. Emulsifiers are often added to kinetically stabilize o/w emulsions and the type being used depends on the desired product shelf life, stability and functionality. Most commonly used emulsifier types in food industry are small molecule surfactants, biopolymers and phospholipids (McClements, 2016b). Besides, there is an increasing interest for more natural ingredients from both costumer and industry sides (Alba & Kontogiorgos, 2017; McClements & Gumus, 2016). Several proteins, polysaccharides and phospholipids belong to this category of emulsifiers which can be extracted from natural resources. In the past, extensive research was already performed to investigate the emulsifying properties of different proteins (e.g. whey protein, β-lactoglobulin and caseinates) to stabilize o/w emulsions (Demetriades, Coupland, & McClements, 1997; Dickinson, 1994; Elizalde, Bartholomai, & Pilosof, 1996; Qian, Decker, Xiao, & McClements, 2012; Tokle & McClements, 2011). By contrast, only limited information is available regarding the emulsion stabilizing properties of certain polysaccharides and

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Abbreviations

CP	citrus pectin
CP82; CP38 or CP10	citrus pectin with a degree of methylesterification of 82%, 38% and 10%, respectively
CP82 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) citrus pectin with a degree of methylesterification of 82%
CP38 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) citrus pectin with a degree of methylesterification of 38%
CP10 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) citrus pectin with a degree of methylesterification of 10%
DB_{abs}	absolute degree of blockiness
DM	degree of methylesterification
GalA	galacturonic acid
HMP	high methylesterified pectin
LMP	low methylesterified pectin
MF	Melamine fluoride
MMP	medium methylesterified pectin
o/w emulsion	oil-in-water emulsion
PC	Phosphatidylcholine
PC emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) phosphatidylcholine
PCCP82 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) phosphatidylcholine and 1% (w/v) citrus pectin with a degree of methylesterification of 82%
PCCP38 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) phosphatidylcholine and 1% (w/v) citrus pectin with a degree of methylesterification of 38%
PCCP10 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 1% (w/v) phosphatidylcholine and 1% (w/v) citrus pectin with a degree of methylesterification of 10%
PME	pectin methylesterase
PS	polystyrene
TW	Tween 80
TW emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 0.5% (w/v) Tween 80
TWCP82 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 0.5% (w/v) Tween 80 and 1% (w/v) citrus pectin with a degree of methylesterification of 82%
TWCP38 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 0.5% (w/v) Tween 80 and 1% (w/v) citrus pectin with a degree of methylesterification of 38%
TWCP10 emulsion	5% (w/v) olive oil-in-water emulsion stabilized with 0.5% (w/v) Tween 80 and 1% (w/v) citrus pectin with a degree of methylesterification of 10%

phospholipids. In this context, pectin represents an interesting polysaccharide, naturally present in plants.

Pectin is a group of polysaccharides rich in galacturonic acid (GalA) units and predominantly located in the primary cell wall and middle lamella of higher plants (Willats, McCartney, Mackie, & Knox, 2001). Pectin can be extracted from several plant sources, but commercially available pectin sources are mainly citrus peel, apple pomace and sugar beet pulp (Chan, Choo, Young, & Loh, 2017). The variation in pectin structure and composition results in different functionalities of which its gel-forming capacity was extensively studied in the past (Fraeye et al., 2010; Lofgren, Guillotin, Evenbratt, Schols, & Hermansson, 2005; Ngouémazong et al., 2012). Recently, more attention is given to the emulsifying and emulsion-stabilizing properties of pectin. These emulsifying and emulsion-stabilizing properties are determined by both intrinsic (e.g. degree of methylesterification, protein content, acetyl groups and molecular weight) as well as extrinsic (e.g. pectin concentration, pH and ionic strength) factors (Alba & Kontogiorgos, 2017; Ngouémazong, Christiaens, Shpigelman, Van Loey, & Hendrickx, 2015). Pectin is a biopolymer used for its emulsion stabilization properties, because the addition of the polymer can lead to an increased viscosity of the aqueous phase of an o/w emulsion (Dickinson, 2003). In addition, it may confer negative charge ($pH > \sim 3.5$) in the surrounding areas of oil droplets due to its anionic nature, contributing to the electrostatic stability of o/w emulsions (Morris, Foster, & Harding, 2000). However, it has been recently suggested that pectin might actually act as a surface active emulsifier. In this context, although being a water-soluble polymer, pectin might have some slightly hydrophobic moieties (e.g. acetyl groups and methylesters) that provide pectin the ability to adsorb at the oil-water interface (Chen, Fu, & Luo, 2016; Kpodo et al., 2018; Schmidt, Schütz, & Schuchmann, 2017; Schmidt, Schmidt, Kurz, Endreß, & Schuchmann, 2015b). For example, commercially available citrus pectin with medium (55%) and high (70% and 84%) degree of methylesterification is able to create stable emulsions at low pH (pH 2–4) (Schmidt et al., 2017). Nevertheless, the exact mechanism and the actual adsorption capacity remains unrevealed as well as the possible interactions between pectin and conventional emulsifiers in o/w emulsions.

Therefore, the first part of this work focuses on exploring the emulsifying properties of citrus pectin with distinct degree of methylesterification at low and neutral pH. More specifically, several physical characteristics of the different pectin samples are evaluated: pectin charge, hydrodynamic diameter and adsorbed layer thickness. In addition, a dynamic interfacial tension evaluation was performed and is measured for both pure pectin solutions as well as for pectin in presence of a conventional emulsifier, namely Tween 80. This dynamic evaluation allows the determination of both the adsorption rate as well as the final emulsion surface tension value. In the second part, the emulsifying properties are evaluated during a short-term storage study using the different citrus pectin samples as single-emulsifier or in a multiple-emulsifier solution in which citrus pectin will be combined with a more conventional emulsifier, such as Tween 80 or phosphatidylcholine. It was hypothesized that possible interactions could occur in case of the multiple-emulsifier emulsions and therefore could influence the organization and stability of the emulsion. The overall results of this work lead to a proposed hypothesis on how pectin is organized in the different emulsions (pectin only, pectin combined with Tween 80 or pectin combined with phosphatidylcholine) at two distinct pH values, which was visualized by fluorescently labeling the pectin and corresponding microscopic images.

2. Material and methods

2.1. Materials

High methylesterified citrus pectin (HMP) was obtained from Sigma Aldrich (Diegem, Belgium) and used to prepare medium and low methylesterified citrus pectin (MMP and LMP, respectively). Orange carrots (*Daucus carota* cv. Nerac), kiwis (*Actinidia deliciosa* cv. Hayward) and olive oil were bought in a local shop. The carrots were peeled, cut into small pieces, frozen with liquid nitrogen and stored at −40 °C until extraction of pectin methylesterase (PME). The PME inhibitor was extracted from ripened kiwis. Melamine fluoride (MF) and polystyrene (PS) microspheres were purchased from microParticles GmbH (Berlin, Germany) and had an average diameter of 1.04 µm (± 0.03) and 1.05 µm (± 0.03), respectively. All analytical chemicals and reagents were purchased from Sigma Aldrich (Diegem, Belgium), VWR Chemicals (Leuven, Belgium) or Acros Organics (Geel, Belgium). Ultrapure water (organic free, 18.2 MΩ cm resistance) was used for all