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Polysaccharide gels as oil bulking agents: Technological and structural properties

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ABSTRACT

Lipid and polysaccharide interactions in various polysaccharide gels prepared for use as oil bulking agents were investigated using Raman spectroscopy. Two different polysaccharide gel matrices containing olive oil were prepared using mixed biopolymer systems of alginate with inulin (OM-A/I) or dextrin (OM-A/D). Stability and textural properties were also evaluated in these matrices. Thermal stability of the different matrices was optimal. The textural behaviour of polysaccharide matrices with olive oil incorporated differed depending on the polysaccharide gels used in their formulation. OM-A/I presented the highest ($P < 0.05$) hardness, adhesiveness, and chewiness. These matrices were stabilized by hydrogen bonding between oil carbonyl groups and water and/or carbohydrate molecules. Lipid acyl chains are relatively fixed through hydrogen bonding and intermolecular order upon micelle formation. Raman spectroscopic results also showed carbohydrate-water hydrogen bonding, in which inulin seemed to be more strongly bonded to water than dextrin. This difference in the structural behaviour of inulin and dextrin in terms of hydrogen bonding to water may explain the differences in textural properties.

1. Introduction

Improving the fat content of foods based on processing strategies (reformulation) is one of the most important current approaches to the development of potential functional foods, especially in the case of meat-based functional foods. Healthier lipid reformulation processes are generally based on replacement of the animal fat normally present in the product with another fat whose characteristics are more in line with health recommendations (Jiménez-Colmenero, 2007). A variety of non-meat fats of plant and marine origin have been used in product formulation (as non-meat ingredients) to partially replaces meat fats (mainly pork or beef). These oils have been incorporated in meat products in liquid and solid forms, encapsulated, or as oil-in-water emulsions (Jiménez-Colmenero, 2007). Strategies for incorporation of healthy oils in a gel-like matrix to form oil's bulking agent (in which this new ingredient acts as an animal fat replacer) could offer new possibilities for improving the fat content of meat products. Polysaccharides, used either individually or in combination, can be used to create a variety of gel structures which may be suitable for immobilizing oil droplets and thus to acting as oil's bulking agents. In this regard, healthy oils in a konjac matrix have been used to improve fat content in dry fermented sausage (Ruiz-Capillas, Triki, Herrero, Rodríguez-Salas, & Jiménez-Colmenero, 2012), fresh merguez sausages (Triki, Herrero, Jiménez-Colmenero, & Ruiz-Capillas, 2013) and frankfurters (Salcedo-Sandoval, Cofrades, Ruiz-Capillas, Solas, & Jiménez-Colmenero, 2013).

Alginate gels may offer interesting possibilities as oil bulking agents. Alginates are of particular interest for their ability to form gels in the presence of calcium salt (Roopa & Bhattacharya, 2010; Zhang, Daubert, & Foegeding, 2005). These gels consist of polymeric molecules cross-linked to form a three-dimensional macromolecular network containing a large fraction of water within their structure which displaying mechanical rigidity. The properties of the gel are the net result of the complex interactions between the components. One of the most important properties of alginate gels, which make them highly versatile, is their capacity for controlled uptake, release and retention of molecules. This capacity is due in turn, to specific interactions of the macromolecular network with the diffusing or retained molecule. In this connection, hydrocolloids as alginate, unlike emulsifiers, generally stabilize emulsions by increasing the viscosity, which inhibits the rate of coalescence between the oil droplets. This compound is adsorbed at the oil/water interface to form an interfacial film and sterically stabilize emulsions against flocculation and coalescence (Huang, Kakuda, & Cui, 2001). In addition to functioning as gelling agents, they also

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exhibit properties as emulsifiers, encapsulating agents, dispersing agents, foam stabilizers, film formers, and crystal inhibitors (Gaonkar, 1991). Alginate gel properties and their utility as oil bulking agents can be modulated by mixing with other biopolymers. Various researchers have investigated the properties of mixed biopolymer gelling systems for that purpose in some cases achieving substantial enhancements in gel strength (Evageliou, Tseliou Mandala, & Komaitis, 2010; Harrington & Morris, 2009; Zimeri & Kokini, 2003).

Inulin is a polysaccharide which offers interesting technological and health-beneficial properties. The technological properties are related to the degree of polymerization of its chains, making it suitable for use as a low-calorie sweetener, fat replacer or texturizing agent (Tungland & Meyer, 2002). The ability of inulin to form gels, and the physicochemical properties of these gels, have been addressed by numerous researchers (Bot, Erle, Vreeker, & Agterof, 2004; Kim, Faqih, & Wang, 2001; Zimeri & Kokini, 2002). Some authors have reported that inulin gels resemble solid fats in texture and may be used as fat mimetic (Bot et al., 2004). Increasing the amount of inulin can result in an increase in the gel strength of gellan (Evageliou et al., 2010).

Another polysaccharide of interest is dextrin, a low-molecular-weight glucose polymer resulting from partial hydrolysis of starch. Dextrin is a widely used material with a variety of applications, particularly in the food industry for adhesives, and also in other applications where it offers considerable potential for hydrogel production (Carvalho, Gonçalves, Gil, & Gama, 2007; Garcia, Barros, Gonçalves, Gama, & Gil, 2008).

The properties of these matrices with oil entrapped in polysaccharide gels are the net result of complex interactions among the components. Raman spectroscopy is a direct, non-invasive technique which has proven useful for providing structural information on the various components (lipids, polysaccharides, etc.) (Choi, Yuen, Phillips, & Ma, 2010; Dobson, 2001) involved in the preparation of these matrices. This spectroscopic technique has been used to identify selected seaweed polysaccharides (Pereira, Amado, Critchley, van de Velde, & Ribeiro-Claro, 2009) and the structural behaviour of oligosaccharides in water (Kačuráková & Mathlouthi, 1996). In particular, some authors have performed Raman spectroscopic analysis of alginate hydrogels (Dumitriu, Mitchell, & Vasile, 2011; Pielesz & Bąk, 2008). In addition, the technique has been used to investigate the conformational behaviour of lipid bilayer systems (dipalmitoylphosphatidylcholine) perturbed by cholesterol and water (Bush, Adams, & Levin, 1980). By means of Raman spectral frequencies and intensities it is possible both to monitor intramolecular changes occurring within the three structurally distinct regions of the phospholipid molecule and to follow alterations in lattice order and packing characteristics. The acyl chain mobilities of bovine milk fat globule lipids and component triglycerides have also been determined by Raman spectroscopy as a function of temperature. This study showed that the CH stretching region is the most useful for lipid chain order analysis (Forrest, 1978). Also, Raman spectroscopy has proven the role of proteins and lipids in emulsion formation (Howell, Henryk, & Li-Chan, 2001; Meng, Chan, Rousseau, & Li-Chan, 2005). Moreover, Raman spectroscopy has been used to characterize the development of polymeric matrices based on chitosan/cashew gum for encapsulation of a natural essential oil (Abreu, Oliveira, Paula, & de Paula, 2012). These findings speak to the feasibility or the potential of this technique as a means to elucidate interactions between the components of matrices of oil molecules involved in polysaccharide gels.

The aim of the present study was to develop olive oil bulking agents using mixed biopolymer systems of alginate with inulin or dextrin with optimal characteristics for use as animal fat replacers in the development of healthier meat products. Two main aspects of these agents were considered: their technological characteristics, since these affect quality properties of the reformulated products in which they will be incorporated; and the other structural characteristics of the system and interactions between their components, in order to establish causal relationships between their structural and technological properties.

2. Materials and methods

2.1. Materials

Ingredients used for preparation of polysaccharide gels as oil's bulking agents included: olive oil (13% SFA, 79% MUFA and 8% PUFA) (Carbonell Virgen Extra, SOS Cuétara SA, Madrid, Spain); sodium alginate (SA) (90% carbohydrates content) (Tradissimo, TRADES S.A., Barcelona Spain); calcium sulfate (CS) (Panreac Química, S.A. Madrid, Spain), tetra-sodium pyrophosphate anhydrous PRS (SP) (Panreac Química, S.A. Madrid, Spain), inulin (I) consisting mainly of chicory inulin (>90% inulin) (TRADES S.A., Barcelona Spain) and white maize dextrin (D) (CARGILL S.L.U- CTS Rubi, Barcelona, Spain).

2.2. Preparation of olive oil bulking matrices based on polysaccharide gels

Different concentrations and combinations of inulin, dextrin, and alginate and olive oil were assayed to determine the best conditions, from a technological standpoint (optimal fat content more in line with health recommendations, without loss of exudate and with a suitable texture for cutting, grinding, etc.), for production of an oil bulking agent that could use as fat replacer (Delgado-Pando, Cofrades, Ruiz-Capillas, Solas, & Jiménez Colmenero, 2010; Herrero, Carmona, Pintado, Jiménez-Colmenero, & Ruíz-Capillas, 2011a, 2011b; Jiménez-Colmenero et al., 2012; Jiménez-Colmenero, Herrero, Pintado, Solas, & Ruiz-Capillas, 2010). Table 1 show the concentrations and combinations of inulin, dextrin, alginate and olive oil assayed. Among them, we chosen OM-A/D and OM-A/I due to they showed the highest content of olive oil, which could provide adequate intake levels, and textural properties (Table 1). It is reasonable to assume that OM-A/D and OM-A/I could be used as animal fat replacer. These matrices were prepared by mixing sodium alginate (1%), $CaSO_4$ (1%), sodium pyrophosphate (0.75%) and dextrin (2.25%) or inulin (2.25%) with water (40%) in a homogenizer (Thermomix TM 31, Vorwerk España M.S.L., S.C, Madrid) to obtaining OM-A/D and OM-A/I matrices respectively. Ca^{2+}-salt and sodium pyrophosphate were used in order to slow the gelling procedure (Weiss, Scherze, & Muschiolik, 2005). The mixtures were prepared at 1500 rpm for 20 s. Olive oil was gradually added to this mixture with the homogenizer in operation (1500 rpm). Each type of sample was stuffed into metal moulds (similar to moulds used for cooked ham) of 2 kg capacity under pressure (which is apply manual as the maximum to permit the moulds employed) to compact them and prevent air bubbles, and stored in a chilling room at 3 °C for 24 h until analysis. Each matrix was prepared in duplicate.

Technological properties, except penetration test, and structural characteristics were determined only in OM-A/D and OM-A/I because these samples showed the highest olive oil content and penetration force values, which indicate that they could be used as fat replacer. The oil content (55%) in this oil bulking agents seems appropriate for use as fat replacer for example in a meat product, which provided adequate intake levels of olive oil.

The same mixtures of polysaccharide in aqueous solution (without added olive oil) were prepared for use as references for