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Influence of a cationic polysaccharide on starch functionality

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ABSTRACT

Fundamental rheology, differential scanning calorimetry and infrared spectroscopy have been used to evaluate the effect of a cationic polysaccharide, chitosan, on the gelatinization, gel formation and retrogradation of maize starch samples, under acidic aqueous conditions. Moderate acidic conditions (0.1 mol L^{-1} acetic acid) have shown a (slight) positive effect on starch gelatinization process and structure development. The presence of chitosan increased the DSC onset gelatinization temperature and also shifted the onset of the storage modulus increase to higher temperatures.

Formation of the starch gel, mainly gelation of the leached-out amylose, is somehow hindered by the presence of the cationic polysaccharide and, therefore, the retrogradation of starch at very early stage can be delayed by addition of chitosan. However, long-term retrogradation was slightly increased. FTIR pectroscopy did not reveal any significant interaction between both polysaccharides what is in accordance with the observed rheological behavior. Small additions of chitosan to starch-rich systems may be a useful strategy to obtain new textures with novel phase transition behaviors.

1. Introduction

Food systems are well recognized as multicomponent soft materials (van der Sman, 2012) whose properties and consumer acceptance are largely dependent on the interactions between the macromolecular components. Tailor-making these interactions is also an advantageous strategy to optimize food formulation and to design products with desired structure or novel textures (Dickinson, 2006).

Due to its abundance, low cost, renewability and functional versatility, starch is widely used in food industry as a thickener, stabilizer and gelling agent, to alter favorably the organoleptic properties of food formulations, or as a processing aid. Not surprisingly, many studies have been done concerning the effects of other polysaccharides on pasting properties, gelatinization and retrogradation of starch (Appelqvist & Debet, 1997; BeMiller, 2011; Elgadir et al., 2012). Nevertheless, the mixture between different biopolymers and the resulting new functionalities are still an open field of research, especially under less common conditions that may find specific useful applications.

Chitosan is a cationic polysaccharide formed by a linear chain of D-glucosamine and *N*-acetyl-D-glucosamine residues linked by β-(1-4) bonds. Chitosan is a versatile functional biopolymer, naturally abundant, biocompatible and biodegradable, exhibits interesting antimicrobial and haemostatic properties (Kumar, 2000). This polysaccharide becomes positively charged in acidic media due to the protonation of its amino groups, and exhibites peculiar properties when compared to most of food polysaccharides, typically neutral or anionic. Although being widely applied in different areas, chitosan is not extensively used as a food additive, what probably explains the few reports of its effect on starch pastes or gels.

In fact, most studies performed for starch-chitosan mixtures concerned the preparation and properties of chitosan/starch composite films (e.g. Bonilla, Atarés, Vargas, & Chiralt, 2013; Liu, Adhikari, Qipeng, & Adhikari, 2013; Xu, Kim, Hanna, & Nag, 2005). Although they are quite scarce, studies involving mixed systems of chitosan and starch under high water contents, namely related to the study of rheological and thermal properties of mixed pastes and/or gels, have been recently described. Yet most of the work done involved not native but modified starch samples, namely oxidized starches, exploring more specific interactions/crosslinks that might occur with the cationic polysaccharide (Horn, Martins, & Plepis, 2011; Serrero et al., 2010). Xu et al. (2012) have shown that chitosan caused a general increase in starch pasting viscosity only for concentrations above 3%, showed minimal effects on amylose leaching and no particular association with starch components. In this study, the pasting behavior of starch dispersions was characterized following the classical approach, i.e. measuring viscosity under shear and during suitable ramp temperatures (heating and

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cooling). Under these conditions obviously shear will be an important variable to be considered. In the particular case of the starch granules, the presence of a polysaccharide in the bulk or on the granule surface might have a stabilizing effect against shear forces (Appelqvist & Debet, 1997; Shi & BeMiller, 2002). One may also expect that rate and extension of any phase separation process and the final structural organization of the multicomponent system will be dependent on shear (Wolf, Scirocco, Frith, & Norton, 2000).

Despite the large number of work related to mixtures of starch with other hydrocolloids, it is still difficult to predict what results will be obtained due to the large number of variables involved, thereby limiting the applicability of this strategy. In fact there is a gap in scientific research concerning the effect of chitosan on starch gel formation, with emphasis on its main functional properties.

In this context, we have studied the influence of chitosan on the gelatinization and retrogradation of starch, under acidic conditions. The main purpose was to characterize the influence of chitosan on starch functionality under unperturbed conditions through small-amplitude dynamic rheological tests and thermal analysis, and under acidic conditions. Our hypothesis is that beneficial interactions between chitosan, a cationic polyelectrolyte with well-known bioactive properties, and the starch components may develop, allowing to obtain novel functionalities with usefulness in particular food-related applications – development of innovative acidic starch-based products without the need to use chemically modified starches.

2. Materials and methods

2.1. Materials

Two maize starch samples were used in this work: (1) A commercial maize starch (CS) (Maizena®, Unilever Jerónimo Martins Lda, Portugal), and (2) a maize starch sample isolated at the laboratory (LS), obtained from a Brazilian maize landrace and characterized as previously described (Raguzzoni, Lopes da Silva, Maraschin, & Delgadillo, 2013) (see Table S1, Supplementary material, for some characteristics of these starch samples).

Chitosan sample (degree of acetylation of 18%, viscosimetric-molecular weight of 7.8×10^4), obtained from shrimp shells, was purchased from Sigma-Aldrich (St. Louis, MO, USA), purified and characterized as previously described (Santos, Seabra, Veleirinho, Delgadillo, & Lopes da Silva, 2006). All other chemicals were reagent grade and were also purchased from Sigma-Aldrich Co. (St. Louis, MO, USA).

2.2. Preparation of the mixed dispersions

Chitosan solutions were prepared in 0.1 mol L^{-1} acetic acid, by dispersion of the chitosan powder overnight under moderate stirring and then centrifuged (10,000*g*, 10 min). Starch was also dispersed in 0.1 mol L^{-1} acetic acid, by moderate stirring during 2 h at room temperature. Starch dispersions were also prepared in water and in 1 mol L^{-1} acetic acid to evaluate the effect of pH/acid on the observed rheological behavior under heating and cooling. Chitosan and starch dispersions were mixed in appropriate ratios to reach the desired concentrations of each biopolymer (constant starch concentration (20 wt.%), chitosan between 0.1 and 2 wt.% (dry weight basis)), under low controlled stirring (2 h, under vacuum). Blended dispersions were then used for the rheological and DSC measurements or frozen and freeze-dried for further spectroscopic analysis.

2.3. Rheological measurements

Oscillatory shear rheological tests within the linear viscoelastic region were performed using a controlled-stress rheometer (CVO 120HR, Bohlin), fitted with a roughish plate–plate geometry (diameter 40 mm, gap 1 mm). The temperature of the bottom plate was controlled with a Peltier system. Each mixture prepared as described above (Section 2.2) was then transferred to the rheometer measuring device. The water loss was minimized by placing a low viscosity mineral oil (d = 0.84 g/mL, Sigma-Aldrich Quimica SA, Portugal) on the exposed edge of the sample. Gelatinization was allowed to occur *in situ* on the rheometer measuring device, while performing a temperature sweep experiments at 1 °C/min, 2 rad/s constant frequency, and 1% strain amplitude. Experiments were done by heating the sample from 40 °C to 90 °C, held at 90 °C for 10 min, then cooled back to 20 °C at the same rate. After cooling, the viscoelastic behavior of the gels was evaluated by frequency sweeps at constant temperature (20 °C), and structure development was assessed by time sweep experiments (20 °C, 2 rad/s, 1% strain).

2.4. Thermal analysis

The effect of chitosan on the gelatinization and retrogradation of starch was studied by thermal analysis using a Power Compensation Perkin-Elmer Diamond DSC, calibrated using indium. Aliquots of ~20 mg of the starch or starch/chitosan dispersions, prepared as described above (§ 2.2), were accurately weighed into aluminium pans and hermetically sealed. For the gelatinization analysis, thermograms were acquired during heating at a rate of 10 °C/min from 20 to 90 °C. For the retrogradation studies, the samples were stored at 4 °C and reheated after 7, 14 and 40 days. An empty pan was used as a reference and nitrogen was used as purge gas at a flow rate of 40 mL/min. The thermal transitions were characterized by the onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization, and the gelatinization enthalpy (ΔH_{gel}), obtained from the gelatinization DSC endotherm, using the equipment software. The gelatinization temperature range (R_{gel}) was calculated as $2(T_p - T_o)$ and the percentage of retrogradation was calculated as the ratio $\Delta H_{ret}/\Delta H_{gel}$ x 100 (Sandhu, Singh, & Lim, 2007), where (ΔH_{ret}) denotes for the retrogradation enthalpy.

2.5. MID- infrared spectroscopy (MIR)

The IR spectra were acquired for the freeze-dried samples (before and after gelatinization into the rheometer) over the range of 4000–600 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer (Bruker, model IFS55), equipped with a 'Golden Gate' attenuated total reflection (ATR) accessory (single reflection). Spectra were recorded with a resolution of 4 cm^{-1} and averaged over 128 scans.

2.6. Statistical analysis

A one-way ANOVA was used to test for any significant difference between samples on each independent variable under study. A Tukey's *post hoc* test was performed to test for specific statistical significance among data means. Significant differences were defined as $p \leq 0.05$. Unless otherwise stated, data are presented as mean and standard deviation of triplicate analyses.

3. Results and discussion

3.1. Chitosan effects on starch gelatinization and gel formation

First, the effect of the acidic conditions on the rheological behavior of the starch dispersions was analyzed, considering that the