



Effect of high-pressure treatment on the structural and rheological properties of resistant corn starch/locust bean gum mixtures



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ABSTRACT

In this study, effects of a 30 min high pressure (HP) treatment (200–600 MPa) at room temperature on the rheological, thermal and morphological properties of resistant corn starch (RS) (5% w/w) and locust bean gum (LBG) (0.25, 0.50 and 1.0% w/v) dispersions were evaluated. Results showed that the storage modulus (G'), loss modulus (G''), and apparent viscosity values of starch/gum (RS/LBG) mixtures were enhanced with an increase pressure level, and demonstrated a bi-phasic behavior. HP treated RS/LBG samples were predominantly either solid like ($G' > G''$) or viscous ($G'' > G'$), depending on the pressure level and LBG concentrations. Differential scanning calorimetry (DSC) analysis of the pressurized mixtures showed a major effect on gelatinization temperatures (T_o , T_p), and it was observed that RS/LBG mixtures gelatinized completely at ≥ 400 MPa with a 30 min holding time. Confocal laser scanning microscopy (CLSM) images confirmed that at 600 MPa, RS/LBG mixtures retained granular structures and their complete disintegration was not observed even at the endpoint of the gelatinization.

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1. Introduction

Starch/hydrocolloid mixtures are frequently used in the food industry as they impart better quality and stability to the final products. Starches, in their native form, often do not exhibit properties prerequisite for a specific application. (Zhu, 2015). Native starches are often chemically modified and/or blended with other components such as hydrocolloids (e.g. guar gum, corn fiber gum, hydroxypropylmethylcellulose (HPMC), xanthan gum) to impart desirable and amending properties for improving product texture and rheology (Qiu et al., 2015; Rosell, Yokoyama, & Shoemaker, 2011), enhancing cold-storage and freeze-thaw stability (BeMiller, 2011), moisture retention (Kohajdová & Karovičová, 2009), syneresis (Yamazaki et al., 2013), and resistance to various physical changes during processing (heat, shear, and acidic medium), retrogradation and breakdown.

Locust bean gum (LBG), also known as Carob gum is a natural hydrocolloid, which has been used in numerous industrial applications (food, cosmetic, textile, pharmaceutical, paint, milling and construction industries) because of its ability to produce highly viscous solutions at relatively low concentrations ($\leq 0.02\%$) to stabilize

emulsions and as a fat replacement (Barak & Mudgil, 2014). In food industry, LBG alone or in combination with other hydrocolloids (e.g. carrageenan, xanthan gum) is widely used in beverages (Dogan, Toker, & Goksel, 2011), bakery products (Kohajdová, Karovičová, & Schmidt, 2009), noodles (Silva, Birkenhake, Scholten, Sagis, & van der Linden, 2013), ice cream (Cropper, Kocaoglu-Vurma, Tharp, & Harper, 2013), low-fat yoghurt (Ünal, Metin, & Işikli, 2003) and as edible coatings (Martins et al., 2012).

Corn starch is also used in many food applications for its desirable rheological properties (Amini, Razavi, & Mortazavi, 2015). Further, starch and its derivatives can be classified on the basis of their digestibility as “rapidly digested starch” (RDS), “slowly digested starch” (SDS) and “resistant starch” (RS) (Englyst, Kingman, & Cummings, 1992). RS is classified into five groups on the basis of its structure and properties: RS I – physically inaccessible starch; RS II – native granular starch; RS III – retrograded starch; RS IV – chemically-modified starch and RS V – amylose-lipid complex (Vamadevan & Bertoft, 2015). RS has been primarily used as a functional ingredient to improve the quality and dietary fiber content (Öztürk & Köksel, 2014) of low-moisture foods such as bakery products (bread and muffins), pasta products, and in breakfast cereals and snacks (Fuentes-Zaragoza, Riquelme-Navarrete, Sánchez-Zapata, & Pérez-Álvarez, 2010). Additionally, being a dietary fibre, it plays several physiological functions against colonic carcinogenesis and reducing the risk of diabetes, obesity,

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high cholesterol and other chronic diseases (Choi, Lee, Cho, Choi, & Moon, 2010).

Several studies have reported that the influence of hydrocolloids on corn starch is dependent on the structure and concentration of the hydrocolloid (Funami et al., 2008; Qiu et al., 2015). The interaction between starch and hydrocolloid is also reported to be dependent on the starch source, differences in granule size (Amini et al., 2015) and crystalline microstructure (Techawipharat, Supphantharika, & BeMiller, 2008). In order to take advantage of starch/gum interactions and enhance their applications in food formulations, it is important to assess the influence of different physical and chemical processes, such as heat, high pressure (HP) and/or enzymatic treatments, on their functional and physico-chemical properties (Li, Bai, Mousaa, Zhang, & Shen, 2012). The majority of earlier reports are focused mainly on the nutritional, functional and digestibility characteristics of resistant starches, while the use of resistant starches in food formulations often involve noticeable presence of other hydrocolloids (gums). Therefore, understanding the interactions between RS and gums are of considerable interest.

High pressure-processing (HPP) is a non-thermal processing technology used in the food industry for preparing products with high functional (Ramaswamy, Singh, & Sharma, 2015), nutritional (Ramaswamy, Chen, & Rattan, 2015) and textural (Alvarez, Ramaswamy, & Ismail, 2008) qualities. Over the last two decades, the influence of HP treatment (i.e. pressure level, treatment time, starch source, concentration, temperature, etc.) on starch gelatinization in general (Ahmed, Ramaswamy, Ayad, Alli, & Alvarez, 2007; Ahmed, Varshney, & Ramaswamy, 2009; Liu, Selomulyo, & Zhou, 2008; Oh, Hemar, Anema, Wong, & Neil Pinder, 2008; Oh, Pinder, Hemar, Anema, & Wong, 2008; Stolt, Oinonen, & Autio, 2000) or more specifically on gelatinization of corn starch (Ahmed, Singh, Ramaswamy, Pandey, & Raghavan, 2014; Błaszczak et al., 2007; Buckow, Heinz, & Knorr, 2007) has been widely investigated. The above studies have been focused on understanding the mechanism of pressure-induced gelatinization and its influence on physicochemical and structural properties of starches. HP treatment has been shown to influence mostly the non-covalent bonds in starches, so this treatment can cause major structural, textural, sensory and nutritional damages (Balny, 2002).

In a recent review covering over fifty studies (BeMiller, 2011), a few have focused on the effect of LBG on different starches but none have included HPP. To the best of our knowledge, there has been no study on the effect of HP treatment on starch/LBG mixtures to date. With this background, the aim of this experimental study was to evaluate the effect of HP treatment on the rheological, calorimetric (gelatinization) and morphological properties of starch-LBG mixtures. From an industrial point of view, this research is significant because of the dearth of basic data on the dynamics of interactions between LBG and RS treated with HP which will be useful in the development of RS-gum based food products.

2. Materials and methods

2.1. Materials

Commercial grade chemically modified resistant starch with average particle size 10–15 μm (Hi Maize 260 corn starch termed as RS) (National Starch and Chemical Co., NJ, USA) was used in the study. The proximate composition of the starch was: moisture content, $10.8 \pm 0.1\%$; ash content, $<0.4\%$; fat content, $<0.8\%$; and protein content, 0.8% (all on dry basis), as provided by the manufacturer. In order to verify moisture content of the starch sample, RS samples were dried (in duplicate) in an oven at 130°C to constant weight. The evaluated moisture content was within 1% of the supplier

data. Laboratory food-grade LBG (galactomannan polysaccharide 100 K0220) was from Sigma Chemicals (St. Louis, USA).

2.2. Preparation of starch and starch/LBG dispersions

Aqueous 5% dispersion of RS was prepared by dispersing 5 g of starch to 95 g deionized water at room temperature. LBG powder was dispersed in deionized water at 0.25, 0.50 and 1% (w/w). Both dispersions were prepared with constant stirring overnight on a magnetic stirrer (400 rpm) to achieve complete hydration. Starch/gum dispersion mixtures were prepared by gradually adding 5% (w/w) RS powder into fully-hydrated gum solutions to achieve samples with the required concentrations of starch/LBG dispersions. The final dispersions were stirred for 2 h, and immediately prepared for HP treatments.

2.3. High pressure treatment

Prepared starch/gum dispersion samples were sealed (approx. 20 mL) in low density polyethylene bags (Whirl Pak®, Nasco, Fort Atkinson, WI, USA) and treated by HP at 200, 400 or 600 MPa for 30 min in a 5 L static HP unit (ACIP 6500/5/12VB; ACB Pressure Systems, Nantes, France) equipped with temperature and pressure regulators. The pressurization and depressurization rates were maintained at 4.4 MPa/s and 26 MPa/s, respectively. The initial temperature of pressure transmission medium (water) was around 18°C , which increased to $23\text{--}30^\circ\text{C}$ up on pressurization to 200–600 MPa due to adiabatic compression. The adiabatic temperature rise is expected to be about 3°C per 100 MPa increase. The final processing temperature became steady between 22 and 25°C during the treatment time because the pressure vessel was operated at room temperature. Each experiment was carried out in triplicate.

2.4. Rheological measurements

2.4.1. Dynamic rheology measurements

Oscillatory rheology measurements of HP treated starch/LBG dispersions were made using a controlled-stress rheometer (AR 2000, TA Instruments, New Castle, DE, USA). A cone plate geometry was used with a diameter of 60 mm and a cone angle of 2° . The gap between the base plate and geometry was set at $64\ \mu\text{m}$. The sample temperature (25°C) was controlled by a Peltier system and monitored by platinum resistance thermometer sensors (accuracy $\pm 0.1^\circ\text{C}$), which were positioned both in the upper and lower plates. The sample perimeter was covered with a thin layer of high-temperature-resistant silicone oil to prevent sample dehydration. Small-amplitude oscillatory strain sweep experiments (0.001–10%) were carried out, and elastic (G') and viscous (G'') shear moduli, at a constant frequency of 0.1 Hz were measured to determine the limit of the linear viscoelastic region (LVR) (Ahmed et al., 2014). The LVR determination was carried out for the entire range (2–5 Pa depending on gel stiffness), and measurements were carried out accordingly. Frequency sweep tests (0.01–25 Hz) were carried out in the linear regime, at constant strain (0.05%) at 25°C (Ahmed et al., 2014). All the rheological measurements were carried out in triplicate and rheological parameters (G' , G'') were obtained directly from the manufacturer supplied computer software (Rheology Advantage software, TA Instruments, New Castle, DE, USA).

2.4.2. Steady flow measurements

Steady flow measurements (shear stress, shear rate, apparent viscosity) made over a shear rate range from 0.1 to $100\ \text{s}^{-1}$ at 25°C in triplicate. Flow curves of HP – treated dispersions at 25°C was modeled using Rheology Advantage software, TA Instruments, New Castle, DE, USA. The Power Law model, represented by the following

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