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Rheometric non-isothermal gelatinization kinetics of high hydrostatic pressure treated chickpea flour slurry

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ABSTRACT

The effect of high hydrostatic pressure (HHP) as a function of treatment pressure (200, 400, 600 MPa), temperature at pressurization (10, 25, 50 °C), and treatment time (5, 15, 25 min) on the subsequent temperature-induced gelatinization of chickpea flour (CF) slurry during non-isothermal heating from 25 to 95 °C was investigated. Temperature-induced gelatinization was sensitive to the changes in pressure, temperature, and time during HHP pre-treatment. During heating, CF gelatinization kinetics from the cross-over of elastic modulus (G') and viscous modulus (G'') to 95 °C were considered for rate estimation. Zero-order reaction kinetics adequately described the CF gelatinization process. Structure development rate (dG'/dt) is described by two exponential functions with activation energies ranging from 51.2 to 577 and −129 to 539 kJ mol^{-1} for downward and upward gelatinization curves, respectively. Changes in dG'/dt vs. temperature seem to be closely related to the degree of gelatinization induced by HHP pre-treatment.

1. Introduction

Starch gelatinizes in a wide range of temperature in the presence of a sufficient amount of water, and thermal starch gelatinization at atmospheric pressure can start at anywhere between 55 and 80 °C (Ahmed, 2012; Stolt et al., 2001). Gelatinization – a thermal transition of hydrated starch – is an important phenomenon for cereal and legume starches and flours. This process disrupts the structure of the starch granules and causes swelling up to several times their original size. HHP treatment of starch in the presence of water can also induce its gelatinization (Bauer and Knorr, 2005; Oh et al., 2008a; Stute et al., 1996; Vallons and Arendt, 2009a, 2009b). However, when heating a barley starch suspension subjected to a pressure higher than 200 MPa, gelatinization takes place at a lower temperature range than when heating at atmospheric pressure (Stolt et al., 2001). In turn, a pressure above 400 MPa at excess water is e.g. not sufficient for potato starch gelatinization but shows effects for wheat starch (Stute et al., 1996). All the factors such as pressure, temperature at pressurization, treatment time, starch type, and other major components (protein and fiber) interact and contribute to the effect of pressure-induced gelatinization of starch. There are also significant differences in the structural and rheological properties between heated and pressurized starches (Vallons et al., 2014).

In addition to starch, CF slurries contain a relatively large amount of protein, which could give a second endothermic peak on heating in water (Meares et al., 2004). Ahmed et al. (2007) studied the effect of HHP treatment of basmati rice flour slurries and found both gelatinization of starch and denaturation of proteins. In turn, Ahmed et al. (2009) studied the thermal characteristics of HHP-treated lentil flour slurries at selected moisture levels and found no starch gelatinization peak during thermal scanning. In contrast, the protein denaturation temperature shifted with applied pressure. It was also assumed that gluten inhibited HHP-induced starch gelatinization, explaining the lower paste consistency of the wheat flour suspensions compared with the isolated starch (Vallons et al., 2010).

Gelatinization kinetics of starch has been studied extensively by different techniques. Most of the researchers have used differential scanning calorimetry (DSC) for the study where the degree of gelatinization is directly measured from gelatinization enthalpy (Ahmed et al., 2008). Other authors used either DSC or rheology to analyze the pressure-induced gelatinization process of sorghum

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and buckwheat starches, and to compare them to the effect of temperature (Vallons and Arendt, 2009a,b). Poor correlation coefficients between gelatinization temperatures determined by DSC and rheology were found, which was explained by the different properties measured with the two methods. While a differential scanning calorimeter measures gelatinization as melting of starch crystals, the rheometer measures gelatinization as an increase in viscosity. In turn, Ahmed (2012) stated that DSC measurement could not able to detect gelatinization temperature for all studied specimen and the endotherm depends upon starch to water ratio and some other factors. According to the author just cited, rheometric measurement (small amplitude oscillation shear (SAOS) measurement) has advantages over DSC and can successfully detect the gelatinization temperature in addition to the gel point during non-isothermal heating and provide reliable information on gelatinization reaction kinetics. Limited information is available on dynamic rheology to characterize the gelatinization process especially non-isothermal studies (Ahmed, 2012; Alvarez et al., 2014a; Yoon et al., 2004). In this work, rheometric measurement of pressurized CF slurries is focused to obtain the temperature induced gelatinization reaction kinetics which are limited in the literature.

Little information is in addition available concerning the impact of pressure on whole flour systems. Screening for variation in starch properties using flour, however, is difficult because of the presence of other seed components, in particular protein, lipid and fiber (Meares et al., 2004). It was observed that pressure combined with thermal treatment resulted in a significant reduction in CF paste rigidity as compared with unpressurized samples (Alvarez et al., 2014b). Elasticity of pressurized CF slurry increased significantly with increasing pressure applied in proportion with the extent of HHP-induced gelatinization of starch. Consequently, weaker pastes are formed in the subsequent heating process, because there is an increase in the amount of starch pre-gelatinized by pressure and pastes are formed solely by melting of the crystallites that still remain. The handling of CF pastes in terms of sheeting, flattening, rolling, and taking form is difficult due to the absence of gluten forming proteins. Therefore, a suitable selection of HHP treatment at appropriate levels can produce chickpea pastes that possess the desirable handling and machinability properties leading to preparation of products.

The objective of this work was to evaluate the combined effects of treatment pressure (0.1, 200, 400, and 600 MPa), temperature at pressurization (10, 25, and 50 °C), and treatment time (5, 15, and 25 min) on the subsequent temperature-induced gelatinization of CF slurry, with a view to providing information that can be translated to develop CF-based food products. Unpressurized and HHP-treated CF slurries at the different combinations were then pasted under non-isothermal (from 25 up to 95 °C) heating conditions and the kinetics of CF gelatinization were established by an oscillatory rheological approach.

2. Materials and methods

2.1. Materials

Spanish chickpea (*Cicer arietinum* 'Castellano') flour was a commercially available product donated by the Los Pisones flour milling company (Zamora, Spain). CF was supplied packed in polyethylene pouches (500 g) and was stored in watertight containers (10 °C and 73 ± 3% relative humidity) until use. Mean values for proximate analysis (g 100 g^{-1}) of CF samples (as analyzed by the AOAC method, 1984) were: moisture, 8.49 ± 0.34, total ash, 2.77 ± 0.24, and crude protein (N × 6.25), 20.64 ± 0.05.

2.2. Sample preparation

CF slurries were prepared at a concentration of 1:5 flour-to-water ratio. The required amounts of CF and distilled water were placed in a 250-ml beaker, hand-mixed with a glass rod, and kept for half an hour at room temperature (25 ± 1 °C) for hydration with stirring at 900 rpm before subjecting each sample to the HHP treatments.

2.3. High hydrostatic pressure treatment

CF slurries (200 ml) were vacuum packaged in a very low gas permeability bag type, Doypack® (Polyskin XL, Flexibles Hispania, S.L.). HHP treatment was performed using a Stansted Fluid Power Iso-lab 900 High Pressure Food Processor (Model: FPG7100:9/2C, Stansted Fluid Power Ltd., Harlow, Essex, UK), with 2925 ml capacity, maximum pressure of 900 MPa, and a potential maximum temperature of 100 °C. Four packed samples were inserted simultaneously into the pressure unit filled with pressure medium (water), then treated at pressures of 200, 400, or 600 MPa, and compared with untreated sample. The pressure was increased at a rate of 500 MPa min^{-1} and maintained at the desired level for holding times of 5, 15, and 25 min; the decompression time was less than 4 s. The temperature of the pressure unit vessel was thermostatically controlled at 10, 25, and 50 °C throughout the different treatment combinations. Pressure, temperature, and time were controlled by a computer program, being constantly monitored and recorded during the process. Increases of up to a maximum of 8 °C ± 1 °C, 13 °C ± 2 °C, or 17 °C ± 2 °C at 200, 400, or 600 MPa, respectively, due to compressive heating, were observed in the temperature of the pressuring fluid, but equilibrated at 10, 25, and 50 ± 2.5 °C during the holding period. Average adiabatic heating during pressurization was ~3.4 °C 100 MPa^{-1}. After HHP treatment, samples were immediately stored in a refrigerator at 4 °C for 24 h before further use. All the HHP treatments were performed twice (two batches).

2.4. Rheological measurements

A Kinexus pro rotational rheometer (Malvern Instruments Ltd, Worcestershire, UK) was used to conduct SAOS measurements under non-isothermal heating conditions in combination with a concentric cylinder geometry (C25 DIN SW1009 SS: PC25 DIN CO155 AL), and a solvent trap was used to minimize moisture loss during tests. Sample temperature was internally controlled by a Peltier system (−40 to 200 °C with an accuracy of ±0.1 °C) attached to a water circulation unit. Following an initial equilibration of CF slurry for 2.5 min at 25 °C, temperature sweep pasting profiles were recorded from 25 to 95 °C at a heating rate of 2 °C min^{-1} and at a frequency (f) of 1 Hz, with the amplitude of the periodic shear stress (σ) ranging between 0.01 and 1 Pa during heating to guarantee the existence of linear viscoelastic (LVE) response. During pasting profiles, values of elastic modulus (G', Pa) and viscous modulus (G'', Pa) were recorded. Moreover, several parameters that provide information about gelatinization characteristic were also obtained from the temperature ramps: the onset elastic modulus at 25 °C ($G'_{initial}$, Pa), the starting gel point temperature (T_{gel}, °C), considered as the temperature where there was cross-over of G' and G'', the temperature where G' achieved its maximum value ($T_{G'max}$, °C), and the G'_{max} (Pa) value itself. All rheological measurements were carried out in triplicate for each batch (six replicates were measured), and rheological properties were obtained directly from the manufacturer-supplied computer software (rSpace for Kinexus v. 1.40, Malvern Instruments Ltd., Worcester, UK).