Calcium chloride effects on the glass transition of condensed systems of potato starch

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ABSTRACT

The effect of calcium chloride on the structural properties of condensed potato starch undergoing a thermally induced glass transition has been studied using dynamic mechanical analysis and modulated differential scanning calorimetry. Extensive starch gelatinisation was obtained by hot pressing at 120 °C for 7 min producing materials that covered a range of moisture contents from 3.7% w/w (11% relative humidity) to 18.8% w/w (75% relative humidity). FTIR, ESEM and WAXD were also performed in order to elucidate the manner by which salt addition affects the molecular interactions and morphology of condensed starch. Experimental protocol ensured the development of amorphous matrices that exhibited thermally reversible glassy consistency. Both moisture content and addition of calcium chloride affected the mechanical strength and glass transition temperature of polymeric systems. Highly reactive calcium ions form a direct interaction with starch to alter considerably its structural properties *via* an anti-plasticizing effect, as compared to the polymer-water matrix.

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1. Introduction

The thermally induced glass transition is an important concept to rationalise the textural consistency and stability of condensed starchy products and starch-based films (Liu, Xie, Yu, Chen, & Li, 2009; Talja, Helén, Roos, & Jopuppila, 2007). Starch granules contain an amorphous phase, which is the main component of linear amylose and some of the partially crystalline branched amylopectin. During vitrification that commonly follows starch gelatinisation, amorphous polymeric segments remain "frozen" in a random conformation resulting in slow molecular motions and effective immobilisation in the glassy state (Zeleznak & Hoseney, 1987). Upon subsequent heating at a given scan rate, the glassy polymer converts into a rubbery system of high viscosity and increased configurational flexibility. This rubber-to-glass transformation is demarcated by the so-called glass transition temperature, T_g, which depends on the amylose/amylopectin content, surrounding relative humidity, molecular interactions between starch and low molecular weight co-solute, and the nature of measuring protocol (Perdomo et al., 2009).

Starch based biomaterials and processed foods experience plasticising or anti-plasticising phenomena that alter considerably glass-transition behaviour. Increase in the plasticizer content of water and polyols depresses the glass transition temperature and reduces the mechanical strength (Hulleman, Janssen, & Feil, 1998; Lourdin, Coignard, Bizot, & Colonna, 1997; Róz, Carvalho, Gandini, & Curvelo, 2006). Glycerol and xylitol, for example, form hydrogen bonds with the hydroxyl groups of starch leading to a reduction in intermolecular polymer associations and entanglements, and retention of backbone flexibility (Chaudhary, Adhikari, & Kasapis, 2011). Conversely, linoleic and oleic acids can act as anti-plasticizers aided by the steric accommodation of the fatty acid molecule within the hydrophobic cavity of amylose helices. This leads to an upward shift of T_g values in the cassava starch matrices at a moisture content lower than 11% and in the presence of at least 2% added fatty acid (Luk, Sandoval, Cova, & Müller, 2013).

Various types of salt are regularly utilised in starch based formulations in order to enhance techno-functionality. Sodium chloride is a traditional preservative widely added in starch to act as a taste and/or flavour enhancer and a water-holding capacity or water activity modifier (Albarracin, Sánchez, Grau, & Barat, 2011). The effect of sodium chloride on the glass transition of condensed starches (more than 80% solids in preparations) was investigated. Differential scanning calorimetry was used and results were rationalised on the basis of non-dissociated (crystalline) salt molecules or dissociated (amorphous) atoms depending on moisture levels (Farahnaky, Farhat, Mitchell, & Hill, 2009).

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Calcium chloride is another common food additive used in bio-materials and composites in order to improve, for example, the thermal engineering of starch-based biodegradable films (Jiang et al., 2012). Application of calcium chloride in the thermal processing of starch takes advantages of its high hygroscopic desiccating ability, better thermal and chemical stability than other salts, desirable thermal conductivity and non-toxicity (Tsoukpoe et al., 2015). Calcium counterion is a stronger electrolyte than the sodium cation because of the dense electric charge. In low-solid aqueous systems, calcium dissolves and forms complexes with ionic polysaccharides supporting the formation of salt bridges that have a firming effect on gels following heat treatment (Luna-Guzmán & Barrett, 2000). It can also bind with the phosphoric acid residues of the amylophosphoric portions of native starch contributing strength and elasticity to the gel upon gelatinization (Noor & Islam, 2006; Tomasik & Schilling, 1998).

There is scant information in the literature on the effect of calcium chloride on the structural properties of high-solid starch preparations. This could take the form of plasticisation by increasing the free volume between adjacent polymer chains, hence depressing the values of T_g. Alternatively, it could interact directly with the chemical moieties of the polysaccharide chains, hence supporting polymeric interactions, reducing mobility and increasing the glass transition temperature. The aim of this investigation, therefore, is to employ a range of suitable physicochemical techniques in order to provide fundamental understanding on the important role of calcium chloride in condensed starch based systems.

2. Materials and methods

2.1. Materials

A food-grade native potato starch was used, which was a white, fine free-flowing powder with a bland taste. It contains <10 mg/kg of sulphur dioxide without known allergens. Typical nutritional value expressed as % per 100 g of the material shows a total carbohydrate content of 84%, water content of 15.08%, protein content of 0.2% and total fat of 0.1% (Penford Starch, Lane Cove, NSW, Australia).

Calcium chloride, anhydrous in a white granule form ($\leqslant 7.0$ mm), with minimum purity by EDTA titration being 98.1%, was purchased from Sigma Aldrich (Castle Hill, NSW, Australia).

Millipore system Elix® 10 water purification system was used to produce the Millipore type 2 analytical-grade water of this investigation (Merck KGaA, Germany).

Desiccating chambers were prepared to achieve a series of moisture and relative humidity values for our starch/calcium chloride samples, with the saturated salt solutions being purchased from Sigma Aldrich, i.e. lithium chloride (LiCl): moisture content 3.71% w/w, RH 11%; potassium acetate (CH$_3$COOK): moisture content 6.07% w/w, RH 23%; magnesium chloride (MgCl$_2$·6H$_2$O): moisture content 6.55% w/w, RH 33%; sodium bromide (NaBr): moisture content 11.49% w/w, RH 58%; magnesium acetate [Mg(CH$_3$COO)$_2$·4H$_2$O]: moisture content 14.40% w/w, RH 65%; sodium chloride (NaCl): moisture content 18.83% w/w, RH 75% (Sablani, Kasapis, & Rahman, 2007).

2.2. Sample preparation

Potato starch powder, with a moisture content of 15.08% (w/w) that was taken into consideration for final sample preparation, was dry mixed with a wide range of added calcium chloride concentrations (0.0%, 1.5%, 3.0%, 4.5% and 6.0% w/w) to achieve a total of 35.0% (w/w) moisture content. In doing so, Millipore type 2 water was introduced piecemeal prior to processing all preparations; weighing was carried out carefully using a four decimal place analytical balance. Then, twin screw Thermo Rheomix OS (HAAKE, Newington, NH, USA) were used to mix the mixture with a screw speed of 200 rpm for 2 min at ambient temperature. Mixture was placed on a stainless steel metal frame (130 mm × 130 mm × 2 mm) sandwiched between two non-stick plastic sheets at the bottom and top of the frame. It was then transferred to a steam preheated hot press at 120 °C for 7 min achieving pressurisation of 59 Bar.

Heated samples were cooled within the same press to about 45 °C (to prevent air bubble formation on the starch film), packaged and sealed separately with a moisture/gas impermeable plastic vacuum bag, and stored at 4 °C. To facilitate subsequent instrumental analysis, samples were cut into the desired shape and size (10 × 10 × 1 mm) and stored in sealed relative-humidity desiccators for 4 weeks containing the aforementioned saturated salt solutions. Relative humidity to the required equilibrium value in the starch/calcium chloride systems was checked periodically with a water activity metre (Novasina aw set-1, Pfäffikon, Switzerland). The final moisture content of these preparations after a 4-week desiccator storage was between 3.71% w/w (RH 11%) and 18.83% w/w (RH 75%), as estimated by oven drying at 102 °C overnight.

2.3. Instrumental protocol

2.3.1. Dynamic mechanical analysis

Diamond DMA from Perkin-Elmer (Akron, Ohio, USA) with an external 60 L liquid nitrogen Dewar was used for monitoring the tensile storage and loss modulus (E' and E'', respectively) of our materials. In doing so, the sample film was set on a twin grip clamp and tensile mode was employed. Cooling from ambient temperature to −100 °C was carried out followed by heating to 150 °C at a scan rate of 2 °C/min, and frequency of 1 Hz. Strain employed was 0.1% throughout, which falls within the linear viscoelastic region (LVR) of the material. To minimise moisture loss during measurement, a thin layer of petroleum vacuum grease was used to coat the sample prior to loading onto the tensile grips. Isochronal routines were carried out in duplicate returning consistent results.

2.3.2. Modulated differential scanning calorimetry

Thermal transfer analyser Q2000 (TA Instruments, New Castle, DE) was used. It was attached to a recirculated cooling system (RCS90), with ultra-pure nitrogen gas purging into the sample analysis chamber at a flow rate of 50 mL/min. About ten mg of the material was placed in a Tzero aluminium pan, hermetically sealed with an aluminium lid and analysed at modulated amplitude of ±0.53 °C for 40 s. An extensive temperature range was accessed with successive cooling and heating routines from −80 to 180 °C at a scan rate of 10 °C/min. All measurements were performed in triplicate to yield effectively overlapping thermograms.

2.3.3. Fourier transform infrared spectroscopy

Data were recorded on a Perkin Elmer Spectrum 100 using MIRacle TMZnSe single reflection ATR plate system (Perkin Elmer, Norwalk, CT). Starch/calcium chloride preparations were analysed at ambient temperature within a wavelength of 4000–650 cm^{-1} and a resolution of 4 cm^{-1}. Spectra are presented in absorbance mode based on 32 average scans. Final results were obtained following removal of the background signal at ambient temperature and have been repeated three times for each measurement.