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ABSTRACT

The effect of heating rate on structural and functional properties of wheat and potato starch-water systems were analyzed in term of gelatinization, swelling and pasting behavior as well as in terms of textural and flow characteristics of gels recovered. Gelatinization temperatures and enthalpy of starch increased with increasing heating rate. Viscosities measured during the pasting procedure increased with the heating rate as a consequence of granule swelling. Slower heating rates resulted in smaller breakdown of viscosity during the pasting procedure. Both wheat and potato starch gels showed shear thinning behaviours, with a consistency index decreasing when the heating rate increased. The hardness of wheat starch gels slightly decreased when the heating rate increased while the hardness and gumminess of potato starch gels increased with the heating rate.

1. Introduction

Native starch granules are insoluble in cold water and less digested by human beings and monogastrics. To induce most of the characteristics of starch-based foods, starch-water systems undergo heat and mechanical treatments aiming to induce the textural and sensory characteristics well accepted by consumers. Most manufactured starchy foods are characterized by their rheological and textural parameters, as well as by their water holding capacity. The ability to induce these functional properties is one of the aspects which make starchy food suitable for numerous uses. Such properties are closely dependent on the structural features of granules and on the pasting procedure applied during the heat-treatment.

When starch is heated beyond the gelatinization temperature, granules swell up to many times their original size, collapse and release amylose in the continuous medium. These phenomena enhance the viscosity of starch-water systems and induce a gel upon cooling, promoting the use of starch as a thickening agent (Nayouf, Loisel, & Doublier, 2003). These properties may however be modulated by the pasting procedure applied, especially by the heating rate (Doublier, Llamas, & Le Meur, 1987) as well as by the presence of small molecular weight solutes and hydrocolloids (Evans & Haisman, 1982; Wootton & Bamunuarachchi, 1979).

Although the influence of the heating procedure is recognized as of particular interest, most previous studies that addressed the effect of heat-treatment on structural and functional properties of starch-water system were performed either isothermally or applied constant heating rates (Okechukwu & Rao, 1996; Lagarrigue, Alvarez, Cuvelier, & Flick, 2008; Chen, Campanella, & Purkayastha, 2007) even if the manufacturing of starch-based food is rarely accomplished isothermally nor by applying a constant heating rate over all the processe.

Most of the papers that addressed the effect of heating rates on starch-water systems were based on differential scanning calorimetry (Andreev. Kalistratova, Wasserman, & Vladimir, (DSC) 1999: Resio & Suarez, 2001; Marchant & Blanshard, 1978; Patel & Seetharaman, 2010; Spigno & De Faveri, 2004; Wootton & Bamunuarachchi, 1979; Yu & Christie, 2001), without linking thermal properties displayed during the DSC with other properties of gel-like products formed upon starch-water systems heating. Some of the DSC-based studies, devoted to the effect of heating rates, led to contradictory results that need to be addressed taking into advantage the performance of current DSC devices. Wootton and Bamunuarachchi (1979) sustained that more rapid heating of starch water-systems resulted in a decrease in the onset temperature and enthalpy of gelatinization, probably because of a shorter time of exposure to the gelatinization temperature range. Spigno and De Faveri (2004) sustained that higher heating rate shifted the temperature of gelatinization towards higher values and attributed this increase of gelatinization temperature to a certain delay of the instrument response to the increasing temperature. Vamadevan and Bertoft (2015) sustained that higher heating rate increased the thermal lag, which delayed the

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transition temperatures observed during the DSC analysis of starch gelatinization. Marchant and Blanshard (1978) performing a small angle light scattering analysis, already rejected the hypothesis of thermal delay to explain the dynamic of starch gelatinization when different heating rates were applied. They sustained that, depending on the heating rate, two different structural processes occurring inside granules may influence the dynamic of gelatinization. Considering the work mentioned above, it is clear that the basis of the changes observed with the heating rate is not yet well mastered.

DSC device have actually been highly improved and are now sufficiently sensitive to detect small changes of heat flow during the analyses, so it seems interesting to assess some hypotheses assumed in previous studies and to highlight the effect of heating rate on functional properties displayed by gelatinized starch-water systems.

The aim of the present study was to assess the effect of heating rate on starch–water systems in term of gelatinization, granule swelling as well as in term of pasting behavior, rheological and textural properties displayed by starch-water systems upon heating at different heating rates. Wheat and potato starches were used as material models.

2. Materials and method

2.1. Materials used

The native wheat and potato starches used in this study were supplied from SIGMA-ALDRICH Ltd (Switzerland). To characterize these materials their moisture contents were determined by oven drying at 105 °C until constant mass. The sample purity was measured by the polarimetric method of Ewers (ISO, 1997) which revealed that their purities were over 99 g of starch in 100 g of sample. The apparent amylose content determined by the polarimetric method as described by Massaux et al. (2008) was 27.8 g/100 g for wheat starch and 29.4 \pm 0.2 g/100 g for potato starch. The purity of these two samples was determined by measuring their residual protein content using Dumas methodology (N \times 6.25) and revealed less than 0.3 g of residual protein per 100 g of starch for both samples. No significant alphaamylase activity was detected in samples using the Megazyme Ceralpha K-CERA 01/12 assay kit. So differences observed between low and high heating rates cannot be attributed to amylolysis during the slow increase of temperatures.

2.2. Differential scanning calorimetry (DSC)

The effect of heating rate on the thermal properties of samples was assessed using a DSC analyzer TA Instruments Q2000 (New Castle, Delaware, USA) with a Refrigerated Cooling Accessory as previously described in Malumba et al. (2016). The empty sample and reference pans were of equal mass, analysis was performed with 50 mL min⁻¹ of dry nitrogen purge flow and the cell was calibrated for temperature and enthalpy using indium and eicosane as standard. Approximately 3 mg of starch were weighed into aluminum pans and mixed with deionized water to obtain 3:1 water: starch ratio. Measurements were performed over a temperature range of 30 °C–95 °C and scanned at heating rates of 0.5; 2 and 5 K/min. The onset temperature and peak temperatures were computed using NV Thermal analysis software (Universal analysis, New Castle, Delaware, USA) and the gelatinization enthalpies were calculated by integrating the area of the gelatinization endothermic signal divided by the amount of dry starch used.

2.3. Granule swelling

To study the granule swelling of starch granules (SG) under different heating rates, 1 L of water-starch suspension (10 g/L) was prepared in a steel vessel, placed in a water-bath (JULABO HC 25/3) as described in Malumba, Jacquet, Delimme, Lefebvre, and Béra (2013). Heating rates of 0.5 and 5 K/min were applied while the suspension was stirred at

approximately 120 rpm using an impeller placed in an axial position inside the vessel. The temperature of the starch suspension inside the steel vessel was monitored by using T-type thermocouples connected to a digital interface Ellab TA 9616. At predetermined temperatures, an aliquot of starch-water suspension was withdrawn and quenched in ice water to stop the effect of the heat treatment before measuring the diameter of the granules. Granule sizes were determined using a laser granulometer (Malvern Instruments Inc, UK) as described in Malumba, Massaux, Deroanne, Masimango, and Béra (2009). The method used in this instrument relies on the fact that the diffraction angle is inversely proportional to particle size. This instrument consists of a fixed wavelength laser light source and a suitable detector. The calculations of granule size parameters use the full Mie theory which completely solves the equations for interaction of light with solid particles (Malvern Instrumets Ltd, Technical paper). The size distribution was described in terms of median diameter d (0.5) that corresponds to the diameter of granules for which 50% of particles are smaller. This measurement was highly repeatable with variation coefficient less than 1% of the measured value.

2.4. Pasting behavior of wheat and potato starch

The Brabender visco-amylograph (Duisberg, Germany) was used to assess the effect of heating rate on pasting behavior of starch-water systems. Starches (10 g in dry basis) were mixed with 100 g of deionized water and then submitted to gradual heating from 30 °C to 95 °C using the heating rates of 0.5; 2 and 5 K/min. After reaching 95 °C, a holding phase of 10 min was maintained, before a gradual cooling step (-4.5 °C/min) to 50 °C. This temperature was maintained for 5 min before the end of pasting. For each pasting procedure the peak of viscosity reach during the heating phase, the breakdown of viscosity during the holding period at 95 °C, the setback of viscosity during the cooling phase and the final viscosity of starch-water suspension were determined and expressed in Brabender units (BU).

2.5. Flow behavior of starch gels

Flow behaviors of gels prepared using an Anton Paar Physica mcr 301 rheometer (Anton Paar, Germany) fitted with an electrical heated cylinder system were determined at 50 °C following a pasting procedure similar to that used in the visco-amylograph.

1.78 g of starch (dry basis) was mixed with 16.02 g of deionized water in an CC26/ST aluminium cup (Anton Paar, Germany). The slurry was then submitted to a gradual heating at 0.5; 2 and 5 K/min from 30 °C to 95 °C at the shearing rate of 300 s⁻¹ using a C-EDT160/ST electrical heated cylinder system fitted with a fluid cooling system and a calibrated stirrer ST24. After reaching 95 °C, a holding phase of 5 min was maintained, before a gradual cooling step (-4.5 °C/min) to 50 °C using the same shearing rate as during the heating. The flow behavior measurements were performed subsequently by shearing the slurry at 50 °C from 0.01 to 400 1/s and back to 0.01 1/s. The recorded shear stress allowed the determination of viscosity, which was expressed in Pa.s. To compare the influence of heating rate and to measure the influence of the shear rate on the apparent viscosity and shear stress, as well as to describe the steady shear rheological properties of slurries obtained, collected data were fitted with the power law model of Herschel-Bulkley.

$$\tau = K\gamma^n \tag{1}$$

Where τ = shear stress (Pa), K = consistency coefficient (Pa.sⁿ), γ = shear rate (1/s), and n = flow behavior index. Furthermore, n is the flow behavior index, which demonstrates the extent to which the liquid departs from a Newtonian fluid.

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