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Devitrification of the amorphous fractions of starch during gelatinisation

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ABSTRACT

Gelatinisation of waxy maize starch (WMS) in excess glycerol was investigated by a temperature modulated DSC in quasi-isothermal and non-isothermal mode. By using the measured specific heat capacities (c_p) at different stages of gelatinisation and the hypothetical enthalpy of melting for 100% crystalline amylopectin, a method was developed to reveal the amorphous fraction which remains glassy in the presence of excess glycerol what can be called “rigid amorphous”. It was suggested that the amorphous part of starch was plasticised at around 40 °C whereas, rigid amorphous fraction underwent a second stage glass transition which showed itself by an increase in c_p under the gelatinisation endotherm. It was also shown that holding WMS in excess glycerol at 100 °C (10 °C above the gelatinisation onset temperature) for 10 days was not enough to gelatinise the whole WMS implicating that the most stable crystals did not melt before the required threshold temperature was reached.

1. Introduction

Starch, one of the most important natural macromolecules due to its universal form of packing and storing carbohydrates in green plants, is a mixture of two molecular entities, a mainly linear fraction; amylose, and its branched counterpart; amylopectin (Randzio, Flis-Kabulska, & Grolier, 2002). Amylose is an essentially linear molecule of α-(1 → 4)-linked D-glucopyranosyl units with a few branches, whereas amylopectin has large molecular weight and highly branched structures consisting of α-(1 → 4)-linked D-glucopyranosyl units with 5–6% non-randomly distributed α-(1 → 6)-D-glucopyranosyl units. These two polymers are organised into a semi-crystalline structure (Chung, Liu, Lee, & Wei, 2011). When starch is composed primarily of amylopectin, it is referred to as “waxy” (Chakraborty et al., 2004). Waxy maize starch is a specialty material characterised by a high (>98%) amylopectin content (Sablani et al., 2007).

Understanding of structure, properties and processing of starch is important to improve the quality of starch based food products, pharmaceuticals and development of functional foods (Appelqvist & Debet, 1997). Starch is also an important raw material for biodegradable plastics due to its low cost, its availability as a renewable resources and its thermal processability using conventional plastics processing equipment such as injection moulding, film blowing, thermoforming and extrusion (Tan, Wee, Sopade, & Halley, 2004).

Starch gelatinisation can be generally defined as an irreversible order–disorder transition, which involves disruption of molecular organisation within the starch granules upon heating in the presence of plasticisers (Tan et al., 2004). Due to the complexity of the underlying mechanism of gelatinisation, many features of gelatinisation are not yet understood completely. However, increase in precision of analytical methods and instruments as well as the accumulation of information through various techniques employed up to date lead to better understanding of the gelatinisation. Detailed information on gelatinisation of starch could be found elsewhere (Ratnayake & Jackson, 2008).

Starch, as a natural semi-crystalline macromolecule carries some aspects of synthetic semi-crystalline polymers. Waigh, Gidley, Komanshek, and Donald (2000) suggested that there was an analogy between starch and a chiral side-chain polymeric liquid crystal and they proposed a gelatinisation theory based on this approach, which is still widely accepted and provides basis for emerging new gelatinisation theories (Tan et al., 2004).

The aim of the present contribution is to investigate the existence of an intermediate phase between crystal and amorphous phases which is well known and called “rigid amorphous” in the field of synthetic polymers (Suzuki, Grebowicz, & Wunderlich, 1985; Wunderlich, 2003). This intermediate phase is non-crystalline and includes amorphous portions of macromolecules

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whose mobility is hindered by the near crystalline structures. The different amorphous fractions are usually classified on the basis of their mobility. The unconstrained amorphous phase, that relaxes at the glass transition (T_g), is usually addressed as the "mobile amorphous fraction" (MAF), whereas the term "rigid amorphous fraction" (RAF) refers to the amorphous chain portions whose mobility is hindered by the near crystalline structures (Maria Laura, 2009; Righetti, Tombari, & Lorenzo, 2008; Schick, Wurm, & Mohammed, 2003; Suzuki et al., 1985; Wunderlich, 2003). The determination of RAF and MAF is commonly based on calorimetric measurements. Despite the calorimetry, particularly DSC, is a standard tool in food research, there are only a few quantitative heat capacity data on starch plasticiser systems available (Bizot et al., 1997; Pyda, 2002; Tan et al., 2004).

In the present study, we measured heat capacity and enthalpy change of starch–glycerol–water systems during gelatinisation by using a high sensitivity heat flux temperature modulated differential scanning calorimeter (TMDSC) in order to understand changes in molecular mobility of starch during gelatinisation and to investigate wheatear a rigid amorphous fraction exists. For this purpose, starch in excess glycerol was exposed to different temperatures within the range of gelatinisation temperatures in quasi-isothermal mode, while the change in c_p was monitored for 15 h to 10 days.

2. Materials and methods

2.1. Reagents

2.1.1. Starch

Waxy maize starch was from National Starch Co. (Manchester, UK). In order to minimise the moisture gain/loss during weighing of the starch, the moisture content of the starch was equilibrated with relative humidity of the closed cabinet where the weighing scale (Sartorius, Micro M500P) used for the experiments was stationed. After a week of equilibration time, the moisture content of the starch determined by theromgravimetry (Setaram Labsys TG/DSC) was ca. 10% (w/w).

2.1.2. Glycerol

Glycerol obtained from Sigma–Aldrich (Germany) was 99% pure however, due to its high hygroscopic nature it is assumed that it might have gained some humidity from the air during sample preparation.

2.2. DSC instrument

A Mettler-Toledo 822e DSC equipped with a Star sensor HSS7 and temperature modulated DSC software was used for the experiments. A Julabo (FT900) cooler was used to achieve the programmed modulation temperature. Dry air was purged through the DSC cell with a flow rate of 20 ml/min. Temperature and heat flow calibrations were done in the standard DSC mode without temperature modulation, using the onsets of the transition temperatures and the heat of fusions for indium and zinc.

2.3. Sample preparation

Starch (8.00 ± 0.01 mg) was weighed in standard Mettler aluminium pans with 40 μl volume. After addition of 19.5 ± 0.1 mg of glycerol, the pans were hermetically sealed and left at room temperature for 1 h before the start of the experiments to ensure standardised starting conditions for all measurements. As reference, 19.5 mg of glycerol sealed in a similar aluminium pan was used. Considering the moisture content of starch, it could be stated that the starch is plasticised with a mixture of water and glycerol at a concentration of 4% and 96%, respectively.

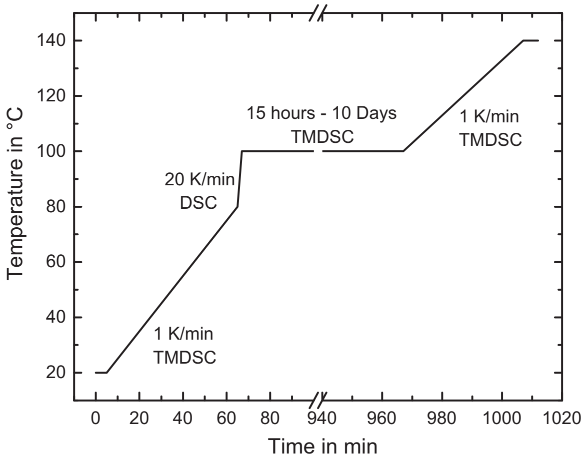

Fig. 1. Schematic presentation of temperature program for quasi-isothermal experiments. Temperatures shown are the mean temperatures of the modulated temperature program except the 20 K min^{-1} segment where modulation was not applied. For temperature scan, $A = 3$ K, $p = 2$ min, $q = 1$ K min^{-1}, for quasi-isothermal segment, $A = 3$ K, $p = 2$ min, $q = 0$ K min^{-1}.

2.4. Evaluation of DSC curves

After a set of experiments to determine the optimum modulation conditions for the chosen pan type, sample and glycerol weights, an underlying heating rate (q_o) of 1 K min^{-1} with 3 K amplitude (A_T) and 2 min period (p) was used for the temperature scanning experiments. Under these experimental conditions thermal lag does not falsify the measured heat capacity or the temperature measurement within 0.5 K. After recording an initial quasi-isotherm at 25 °C for 5 min, temperature scan was performed up to 140 °C. After the end of temperature scan, a second 5 min isotherm at 140 °C was recorded for baseline correction. In the case of any difference in between the initial and final isotherms, a linear correction was performed in such a way that the heat flow signals were reduced to zero for both initial and final isotherms.

From the measured modulated heat flow rates the total specific heat capacity, $c_{p\ total}$, and the reversing specific heat capacity, $c_{p\ reversing}$, were determined according the standard procedures (Wunderlich, Jin, & Boller, 1994). In the case of our study with starch, $c_{p\ total}$ represents the sum of baseline and excess heat capacities, while $c_{p\ reversing}$ is a measure of baseline heat capacity alone. For simplification $c_{p\ reversing}$ is abbreviated by c_p.

The specific heat capacity (c_p) of glycerol was determined separately. Any variation in the weight of the glycerol (±0.1 mg) in sample and reference side was taken into account when calculating the total c_p of starch with 10% (w/w) moisture in excess glycerol. Unless otherwise stated, all the enthalpy and c_p values reported in this study are for WMS (containing ca. 10% moisture) in excess glycerol.

2.5. Quasi-isothermal measurements for determination of rigid amorphous fraction of starch

Fig. 1 shows the temperature program and the parameters of modulation used for quasi-isothermal experiments. Initial 1 K min^{-1} heating up was designed to understand the starch–water–glycerol interactions below gelatinisation temperatures. Non modulated segment of temperature program (20 K min^{-1}) was designed to bring the sample to quasi-isothermal temperature without exposing the samples to higher temperatures