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Comparison of methods to determine the degree of gelatinisation for both high and low starch concentrations

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Abstract

A general procedure was developed to measure the degree of gelatinisation in samples over a broad concentration range. Measurements based on birefringence, DSC (Differential scanning calorimetry), X-ray and amylose–iodine complex formation were used. If a 10 w/w % wheat starch–water mixture was used, each method resulted in approximately the same degree of gelatinisation vs. temperature curve. In case the gelatinisation of a 60 w/w % wheat starch–water mixture was followed as a function of the temperature, each method resulted in a different degree of gelatinisation vs. temperature curve. DSC and X-ray measurements are preferred, because they can be used to determine when the final stage of the gelatinisation process has been completed. Birefringence and amylose–iodine complex formation measurements are suitable alternatives if DSC and X-ray equipment is not available, but will lead to different results. The differences between the methods can be explained by considering the phenomena that take place during the gelatinisation at limiting water conditions.

Based on the experimental data obtained with DSC and X-ray measurements, the gelatinisation of 10 w/w % and 60 w/w % wheat starch–water mixtures started at the same temperature (approximately 50 °C). However, complete gelatinisation was reached at different temperatures (approximately 75 °C and 115 °C for, respectively, 10 w/w % and 60 w/w % wheat starch–water mixtures) according to the experimental DSC and X-ray data. These results are in accordance with independent DSC measurements that were carried out.

The Flory equation was adapted to provide a quantitative explanation for the curves describing the degree of starch gelatinisation as a function of the starch–water ratio and the temperature. The gelatinisation curves that were obtained with the model are in good agreement with the experimentally determined curves. The parameters T_m^0, ΔH_u and χ_{12} that resulted in the lowest sum of the squared residuals are 291 ± 63 °C, 29.2 ± 3.9 kJ/mol and 0.53 ± 0.05 (95% confidence interval). These values agree with other values reported in literature.

Keywords: Starch gelatinisation; Flory equation; Melting temperature of starch; Wide angle X-ray scattering (WAXS); Differential scanning calorimetry (DSC); Amylose–iodine complex formation; Birefringence

1. Introduction

Starch is a biopolymer that occurs naturally as water-insoluble and birefringent granules. Each granule consists of concentric growth rings of alternating amorphous and semi-crystalline composition. The semi-crystalline growth rings contain stacks of amorphous and crystalline lamellae. The crystalline lamellae consist of chain sections of amylopectin that form double helices (type A), while other chain sections of amylopectin form connections between the helices (type B). Branching points of both A and B chains of amylopectin are usually found within the amorphous lamellae (Jenkins et al., 1994; Waigh, Gidley, Komanshek, & Donald, 2000).

When a suspension of starch is heated in the presence of excess quantities of water, an irreversible order–disorder transition called gelatinisation takes place (Cooke &

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Gidley, 1992; Jenkins & Donald, 1998; Liu & Lelievre, 1993). During gelatinisation, starch granules take up water, swell, lose crystallinity and leach amylose (Parker & Ring, 2001). In addition, heat is taken up, according to the characteristic gelatinisation endotherm that can be measured with Differential scanning calorimetry (DSC). If the amount of water is insufficient to provide complete swelling and disruption of the starch granules, only part of the crystallinity of the starch granules is lost. The remaining crystallinity only disappears after heating to higher temperatures. A melting transition occurs giving rise to an additional DSC endotherm (Donovan, 1979; Eliasson, 1980; Randzio, Flis-Kabulska, & Grolier, 2002; Whittam, Noel, & Ring, 1990). For a brief overview of the qualitative models describing the gelatinisation of starch we refer to Jenkins and Donald (1998). A more recent qualitative model was developed by Waigh et al. (2000) using a liquid-crystalline approach to describe the gelatinisation of starch. The Flory equation has been used by several authors for a quantitative description of the gelatinisation or melting temperature as a function of the starch concentration (Burt & Russell, 1983; Donovan, 1979; Donovan & Mapes, 1980; Donovan, Lorenz, & Kulp, 1983; Parker & Ring, 2001; Russell, 1987; Whittam et al., 1990).

Several analysis techniques are used to study different aspects of the gelatinisation process. Birefringence is used to follow the ordering in the granule on the length scale of the wavelength of light (approximately 500 nm) (Lelievre, 1974; Waigh et al., 2000). Wide angle X-ray scattering (SAXS) and short angle X-ray scattering (WAXS) can be used to follow, respectively, short-range order (crystalline double helices) and long-range order (alternating crystalline and amorphous lamellae) (Jenkins et al., 1994). Where X-ray scattering probes the double helices packed in regular arrays, solid state NMR detects the double helix content at a molecular order level (Cooke & Gidley, 1992; Gidley & Bociek, 1985). IR spectroscopy can also be used to follow the gelatinisation of starch on a short-range molecular level, because the IR spectrum of starch is affected by changes in structure such as starch chain conformation, helicity and crystallinity (Van Soest, Tournois, de Wit, & Vliegenthart, 1995). Liu, Lelievre, and Ayoung-Chee (1991) have found a quantitative correlation between crystallinity loss and thermal transitions during the gelatinisation of starch, since melting is a first order transition accompanied by a heat effect that can be measured well. Therefore, DSC measurements can also be used to follow the loss of order that takes place during the gelatinisation process. Amylose chains are released during the gelatinisation process and these chains can be determined colorimetrically (Birch & Priestley, 1973), as dissolved amylose forms a blue complex with iodine (Calabrese & Khan, 1999). When a starch–water mixture gelatinises, the water distribution and manner at which water is bound to the starch matrix changes (Tang & Hills, 2001). These changes affect the dielectric properties of the starch–water system and for this reason conductance measurements can be used to monitor the gelatinisation process (Karapantsios, Sakonidou, & Raphaelides, 2000). Besides the conductance, the viscosity of the starch–water mixture also changes during gelatinisation due to swelling of the granules. Monitoring the viscosity can therefore also be used to follow the gelatinisation. After starch has been gelatinised, it is susceptible to hydrolytic enzymes (Tester & Sommerville, 2001). For this reason, enzymatic methods have also been used to investigate the gelatinisation process indirectly (Roussel, Vieille, Billet, & Cheftel, 1991).

Comparisons between the analysis methods were made to elucidate the mechanisms that take place during the order–disorder transition of the gelatinisation process (Chaiwanichsiri, Ohnishi, Suzuki, Takai, & Miyawaki, 2001; Cooke & Gidley, 1992; Liu et al., 1991; Waigh et al., 2000). Liu et al. compared birefringence and X-ray measurements during the gelatinisation of a 2 w/w % corn starch suspension. However, these authors did not compare these measurements at higher starch concentrations.

In this article, DSC, X-ray, birefringence and amylose–iodine complex formation measurements will be used to determine the degree of gelatinisation in 10 w/w % and 60 w/w % starch suspensions in water. A general procedure was developed to measure the degree of gelatinisation at both low and high starch concentrations. Furthermore, the observed differences between the analysis techniques will be discussed. In addition, the differences between the gelatinisation behaviour of diluted and concentrated starch suspensions will be explained based on the Flory equation. The Flory equation is adapted to describe the degree of gelatinisation as function of both temperature and starch concentration.

2. Theory

The Flory equation is often used to relate the melting temperature T_m of a polymer in a polymer–diluent mixture to the volume fraction ϕ_1 of the diluent (Flory, 1953):

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\frac{V_2}{V_1}\right) \cdot \left[\phi_1 - \chi_{12}\phi_1^2\right] \quad (1)$$

where T_m^0 is the melting point of the pure polymer, R is the gas constant, ΔH_u the heat of fusion per repeating unit, V_1 and V_2 are the molar volumes of the diluent and the repeating unit of the polymer and χ_{12} is the Flory–Huggins polymer–diluent interaction parameter. In addition, we have assumed that the ratio V_2/V_1 and χ_{12} are temperature independent. The Flory–Huggins interaction parameter is known to depend linearly on the reciprocal of the absolute temperature (Rudin, 1999). Therefore, χ_{12} decreases with 20% over the temperature interval of interest (50–115 °C). This variation is not too large and for this reason the assumption of a constant χ_{12} parameter seems justified. In the derivation of Eq. (1), it is assumed that the heat of fusion and the entropy of fusion do not depend on the temperature. According to Hoffman (1958), Van Krevelen