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Effect of amylose content on estimated kinetic parameters for a starch viscosity model

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ABSTRACT

The apparent viscosity profile of starches during gelatinization varies with different amylose content. This study focused on the influence of amylose content on the kinetic parameters of a starch viscosity model for corn starches. The five parameters were: gelatinization rate constant (k_g), gelatinization activation energy (E_g), relative increase in apparent viscosity during gelatinization (A^α), relative decrease in apparent viscosity during shearing (B), and viscous activation energy (E_v). The parameters were estimated at different amylose content using both ordinary least squares nonlinear regression and the sequential method. The mixer viscometry approach was used to measure apparent viscosity. The first part of this paper presents parameter estimation results for waxy corn starch. The model was validated by using the parameters to predict viscosity for the same starch in a different measuring system, i.e., the RVA. The second part of this paper presents the estimated parameters for corn starch blends at different amylose content. The following parameters were significantly affected by amylose content: k_g and E_g both decreased with amylose content by an power-law relationship. Activation energy of gelatinization ranged from 121 to 1169 kJ/mol. The other parameters A^α, B, and E_v were not significantly influenced by amylose content. In summary, the gelatinization parameters k_g and E_g dramatically decreased as amylose increased from 3% to 35% (waxy corn starch blends).

1. Introduction

Starch is one of the major components in the diet of the world population. Starch plays a very important role in food functionality and nutritional quality enhancement, leading to increasing interest in starch research (Yuryev et al., 2002). Starch is mainly composed of two types of glucose molecules: amylose (AM) and amylopectin (AP). The amylose content present in starch depends on the botanical source (Jane et al., 1999; Yuryev et al., 2002). Corn starch is a notable example of cereal starch that has varying amylose content due to three varieties available commercially: waxy, normal, and high amylose starches. Some researchers have done studies on the behavior of corn starch regarding gelatinization, solubility, thermal properties, rheological properties, and molecular structure (Jane et al., 1999; Juhasz and Salgo, 2008; Liu et al., 2006, 2010; Matveev et al., 2001; Dail and Steffe, 1990a; Dolan and Steffe, 1990; Ratnayake and Jackson, 2006; Xie et al., 2009; Cheetham and Tao, 1997; Cheetham and Tao, 1998; Uzman and Sahbaz, 2000; Villwock et al., 1999; Wu et al., 2006).

Waxy starch contains the highest amount of amylopectin, and when heated in water produces the most dramatic increase in peak viscosity among other varieties of starches (Juhasz and Salgo, 2008). Waxy starch is used to address certain common problems in the food industry for example: (1) to avoid the texture of pourable dressing being too thin, waxy starch content in the formulation is increased; (2) to avoid having a gummy texture of dressings, waxy starch content in the formulation is decreased; (3) to have a uniform cell structure, desired moistness and high volume of final product in bakery products, waxy starch is added in the formulation; (4) to have crispness in extruded products, amylose content is increased if high-shear conditions are used or amylopectin content is increased if low-shear conditions are used (Thomas and Atwell, 1999).

Viscosity profiles (pasting curves) are powerful tools to represent starch functional properties. Each starch produces a different viscosity profile even under the same processing conditions. This paper is focused on the influence of starch amylose content on gelatinization kinetic parameters using parameter estimation

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Nomenclature

A^{α}	relative increase in apparent viscosity, dimensionless
AM	amylose
AP	amylopectin
B	relative decrease in apparent viscosity, dimensionless
b	concentration parameter, $\%^{-1}$
BF	Brookfield viscometer
CON A	concavalin A
C	starch concentration, %
E_v	viscous activation energy, kJ/mol
E_g	gelatinization activation energy, kJ/mol
d	shear-decay rate parameter, rev^{-1}
k_g	gelatinization rate constant, $(Kmin)^{-1}$
K_r	pseudo consistency coefficient, Nm min^n
M	torque, mN mm
N	speed, rpm
n	flow behavior index, dimensionless
RMSE	root mean square error, mN mm
RTD	resistance temperature detector
RVA	rapid visco analyzer
S	parameter combine shear rate and concentration term, mNmm min^n
SS	sum square of error
t	time in min
t_f	time when the experiment ends, min
t_{SH}	time when the shear history begin, min
T	temperature, Kelvin
T_{rg}	gelatinization reference temperature on Arrhenius equation, Kelvin
T_{rt}	reference temperature on Arrhenius equation for temperature term, Kelvin
α	dimensionless parameter
Ψ	time–temperature history, (K min)
Φ	shear history, rpm min

techniques on the viscosity model presented by Dolan and Steffe (1990) for gelatinizing starch solutions. To the best of our knowledge, no such study has been reported. The results of this study will be useful for (1) food engineers when calculating the velocity profile of products, since viscosity plays a major role in the flow characteristics; and (2) product developers when formulating a product, especially when corn starch is used as the product thickener.

2. Overview of method

2.1. Sample preparation

Commercial native waxy, Melojel, and high amylose corn starches (Hylon V and Hylon VII) were obtained from a starch company (National Starch, NJ). Corn starch blends with different AM content of starch were prepared by adding higher AM content starches to lower AM content starches. Samples at different AM were prepared as follows: System I contained waxy and normal corn starch mixtures (0%, 10%, and 27% AM); System II contained waxy and high amylose Hylon V mixtures (10%, 20%, 30%AM); System III contained waxy and high amylose Hylon VII mixtures (10%, 20%, 30%, 40%, 50%). There were a total of 11 samples. Each sample, weighing 5 g, was placed in a small glass vial and mixed well by vigorous manual shaking and a vortex mixer. The samples were then used to measure the apparent AM content experimentally, and the pasting curves.

2.2. Starch apparent AM/AP ratio determination

The apparent AM/AP content of the samples was determined experimentally by the Con A method using the Megazyme AM/AP content assay kit (Megazyme, 2006). The Con A method has been used to measure the amylose content in starch and flours (Gibson et al., 1997). In this study, the exact method given by Megazyme was used with slight modifications. Samples were centrifuged using the bench centrifuge at 4000*g* for 10 min instead of 2000*g* for 5 min. The measurements were done at least in duplicate. The amylose content present in the sample was determined based on Con A supernatant and total starch aliquot absorbance readings at 510 nm as follows:

$$\text{Amylose experimental, } \%(\text{w/w}) = \frac{\text{Absorbance (Con A Supernatant)}}{\text{Absorbance (Total Starch Aliquot)}} \times 66.8$$

2.3. Rheological measurement

2.3.1. Mixer viscometer data collection

Equipment set up consisted of a RVDV Brookfield viscometer equipped with three ethylene glycol baths (temperatures set at 96, 60, and 5 °C) and a solenoid valve system to switch between baths. The Brookfield flag impeller and small cup adapter with RTD on the bottom of the sample cup, was used to hold the sample during agitation. Calibrations of instrument voltage and torque were done using a few standard sample fluids of silicon oil. Calibration of voltage and temperature were done by using ice, boiling water, and also by heating the water at fixed water bath temperatures. A data acquisition system (USB 6008), and a block diagram using Lab View, were used to collect the continuous raw data of time, temperature, and torque.

A starch solution at 6%w/w concentration in starch: water system was prepared. A small sample size of 0.829 g in 13 mL water was used. The sample was mixed with a vortex for 30 s in a test tube before the sample was ready for measurement. The sample, at room temperature, was poured into the heated cup while the impeller was being agitated to avoid sample settling. A fixed temperature profile was maintained: from 60 to 95 °C in 2 min, hold at 95 °C for 12 min, cool to 60 °C in 13 s, and hold constant at 60 °C for 10 min.

2.3.2. Rapid visco analyzer (RVA) data collection

Standard profile 1 of RVA was used for the time–temperature profile. Native waxy corn starch (National Starch, NJ) at 6% w/w concentration in starch: water system was prepared. Total sample volume was 25 mL. Time, temperature, and viscosity of the samples during the 13 min test were obtained from the RVA data.

2.4. Starch viscosity model

In this study, the starch viscosity model proposed by Dolan and Steffe (1990) was used with some modification by including the reference temperature in the Arrhenius equation: in the time–temperature history term (T_{rg}) and in the temperature term (T_{rt}) as shown in Eq. (1). There were no other models found in the literature for viscosity development during gelatinization that incorporated simultaneously the four independent variables in the present model: shear rate, temperature, temperature–time history, and shear history. The model discussed in this study has been shown to be suitable for studying the apparent viscosity changes