Journal of Food Engineering 209 (2017) 45–51

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Predictive model for viscosity development of modified rice starch suspension under unsteady temperature change

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ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form
3 April 2017
Accepted 8 April 2017
Available online 12 April 2017

Keywords:
Rice starch
Gelatinization
Kinetics
Rheology
Modeling
Granule growth

ABSTRACT

This study aimed to establish a predictive model that takes into account the effect of thermal history on the viscosity development of modified rice starch dispersions subject to unsteady temperature change. Experiments were conducted in a modified rheometer allowing fast heating/cooling similar to an industrial heat exchanger. The model was developed on two assumptions: (1) starch granule growth is responsible for the viscosity evolution and (2) thermal history controls the gelatinization and the granule growth of the starch dispersion. To identify the rheological parameters, modified rice starch dispersions (3%–5%) were heated from 20 °C to temperatures normally used in heat exchangers (105–120 °C) in a Couette rheometer under high heating rates (0.5–2.0 °C s^{-1}) and shear rates (400 and 800 s^{-1}). The predictive model was successfully employed to predict the viscosity of modified rice starch dispersion gelatinized under vigorous conditions.

1. Introduction

A major problem encountered in the thermal processing of liquid food containing starch is the difficulty to have an accurate prediction of rheological behaviors and hence the control of flow and heat transfer upon the gelatinization of starch. When gelatinization commences, starch granules imbibe great amount of water and, eventually, rupture. As a consequence, a) the volume fraction of particles increases, b) amylose and eventually amylopectin molecules leach out into the medium; these two phenomena cause the food's viscosity to rise rapidly (Tseng and Lin, 2003). The viscosity and rate of viscosity development are governed by starch botanical source, starch concentration, mechanical and thermal history. Native starches are more susceptible to heat and shear compared to chemically bonded starches. When subjected to heat and shear in presence of water, native starches tend to gelatinize and give a peak viscosity which decreases as gelatinization proceeds towards the end (Ibarz et al., 1987). On the contrary, modified, especially cross-bonded, starches would give a peak viscosity that stays relatively constant throughout gelatinization process even under highly vigorous conditions (Saravacos, 1970). Upon cooling, the linear chain of leached amylose molecules tends to reassociate resulting in a more ordered network. As a result, the dispersion viscosity increases. Mechanical and thermal history greatly influences viscosity development of the starch during gelatinization and the final structure of the gelatinized starch. In turn, the final structure of gelatinized starch defines the organoleptic characteristics of foods containing starch. Thus, it is important to correctly characterize the effect of mechanical and thermal history on starch gelatinization. There have been numerous works stating the relationship between viscosity development of food containing starch as a function of starch concentration, mechanical and thermal history under mild gelatinization conditions (Dolan and Steffe, 1990; Doublier et al., 1987; Harrod, 1989a, b; 1989c) and under high gelatinizing temperatures (Abdelrahim et al., 1995; Heydon et al., 1996; Liao, 1998; Rao and Tattiyakul, 1999; Tattiyakul and Rao, 2000). However, rheological data under vigorous processing conditions; high heating rates and shear rates, is missing (Tattiyakul et al., 2006).

Continuous heat exchanger is widely used in liquid food sterilization. When processed in a heat exchanger, especially under an ultra-high temperature (UHT) condition, food is subjected to vigorous conditions, that is, heat treatment at a temperature as

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http://dx.doi.org/10.1016/j.jfoodeng.2017.04.012

Nomenclature

A_m	Inner cylinder vertical surface (m^2)
C	Starch concentration (%)
C_0	Constant related to starch concentration (%)
c_p	Specific heat of the fluid in the gap (J kg^{-1} K^{-1})
c_{pm}	Specific heat of the inner cylinder (J kg^{-1} K^{-1})
D_0	Initial starch granule average diameter (m)
D_t	Starch granule average diameter at time t (m)
D_e	Starch granule equilibrium average diameter (m)
E_a	Energy of activation (J mol^{-1})
e	Gap thickness (m)
K	Consistency index (Pa s^n)
K_0	Consistency index concentration constant (Pa s^n)
K_C	Consistency index temperature constant (Pa s^n)
l	Height of the inner cylinder (m)
m_m	Inner cylinder mass (kg)
n	Flow behaviour index (dimensionless)
n_{av}	Average flow behaviour index in the 30 °C –60 °C range (dimensionless)
R	Universal gas constant, 8.314 J mol^{-1} K^{-1}
R_o	Radius of the outer cylinder (m)
R_i	Radius of the inner cylinder (m)
t	Time (s)
t′	Time t + dt (s)
t_f	Final process time (s)
T	Temperature (K)
T_1	Initial temperature of the inner cylinder (K)
T_a	Onset temperature of the starch gelatinization (K)
T_g	Gelatinization temperature (K)
T_i	Temperature at the surface of the inner cylinder (K)
T_m	Mean temperature in the gap of concentric cylinders (K)
T_o	Temperature at the surface of the outer cylinder (K)
V_T	Starch gelatinization reaction rate constant at temperature T (s^{-1})
V_a	Parameter associated with the starch gelatinization kinetics (s^{-1} K^{-1})
w_1	Fraction of raw starch granules
w_2	Fraction of swollen starch granules
X	Extent of starch gelatinization (dimensionless)
Y	Temperature-time integral (K s)
Greek letters	
$\dot{\gamma}$	Shear rate (s^{-1})
η_a	Apparent viscosity (Pa s)
η_{ac}	Calculated apparent viscosity (Pa s) using the estimate values
$\eta_{a,max}$	Maximum apparent viscosity (Pa s) in the data set
ρ	Density of the fluid in the gap (kg m^{-3})
λ	Thermal conductivity of the fluid in the gap (W m^{-1} K^{-1})
τ	Time delay (s)

high as 270 to 300 °F (around 132–149 °C) for a few seconds (David, 2013) and a shear rate as high as 1000 s^{-1} (Steffe, 1996). When food containing starch is processed under such conditions, difficulty in prediction of viscosity evolution is encountered. Due to high heating rate, a large temperature gradient results. Also inside a rheometer, when applying high heating rate, the set point temperature cannot be taken as the effective temperature that induces rheological changes of the food. Lagarrigue et al. (2003) showed that, when heating glycerol and 60% w/w sucrose solution in the gap between concentric cylinders (1 mm gap size), the temperature deviation between the outer cylinder and the fluid in the gap was as high as 7.5 °C in the case of glycerol and 6 °C for 60% w/w sucrose solution. If the outer cylinder (set) temperature was to be used to calculate the viscosity change, a 25% and 60% deviation would result for the viscosity prediction of 60% w/w sucrose solution and glycerol, respectively. In such case, the authors showed that the fluid viscosity change was a function of the mean value of the outer cylinder temperature and inner cylinder temperature. Moreover, at high heating rates, starch granules were not allowed to sufficiently hydrate to their typical capacity at certain temperatures. Thus, delay in granules growth could be expected.

The objective of this study was to characterize viscosity development of modified rice starch dispersion under unsteady thermal conditions at high heating rates and high shear rates.

2. Theory

With presence of excess water at low temperature ($T < 50$ °C), raw starch granules imbibe water and swell. The extent of swelling is not so large that the viscosity of the dispersion changes noticeably in this step, and changes are reversible. When heat is supplied to the dispersion so that the starch gelatinization temperature of T_g is exceeded, starch granules swell to a great extent; 4–5 times their original size, resulting in an increase in the dispersion viscosity (Rao and Tattiyakul, 1999). Changes that occur after T_g is reached are not reversible. With continuing heat and shear, the swollen granules lose their integrity causing a decline in viscosity. For cross-bonded starches, it can be assumed that the starch granules withstand vigorous conditions and, hence, retain their integrity throughout the gelatinization process. Therefore, a single-stage gelatinization reaction can be assumed.

Following Okechukwu and Rao (1995), the extent of gelatinization (X) can be expressed as

$$X = \frac{D_t - D_0}{D_e - D_0} \tag{1}$$

Where, D_0, D_t and D_e are respectively the initial diameter, the diameter at time t and the diameter of completely swollen granules (after a long heat treatment).

The fraction of raw starch granules (w_1) and swollen starch granules (w_2) equals 1-X and X, respectively. The rate of starch gelatinization that follows second-order reaction kinetics (Lagarrigue et al., 2008) can be written as following:

$$\frac{dw_1}{dt} = -V_T(t)w_1^2 \tag{2}$$

where, $V_T(t)$ is the gelatinization reaction rate constant that changes as a function of temperature after starch gelatinization commences:

$$V_T(t) = 0, \text{ for Tm(t)} < \text{Ta} \tag{3}$$

$$V_T(t) = V_a(T_m(t) - T_a), \text{ for Tm(t)} \geq \text{Ta} \tag{4}$$

where, $T_m(t) = \frac{T_o(t)+T_i(t)}{2}$ is the mean temperature (in the gap of the