Food Chemistry 115 (2009) 563–568

Contents lists available at ScienceDirect

Food Chemistry

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

Preparation and characterisation of crosslinked waxy potato starch

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ARTICLE INFO

Article history:
Received 5 June 2008
Received in revised form 24 November 2008
Accepted 18 December 2008

Keywords:
Modified waxy potato starch
Acetylated distarch adipate
Degree of substitution

ABSTRACT

Using waxy potato starch as the raw material, the preparation, and determination of physical and chemical properties of acetylated distarch adipate (ADA) were studied systematically. The experimental variables investigated include temperature, pH, and reaction time, which all have influence on the degree of substitution (DS) of crosslinked waxy potato starch. Results show that the optimal reaction was obtained at a pH range of 9.0–9.5, a temperature of 35 °C, and a reaction time of 2 h. The structures of ADA starch were characterised by FT-IR, and the results indicate a new absorption peak at 1732 cm^{-1} which is assigned to the C=O stretching vibration. It was found through polarised light microscopy and scanning electron microscopy (SEM) that the starch granule structure did not substantially change after crosslinking. The modified waxy potato starch paste exhibited excellent viscosity stability, acid resistant, salt tolerance properties and good breakdown. The swelling of ADA starch granules was gradual over a wide range of temperatures.

1. Introduction

Waxy potato starch has been developed from a potato mutant where amylose biosynthesis was inhibited resulting in tubers containing about 99% amylopectin (Visser, Suurs, Bruinenberg, Bleeker, & Jacobsen, 1997a).

Waxy potato starch combines the properties of normal potato starch with the advantage of lower viscosity and enhanced stability in pastes. Moreover, it shows a lower tendency to retrograde resulting in more stable and less turbid systems with lower viscosity (Kortstee et al., 1998; Nuessli, Handschin, Conde-Petit, & Zurich, 2000; Visser, Suurs, Bruinenberg, Bleeker, & Jacobsen, 1997b). However, it has some disadvantages which make it unsuitable for food systems and processing such as: narrow peak viscosity, undesirable texture, poor stability, and poor process tolerance (Light, 1990).

Cross-linking reagents may be any chemical containing two or more functional groups capable of reacting with at least two of the hydroxyl groups on the starch molecule, and thus causing a linkage of those groups. The most widely used cross-linking reagents for modifying food starches are mixes of adipic/acetic anhydride, and phosphorus oxychloride or sodium trimetaphosphate, which yield distarch adipates, distarch phosphates, respectively (Mali & Grossmann, 2001; Wurzburg, 1986). Adipic acid reacts with starch and produces both cross-linked starches and monoderivatives (Wurzburg, 1960). Some advantages of cross-linked starches over native starches are: increased stability towards heat, pH, shear, and freeze-thaw stability (Ellis, Cochrane, & Daley, 1998). When acetyl groups are introduced on starches, the tendency of sols of these starches to deteriorate in clarity, texture, and to syneresis when held at low temperatures, is greatly reduced. These constituent groups are stabilized starches by interrupting the linearity of amylose chains and segmenting of amylopectin branches. Cross-linked starches have been applied in soups, gravies, sauces, baby foods, fruit filling, pudding, and deep fried foods (Rutenberg & Solarek, 1984).

The present paper studies the chemical modification of waxy potato starch and its characterisation. The objectives of this study were to develop a greater understanding of how critical reaction parameters (temperature, pH and reaction time) in aqueous slurry affect the degree of substitution of acetylated distarch adipates (ADA) of waxy potato starch, and to study the structure of ADA starch and their physiochemical properties.

2. Materials and methods

2.1. Materials

Waxy potato starch was obtained from AVEBE Company (Veendam, Netherlands). Adipic acetic mixed anhydride was prepared by mixing adipic acid and acetic anhydride (mass ratio 1:30) (Wurzburg, 1960), which were purchased from Guang Zhou chemical reagent company (Guang Zhou, China). The other chemicals used in the study were all of analytical grade.

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doi:10.1016/j.foodchem.2008.12.052

2.2. Preparation of acetylated adipate crosslinked waxy potato starch

The general methodology for reactions of mixing adipic acid and acetic anhydride with waxy potato starch is given below. Starch slurry was prepared by adding 500 g waxy potato starch (dry basis, db) to 930 g deionized water at room temperature in a 2 L reaction vessel equipped with a mantle. The pH was maintained between 9.0 and 9.5 using a 3% (w/w) aqueous NaOH solution. The temperature was increased to 35 °Cwith a temperature controller and then 20 g mixed anhydride was added drop-wise to the slurry. The slurry was maintained at 35 °C for 2 h and then the pH was adjusted to 6.5 using diluted HCl (0.1 N). The resulting starch suspension was vacuum-filtered through filter paper (Whatman 110 mm, Whatman international Ltd. Maidstone, England) and washed twice with distilled water (used 1.25 L at a time) and once with alcohol. Afterwards the recovered starch was dried in a force-air oven (Model: CS101, Chong Qing experimental equipment factory, Chong Qing, China) at 40 °C for 24 h. The dried starch was ground gently in a mortar to pass through a standard 100-mesh sieve. The degree of substitution (DS) of ADA starch was determined according to the methods of Sanders and Brunt (1994). The preparation of ADA starch was duplicate following the same procedure.

2.3. Polarised light microscopy

Polarised light microscopy was performed using an OLYMPUS VANOX BHS-2 (Tokyo, Japan). ADA starch was suspended in distilled water (1% w/v). The starch slurry was then dropped on a glass slide; spread around then cover slip was placed. The sample was observed with a magnification of 400×.

2.4. Scanning electron microcopy (SEM)

The appearance of native waxy potato starch and ADA starch granules were observed using a SEM according to the method of Hung and Morita (2005). Starch was suspended in 95% ethanol for a few minutes and sprinkled on double-sided adhesive tape mounted on an aluminium stub, and then coated with a thin film of Pt-Pd. Scanning was performed using a S-550 Scanning Electronic Microscope (Hitachi Ltd. Tokyo, Japan). The sample was observed with a magnification of 1000×.

2.5. Fourier-transform infrared (FT-IR) spectroscopy

The IR spectra were obtained from samples in KBr pellets using a Vector 33 FT-IR spectrophotometer (Bruker Company, Ettlingen, Germany).

2.6. Swelling power of native waxy potato and ADA starches

Swelling power was determined using the method of Leach, McCowen, and Schoch (1959). Starch samples (0.25 g, db) were accurately weighed and transferred into clear dried test tubes and weighed with the test tubes (W_1). Distilled water (50 mL) was added to the test tube and mixed thoroughly with a Variwhirl mixer (Model: A901, Salver Chem. Chicago, IL, USA) for 30 s. Because of the different swelling properties of native waxy potato starch and ADA starch, The resultant slurries were then heated in water bath at selected temperature; from 62 °C to 74 °C at two degree intervals for waxy potato starch and from 64 °C to 92 °C at four degree intervals for ADA starch. The suspension was then cooled rapidly to room temperature and centrifuged (5000g, 15 min) and sediment recovered. The weight of the residue (after decanting the supernatant) was obtained (W_2).

Swelling of starch was then calculated to be W_2-W_1/Weight of starch (dry matter basis).

2.7. Rheological measurements

Steady shear properties were studied at pH values of 3.0, 4.0, 5.0, 6.0 and 7.0 using a rheometer (Brookfield DV-I, Brookfield Engineering Laboratories, INC, Massachusetts, USA).

2.8. Pasting properties of starches

Native waxy potato and ADA starches were analysed using a Brabender viscograph "E" (C.W. Brabender instruments INC, Duisburg, Germany). Dry sample (13.8 g) was suspended in 446.2 mL distilled water or 1% (w/w) NaCl solution. Brabender cartridge (700 cm/g) was fitted with the rotation speed set to 75 rpm. The starch suspension was heated at 1.5 °C/min to 95 °C from 30 °C, then held for 30 min at 95 °C, cooled to 50 °C at a rate of 1.5 °C/min, and then held for 30 min at 50 °C.

2.9. Statistical analysis

Analyses of mean separation were performed performed by Tukey's HSD test using SigmaStat Version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL, USA).

3. Results and discussion

3.1. Effect of pH of aqueous on the reaction

The effect of pH on the reaction was studied at the pH range of 7.0 to 10.5 whilst the other reaction parameters were kept constant. Inspection of Fig. 1 A shows that the highest degree of substitution was reached at the pH range of 9.0–9.5. However, pH above or below of this range had substantially detrimental effects on the reaction. These results may be explained by the fact that pH values >9.5 favour anhydride hydrolysis whereas pH values <9.0 do not satisfactorily activate the hydroxyl groups of starch molecules for the nucleophilic attack of the anhydride moieties. Hence, the pH range of 9.0–9.5 was used in subsequent experiments.

3.2. Effect of reaction temperature

Fig. 1B gives the results of variation in reaction temperature whilst holding the starch concentration at 35%, the anhydride at 4.0% (w/w) relative to dry starch, pH at 9.0–9.5 and reaction time of 2 h. Fig. 1B shows both positive and negative effects of temperature on the reaction efficiency. An increase in the reaction temperature from 20 °C to 35 °C resulted in a large increase in the degree of substitution. Further increase in the reaction temperature from 35 °C to 50 °C resulted in a decrease in the degree of substitution. A complex set of variables is expected to come into play when the reaction temperature is changed. For example, an increase in temperature will result in increased hydrolysis of anhydride. However, a higher temperature would be expected to also enhance the swelling of native starch granules which will increase the esterification. These results indicate that a better understanding how temperature affects hydrolysis of anhydride and starch granule swelling would help in explaining the above results.

3.3. Effect of reaction time

Variations in the reaction time and its effect on reaction efficiency were studied (Fig. 1C). Increasing the reaction time from 0.5 to 2 h resulted in higher reaction efficiency. However, prolonging the reaction time beyond 2 h resulted in decreased reaction efficiency. This could be due to that as the reaction progress, the