Thermochimica Acta 552 (2013) 46–53

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

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

Effect of emulsifiers on complexation and retrogradation characteristics of native and chemically modified White sorghum (*Sorghum bicolor*) starch

Tahira Mohsin Ali*, Abid Hasnain

Department of Food Science and Technology, University of Karachi, 75270 Karachi, Pakistan

ARTICLE INFO

Article history:
Received 12 July 2012
Received in revised form
12 November 2012
Accepted 14 November 2012
Available online 23 November 2012

Keywords:
Starch
Sorghum
Retrogradation
Emulsifiers

ABSTRACT

The effect of emulsifiers on complexation and retrogradation characteristics of native and chemically modified white sorghum starches was studied. Complex forming tendency of white sorghum starch with commercially available emulsifiers GMS and DATEM improved after acetylation. Presence of emulsifiers reduced λ_{max} (wavelength of maximum absorbance) both for native and modified sorghum starches suggesting lower availability of amylose chains to complex with iodine. In native white sorghum starch (NWSS) and oxidized white sorghum starch (OWSS), both Type I and Type II starch–lipid complexes were observed on addition of 1.0% GMS prior to gelatinization. Acetylated-oxidized white sorghum starch (AOWSS) formed weakest complexes among all the modified starches. The results revealed that antistaling characteristics of modified sorghum starches were enhanced when used in combination with emulsifiers. The most prominent decline in reassociative capability among modified starches was observed for acetylated starches.

1. Introduction

Native and modified starches are incorporated as additives in a wide variety of food products [1]. Depending upon the processing conditions, starches interact with other co-ingredients like sugars, gums, lipids, proteins, etc. and significantly alter the physicochemical and textural properties of such products. One of the most noteworthy interactions is between starches and emulsifiers as amylose component of starch has the capability to form inclusion complex with amphiphilic molecules called emulsifiers. Guest molecules like fatty acids, alcohols and esters because of their hydrophobic nature have limited affinity for aqueous environment and thus are hosted in the hydrophobic lumen of amylose [2]. The single helical left-handed inclusion complex called V-amylose thus formed is stabilized by forces that are hydrophobic in nature [3].

Emulsifiers are present together with both native and modified starches in confections, spreads, dressings, custards, mayonnaise, breads, biscuits, cakes, etc. According to Heinemann et al. [4], amylose–lipid complex formation even takes place in more complex systems like dressings, spreads and custards. Such products usually contain modified starches instead of native starches. Wulff et al. [5] carried out investigation on inclusion behavior of modified amylose chains. Chemical modifications introduce functional groups on amylose chains which subsequently improve solubility of amylose chains and the complexes formed by such modified amylose chains are also soluble in water [5]. Because of the higher solubility of modified amylose–lipid complexes they could be used as a carrier to solubilize compounds like flavors, fatty acids and triglycerides that are otherwise insoluble in water. The presence of soluble and insoluble complexes affects the colloidal properties of starch–water systems in a different way. Presence of suitable guest molecules induces single helical conformation of amylose [6]. However, in the absence of guest molecules linear amylose chains characterized by random coils and having low solubility in aqueous phase associate with each other to form double helices. These double helices act as nuclei for retrogradation by co-crystallizing with amlopectin [7]. The unavailability of amylose in double helical form therefore curtails retrogradation phenomenon in starches. Differential Scanning Calorimetry is a powerful tool to study the retrogradation characteristics of starches. In long term, retrogradation is due to recrystallization of amylopectin chains [8] and DSC is used to measure the enthalpy required to melt these recrystallized amylopectin chains.

Many research studies have been carried out to investigate starch–lipid complexes in potato, corn, rice, pigeon pea, cowpea, cassava and wheat starches on addition of emulsifiers [9–14]. However, very little work has been done to investigate the effect of emulsifiers on complexing tendency of sorghum starch which is used in a number of gluten free products. Sorghum is characterized by high drought tolerance and can even grow in limited water supplies [15]. Such agronomic properties highlight importance of

* Corresponding author. Tel.: +92 21 34823115; fax: +92 21 99243206.
E-mail addresses: tahira.mohsin@uok.edu.pk (T.M. Ali), abidhasnain@uok.edu.pk (A. Hasnain).

0040-6031/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2012.11.016

sorghum for countries with limited water resources. Owing to functional similarity between sorghum and corn starch [16], the former could easily substitute corn starch. Secondly, most of the previous work done focused on acetylated starches [17,18], while investigations on other single and dual modified forms of starches commonly used in food products is still scanty.

The emulsifiers are often present as co-ingredients with modified starches in many solid and semi-solid food products and thus could interact with each other and may affect the textural and rheological properties of starch gels. Therefore, the aim of present study was to investigate the effect of emulsifiers on complexation, gelatinization and retrogradation characteristics of acetylated, oxidized, acid thinned and acetylated-oxidized white sorghum starches.

2. Materials and methods

Cleaned white sorghum grains from a single cultivar were used for isolation of starch. The amylose and amylopectin content in starch was found to be 26.5% and 73.5% using the method of Landers et al. [19]. Emulsifiers namely glycerol monostearate (GMS-90), diacetyl tartaric acid esers of monoglycerides (DATEM) and sodium stearoyl lactylate (SSL) were kindly provided by ZTCC (Henan Zheng Tong, China). All other chemicals used were of reagent grade.

2.1. Isolation of starch

Starch was isolated from white sorghum grains using the procedure of Ali and Hasnain [20].

2.2. Starch oxidation

The method of Forssell et al. [21] was used for preparing oxidized white sorghum starch.

2.3. Acetylation

Acetylated white sorghum starch was prepared by adding 6 g of acetic anhydride (Merck KGaA, Darmstadt, Germany) to 100 g of starch using the procedure of Philips et al. [22].

2.4. Acid thinning

Acid thinning was carried out using the procedure of Gunaratne and Corke [23]. A 40% (dry basis) starch slurry was acid modified using 0.1 M HCl at 50 °C in water bath with constant stirring for 1.5 h. The slurry was then adjusted to pH 7 using 0.5 M NaOH. The sedimented starch was washed at least five times with distilled water, followed by drying at 45 °C in a forced air oven.

2.5. Dual modified acetylated oxidized starch

Oxidized white sorghum starch prepared by using the aforementioned method was further modified by acetylation using the procedure of Philips et al. [22] to prepare dual modified acetylated-oxidized starch.

2.6. Determination of carboxyl content (%)

Carboxyl content was determined using the procedure of Chattopadhyay et al. [24].

2.7. Determination of carbonyl content (%)

Carbonyl content was determined using the procedure of Smith [25].

2.8. Determination of degree of acetylation (%)

The method of Wurzburg [26] was used to determine percent acetylation and degree of substitution in acetylated white sorghum starch.

2.9. Preparation of emulsion gels

Emulsion gels were prepared by mixing emulsifier and water in the ratio of 1:10 (w/v). For GMS-90, the emulsifier suspension was heated at 65 °C for 30 min in a water bath whereas DATEM and SSL suspensions were heated at 45 °C for 30 min. To study the effect of emulsifiers on the properties of starches, the emulsifiers were added at 0.5%, 0.75% and 1.0% based on starch weight (dry basis).

2.10. Complexation index (CI), maximum absorbance (A_{max}) and wavelength of maximum absorbance (λ_{max})

Complexation index was determined using the method of Gilbert and Spragg [27]. One milliliter of DMSO was added to starch (20 mg) followed by heating in a boiling water bath for 15 min to completely gelatinize the starch. Five milliliter of ethanol was added to starch and solutions were kept in water bath at 60 °C. After 30 min, starch solutions were centrifuged at 3000 × *g* for 15 min. The pellets obtained after centrifugation were dissolved in 5 mL of distilled water followed by addition of emulsifiers at 0.5%, 0.75% and 1.0% based on starch weight (dry basis) and were then heated at 60 °C for 1 h. An aliquot of 0.1 mL starch solution was added to 5 mL of distilled water, with subsequent addition of 0.05 mL iodine solution (0.1% (w/v) I_2 and 0.3% (w/v) KI in water) and the resulting solution was allowed to stand for 30 min for color development followed by measurement of absorption spectra from 400 nm to 800 nm using JASCO V-670 Spectrophotometer. Complexation index was calculated using following formula:

$$\%CI = \frac{(A_s - A_{se}) \times 100}{A_s}$$

A_s is the absorbance of starch without emulsifier at 620 nm. A_{se} is the absorbance of starch with emulsifier at 620 nm.

Wavelength of maximum absorbance (λ_{max}) was also determined from the absorption spectra.

2.11. Differential Scanning Calorimetry

Starch–lipid complexes, gelatinization and retrogradation characteristics of native and modified starches in the presence of emulsifiers were studied using Differential Scanning Calorimetry (DSC Q10, TA instruments, USA). Briefly, 2 mg of starch was placed in 40 μL capacity hermetic aluminum pans followed by addition of 6 μL of water using a microliter syringe. The pans were then hermetically sealed and allowed to equilibrate for 24 h at room temperature before the thermal scan. The pans were scanned from 30 °C to 130 °C at a scanning rate of 10 °C/min using an empty pan as a reference. The same pans were then stored for 14 days at 6 °C to observe the retrogradation characteristics of native and modified white sorghum starches by scanning from 30 °C to 130 °C at a scanning rate of 10 °C/min.