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Utilization of chemically modified pearl millet starches in preparation of custards with improved cold storage stability

Marium Shaikh*, Tahira Mohsin Ali, Abid Hasnain

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

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ABSTRACT

Custards were prepared using five ingredients: milk powder, modified pearl millet starch, sugar, vanilla essence and water. The effect of adding hydroxypropylated starch (HPS), succinylated starch (SUS), oxidised starch (OXS) and acetylated starch (ACS) on cold storage stability, pasting, textural and sensory properties was studied and compared to custards containing native pearl millet starch (NS). Interestingly, all chemically modified starches reduced syneresis and no water weeping was observed in custard sample incorporating hydroxypropylated starch (HPC) even after 7 days of cold storage. Viscoamylographic analysis revealed that custard containing succinylated starch (SUC) had the highest peak viscosity (108.8 BU), whereas HPC showed the least set back viscosity (19.0 BU). Sensory results suggested that assessors preferred HPC over other custards. Custards are preferred for their chewy semi-solid texture. Incorporation of hydroxypropylated starch (HPS) increased hardness, gumminess and chewiness which subsequently led to higher sensory scores during subjective analysis. Also, no retrogradation peak was observed for HPS and acetylated starch (ACS) when rescanned after 14 days. Thus, it could be concluded that HPS could be used in custards to confer low temperature stability by reducing syneresis.

1. Introduction

Starch is a multifunctional storage carbohydrate that plays a vital role in human nutrition as well as maintains texture, body, mouth feel and several other characteristics of a wide variety of food products. It is comprised of two types of molecules: amylose (linear polymer of α-D-glucose units linked by α-1,4 glycosidic linkages) and amylopectin (branched polymer of α-D-glucose units linked by α-1,4 and α-1,6 glycosidic linkages). These two components are arranged in such a manner which generates a typical semi-crystalline granular structure. Native starches are those starches which are derived from different parts of the plants but due to their instability towards certain processing conditions of food, they are generally modified either chemically, physically or using a combination of both. Both native and chemically or physically modified starches are commonly employed in dairy products. However, the use of modified starches is increasing as they show superior thermo-mechanical resistance and extra stability as compared to native starches producing dairy desserts with better texture and without syneresis. Native starches can be chemically modified via succinylation, oxidation, acetylation and hydroxypropylation [1–4]

Custard is basically a starch based dairy product which is widely consumed in different regions of the world as a dessert. The chief ingredients for custard formulation include: milk solids, starches (from corn, cassava etc/modified starches), sucrose, colorant, and flavour [5]. To this mixture normally water is added and then heated to prepare a viscous slurry which upon cooling turns into a semi solid gel. Custards are famous due to their consistency, semisolid structure and different available flavours like chocolate, vanilla, strawberry etc [6]. The particular characteristics of some ingredients, like fat content of milk, type and concentration of starch, and/or type and concentration of hydrocolloids strongly influence the rheological and sensory properties of custards. One of the major technological challenges in maintaining the shelf life of custard is to reduce or eliminate the water separation phenomenon upon cold storage. Generally corn starch is added to the custard formulation as it provides structure and texture to the product. However, corn starch can be substituted with other starch sources.

Pearl millet (*Pennisetum glaucum*), locally known as '*Bajra*', is widely grown in different regions of the world including Pakistan. It is highly tolerant to drought, salt and adverse climatic conditions. Being resilient in nature, pearl millet efficiently utilizes more moisture and has a high heat tolerance in comparison to sorghum and corn [7]. The starch content of pearl millet constitutes about 55-65% and it could also be a cheap source of starch in comparison to corn. Despite of its beneficial agronomic properties, pearl millet is considered as a crop with poor economic value. However, it could

* Corresponding author.
E-mail addresses: marium.shaikh@uok.edu.pk (M. Shaikh), tahira.mohsin@uok.edu.pk (T.M. Ali), abidhasnain@uok.edu.pk (A. Hasnain).

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be exploited for the starch extraction which could be used in various commercial and domestic food applications. This study aimed to investigate the effect of incorporating native as well as different chemically modified pearl millet starches into custard samples. These effects were studied in terms of syneresis, texture, viscosity and sensory properties. Special attention was given to develop cold stable custards by incorporation of chemically modified pearl millet starches which were less prone to water separation upon storage.

2. Materials and methods

2.1. Materials

Good quality pearl millet grains (WCA-78), free from defects were obtained from PARC (Pakistan Agriculture Research Council). These were planted in Islamabad under the supervision of PARC. After fumigation, grains were stored at room temperature (±25 °C) in paper bags. The following analytical grade reagents were procured: succinic anhydride (Daejung, CAS: 108-30-5), propylene oxide (Sigma-Aldrich Chemical Co., CAS: 75-56-9), acetic anhydride (Riedel-de Häen AG, Seelze, Germany, CAS: 108-24-7), and sodium hypochlorite (Riedel-de Häen AG, Seelze, Germany, CAS: 67-63-0).

2.2. Isolation of starch and chemical modification

Starch was isolated from pearl millet grains in accordance with the method explained by Shaikh et al. [8]. Cleaned pearl millet grains were washed and steeped in 0.5% lactic acid and 0.3% (w/v) sodium metabisulfite solution for 24 h at 40 °C. The steeping solution was completely removed by washing the grains thrice with tap water. Grains were then coarsely ground and blended in a waring blender (Black & Decker, model BX380G, England) for 5 min at 8000 rpm. The resultant slurry was sieved through a pile of 80 and 300 wire mesh sieves from top to bottom. The overs from the sieves were reblended in a waring blender for 2 min, followed by sieving. This step was repeated twice. The pH of the obtained slurry was adjusted to 9.0 using 0.5 mol/L NaOH solution, stirred for 2 h in a magnetic stirrer (Jenway 1200, UK) and then allowed to sediment at 4 °C. Afterwards, the protein layer was scraped off using a spatula. The sedimented starch was washed with water and homogenized again to remove the residual protein. The washed starch was then dried at 45 °C for 24 h in a forced air oven (Daihan Labtech Co.Ltd., Korea).

2.2.1. Succinylation of starch

Succinylated starch was prepared according to the method described by Mehboob et al. [9]. A 40% (w/w, dry basis) starch slurry was prepared in distilled water. The pH of the slurry was regulated to 9.5 by adding 3% (w/v) NaOH solution. Succinic anhydride (3%, db of starch) was added gradually while maintaining the pH between 9.0-9.5. The reaction was allowed to proceed for 2 h and thereafter terminated by addition of 0.5 mol/L HCl solution to achieve a pH of 7.0. The slurry was washed thrice with distilled water. The succinylated starch was then dried at 45 °C for 24 h and stored in refrigerator prior to use. Percent succinyl content was calculated using the following equation:

$$\%\,\text{Succinyl content} = \frac{(\text{blank} - \text{sample})\,\text{mL} \times \text{normality of standardized acid} \times 100}{\text{weight of sample (g)}}$$

2.2.2. Acetylation of starch

Starch was acetylated as per the method explained by Phillips et al. [10]. A 42% (w/w, db) starch slurry was prepared by dissolving pearl millet starch (150 g, dry basis) in 353 mL distilled water. The pH was adjusted to 8.0 by addition of 3% NaOH (w/v) solution. Acetic anhydride (6%, db of starch) was added drop wise while pH was simultaneously maintained between 8.0-8.5. The reaction continued for 15 min and then 0.5N HCl was added to attain the pH of 4.5. The starch was allowed to sediment and the resultant cake was washed thrice with distilled water. The acetylated starch was dried at 45 °C for 24 h and stored in refrigerator prior to use. Percent acetyl groups in starch were determined as:

$$\%\,\text{Acetyl content} = \frac{(\text{blank} - \text{sample})\,\text{mL} \times \text{molarity of standardized HCl} \times 0.043 \times 100}{\text{weight of sample (g)}}$$

2.2.3. Oxidation of starch

Oxidation of starch was performed in accordance with the method described by Lawal et al. [11]. Starch (150 g, db) was dissolved in 750 mL of distilled water to prepare 20% (w/w, db) slurry and pH was maintained at 9.5 with 1 mol/L NaOH solution. Sodium hypochlorite (5 g) was added to the slurry over a period of 30 min with continuous stirring, while maintaining pH in the range of 9.0–9.5. The pH was controlled with 0.5 mol/L HCl or 0.5 mol/L NaOH. After 15 min, the reaction was stopped by adding 1 mol/L H_2SO_4 thereby obtaining a pH of 7.0. The resultant starch was filtered and washed four times with distilled water. The oxidized starch was then dried at 45 °C for 24 h and stored in refrigerator prior to use.

The carboxyl content of oxidized starch was calculated as follows:

$$\frac{\text{Milliequivalents of Acidity}}{100\text{ g Starch}} = \frac{(\text{sample} - \text{blank})\,\text{mL} \times \text{normality of standardized NaOH} \times 100}{\text{weight of sample (g)}}$$

$$\%\,\text{Carboxyl content} = \left[\frac{\text{Milliequivalents of acidity}}{100\,\text{g starch}}\right] \times 0.045$$

The carbonyl content of oxidized starch was calculated as follows:

$$\%\,\text{Carbonyl content} = \frac{(\text{blank} - \text{sample})\,\text{mL} \times \text{normality of standardized acid} \times 0.028 \times 100}{\text{weight of sample (g)}}$$

2.2.4. Hydroxypropylation of starch

Hydroxypropylation of pearl millet starch was conducted as per the method of Lawal [12]. Starch (150 g, db) was weighed in a 500 mL screw capped glass jar and 250 mL distilled water was added to prepare slurry. To this slurry, 15 g of sodium sulphate was added, stirred for 30 min in a magnetic stirrer and then the pH was adjusted to 11.5 with 1 mol/L NaOH solution. Propylene oxide (30%, based on dry weight of starch) was added, the slurry was thoroughly homogenized and the glass jar was placed in water bath at 40 °C for 24 h. Afterwards, the reaction was terminated with the addition of 0.1 mol/L HCL solution and the pH was adjusted to 7.0. The suspension was then allowed to sediment and the resultant starch cake was washed with distilled water until it was negative for sulphate content when tested with 1% barium chloride solution. The starch cake was finally dried at 45 °C for 24 h in a forced air oven and stored in refrigerator prior to use. Percent hydroxyl groups were estimated by using the following equation:

$$\%\,\text{hydroxypropyl content} = \frac{\text{Amount of propylene glycol}\left(\frac{\mu g}{mL}\right) \times 0.7763 \times 10 \times F}{\text{weight of sample (mg)}}$$

Where F is the dilution factor (if a further dilution has been necessary) and 0.7763 is the factor to convert micrograms of glycol to hydroxypropyl group equivalent.