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Influence of potato and corn modified starches as fat replacers on sensory and physicochemical properties of milk

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ABSTRACT: Current interests towards lowering fat content in food products and producing healthier and safer foods, have convinced milk manufacturers to substitute milk fat with either carbohydrate based fat replacers. In this study, modified starch was used as a fat replacer in the milk. Fat replacer was manufactured from various modified starch such as acid treated, pre-gelatinized and cross–linked starch by replacing 0.15, 0.3 and 0.45% of milk. Modified starches were produced from two source of starch (potato and corn) using citric acid. Physicochemical and sensory properties of milk samples were evaluated. The effect of plant source and kind of modification on physicochemical and sensory properties of the milk sample was significant. The results indicated that acid-modified starch at concentration of 0.15%, pre-gelatinized starch at concentration of 0.45% and cross-linked starch at concentration of 0.3% can be a good choice for adding to skim milk but milk samples with cross-linked corn starch were better due to its acceptable texture and flavor.

Keywords**:** Chemical modification, Corn starch, Potato starch, Cross-linked starch

INTRODUCTION

Starch, one of the main polysaccharides, plays an important role in textures of many kinds of food products and serves as a great source of energy for humans. Nevertheless, native starch does not meet the functional properties required in food products such as thickening and stabilization. Hence starch modification improve its functional characteristics, can be used to tailor starch to specific food applications (Hermansson and Svegmark, 1996). Starch modification is generally achieved through derivatization such as etherification, esterification, cross-linking and grafting of starch; decomposition of starch applying acid or enzymatic hydrolysis and oxidization or physical treatment of starch using heat or moisture, etc. Chemical modification involves the introduction of functional groups into the starch molecules, resulting in marked changes in starch physico-chemical properties (Thomas and Atwell, 1999, Ratnayake and Jackson, 2008).

Cross-linked starch is an example of chemically modified starches. Chemical modification is intended to facilitate intra- and intermolecular bonds at random locations in the starch granules for their stabilization (Singh et al., 2007, Carmona-Garcia et al., 2009). Pastes of cross-linked starch are more resistant to shear and acidic conditions. Cross-linking is generally performed by treatment of granular starch with multifunctional reagents capable of forming either ether or ester inter-molecular linkages between the hydroxyl groups of starch molecules. The main reagents used for cross-linking are sodium trimetaphosphate, mono-sodium phosphate, sodium tripolyphosphate, phosphoryl chloride (POCl3), a mixture of adipic acid, acetic anhydride, and vinyl chloride (Ratnayake and Jackson, 2008, Singh, 2007).

Pre-gelatinized starch is a common type of physically modified starch with wide applications, especially in food industry. Pre-gelatinized starch also referred to as "pre-gel" or "instant starch", is generally produced by drum drier, spray drier, and, less commonly, by extruder (Anastasiades, 2002, Kalogianni, 2002, Mounsey and O'Riordan, 2008). Depending on the method, condition and source of starch, the produced pre-gelatinized starch has different properties (Kalogianni, 2002, Mercier, 1987).

The process of gelatinization causes substantial changes in both chemical and physical nature of granular starch due to the rearrangement of intra- and intermolecular hydrogen bonding between water and starch molecules resulting in the collapse or disruption of molecular orders within the starch granules. This causes irreversible changes in the starch properties including loss of organized structure of starch, granule swelling, loss of birefringence and crystallinity (Anastasiades, 2002, Cooke and Gidley, 1992).

Decomposition of starch using acid hydrolysis is a convenient method to modify starch in food industry. This process involves suspending starch in an aqueous solution of hydrochloric acid or sulfuric acid at certain temperatures. In the presence of a strong acid and heat, the glycosidic bond between monosaccharides in a polysaccharide is cleaved. In this research citric acid was chosen as the aqueous solution to modify starch. It is also important as a sour basic substance for difference tests on the sensory evaluation (Ratnayake and Jackson, 2008).

However, a limited amount of work has focused on the effects of these modified starches on the physicochemical and sensory properties of milk by fat replacer. The aim of this study was to modify starches (acid treated, pre-gelatinized and cross–linked starches) from two botanical sources (potato and corn) and using them as a fat replacer in milk then to characterize the physicochemical and sensory properties of milk samples, in order to facilitate applications in food and/or other related industries.

MATERIALS AND METHODS

Materials

Pure potato and corn starches were purchased from GlucosinCo. Qazvin, Iran. Other chemicals including POCl3, NaOH, HCl, NaHSO4, ethanol, zinc acetate, citric acid and KOH were analytical grades and obtained from Merck, Germany.

Methods

1. Production of modified starches

1.1. Preparation of acid-modified starches

50 gram (dry basis) of starch was hydrolyzed by suspending in 67 ml of (1M) HCl solution at 25 °C for 2h without stirring. After hydrolysis time, the suspension was neutralized with diluted NaOH solution, and washed five times with distilled water. The water was then removed by centrifugation (Sorvall RC 3B Plus, Delaware, USA) at 1000 rpm for 2 min and decanting. The acid-modified starch slurry was spray-dried with a mobile minor spray dryer (Gea-Niro, Denmark) at the inlet and outlet temperatures of 160 and 60 °C, respectively. The dried powder was sieved through 100-mesh sifter to achieve acid-modified starch powder.

1.2. Preparation of pre-gelatinized starch

pre-gelatinized starch was produced using gelatinizing starch in Brabender Viscoamylograph Type E (Duisburg, Germany). A starch suspension 6% (w/v) was heated from 25 to 95 °C at the rate of 1.5 °C/min, held at 95 °C for 15 min and cooled to 50 °C at the same rate. The suspension of starch was spreaded to form thin layer before drying overnight in an oven (60 °C). The pre-gelatinized starch sample (containing 10% water) was blended and sieved through a 100-mesh sifter to achieve the starch powder sample.

1.3. Production of Cross-linked starch

50 g of starch was suspended in 67 mL of distilled water containing 1 g $NaHSO_4$ and the pH was adjusted to 11 ± 0.1 by employing NaOH 1N. Then 0.1g $POCl_3$ was added to the mixture while stirring for 1 h to start the reaction. The reaction was terminated by adjusting the pH to 5.5 using HCl 1N. The suspension was washed with distilled water and centrifuged several times for 10 min at 15000 g and was dried in an oven at 40°C.

2. Physico-Chemical analysis

Total solid of individual sample was measured according to AOAC method 990.19 and AOAC 2000.18 was used to determine fat contents in each sample (AOAC, 2005). Titrable acidity of each sample was determined as described in AOAC method 974.05 and protein content was analyzed using AOAC 975.17. The pH was determined by pH meter with a combined glass electrode and temperature probe (pH meter Micro pH 2002; Crison, Spain). Before analyzing, instrument was calibrated, by using buffer solutions at pH 4.0 and 7.0. Viscosity of prepared milk samples were determined using a Brookfield DV-III Ultra Programmable Rheometer (Brookfield Engineering Lab Inc., Massachusetts, USA)

3. Sensory Evaluation

The sensory evaluation of milk samples performed through the judgment of 18 trained panelists. The samples were coded with three digit random numbers in odorless plastic cups with all the orders of servings completely randomized. A 9-point hedonic scale was employed to determine the degree of liking of the products (9= Extreme like, 5= Neither like nor dislike, 1= Extreme dislike). The samples were rated for color and appearance, flavor/taste, texture and overall acceptability as prescribed by Herald, (2008). Physicochemical and sensory analyses of the final products were conducted 1 day past production.

4. Statistical Analysis

The experiments were performed in a completely randomized design. All experiments were conducted in triplicates and the mean values and standard deviations were calculated. Analysis of variance (ANOVA) was performed and the results were separated using the Multiple Ranges Duncan's test using statistical software of SPSS 19 (SPSS, Inc., New Jersey, USA)

RESULTS AND DISCUSSION

According to primary test results, the viscosity and sensory evaluation of samples containing acid-modified starch at concentration of 15%, pregelatinated starch at concentration of 45% and cross-linked starch at concentration of 30%, can be a good choice for adding to skim milk. Physicochemical characteristics and sensory property of these samples were evaluated. Viscosity values, total solid, protein, acidity, fat content and pH for samples containing modified starches are presented in Tables 1.

Table 1.Physicochemical properties of milk samples containing various modified starches

Samples	Viscosity (cP)	Total solid (% w/v)	Protein (% w/v)	Acidity	pH	Fat (%w/v)
Acid treated potato starch 0.15%	1.5±0.13^{cd}	9.56±0.33^{bc}	3.70±0.12	14.40±0.22	6.62±0.10	0
Pre-gelatinized potato starch 0.45%	1.3±0.09^{e}	9.55±0.3^{bc}	3.70±0.10	14.40±0.30	6.62±0.20	0
Cross-linked potato starch 0.3%	1.7±0.10^{bc}	9.62±0.25^{bc}	3.70±0.08	14.40±0.40	6.62±0.10	0
Acid treated corn starch 0.15%	1.5±0.13^{cd}	9.60±0.20^{bc}	3.70±0.10	14.40±0.25	6.62±0.30	0
Pre-gelatinized corn starch 0.45%	1.4±0.1^{de}	9.64±0. 20^{bc}	3.70±0.14	14.40±0.20	6.62±0.10	0
Cross-linked corn starch 0.3%	2.3±0.12^{a}	9.72±0.12^{b}	3.70±0.07	14.40±0.30	6.62±0.30	0
Milk with 1.5% fat	2.0±0.1^{ab}	10.47±0.12^{a}	3.70±0.12	14.40±0.50	6.62±0.10	1.5
Skim milk	1.3±0.13^{e}	9.464±0.23^{c}	3.70±0.10	14.40±0.25	6.62±0.10	0

Data are means ± S.D of triplicate measurements. Values with different superscript upper case letters in a column are statistically significant at P < 0.01.

The information in Table 1 shows that the viscosity values of the samples containing modified starch were significantly higher than that of skim milk (P< 0.01). The highest value was obtained for the sample with 0.3% of cross-linked corn starch and no significant difference (P> 0.01) found with sample milk containing 1.5% fat. Viscosity is an important parameter for estimating physicochemical property of milk**.** The molecules of cross-linked starch may have less mobility as a result of cross-linking. The presence of cross-linkages may also reduce interactions of starch molecules with water molecules. Similarly, it has been reported that cross-linking can increase the granular resistance against temperature and heating time (Singh, 2007, Mirmoghtadaei, 2009). Samples containing Pre-gelatinized starch had lower values of viscosity than samples with other modified starches but the results indicate that the Pre-gelatinized had the ability to increase the viscosity at temperatures below gelatinization temperature of native starch. Pre-gelatinized starch had significantly higher water solubility and absorption indices compared to the native starch. This can be attributed to the destruction of starch granules, reduction of the degree of crystallinity, and degradation of starch molecules during pre-gelatinization. Apparently, the porous structure of Pre-gelatinized starch can readily absorb more water compared to the native starch. Slaughter, (2001) also reported higher water solubility and swelling for fully gelatinized wheat, maize, and rice starches. Higher solubility and water absorption values were also reported for pre-gelatinized banana starch by Waliszewski,(2003).

As can be seen from Table1, the highest value for total solid was obtained for the control and follows it, sample with 0.3% of cross-linked corn starch. Hirsch et al., Gunarantne et al., and Mirmoghtadaei et al. also reported a reduction in solubility and swelling of various cross-linked starch systems. They have indicated that the resistance of a cross-linked starch towards solubility and swelling increases by increasing the concentration of cross-linking agent. Kaur et al. indicated that the cross-linkages may reduce the movement of starch molecules, causing reduction in water solubility and water absorption of cross-linked starch.

Additionally, viscosity values and total solid content for samples with modified corn starch were significantly higher than those for modified potato starch. Choi et al. indicated that the extent of the changes depends on the botanic source of starch, concentration, and type of cross-linking reagent and the reaction condition. Jane, Radosavljevic, and Seib (1992) reported that cross-linking of starch chains occurred mainly in amylopectin. Another factor that may influence the extent of cross-linking is the size distribution of starch granule population (Hung and Morita, 2005). During cross-linking small size granules have been reported to be derivatized to a greater extent than the large size granules (Bertolini, 2003). According to data presented in Table 1, no significant difference was observed between protein, acidity, fat and pH values of samples containing modified starch. Sensory properties of milk containing the three types and their levels of modified starch are presented in Table 2.

Table 2. Sensory properties of milk samples containing various modified starches

Samples	Color	Flavor	Texture	Overall acceptance
Acid treated corn starch 0.15%	3.00±1.00^{e}	4.33±0.57^{de}	4.67±0.57^{cd}	4.33±0.57^{ef}
Pre-gelatinized corn starch 0.45%	4.00±1.00^{cd}	3.33±0.57^{ef}	3.67±0.57^{d}	3.33±0.57^{f}
Cross-linked corn starch 0.3%	5.33±0.57^{ab}	6.33±0.57^{abc}	6.67±0.57^{ab}	6.33±0.57^{bc}
Acid treated corn starch 0.15%	3.67±0.57^{cde}	5.00±1.00^{cd}	5.67±0.57^{bc}	5.33±0.57^{cde}
Pre-gelatinized corn starch 0.45%	5.33±0.57^{ab}	6.33±0.57^{abc}	6.67±0.57^{ab}	6.00±1.00^{cd}
Cross-linked corn starch 0.3%	6.33±0.57^{a}	6.67±0.57^{ab}	7.67±0.57^{a}	7.33±0.57^{ab}
Milk with 1.5% fat	7.00±1.00^{a}	7.67±0.57^{a}	8.00±1.00^{a}	7.67±0.57^{a}
Skim milk	3.33±0.57^{de}	4.00±1.00^{de}	4.67±0.57^{cd}	4.33±0.57^{ef}

Data are means ± S.D of triplicate measurements. Values with different superscript upper case letters in a column are statistically significant at $P < 0.01$. Based on 9-point hedonic scoring: 9 for excellent, 1 for very poor.

According to the data in Table 2, color, flavor, texture and overall acceptance of milk samples containing three types of modified starch at their contents significantly differ ($P > 0.01$). Color of the sample containing 0.3% of cross-linked corn starch was higher than for the other samples and also its difference with Milk with 1.5% fat was not significant ($P > 0.01$). Similar results were obtained from flavor score, texture and overall acceptance of the samples. Overall, the most acceptable sample as regards sensory attributes was the milk sample with 0.3% of cross-linked corn starch. In this research citric acid was applied as the aqueous solution to modify starch for the following reasons. First of all, as a result of its multi-carboxylic structure, interaction could take place between the carboxyl groups of citric acid and the hydroxyl groups on the starch. Such an interaction would improve the water resistibility due to reducing available OH groups of starch (Borredon, 1997). On the other hand the carboxyl groups of citric acid can form stronger hydrogen bonds with the hydroxyl groups of starch molecules, so as to prevent recrystallization and retrogradation. Furthermore, because of the multi-carboxyl structure, citric acid may serve as a cross-linking agent and hence, it may improve the mechanical properties and water resistibility (Shi, 2007). And as a third point, citric acid is rated as nutritionally harmless since it is a nontoxic metabolic product of the body (Krebs or citric acid cycle) and it has already been accepted by FDA for using in food formulations (Yang, 2004).

CONCLUSION

We produced three kinds modified starches as fat replacer from two source of starch (potato and corn) using citric acid. Physicochemical and sensory properties of prepared milk samples were evaluated. Results demonstrate that the effect of plant source and kind of modification on physicochemical and sensory properties of the milk samples was significant and milk samples with cross-linked corn starch were better due to its acceptable texture and flavor.

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