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The Effect of Modified Starch Based Fat Replacer on Milk Properties

A. Hajibabaei [a]****, F. Abdolmaleki*** [b]

[a] *Department of Food Science and Engineering, Buinzahra Branch, Islamic Azad University, Buinzahra, Iran.*
[b] *Academic Member of the Department of Food Science and Engineering, Faculty of Industrial and Mechanical Engineering, Qazvin Branch, Islamic Azad University, Iran.*

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ABSTRACT: In this study, modified starch was used as a fat replacer in the milk. The fat replacer was manufactured from modified starch such as pre-gelatinized and cross–linked starches. Modified starches were manufactured by hydrochloric acid and citric acid treatments from potato and wheat and were added to skim milk at concentrations of 0.15%, 0.30% and 0.45%. Viscosity, total solid, fat content, titrable acidity, pH and sensory scores were evaluated for the prepared milk samples. The plant source and kind of modification affected the physicochemical and sensory properties of the milk sample significantly. The impact of modified starch concentration and kind of acid used for modification on sensory property and viscosity of the milk samples was significant. The results indicated that pre-gelatinized starch at the concentration of 0.45% and cross-linked starch at concentration of 0.3% might be selected for the addition to skim milk but milk sample with cross-linked starch was superior due to its acceptable texture and flavor.

Keywords: *Chemical Modification, Cross-linked Starch, Fat Replacer, Starch, Wheat Starch.*

Introduction

Starch, the dominant carbohydrate reserve material of higher plants, plays an important role in textures of many kinds of food products and serves as a great source of energy for humans. Starches meet the functional properties required in food products such as thickening and stabilization, gelling, bulking and play as water retention agent. Hence starch modification improves its functional characteristics, it might be used in many specific food applications (Hermansson and Svegmark, 1996). Starch modification is generally carried out by changing its molecular structure. Modification of starch is achieved through chemical, physical, enzymatic, and genetic methods or their combinations. Chemical modification causes marked changes in physico-chemical properties of starch due to the introduction of functional groups into the starch molecules (Murphy, 2000; Choi and Kerr, 2003; Deetae *et al.*, 2008).

Cross-linked starch is common type of chemically modified starches. Cross-linking modification is intended to facilitate intra- and inter-molecular linkages at random locations in the granules of starch (Acquarone and Rao, 2003). Starch pastes from cross-linked starches are more resistant to shear and acidic conditions. Cross-linking increases the granular resistance against temperature and decrease granule rupture (Woo and Seib, 1997). Cross-linking is carried out by treatment of granular starch using multifunctional reagents which forms inter-molecular bonds between the hydroxyl groups of starch molecules (Rutenberg and Solarek, 1984; Wurzburg, 1986a, 1986b). Cross-linking modification is achieved through the main reagents such as sodium trimetaphosphate, mono-sodium phosphate, sodium tripolyphosphate, acetic anhydride,

*Corresponding Author: Hajibabaei.al@gmail.com

phosphoryl chloride ($POCl_3$), a mixture of adipic acid and vinyl chloride although $POCl_3$ is a common agent for cross-linking modification in the presence of a neutral salt (Felton and Schopmeyer, 1943; Wattanchant *et al.*, 2003; Woo and Seib,1997; Yeh and Yeh, 1993; Yook *et al.*, 1993).

Pre-gelatinized starch is an example of physically modified starch with wide applications, especially in food industry. Pre-gelatinized starch is commonly produced using drum drier, spray drier, and, less regularly, by extruder (Kalogianni *et al.*, 2002; Mounsey and O'Riordan, 2008). The condition, method and source of starch used for gelatinization have great influence on different properties of the starch (Mercier, 1987; Kalogianni *et al.*, 2002).The process of gelatinization involves the rearrangement of intra- and intermolecular hydrogen bonding between water and starch molecules resulting in marked changes in both chemical and physical nature of granular starch. Gelatinization causes structural changes such as loss of organized structure of starch, granular swelling, loss of birefringence and solubilization of starch (Cooke and Gidley, 1992; Anastasiades *et al.*, 2002).

Therefore, little research has been carried out on the effects of modified starches on the physicochemical and sensory properties of milk as fat replacer. The main purpose of the present research is to compare the physicochemical and sensory properties of milk samples that were prepared with modified starch (pre-gelatinized and cross–linked starches) from two different plant sources (potato and wheat) as a fat replacer.

Materials and Methods

Skim milk was obtained from a Sahar Dairy Co., Qazvin, Iran. Pure potato and wheat starches were obtained from Glucosan Co., Qazvin, Iran. All the chemicals were purchased from Merck, Chemical Company, Germany.

- *Production of modified starches*

- *Preparation of pre-gelatinized starch*

Pre-gelatinized starch was prepared by gelatinizing the 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 and held for 15 min at 95 °C and then cooled to 50 °C at the same rate. The suspension of starch was spreaded to form thin layers. The sample was dried overnight in an oven (60 °C). The pre-gelatinized starch sample (containing 10% water) was milled and sieved using a proper mesh sifter to obtain starch powdered sample.

- *Production of cross-linked starch*

50 gram of starch was hydrolyzed by suspending in 67 ml of (1M) HCl solution or (1M) citric acid at 25 °C for 2h without stirring. After the period of hydrolysis the terminated mixture was suspended in 67 mL of distilled water containing 1 g $NaHSO_4$. The pH was regulated to 11 ± 0.1 by employing 1N NaOH. The reaction was started by the addition of 0.1g of $POCl_3$ to the mixture while stirring for 1 h. The reaction was terminated by regulating the pH to 5.5 using 1N HCl. The suspension of starch was washed with distilled water and centrifuged several times at 15000 g for 10 min and then was dried at 40°C in a vacuum oven.

- *Physico-chemical analysis*

Fat content of individual sample was measured according to AOAC method number 2000.18. Total solid in each sample was determined using AOAC method number 990.15 (2000). Titrable acidity of each sample was determined as described by AOAC method number 974.05. The pH was measured employing a calibrated pH meter with a combined glass electrode and temperature probe. A Brookfield DV-III Ultra Programmable Rheometer was employed to determine the viscosity of the prepared milk samples. Sample with different concentrations of modified starch were loaded into the gap of the cylinder Rheometer and then the apparent viscosities of the samples were determined at different speeds consisted of 40, 60, 80, 100, 120 and 140 RPM at 25°C.

- *Sensory Evaluation*

18 trained panelists were employed to evaluate the sensory properties of the milk samples. The evaluations were based on color, appearance, flavor/taste, texture and overall acceptability in a 10 point hedonic scale to determine the degree of liking or disliking of the products (10= Extreme like, 1= Extreme dislike) Herald *et al.* (2008).

- *Statistical Analysis*

In order to calculate significant differences among the different treatments, analysis of variance (ANOVA) was applied and two-tailed independent-sample T-test in SPSS 19.0 software (SPSS Inc., Chicago, IL, USA) was performed. To approve the statistical significance of all data, total experiments were carried out in triplicate orders and values of means ± S.D (standard deviation) were reported.

Results and Discussion

The sensory and physicochemical properties of prepared milk samples with different concentrations of modified starches were evaluated. Sensory evaluation of milk samples containing modified starches are presented in Table 1.

Table 1 compares the color, flavor, texture and overall acceptance of the samples containing modified starches from different plant sources. It is indicated that modified wheat starch behavior was significantly different from the modified potato starch. Flavor and overall acceptance scores of the samples containing modified potato starch were lower than the samples containing wheat starch. Texture scores were recorded higher for samples with wheat starch. As the result, the source of starch had significant effect on the sensory evaluations of the milk samples.

In this work the samples containing cross-linked starch had higher flavor and overall acceptance score than samples with pre-gelatinized starches at the same concentration. Samples containing cross-linked starch treated with hydrochloric acid had yellow color and sweet flavor while samples with pre-gelatinized starches and cross-linked starch treated with citric acid had acceptable colors and flavors. The kind of acid used for cross-liking of starch resulted significant differences in sensory characteristics. Consequently the modification and kind of acid employed affected the sensory properties of the milk sample significantly.

Scientist believe that citric acid improves some properties due to its multi-carboxylic structure and interaction between the carboxyl groups of the acid and the hydroxyl groups on the starch. Such an interaction would improve the water resistibility due to reducing the available OH groups of starch (Borredon *et al.*, 1997). The carboxyl groups of citric acid might form stronger hydrogen linkages with the hydroxyl groups of starch molecules, therefore it might serve as a cross-linking agent and could improve the water resistibility and mechanical characteristics (Shi *et al.*, 2007). Citric acid is also rated as nutritionally harmless since it is a nontoxic metabolic product of the body and it has been approved by FDA to be employed in food formulations (Yang *et al.*, 2004). Additionally, researchers have reported the content of amylopectin (Jane *et al.*, 1992) and the size distribution of starch granule population (Hung and Morita, 2005) that might influence the starch modification and its characteristics.

The results (Table 1) indicated that different concentrations of modified starches that were added to milk samples obtained significant differences in respect of sensory properties. Milk sample with 0.45% cross-linked starch had starchy flavor, while samples with 0.45% pre-gelatinized starch had higher flavor score than the samples containing pre-gelatinized starch at lower concentrations. Milk samples treated with pre-gelatinized starch (0.15 and 0.3%) had unacceptable textures. The control (milk with 1.5% fat) received the highest overall acceptance score followed by the sample with cross-linked starch at concentration of 0.3% and samples with 0.45% pre-gelatinized starch. Table 2 shows the results of the physicochemical properties of the milk containing modified starches.

According to the data in Table 2, the viscosity values of the samples containing modified starches were significantly higher than those of skim milk ($P < 0.01$). The viscosity of the samples containing modified starches from different plant sources indicated that modified potato starch showed significantly lower values than those from modified wheat starch. Therefore the effects of plant source on viscosity and total solid were significant. This finding is consistent with the results by other researchers Choi and Kerr, (2004) and Jane *et al.* (1992).

The information in Table 2 also shows that the viscosity values of the samples containing pre-gelatinized starch were significantly higher than that of cross-linked starch at the same concentration ($P < 0.01$) and the highest value was obtained for the sample with pre-gelatinized potato starch. Mirmoghtadaei *et al.* (2009) claimed that cross-linkages reduces the movement of starch molecules and this modification might also reduce interactions of starch molecules with water molecules. Therefore cross-linked starch shows lower viscosity values at different conditions as compared to the native starch. The highest value of total solid

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

Source	Modification	Acid used	Concentration	Color	flavor	Texture	Overall acceptance
Wheat	Pregelatinized starch	0.15%		5.00±0.55^{bcd}	5.33±0.85^{de}	6.45±0.45^{c}	5.33±0.80^{ef}
		0.3%		6.00±0.89^{abc}	6.00±0.45^{cd}	7.60±0.85^{ab}	6.45±0.55^{cde}
		0.45%		7.33±0.57^{a}	7.00±0.97^{bc}	8.55±0.47^{a}	7.33±0.97^{bc}
	Cross-linked starch	Hydrochloric acid	0.15%	6.00±0.84^{abc}	6.45±0.80^{bcd}	6.00±0.50^{c}	7.00±0.40^{cd}
			0.3%	7.67±0.55^{a}	7.33±0.47^{abc}	7.67±0.97^{ab}	8.00±0.97^{b}
			0.45%	5.33±0.97^{bc}	6.00±0.85^{cd}	6.67±0.45^{bc}	6.00±0.45^{de}
	Cross-linked starch	Citric acid	0.15%	6.33±1.00^{ab}	6.67±0.97^{bc}	6.67±0.57^{bc}	7.00±0.57^{cd}
			0.3%	8.00±0.47^{a}	7.67±0.45^{ab}	8.67±0.65^{a}	8.33±0.45^{ab}
			0.45%	6.33±0.55^{ab}	6.33±0.57^{bcd}	7.00±0.98^{b}	6.33±0.57^{cde}
Potato	Pregelatinized starch	0.15%		4.33±0.45^{cde}	5.00±0.55^{de}	5.00±0.45^{d}	4.33±0.85^{f}
		0.3%		5.00±0.81^{bcd}	6.00±0.49^{cd}	7.00±0.89^{b}	6.00±0.45^{de}
		0.45%		6.80±0.49^{ab}	6.33±0.97^{bcd}	7.00±0.55^{b}	7.33±0.57^{bc}
	Cross-linked starch	Hydrochloric acid	0.15%	5.33±0.55^{bc}	5.45±0.84^{de}	4.67±0.84^{d}	5.67±0.80^{def}
			0.3%	7.33±0.55^{ab}	7.00±0.55^{bc}	7.00±0.55^{b}	7.33±0.47^{bc}
			0.45%	5.00±0.87^{bcd}	4.33±0.97^{ef}	6.67±0.57^{bc}	5.33±0.85^{ef}
	Cross-linked starch	Citric acid	0.15%	6.00±1.10^{abc}	6.00±0.55^{cd}	5.67±1.00^{cd}	6.33±0.57^{cde}
			0.3%	7.55±0.47^{a}	7.45±0.47^{abc}	7.67±0.97^{ab}	8.00±0.45^{b}
			0.45%	5.40±0.45^{bc}	5.00±0.85^{de}	7.00±0.51^{b}	5.67±0.97^{def}
Milk with 1.5% fat				8.40±0.97^{a}	8.60±0.57^{a}	9.00±0.57^{a}	8.67±0.47^{a}
Skim milk				4.33±0.55^{cde}	5.00±0.85^{de}	5.67±0.45^{cd}	5.33±0.95^{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 10-point hedonic scoring: 10 for excellent, 1 for very poor.

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

Source	Modification	Acid used	Concentration	Viscosity (cP)	Total solid (% w/v)	Acidity	pH	Fat (%w/v)
Wheat	Pregelatinized starch	0.15%		2.16 ± 0.14^{de}	9.54 ± 0.25^{bc}	14.40 ± 0.25	6.62 ± 0.10	0
		0.3%		2.20 ± 0.21^{bc}	9.58 ± 0.15^{bc}	14.40 ± 0.40	6.62 ± 0.20	0
		0.45%		2.25 ± 0.15^{a}	9.87 ± 0.27^{b}	14.40 ± 0.22	6.62 ± 0.20	0
	Cross-linked starch	Hydrochloric acid	0.15%	1.77 ± 0.13^{m}	9.54 ± 0.20^{bc}	14.40 ± 0.40	6.62 ± 0.30	0
			0.3%	1.81 ± 0.12^{k}	9.64 ± 0.27^{bc}	14.40 ± 0.25	6.62 ± 0.10	0
			0.45%	1.84 ± 0.15^{k}	10.30 ± 0.15^{ab}	14.40 ± 0.20	6.62 ± 0.20	0
	Citric acid Cross-linked starch		0.15%	1.80 ± 0.13^{l}	9.55 ± 0.27^{bc}	14.40 ± 0.30	6.62 ± 0.10	0
			0.3%	1.83 ± 0.14^{k}	9.81 ± 0.25^{b}	14.40 ± 0.30	6.62 ± 0.30	0
			0.45%	1.87 ± 0.15^{j}	10.40 ± 0.18^{ab}	14.40 ± 0.25	6.62 ± 0.10	0
potato	Pregelatinized starch	0.15%		2.19 ± 0.14^{cd}	9.55 ± 0.15^{bc}	14.40 ± 0.25	6.62 ± 0.20	0
		0.3%		2.23 ± 0.21^{b}	9.64 ± 0.49^{bc}	14.40 ± 0.20	6.62 ± 0.10	0
		0.45%		2.27 ± 0.15^{a}	10.13 ± 0.27^{b}	14.40 ± 0.30	6.62 ± 0.10	0
	Cross-linked starch	Hydrochloric acid	0.15%	2.06 ± 0.13^{h}	9.58 ± 0.15^{bc}	14.40 ± 0.50	6.62 ± 0.20	0
			0.3%	2.10 ± 0.12^{fg}	9.80 ± 0.15^{b}	14.40 ± 0.25	6.62 ± 0.20	0
			0.45%	2.14 ± 0.15^{e}	10.42 ± 0.25^{ab}	14.40 ± 0.30	6.62 ± 0.10	0
	Cross-linked starch	Citric acid	0.15%	2.08 ± 0.13^{g}	9.61 ± 0.17^{bc}	14.40 ± 0.30	6.62 ± 0.30	0
			0.3%	2.12 ± 0.14^{f}	9.87 ± 0.15^{b}	14.40 ± 0.25	6.62 ± 0.10	0
			0.45%	2.15 ± 0.15^{e}	10.59 ± 0.28^{a}	14.40 ± 0.22	6.62 ± 0.20	0
Milk with 1.5% fat				1.93 ± 0.12^{i}	11.07 ± 0.18^{a}	14.40 ± 0.20	6.62 ± 0.10	1.5
Skim milk				1.60 ± 0.15^{n}	9.46 ± 0.23^{c}	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 $P < 0.01$.

was obtained for the sample with cross-linked potato starch. Hirsch and Kokini (2002), Gunarantne and Corke (2002) and Mirmoghtadaei *et al.*, (2009) also reported a reduction in solubility and swelling of various cross-linked starch systems. They have confirmed that the resistance of a cross-linked starch towards solubility and swelling increases by increasing the concentration of cross-linking agent.Furthermore, Kaur *et al.,* (2004) found that the cross-linkages might reduce the movement of starch molecules, causing reduction in water solubility and water absorption of cross-linked starch. But, pre-gelatinized starch had significantly higher water solubility and absorption indices as compared to the native starch. This can be related to the destruction of starch granules and degradation of starch molecules during pre-gelatinization. It would appear that, the porous structure of Pre-gelatinized starch can readily absorb more water as compared to the native starch.

According to the data presented in Table 2, increasing the level of modified starches would lead to an increase in viscosity for both types of starches ($P< 0.05$). However, samples containing 45% pre-gelatinized starch, had higher values of viscosity followed by 45% cross linked starches. Similarly, many researchers have reported that using higher levels of modified starches would lead to increases in viscosity for dairy products (Kaya and Tekin, 2001; Minhas *et al.*, 2002; Muse and Hartel, 2004; Moeenfard and Mazahri, 2008; Soukoulis and Tzia, 2008; Milani and Koocheki, 2010).

Increasing modified starch level had no significant effect on acidity, fat and pH values of the milk samples. Similarly, plant source, type of starch modification and kind of acid treatment did not affect the physical property of the milk samples significantly ($p < 0.01$). Thus, no significant difference was observed between acidity, fat and pH values of samples containing modified starch.

The results of sensory and physicochemical properties of milk samples indicated that pre-gelatinized starch at concentration of 0.45% and cross-linked starch at concentration of 0.3% might be regarded as good choices for addition to skim milk. Accordingly, Shear thinning behavior of these samples is shown in Figure 1.

As it shown, at low shear rates, the apparent viscosity was reasonably high, where as with increasing the shear rate, the viscosity was slowly reduced. These findings indicate that any variations in modified starches as fat replacement with various concentrations might affect the viscosity of the samples. Although, milk samples with 0.3% cross-linked wheat starch had better attribution regarding the acceptable sensory and physicochemical properties.

Our finding also demonstrated that modification of milk by using carbohydrate based fat replacers could be considered as an effective way to lower the fat content in food products and provide healthier and safer foods. This work could be extended by employing other fat replacer in other dairy products in the future.

Conclusion

Two kinds modified starches as fat replacer from two sources of starch (potato and wheat) were produced using citric and hydrochloric acids. Physicochemical and sensory properties of the prepared samples were evaluated. The results demonstrated that the effect of plant source, type of modification, different concentrations and kind of acid used for modification were significant on sensory property and viscosity of the milk samples and the sample with 0.3% cross-linked wheat starch were scored better due to the acceptable texture and flavor.

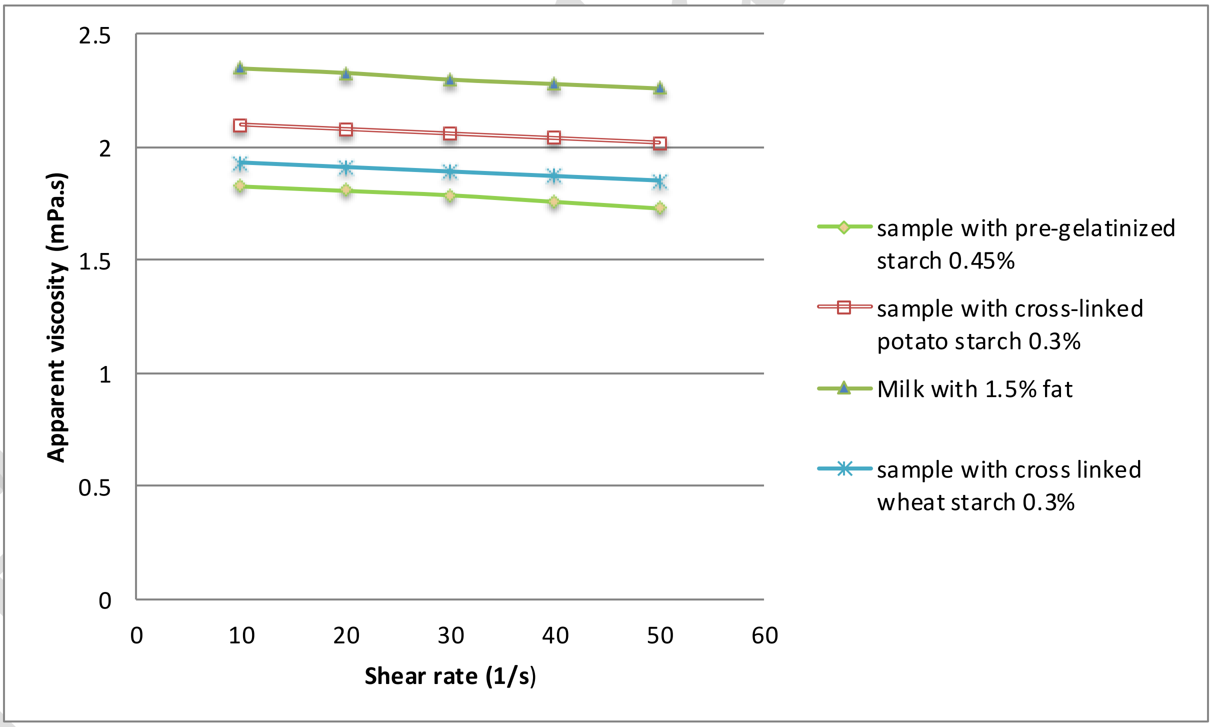

Fig. 1. Viscosity versus shear rate plot of milk samples at 25°C

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