Influence of pregelatinized and granular cold water swelling maize starches on stability and physicochemical properties of low fat oil-in-water emulsions

Sara Hedayati a, Fakhri Shahidi a,*, Arash Koocheki a, Asgar Farahnaky b, c, Mahsa Majzoobi b, c

a Department of Food Science and Technology, Faculty of Agriculture, Ferdowsi University of Mashhad (FUM), Mashhad, Iran
b Department of Food Science and Technology, School of Agriculture, Shiraz University, Shiraz, Iran
c School of Science, RMIT University, Bundoora West Campus, Melbourne, VIC, 3083, Australia

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ABSTRACT

The stability, color, textural parameters, rheological properties, zeta potential, surface and interfacial tensions of oil-in-water emulsions stabilized by pregelatinized (PG) and granular cold water swelling (GCWS) starches were investigated and compared with each other. The emulsions showed a pseudoplastic behavior over the studied shear rate range. Nevertheless, the pseudoplasticity of the emulsions was increased with starch concentration. Apparent viscosity, consistency coefficient (k) and flow behavior index (n) values were higher for the emulsions with GCWS starch compared to the emulsions made with PG. The textural parameters obtained from back-extrusion test increased with starch concentration and GCWS starch had greater values for all of the measured parameters. Both modified starches increased the emulsion stability however, the samples incorporated with GCWS starch were more stable during storage period. The zeta potential of the control emulsion was more negative than starch stabilized samples and PG containing samples were less negatively charged. However, starch concentration did not affect the zeta potential. The lightness increased while the yellowness decreased with starch concentration and GCWS samples were brighter and less yellowish. The surface and interfacial tensions were reduced with the increase of modified starches and GCWS was more effective in reducing these values.

1. Introduction

Mayonnaise and salad dressings are oil-in-water (O/W) emulsions which are widely consumed due to their desirable flavor and texture (Rahmati, Tehrani, & Daneshvar, 2014). These products usually contain high levels of fat in order to maintain their quality (Ma & Boye, 2013). However, fat has the highest calories per unit mass compared with any other major food components (i.e. proteins and carbohydrates) (Akoh, 1995) and overconsumption of fat leads to obesity and have been linked to serious health problems. Therefore, tendency toward reducing the fat content of food emulsion products has been increased (Chung Degner & McClements, 2014). Nevertheless, oil-in-water emulsions are thermodynamically unstable and their instability increases when their fat content reduces below 60–65% (Drakos & Kiosseoglou, 2008). On the other hand, fat has a leading role in texture, color and flavor of these products and its reduction can bring about undesirable changes in physicochemical and organoleptic aspects. Hence finding a suitable fat replacer for production of reduced fat mayonnaise and salad dressings with similar attributes as full-fat products is a major challenge for food manufacturers (Ma & Boye, 2013). Carbohydrate-based fat replacers have been shown to have remarkable effects on improving the emulsion stability by changing rheological properties and decreasing the movements of droplets. Starch as an important source of carbohydrates is extensively employed in the food industry as thickening, stabilizing, and gelling agent and fat replacer. However, application of native starch in food emulsions is limited because starch granules are not soluble in cold water and will only thicken upon heating in excess water (Dolz, Hernandez, & Delegido, 2006). To conquer this defect pregelatinized (PG) starches have been developed. These physically modified starches offer many benefits including being cost and energy efficient, having shorter cooking time and providing higher water uptake and viscosity at ambient temperature. PG starch is commonly prepared by drum drying due to its high production rate and efficiency, low costs, being less labor intensive (Moore, 1995). Nevertheless, drum dried PG starches give

* Corresponding author.
E-mail address: fshahidi@um.ac.ir (F. Shahidi).

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lower viscosity values than their counterpart starches and have a grainy appearance due to the destruction of starch granules and chains caused by the high temperature (above 150 °C) during drum drying. Thus, GCWS starch has been developed by using several techniques such as aqueous-alcohol treatment, spray drying and alcoholic-alkaline treatment (Dries, Gomand, Goderis, & Delcour, 2014; Rajaopalan & Seib, 1992). Alcoholic-alkaline treatment is preferred to other processes because of its wide applicability for a wide range of starches, providing higher viscosities and being more resistant to freeze-thaw cycles (Chen & Jane, 1994b; Hedayati, Majzoobi, Shahidi, Koocheki, & Farahnaky, 2016a). GCWS starch can disperse more easily and absorb more water at room temperature compared to PG starch. Hence GCWS starch has found growing applications in food products (Hedayati et al., 2016b; Bortnowska, Balejko, Tokarczyk, Romanowska-Osuch, & Krzeminska, 2014; Bortnowska, Balejko, Schube, Tokarczyk, Krzeminska & Mojka, 2014) investigated the influence of PG potato and waxy maize starches on physicochemical properties and stability of model salad dressings and reported that these starches improved the stability, viscosity and textural attributes of dressings. Ansari, Mohsin Ali & Hasnain (2016) studied the effect of chemically modified water-chestnut starch in low-fat mayonnaise and stated that incorporation of 10% starch paste lead to 80% oil replacement and the low-fat mayonnaise had similar textural and sensory attributes compared with full fat mayonnaise. Villamonte, Jury & Lamballerie (2015) studied the emulsion stabilization properties of high pressure treated corn starch. They used 5–40 mg/mL starch and found that this type of physically modified starch could be used to produce stable emulsions and the samples with the highest starch concentration was the most stable sample. Hedayati et al. (2016c) studied the physicochemical properties of PG and GCWS starches and found that GCWS starches are more resistant to syneresis, retrogradation and pH changes. They also noted that GCWS starch gives higher viscosity compared with PG starch. Despite the advantages of GCWS starch, there is no report studying its influences in low fat food emulsions and comparing its performance with drum dried pregelatinized starch which is commonly used in salad dressings. Hence, the objective of this project was to characterize the properties of low fat oil-in-water emulsions stabilized by 1–5% of PG or GCWS starches and investigate the stability, color, textural parameters, rheological properties, zeta potential, surface and interfacial tensions of oil-in-water emulsions stabilized by (PG) or (GCWS) starches.

2. Material & methods

2.1. Materials

Native maize starch with 9.64% moisture, 0.74% fat, 0.45% protein, 0.17% ash (measured by the approved methods of AACC, 2000) and 28.30% amylose (determined by the method of Morrison & Laingneet, 1983) was purchased from Mahshad Starch Company (Yazd, Iran). Whey protein concentrate (WPC) was kindly gifted by Mashhad Milk Powder-Multi Company (Mashhad, Iran). Ethanol was supplied by Parsian Company (Shiraz, Iran). Sodium hydroxide, sodium azide and hydrochloric acid were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of PG starch

Pregelatinized maize starch was prepared according to Majzoobi et al. (2011). An aqueous slurry of 10% (w/w) maize starch was dried in a twin drum drier (Mathis Machine Corporation, Benton Harbor, Michigan, USA) at 185 °C. The dried sheets were then ground and passed through a screen (125 μm aperture) and stored in enclosed containers for further analysis.

2.3. Preparation of GCWS starch

GCWS starch was produced by alcoholic-alkaline treatment following the modified method of Chen and Jane (1994a). Ten g of native starch was suspended in 70 g of ethanol solution (40%, w/w) and mixed by a magnetic stirrer (LABINCO L-81, Amsterdam, The Netherlands) until its temperature reached 35 °C. Then 50 g of NaOH solution (3M) was slowly added to the suspension and after 15 min of stirring it was Büchner filtered. The separated liquid was removed and the collected starch was mixed with fresh ethanol solution (40%) and was neutralized by adding HCl solution (3M in absolute ethanol). The mixture was agitated for 1 h followed by washing with 60 and then 95% (w/w) ethanol solutions. Subsequently the suspension was filtered and dehydrated by absolute ethanol. The alcoholic-alkaline treated starch was oven dried at 50 °C for 12 h. Finally, the modified starch was milled and sieved to reach an average particle size of 125 μm, poured into air tight containers and stored at ambient temperature.

2.4. Preparation of oil-in-water emulsions

Emulsions were prepared according to the method described by Bronskowa et al. (2014a). The prepared samples contained 20.0% (w/w) sunflower oil, 2.0% (w/w) emulsifier (WPC), 0.02% (w/w) sodium azide, and 0–5% (w/w) of PG or GCWS starch. To produce the emulsions aliquots of WPC, PG and GCWS starch powders were separately hydrated in deionized water. To inhibit the microbial growth, sodium azide was also added to the suspensions. The samples were gently mixed over a magnetic stirrer at 22 °C overnight. Then the emulsions were produced by homogenizing the WPC solution with sunflower oil using a laboratory homogenizer (Ultra Turrax T-25, IKA Instruments, Germany) operating at 24000 rpm for 1 min. Subsequently the starch suspensions were added to the mixtures with a kitchen mixer (Moulinex, HM 1010, China).

2.5. Color assessment

Color parameters of the emulsions were measured with the method described by Afshari-Jouybari and Farahnaky (2011). The samples were positioned in an image-capturing box and pictures were taken with a digital camera (Canon, model IXUS 230 HS, 14.0 Megapixels, Japan) that was fixed 25 cm above the samples. Resolution, contrast and lightness of pictures were set to 300 dots per inch (dpi), 62 (%) and 62 (%), respectively and images were saved in JPEG format. The “Lab” mode of the Photoshop 8 software(Adobe Systems Inc., San Jose, United States) was employed to measure L*, a*, and b* values for each sample.

2.6. Emulsion stability

To study the creaming index, emulsion samples (15 mL) were transferred to screw cap tubes and incubated at 25 ± 2 °C for 30 days. The creaming index was determined periodically (5 day intervals) during the storage period using the following equation:

\[ \text{Creaming Index} \ (\%) = \frac{HC}{HE} \times 100 \]

where HE is the initial height of the emulsion (mm) and HC is the height of cream layer (mm).

2.7. Rheological measurements of emulsions

The rheological properties of freshly made emulsions were measured by a rotational viscometer (Viscom 88, Bohlin Instruments, UK) with a heating circulator (F12-MC, Julabo Labortechnik, Germany). 16 g of each sample was transferred into the cup of the instrument and submitted to a shear rate increasing linearly from 10 to 200 s⁻¹ at 25 °C. The experimental data were fitted to Power-law model with the following equation:

\[ \tau = k \cdot \gamma^n \]
Where \( \tau \) is the shear stress (Pa), \( k \) is the consistency coefficient (Pa s\(^n\)), \( \gamma \) is the shear rate (s\(^{-1}\)), and \( n \) is the flow behavior index.

### 2.8. Textural measurements of emulsions

The textural properties of emulsions were evaluated using a back-extrusion test on a Texture Analyzer (Stable Microsystems, TAXT-2 Texture Analyzer, Surrey, England) at ambient temperature. The freshly made emulsions (50g) were placed into glass beakers of 55 mm internal diameter in which a 40 mm aluminum probe with pre-test speed of 2 mm/s, test speed of 2 mm/s, post-test speed of 10.0 mm/s, distance of 8.0 mm and trigger force of 5.0g was entered. Textural parameters such as firmness (maximum force in compression), consistency (positive area of the curve), cohesiveness (maximum force in compression) and indices of viscosity (negative area of the curve) were calculated from the curves using Texture Exponent Lite software (Cevoli, Balestra, Ragni, & Fabbri, 2013; Ciron, Gee, Kelly, & Auty, 2010).

#### 2.9. Zeta potential

Emulsions were diluted 100 times with deionized water and the zeta potential was measured by a particle electrophoresis instrument (Zetasizer Nano ZS, Malvern Instrument, UK).

#### 2.10. Measurement of surface and interfacial tension

The surface tensions of PG and GCWS starches in deionized water alone and in combination with 2% WPC and interfacial tensions of oil-water interfaces in the presence and absence of modified starches were measured with Du Nouy ring method (Kruss K100 Tensiometer, Germany) at 20 °C.

#### 2.11. Statistical analysis

All experiments were replicated at least three times. Analysis of variance (ANOVA) was performed using SPSS software version 22 (SPSS Inc., Chicago, USA). Duncan’s multiple range test was applied to compare any significance within samples at the 95% probability level.

### 3. Results and discussion

#### 3.1. Stability of emulsions

The influence of starch type and concentration on the stability of oil-in-water emulsions are illustrated in Fig. 1. It can be seen that both modified starches increased the stability of emulsions. The emulsion stability depends on viscosity of the liquid surrounding oil droplets. Increasing the viscosity of continuous phase decreases the movement of droplets and increases their stability against creaming. Moreover, addition of starch to the continuous phase leads to the formation of a three-dimensional network in which the starch particles or granules trap oil droplets and prevents them from moving (McClements, 2005). Emulsions with GCWS starch were more stable than samples prepared with PG starch. This behavior could be explained by the higher water absorption of GCWS starch compared to PG starch (Hedayati et al., 2016b) which is more effective in increasing the viscosity of continuous phase and preventing the collision of droplets with each other so that droplets are prevented from creaming. The results revealed that the emulsion prepared with 3% GCWS starch was the most stable sample. Whereas, increasing the concentration of starch lead to instability of emulsions. Starch particles or granules are insoluble and their excessive concentration in the continuous phase can make their embedding impossible (Protonotariou, Evangelou, Yanniotis, & Mandala, 2013). On the other hand, in high levels of starch, the aqueous phase volume is reduced due to the swelling and water absorption of GCWS starch granules or PG starch particles. As a result, the possibility of interactions between droplets increases and emulsions become unstable (Chung, Degner, & McClements, 2014).

#### 3.2. Textural measurements

The textural parameters of different emulsion samples obtained from back-extrusion test are presented in Table 1. The modified starches acted as texture modifier and with raising starch concentration greater values of textural parameters were observed. Water absorption by modified starches decreased the amount of free water and increased the interactions between starch, emulsifier, oil and water. As a result, the emulsion firmness increased. These results are in agreement with the results reported by Bortnowska, Balejko, Tokarczyk, Romanowska-Osuch, and Krzeminska (2014a, b) for emulsions with PG potato and waxy maize starches. Generally, samples with GCWS starch had significantly (\( p < 0.05 \)) higher values for all the measured parameters. Firmness is defined as the positive force required to press the extrusion probe into the sample. As mentioned previously, GCWS starch has higher water absorption due to its granular integrity which can improve the firmness of the emulsions. Consistency and index of viscosity are related to each other. Consistency indicates the thickness of emulsions and is the positive areas under the back-extrusion curve. Whereas, index of viscosity shows the resistances of a sample to flow off the back-extrusion and is determined from the negative area under the curve (Ciron et al., 2010). The higher values of these parameters in GCWS starch is also related to its higher water absorption compared with PG starch. Cohesiveness determines the resistance of emulsions to extraction from the plunger being lifted (Ciron et al., 2010). Commonly, samples with stronger network have greater cohesiveness values. GCWS starch granules are smaller and more homogenous than PG starch particles which increase the contact surface area and generates a consistent and cohesive system (Hedayati et al., 2016b).

![Fig. 1. Influence of starch type and concentration on the creaming of the emulsions. A) samples containing PG starch; B) samples containing GCWS starch.](image_url)
The impurities such as pigments and fats were removed from the starch granules and GCWS starches had a white color but these impurities were not removed in PG starches which may have slight effects on the yellowness of the samples.

### 3.3. Color parameters

The color parameters of the emulsions are presented in Table 2. The color of emulsions depends on their composition as well as microstructure (McClements, 2002). Lightness (L) of the emulsions increased with the increase in starch concentration which may be due to the increasing of light scattering with raising the concentration of starch granules or particles in the continuous phase (Chung, Degner, & McClements, 2013). The L-value in samples prepared with GCWS starch was higher than PG starch containing samples due to the smaller droplets in these samples which affect the light scattering. The a-values of emulsions were not statistically different (p < 0.05) while significant differences were observed in b-values within different treatments. The yellowness of emulsions slowly decreased with the increase of starch concentration. Sunflower oil is yellow and WPC has a creamy color. Addition of starch to the emulsions decreased the concentration of these chromophoric materials in the emulsions and decreased their b value. The samples with GCWS starch were less yellowish due to the smaller particles of GCWS starch compared to PG starch which increases the light scattering in the emulsion samples. Moreover, during alcoholic-alkaline treatment the impurities such as pigments and fats were removed from the starch granules and GCWS starches had a white color.

### 3.4. Viscosity

The results of steady flow measurements are shown in Fig. 2. All of the samples exhibited shear thinning behavior. This is caused by the droplet deflocculation of the disperse phase, orientation of starch granules or particles in the continuous phase with the flow direction and destruction of entanglements within emulsion components (Samavati, Emam-Djomeh, MohammadiFar, Omid & Mehldinia, 2012). The apparent viscosity of emulsions with GCWS starch was higher than those with PG starch which is related to the higher water absorption of GCWS compared with PG starch.

The n and k parameters as well as determination coefficient (R²) are given in Table 3. The highest n value was observed in the control emulsion and was decreased with the increase in starch concentration, indicating that the pseudoplasticity was increased in higher levels of starch. The n parameter in samples containing GCWS starch were higher than those with PG starch which meant that GCWS starch was more shear resistant. This behavior is due to the granular integrity of GCWS starch which makes it more stable during processing (Meng & Rao, 2005). The changes in consistency coefficient were in line with the apparent viscosity and this value was increased with the increase in starch concentration. The k value was also higher in samples prepared with GCWS.

### 3.5. Interfacial characteristics

Determination of surface or interfacial characteristics provides useful information about liquid–liquid and solid–liquid interactions in an emulsion system which are significant factors in determination of emulsion stability. The interfacial tension of oil-water interface can affect the size of the droplets generated during homogenization and the droplet size is reduced with the reduction of interfacial tension (McClements, 2005). The influence of starch type and concentration on surface and interfacial tensions for the systems composed of WPC-modified starch is given in Table 4. WPC-modified starch (at different concentrations) decreased the surface and interfacial tensions compared with the surface tension at the air/water and interfacial tension at sunflower oil/water interfaces, respectively (Table 4). The interfacial tension significantly decreased with the addition of WPC. However, PG and GCWS starches were less effective in reducing the interfacial tension than WPC because polysaccharides are less effective to screen the thermodynamically unfavorable contacts between water and non-polar groups (McClements, 2015). Bai, Huan, Li, and McClements (2017) have also reported that gum Arabic, beet pectin and corn fiber gum do not bring about a large reduction in interfacial tension. As inferred from our data, the lowest interfacial tension value was observed in sample with 2%WPC and 2% WPC with 3% GCWS starch. However, the...
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starch at increasing the emulsion stability by viscosity development, texture modification and reducing the surface and interfacial tensions. Therefore, PG starch can be used in food emulsions with short shelf life while GCWS starch are suggested to be used in products with longer shelf life. Moreover, the emulsions containing GCWS starch had lighter and less yellowish color which is more favorable for consumers. These findings have important practical applications and may help food manufacturers to produce reduced calorie food emulsions with good eating quality which could help reduce fat related chronic diseases such as obesity and overweight.

CRediT authorship contribution statement


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