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Effect of Milling Process on Colloidal Stability, Color and Rheological Properties of Pistachio Paste

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Abstract

Pistachio paste is produced from ground roasted kernel. This study focused on the influence of the milling process on colloidal stability, rheological behavior and color of pistachio paste. The colloidal stability of pistachio paste samples increased with a reduction of particle size from 31.4 to 15.10µm. The Herschel-Bulkley model was found to be the best model to describe the flow behavior of pistachio paste. The storage modulus (G') values were higher than the loss modulus (G") values for all frequencies studied. The results showed that utilizing a gap size of 60µm was the best milling condition for the production of pistachio paste.

Keywords: Colloidal stability, Colour, Pistachio paste, Particle size, Rheological property.

Introduction

The pistachio nut (*Pistacia vera L.*) is a nutritious and popular tree nut that is consumed as a roasted and salted nut. The unsplit form can be used for the production of pistachio products, such as pistachio milk (Shakerardekani *et al.*, 2012), pistachio butter (Ardekani *et al.*, 2009), and pistachio nut spread (Shakerardekani *et al.*, 2013a; Shakerardekani *et al.*, 2013b). It is also used as the main ingredient in many desserts. Pistachio nuts contain 25% protein, 16% carbohydrate and 55% fat (of which, 80% are unsaturated fatty acids) (Alasalvar and Shahidi, 2008). Pistachio nuts are also a good source of dietary fibre, vitamin B6, thiamine, magnesium, phosphorus and copper (Hebbar and Ramesh, 2005). During the production of pistachio paste, pistachio kernels are unhull roasted and grounded into a paste (Ardekani *et al.*, 2009; Maskan and Göü, 1997).

The particle size distribution and rheological behavior of semi-solid food products like pistachio paste affect their preparation, processing and storage (Abu-Jdayil, 2004; Lokumcu-Altay and Ak, 2005). Pistachio nuts are usually shelf stable, but oil separation that occurs when the paste is stored has a negative effect on consumer acceptability. Oil separation is a concern in the stability of nut butter (Gills and Resurreccion, 2000). Due to the high nutritional value and favorable color of pistachio paste, it can be used as an ingredient in ice cream, desserts, and sauces. Therefore, it is important to improve and extend its shelf stability (Bellomo *et al.*, 2009; Ciftci *et al.*, 2008). Since the structure of products was shown to be changed during milling, rheological properties of these products were also changed (Moelants *et al.*, 2014). Although there are several published works on the rheological properties of semi-

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solid pastes such as sesame paste (Razavi *et al.*, 2008) and peanut butter (Guillaume *et al.*, 2001), there have been few studies on the rheological properties of pistachio paste (Emadzadeh, Razavi and Hashemi, 2011; Emadzadeh, Razavi and Mahallati, 2011; Razavi *et al.*, 2010). Stability and rheology of food colloidal such as chocolate, peanut butter, milled flaxseed and sesame paste are strongly influenced by particle size distribution (Chevalley, 1999; Dickinson, 2010; Friberg *et al.*, 2004; Genovese *et al.*, 2007; McClements, 2005; Schorno *et al.*, 2010). The size distribution of particles in peanut butter influences the oil separation of the product (Gills and Resurreccion, 2000). This is because decreasing the particle size improves the dispersion of the solid phase in oil phase. As a result, the interaction of solid and oil phases increased cohesiveness and oil stability (Barnes *et al.*, 1993). Ciftci and others reported that smaller particle size increased sesame paste stability (Ciftci *et al.*, 2008). Matsunobu showed that if the almond paste contained a substantial number of coarse particles having a diameter over about 105µm, it became difficult to prevent precipitation of coarse particles, which was an indicator of instability (Matsunobu *et al.*, 1987). Taghizadeh and Razavi found that pistachio butter behaved as a non-Newtonian fluid, indicating that there was a non-linear shear stress-shear rate relationship (Taghizadeh and Razavi, 2009a). None of these studies discussed the impact of the particle size distribution on the rheological properties and colloidal stability, nor the effect on color of pistachio paste. Thus, this study was conducted to determine the effect of different particle sizes on the colloidal stability, viscoelastic behaviour and color of pistachio paste.

Materials and Methods

Preparation of Kernels

Raw and dried pistachio nuts (Ohadi variety) were obtained from Iran Pistachio Research Institute (Kerman, Iran). The pistachios were stored in the freezer before processing. The nuts were manually broken to obtain the kernels. Fifty grams kernels were placed in a single layer in glass petri dishes (9 cm in diameter) and were roasted in the convection oven (UNB 500, Memmert, Germany) at 134°C for 30 minutes before milling at 1000 rpm into a paste using a supermass colloider (Masuko, model MKZA6-5, Japan). Four grinding gap sizes (20, 40, 60 and 80 µm) were selected to produce pistachio pastes with different particle sizes. One kilogram pistachio kernel was milled for each gap size. The pastes (100 g) were stored at -18°C in individual plastic containers before analysis. Three batches of pastes were prepared for each gap size.

Determination of Paste Particle Size

The particle size of the pistachio paste samples was determined using a particle size analyser (Mastersizer 2000, Malvern Instruments, and UK). The measurements were performed using paste samples diluted in water (1:10 w/v). The data were analysed using the Malvern software Version 5.60. Five replicates analyses were carried out for each sample, and the mean was reported.

Determination of Colloidal Stability

Colloidal stability was determined according to the method described by Wu (2001) and Ciftci *et al.* (2008). Sixteen grams of pistachio paste of different particle sizes were placed in separate 10 mL glass centrifuge tubes (1.5 cm diameter, 11cm height), heated in an 80˚C water bath for 30 minutes, cooled in water at room temperature for 15 minutes, and then centrifuged at 4000×*g* at 20°C for 10 minutes. The height of oil layer that separated from the pastes was determined using a dial micrometer. Colloidal stability (CS) was expressed as % oil and determined using the following equation, where H_0 is the height of the separated oil, and H_t is the total height of the pistachio paste in the test tube at the start of the experiment: (Ciftci *et al.*, 2008; Wu, 2001)

$$CS\ (\%\ oil) = (H_{total}-H_{oil}/H_{total}) \times 100\ldots \qquad \text{Equation 2}$$

Determination of Rheological Properties

The rheological properties of the pastes were determined using a cone-and-plate rheometer (Haake Rheostress 600, Karlsruhe, Germany). The measurement was performed using a PP 35Ti probe at 20 ± 0.5˚C (Haake Universal Temperature Controller). The paste (two grams) was loaded into the rheometer sample plate and was allowed to rest for two minutes before the flow characteristics were measured at 20°C (shear rate from 0 to 300 s^{-1} during 120s). Flow curves were analysed using the Herschel-Bulkey model to describe the rheological behavior of pistachio paste samples. Oscillatory stress sweeps were performed at a constant angular frequency of one Hz in a stress range of 0.5 Pa to 1000 Pa. Oscillatory frequency sweeps were performed at 20˚C over a frequency range of 0.1 to 14 Hz at a constant stress amplitude of 150 Pa. Viscoelastic parameters, including the storage modulus (G') and the loss modulus (G''), were obtained. The measurement was carried out three times.

Colour Determination

The effect of particle size on color (L, a and b values) of the pistachio pastes was determined using an Ultrascan PRO Spectrocolorimeter (Hunter Lab).Twenty grams of sample were placed in the glass container of Hunter Lab before the measurements were made. The analysis was replicated three times.

Statistical Analysis

Analysis of variance (ANOVA) was utilized to determine the effect of the particle size on the colloidal stability, rheological properties and the color of the pistachio paste samples. The ANOVA tests were performed using Minitab 16.1.0.0 (Minitab Inc., USA). Tukey's test was applied to detect the differences among the pistachio paste samples ($p< 0.05$). The correlation coefficient (R^2) was determined using the Rheowin Data Manager Version 3.30.0000.

Results

Effect of Particle Size on Colloidal Stability of Pistachio Paste

The particle sizes of the pistachio paste samples are listed in Table 1. All results had similar bimodal distributions (Fig. 1).

Table 1. Physicochemical and rheological properties, and colloidal stability of pistachio paste at different mill Gap Size

Properties	Gap Size of Colloid Mill (µm)			
	20	40	60	80
Particle size (µm)	15.10 ± 0.20d*	19.00 ± 0.50c	22.70 ± 0.50b	31.40 ± 1.50a
Colloidal stability	99.3 ± 0.1a	99.0 ± 0.1ab	98.9 ± 0.3ab	98.8 ± 0.1b
Flow behavior:				
Consistency index (Pa s)	3.97 ± 0.70d	19.82 ± 0.30c	21.50 ± 0.40b	24.20 ± 0.20a
Flow behavior index	0.60 ± 0.02a	0.60 ± 0.02a	0.60 ± 0.01a	0.60 ± 0.03a
Yield stress (Pa)	11.30 ± 0.60d	15.10 ± 0.60c	18.50 ± 0.50b	28.20 ± 0.70a
Dynamic oscillatory property:				
Storage modulus (Pa)	42943 ± 250d	54020 ± 1095c	79797 ± 257a	66990 ± 111b
Loss modulus (Pa)	6370 ± 250c	10183 ± 76a	10260 ± 75a	8606 ± 76b
Color parameters:				
L value	37.67 ± 0.20a	37.10 ± 0.30a	37.74 ± 0.40a	37.88 ± 0.4a
a value	1.34 ± 0.03a	1.38 ± 0.04a	1.43 ± 0.09a	1.49 ± 0.06a
b value	15.88 ± 0.20a	15.98 ± 0.20a	15.95 ± 0.30a	15.56 ± 0.6a

Note: *Different letters show significance difference (*P*<0.05); ± Standard error

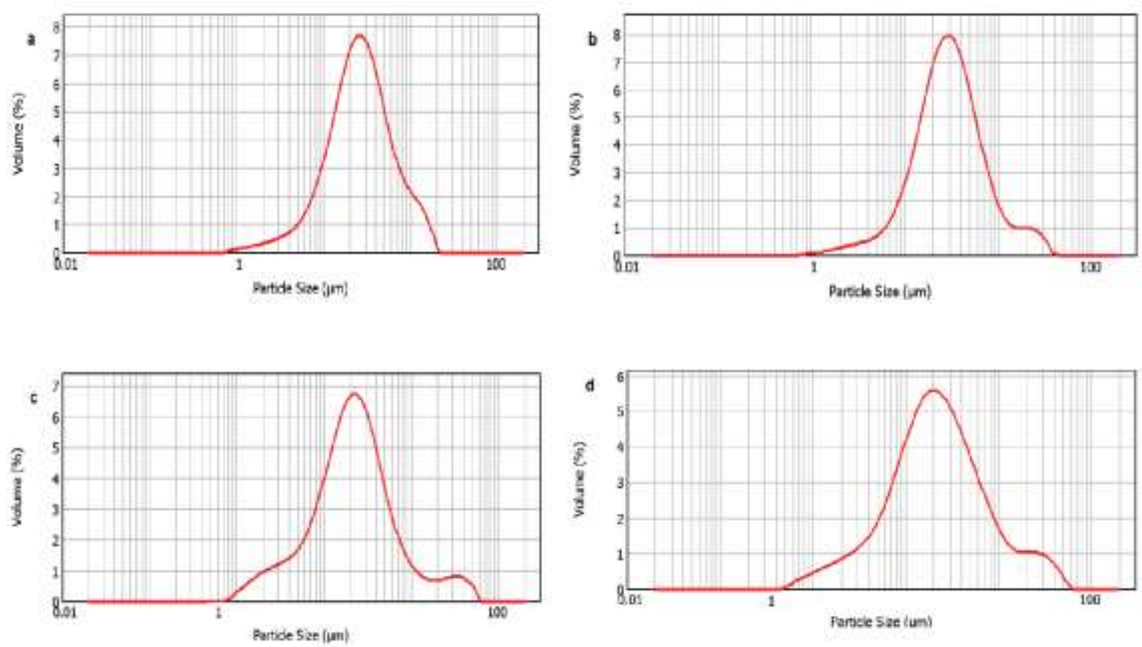


Fig. 1. Particle size distribution curve of pistachio paste produced using a Colloid mill at different gap size (a=20 µm; b= 40µm; c=60µm and d=80µm)

A reduction in the mill gap size resulted in a decrease in pistachio paste particle size, and as expected, the narrowest gap size produced paste with the smallest particle size. Visual observation showed that the paste was smoother than the rest, especially the one that was obtained when the gap size was the lowest. The particle sizes raged 0.9-46.7, 1.0-76.3, 1.2-85.9 and 1.9-97.3 µm for mill gap size of 20, 40, 60 and 80 µm, respectively. A significant ($P < 0.05$) difference was observed in the particle size of the paste as the mill gap size was increased. At a smaller gap size of 20 µm, the efficiency of the milling process was contributed by friction of the disc surfaces of the mill that were in contact with the kernels surfaces. As the mill gap size was increased from 20 to 80 µm, more kernels could enter the spaces between the discs of colloid mill to produce a uniform paste at a faster rate with larger particle size. Alterations in the colloidal stability of pistachio paste are shown in Table 1. It was obvious that decreasing the particle size (from 80 to 20 µm) improved the colloidal stability. A significant difference ($P<0.05$) was observed between the colloidal stability of pistachio paste produced using mill gap size of 80 µm and the pastes produced using the other gap sizes (20, 40 and 60 µm). It was clear that the pistachio paste was less stable when it was in the range of 31.4 µm. This was because the paste forms a smaller dispersion of solid phase in the oil phase when the number of larger particles increased and hence, it became less stable.

Rheological Properties of Pistachio Paste

Flow behaviour

The rheological properties of pistachio paste at different mill gap size are shown in Table 1. The consistency index (K) and yield stress (τ_0) decreased as the gap size. The particle size also decreased. It was found that the flow behavior index (n) of all the pistachio paste was less than 1, indicating that these pastes behaved as a Herschel-Bulkey material. Taghizadeh and Razavi studied pistachio butter and observed non-linear relationships between shear stress and shear rate with n of less than 1, indicating similar behavior as pistachio paste (Taghizadeh and Razavi, 2009b). The flow behavior of pistachio paste samples was also compared with several rheological models, including the Bingham, Power Law, Herschel-Bulkey and Casson Models). The Herschel-Bulkey Model was found to be the best model to describe the rheological properties of the pistachio paste studied based on the highest R^2 as shown in Table 2.

Table 2. Correlation coefficient (R^2) of pistachio paste using different rheological models.

Type of rheological model	Model	Correlation coefficient (R^2)
Bingham	$\tau = \tau_0 + \eta\ \gamma^n$	0.9755 d*
Ostwald	$\tau = k\ \gamma^n$	0.9962 b
Power law	$\tau = k\ \gamma^n$	0.9962 b
Herschel-Bulkley	$\tau = \tau_0 + k\ \gamma^n$	0.9968 a
Casson	$\tau^{1/n} = \tau_0^{1/n} + (\eta\ \gamma)^{1/n}$	0.9934 c

*Different letters shows significant difference at *P < 0.05*

K: consistency index (Pa.s); n: flow behaviour index; τ: stress (Pa); τ_0: yield stress (Pa); η: Bingham viscosity (Pa.s)

Dynamic oscillatory property

The dynamic oscillatory property was applied to measure the structural changes in pistachio pastes with different particle size distributions. In the pistachio pastes, G' was higher than G", indicating that the elastic behavior was greater than the viscous behavior at all frequencies studied (Table 1 and Fig. 2). A larger value of the storage modulus implied that the pistachio paste had a prevalent solid-like behavior which was related to higher stability. The results of flow behavior and dynamic oscillatory property of pistachio paste confirmed that the pistachio paste produced using 60µm gap size had the highest stability among all gap sizes used in this study.

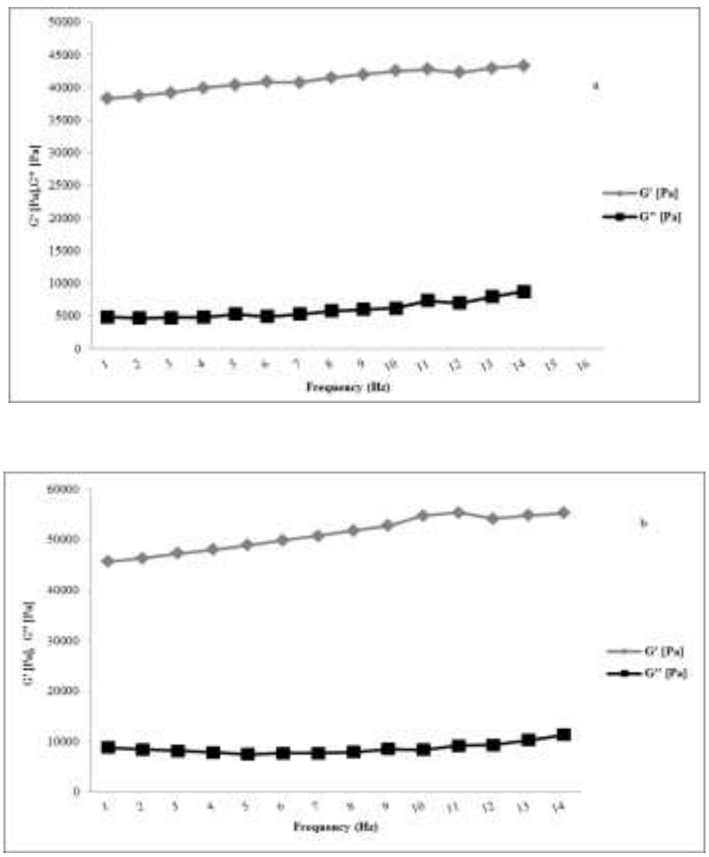
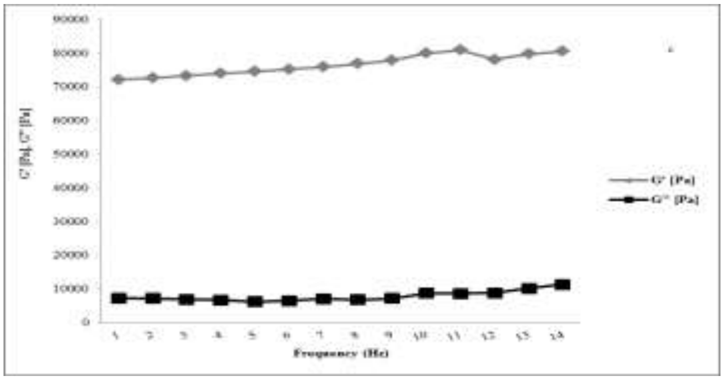


Fig. 3. Effect of frequency on storage and loss modulus of pistachio paste produced at different mill gap size (a=20 µm;b= 40µm;) at a constant stress amplitude of 150 Pa



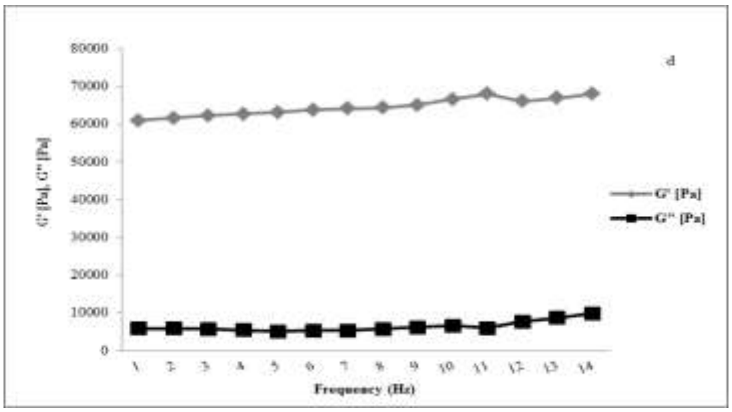


Fig. 3. Continued. c=60µm d=80µm

Effect of Particle Size on Colour of Pistachio Paste

The result of color measurements showed that there was no significant difference ($p<0.05$) in the *L*, *a* and *b* values of pistachio pastes produced using different gap sizes.

Discussion

The findings obtained from this study clearly indicated that the particle size of pistachio paste influenced the colloidal stability. Similarly, Barnes (1994) reported that decreasing the particle size improved the dispersion of the solid phase in oil phase and increased the cohesiveness of the final product and resulted in a more stable colloid. On the other hand, no significant ($P > 0.05$) difference in colloidal stability was observed when the mill gap size was below 80 µm (20, 40 and 60 µm) due to the narrow range of size among the paste particles. Matsunobu et al. (1987) claimed that the instability of almond paste was only detected when the particle size was more than 105 µm.

The Herschel-Bulkey model was found to be the best model to describe the rheological properties of the pistachio paste studied based on the highest R^2. The yield stress in Herschel-Bulkley model can be used to calculate whether a sample is likely to settle in-situ or whether it will be difficult to start pumping or stirring. Good rheological product design will enhance processing and end use.

The result of color measurements showed that there was no significant difference ($p<0.05$) in the color values of pistachio pastes produced using different gap sizes. Ciftci *et al.* reported similar results for sesame paste (Ciftci *et al.*, 2008). The color change was related to the roasting process (Kahyaoglu and Kaya, 2006). The presence of colorants like green pigments and chlorophyll also affected the color of pistachio paste (Ciftci *et al.*, 2008).

The results of flow behavior, dynamic oscillatory property and color properties of pistachio paste confirmed that the pistachio paste produced using 60µm gap size had the highest stability among all gap sizes used in this study.

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