CHEMICAL COMPOSITION AND RHEOLOGICAL CHARACTERIZATION OF PISTACHIO GREEN HULL'S MARMALADE

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ABSTRACT

This research aimed to study the effect of different levels of pistachio green hull (40–60%) and pectin (0–0.4%) on the flow characteristics of pistachio green hull's marmalade. It was found that pistachio hull's marmalade behaved as a pseudo-plastic fluid. Seven models were used to describe time-independent behavior of samples. To evaluate the ability of this models, two statistical parameters namely; R^2 *and root mean square error were used and finally power-law model was found to be the most appropriate to fit the flow curves of pistachio hull's marmalade. Overall, the results showed that increasing the percent of pistachio hull increased the consistency coefficient in the range of 1.9–121 Pa·*s^n *and apparent viscosity in the range of 0.67–7.95 Pa·s, whereas it decreased the flow behavior index in the range of 0.82–0.28. The change of flow behavior index and consistency coefficient with pectin did not follow a descriptive trend.*

PRACTICAL APPLICATIONS

Rheological properties of semisolid foods are important for quality control and process engineering calculations. Pistachio hull's marmalade is a

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semisolid gel made from puree of pistachio green hull, sugar, acid and pectin, which can be used in different formulations such as cake and cookies. Regarding the rheological data of marmalades in literature, comparisons in absolute terms do not provide useful information, possibly because of two reasons. Due to their complex mathematical geometries, some viscometers might not allow shear rate calculations and, hence, can only produce comparative rather than absolute flow behavior data. Another reason could be the differences in the production method or raw material used. Even very minor changes in composition or processing variables can dramatically influence the rheological properties. The knowledge obtained in this work will enable the pistachio processors to increase the efficiency of the design and quality control throughout the processing of this new product.

KEYWORDS

Marmalade, modeling, pistachio hull, pseudo-plastic, rheology

INTRODUCTION

Soft green hull (endocarp), branch, leave, remaining kernel and wood shell are by-products of the fresh pistachio processing. The green hull is the major waste of pistachio industry, which is estimated averagely 60% of the production (Bohluli Ghaen 2006). Pistachio green hull is a promising source of protein, fat, mineral salts and vitamins, and is also one of the richest sources of antioxidant, phenolic compounds and essential oil such as a-pinene and alpha-terpinolene (Alizadeh and Rusta Azad 2003; Goli *et al.* 2005; Chahed *et al.* 2007).

The market of preserves has been stable during the last decade as a consequence of changes in consumption patterns and economical aspects. Therefore, the preserve industry needs to improve its competitiveness, and developing new products may be a way of achieving this objective. Pistachio hull's marmalade is a semisolid food resulting from the homogenous and consistent mixture obtained upon cooking the pistachio green hull's puree with sugar and other ingredients like acidifying and gelling agents. This product cannot only be consumed as a new preserve, but can also be used in different food products such as cake and cookies. The rheological properties and chemical constituents of foods belong to their fundamental characteristics. There are a number of published researches about the rheological properties of jams such as strawberry jam (Costell *et al.* 1987; Grigelmo-Miguel and Martin-Belloso 1999), apricot jam (Villarroel and Costell 1989), strawberry, peach, plum and apricot jam (Carbonell *et al.* 1991a), strawberry and peach jam (Carbonell *et al.* 1991b), sheared strawberry and peach jams (Costell *et al.* 1993), raspberry, strawberry, peach and prune jam (Maceiras *et al.* 2006), black currant jam (Rubinskiene *et al.* 2007), and pineapple jam (Basu *et al.* 2007). However, no published literature was found on the physicochemical properties of pistachio hull's marmalade as a new food product. The objectives of this study were to (1) characterize the chemical composition and rheological behavior of pistachio hull's marmalade; (2) determine the best time-independent model to describe the flow curves; and (3) analyze the effect of different levels of pistachio green hull and pectin on the rheological characteristics of pistachio hull's marmalade.

MATERIALS AND METHODS

Preparation of Marmalade

Raw materials included dried pistachio green hull, high methylester pectin (62 degree esterification), sugar, citric acid and ascorbic acid. Dried pistachio green hull were supplied by Pistachio Research Institute of Iran, pectin by Azma Laban Shargh Co. (Khorasan Rzavi, Iran), citric acid by Kimya Pars Co. (Tehran, Iran), sugar from local market in Mashhad, Iran, and ascorbic acid by Merk Co., Brussels, Germany.

The dried pistachio hulls were cleaned manually to remove all foreign matter such as dust, stones, black hulls and wood shells. Then, the hulls were soaked in water and boiled two times for 15 min to remove poignancy and astringency tastes. In the next stage, the hulls were mixed with water in equal proportion and homogenized using a high-speed blender. Then, the mixture was filtered through a cloth leach in order to obtain the puree of pistachio hull. To produce marmalade, sugar syrup was firstly prepared by dissolving the food grade commercial sucrose in water until it formed a 90°Brix solution, then mixed with the puree of pistachio hull and stored in a refrigerator for at least 12 h. The mixture was then cooked to 65–70°Brix. When the mixture achieved 60°Brix, the pectin, citric acid and ascorbic acid were added. Finally, the marmalade samples were cooled and filled in little containers and stored in a refrigerator for at least 24 h to ensure that gelation was achieved. Regarding the marmalade formulation, the ratio of pistachio hull's puree over syrup was set at five levels (40–60, 45–55, 50–50, 55–45 and 40–60), and pectin was added at five concentrations (0, 0.1, 0.2, 0.3 and 0.4%).

Chemical Analysis

The chemical compositions of the pistachio hull, pistachio hull's puree and marmalade samples were analyzed as total solid (by the oven method at

TABLE 1.
CHEMICAL CHARACTERIZATION (MEAN VALUE ± SD) OF PISTACHIO HULL SAMPLES

Compound	Dried pistachio hull	Puree of pistachio hull
Protein (%)	13.1 ± 1.2	Not determined
Fat (%)	9.67 ± 0.12	Not determined
Ash (%)	13.1 ± 0.24	Not determined
Pectin (%)	5.75 ± 0.54	0.84 ± 0
pH	Not applicable	6.41 ± 0.01
Acidity	Not applicable	0.01 ± 0
Brix	Not applicable	0.0 ± 0
Insoluble solids (%)	Not applicable	3.25 ± 0
Total solids (%)	94.5 ± 1.2×10^{-13}	3.25 ± 0.04

70C), crude protein (by the micro-Kjeldal method), ash (oven at 550C for 4 h) and pectin (AOAC 2005). The crude oil content was measured according to the Soxhlet method with dietyl ether as oil solvent. To determine the acidity, diluted samples were titrated with 0.1 N NaOH, and results were given as percent anhydrous citric acid. Soluble solid (°Brix) was measured at 20C by using a refractometer (RHBO_80, Link, Fuzhou, China). The pH was controlled with a pH meter (Sartorius PB_11, Göttingen, Germany). The chemical characteristics of died pistachio hull, pistachio hull's puree and marmalade are summarized in Tables 1 and 2.

Rheological Measurements

Rheological properties of pistachio hull's marmalade were measured with a Bohlin Visco 88 viscometer (Bohlin Instrument, Cirencester, U.K.) equipped with a bob and cup geometry (bob length: 60 mm; bob diameter: 14 mm; gap width: 1 mm) and a heating circulator (model F12- MC, Julabo Labortechnik, Seelbach, Germany). The software Bohlin v06.32 was used to generate shear stress–shear rate data. The flow curves of pistachio hull's marmalade were measured at 25 ± 0.5C by increasing the shear rate from 14 to 100/s over a time lapse of 180 s. The apparent viscosity of pistachio hull's marmalades was determined at a shear rate of 40/s.

Modeling Time-Independent Behavior. In the flow curves measurements, the shear stress (σ) was measured as a function of shear rate ($\dot{\gamma}$). Then, the apparent viscosity (η_a) at a given shear rate can be calculated using the following equation (Steffe 1996; Tabilo-Munizaga and Barbosa-Canovas 2005):

$$\sigma = \eta_a \dot{\gamma} \tag{1}$$

TABLE 2.
CHEMICAL COMPOSITION (MEAN VALUE ± SD) AND RHEOLOGICAL PARAMETERS OF POWER LAW MODEL OF PISTACHIO GREEN HULL'S MARMALADE*

Pistachio hull (%)	Sugar (%)	Pectin (%)	pH	Acidity	°Brix	Total solids (%)	Insoluble solids (%)	Total pectin (%)	Flow behavior index	Consistency coefficient (Pa·s^n)	Apparent viscosity (Pa·s)†
40	60	0	3.15 ± 0.09	0.33 ± 0.01	66.6 ± 0.8	67.8 ± 1.2	1.3 ± 0.4	2.3 ± 0.4	0.75 ± 0.07	1.9 ± 1.5	0.7 ± 0.3
45	55	0	3.12 ± 0.15	0.33 ± 0.03	69.8 ± 0.3	73.9 ± 0.3	4.1 ± 0.1	3.7 ± 1.2	0.58 ± 0.04	10.8 ± 2.2	2.3 ± 0.2
50	50	0	3.25 ± 0.15	0.35 ± 0.08	69.2 ± 0.6	72.0 ± 1.1	2.8 ± 0.4	1.3 ± 0.6	0.45 ± 0.01	22.1 ± 3.0	3.0 ± 0.4
55	45	0	3.25 ± 0.07	0.41 ± 0.05	69.5 ± 0.7	72.0 ± 0.9	2.5 ± 0.2	1.9 ± 0.9	0.43 ± 0.05	18.1 ± 13.6	2.0 ± 1.3
60	40	0	3.25 ± 0.05	0.41 ± 0.06	68.3 ± 0.6	70.6 ± 0.5	2.3 ± 0.1	1.7 ± 0.7	0.30 ± 0.02	68.3 ± 21.9	5.1 ± 1.5
40	60	0.1	3.13 ± 0.08	0.32 ± 0.03	66.7 ± 0.8	69.3 ± 1.2	2.6 ± 0.4	2.0 ± 1.0	0.67 ± 0.01	3.6 ± 0.5	1.1 ± 0.1
45	55	0.1	3.19 ± 0.09	0.35 ± 0.02	68.0 ± 0.6	70.6 ± 0.8	2.6 ± 0.2	2.1 ± 0.6	0.60 ± 0.05	7.8 ± 3.7	1.7 ± 0.6
50	50	0.1	3.15 ± 0.04	0.40 ± 0.04	68.8 ± 0.5	72.4 ± 1.9	3.6 ± 1.4	2.5 ± 0.3	0.49 ± 0.05	20.1 ± 9.2	2.9 ± 0.9
55	45	0.1	3.30 ± 0.13	0.38 ± 0.04	68.7 ± 0.8	73.9 ± 2.1	5.2 ± 1.4	1.3 ± 0.2	0.46 ± 0.06	31.1 ± 21.6	3.9 ± 2.4
60	40	0.1	3.28 ± 0.07	0.41 ± 0.09	68.2 ± 0.7	71.6 ± 1.0	3.5 ± 0.3	2.1 ± 0.4	0.36 ± 0.05	52.1 ± 26.9	4.7 ± 1.9
40	60	0.2	3.15 ± 0.01	0.28 ± 0.01	70.0 ± 0.4	73.9 ± 0.8	3.9 ± 0.4	1.7 ± 0.4	0.67 ± 0.06	6.0 ± 2.4	1.7 ± 0.3
45	55	0.2	3.32 ± 0.07	0.38 ± 0.03	68.5 ± 0.4	70.4 ± 1.8	1.9 ± 1.4	4.3 ± 1.2	0.52 ± 0.02	12.6 ± 4.9	2.1 ± 0.7
50	50	0.2	3.17 ± 0.04	0.37 ± 0.02	68.9 ± 0.4	70.6 ± 1.2	1.7 ± 0.8	2.3 ± 0.6	0.49 ± 0.05	18.8 ± 7.1	2.7 ± 0.6
55	45	0.2	3.24 ± 0.06	0.37 ± 0.02	68.0 ± 0.5	69.8 ± 1.3	1.8 ± 0.9	1.9 ± 0.2	0.34 ± 0.06	65.8 ± 35.8	5.4 ± 2.0
60	40	0.2	3.22 ± 0.06	0.44 ± 0.04	68.5 ± 1.0	69.9 ± 0.8	1.4 ± 0.3	1.2 ± 1.0	0.30 ± 0.03	104.9 ± 38.5	7.6 ± 2.1
40	60	0.3	3.28 ± 0.01	0.30 ± 0.08	68.0 ± 0.2	70.5 ± 1.2	3.5 ± 0.9	1.9 ± 0.4	0.82 ± 0.24	3.4 ± 2.2	1.0 ± 0.6
45	55	0.3	3.25 ± 0.03	0.29 ± 0.03	68.3 ± 0.3	71.3 ± 0.5	3.0 ± 0.2	1.7 ± 0.2	0.53 ± 0.09	17.4 ± 11.9	2.7 ± 0.8
50	50	0.3	3.24 ± 0.06	0.40 ± 0.03	67.9 ± 0.4	69.9 ± 0.9	2.0 ± 0.4	3.1 ± 0.6	0.42 ± 0.04	29.2 ± 7.6	3.5 ± 0.5
55	45	0.3	3.24 ± 0.03	0.38 ± 0.03	67.5 ± 0.0	69.5 ± 0.9	2.0 ± 0.9	4.4 ± 1.3	0.31 ± 0.06	65.5 ± 22.2	4.9 ± 1.1
60	40	0.3	3.28 ± 0.13	0.43 ± 0.06	67.9 ± 0.3	70.6 ± 1.0	2.8 ± 0.8	2.1 ± 0.7	0.30 ± 0.01	94.4 ± 41.6	7.0 ± 2.8
40	60	0.4	3.26 ± 0.05	0.27 ± 0.04	69.3 ± 0.2	74.0 ± 0.4	4.8 ± 0.2	1.7 ± 0.3	0.62 ± 0.04	10.9 ± 2.3	2.6 ± 0.2
45	55	0.4	3.26 ± 0.03	0.34 ± 0.01	68.5 ± 0.2	71.1 ± 1.3	2.7 ± 1.0	2.0 ± 0.6	0.53 ± 0.04	12.2 ± 6.2	2.1 ± 0.8
50	50	0.4	3.17 ± 0.04	0.40 ± 0.01	68.4 ± 0.3	73.1 ± 1.3	4.8 ± 1.0	2.4 ± 0.3	0.45 ± 0.02	26.0 ± 4.6	3.4 ± 0.4
55	45	0.4	3.18 ± 0.10	0.41 ± 0.03	69.3 ± 1.4	69.9 ± 1.4	0.6 ± 0.0	2.3 ± 0.5	0.40 ± 0.08	72.8 ± 51.3	6.7 ± 4.0
60	40	0.4	3.26 ± 0.11	0.41 ± 0.09	68.2 ± 2.4	72.2 ± 3.0	3.9 ± 0.6	3.1 ± 1.4	0.28 ± 0.09	120.8 ± 61.8	8.0 ± 2.5

* All data represent four determinations.
† Apparent viscosity calculated at a shear rate of 40/s.

The flow curves of pistachio hull's marmalade samples were described by power-law (or Ostwald -Waele), Herschel–Bulkley, Casson, Bingham, Mizrahi and Berk, Vocadlo and Sisko models (Steffe 1996).

Statistical Analysis

To analysis of variance (ANOVA), Minitab software (version 13, Minitab Inc., State College, PA) was used to determine significant differences ($P = 0.05$) among marmalades with different levels of pistachio hull's puree and pectin used, and Duncan's multiple range test was employed to determine difference among formulations. To select the best model describing time-independent rheological properties of pistachio hull's marmalade samples, two statistical parameters including root mean square error (RMSE; Eq. 2) and coefficient of determination (R^2; Eq. 3) were determined using Microsoft Excel (Microsoft Office, Package 2003) and Slidewrite software (Computer package version 2.0, Advanced Graphics Software, Inc., Encinitas, CA) for the seven aforementioned rheological models.

$$RMSE = \left[\frac{1}{n}\sum_{1}^{n}\left(x_{\text{exp.}} - x_{\text{pred.}}\right)^2\right]^{\frac{1}{2}} \tag{2}$$

$$R^2 = \frac{\sum_{1}^{n}\left(x_{\text{pred.}} - \bar{x}\right)^2}{\sum_{1}^{n}\left(x_{\text{exp.}} - \bar{x}\right)^2} \tag{3}$$

where n is the number of experimental data, $x_{\text{exp.}}$ is the value obtained from experiment, $x_{\text{pred.}}$ is the predicted value by the corresponding model and $\bar{x}$ is the grand mean. The value resulted from Eq. (2) must be divided by the mean value of each treatment to achieve the final RMSE value. Values less than 0.1 represent excellent fitting.

RESULTS AND DISCUSSION

Flow Curves

Figure 1 shows the typical flow curves of pistachio hull's marmalade samples (40% puree of pistachio hull and 60% sugar) at different levels of pectin used. The results showed that the shear stress-shear rate relationship is nonlinear, indicating that all pistachio hull's marmalades behave as non-Newtonian fluid, pseudoplastic type. This behavior is similar to those previously observed for strawberry jam (Costell *et al.* 1987), apricot jam (Villarroel and Costell 1989), strawberry, peach, plum and apricot jam (Carbonell *et al.*

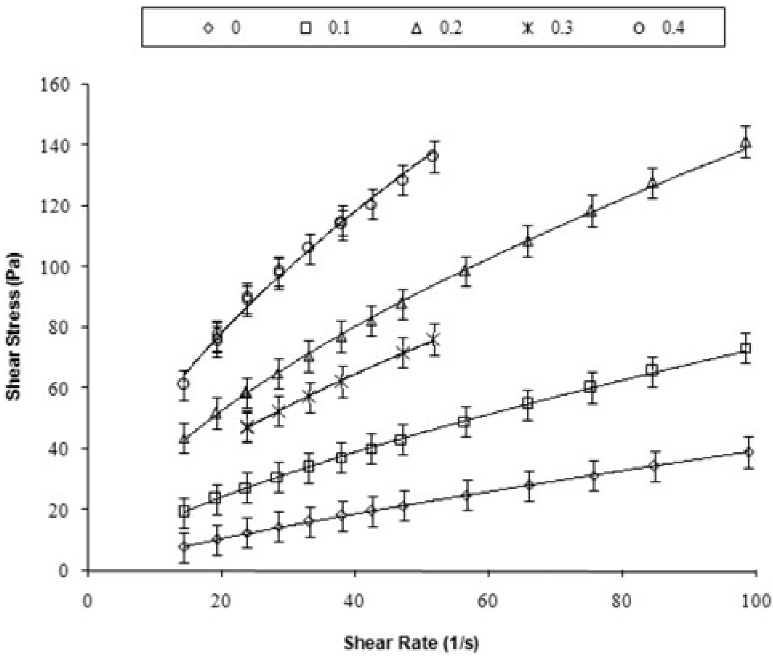

FIG. 1. THE TYPICAL FLOW CURVES OF PISTACHIO HULL'S MARMALADE (40% PUREE OF PISTACHIO HULL AND 60% SUGAR) FITTED WITH THE POWER MODEL AT DIFFERENT LEVELS OF PECTIN INDICATED

1991a), strawberry jam (Grigelmo-Miguel and Martin-Belloso 1999), raspberry, strawberry, peach and prune jam (Maceiras *et al.* 2006).

Selection of the Best Model

Table 3 shows the two statistical parameters determined for validation of the seven rheological models used in this study. It can be found that the Sisko model was generally the poorest and it was not applicable for most samples. The Herschel–Bulkley model was not applicable for two samples (40% puree of pistachio hull, 60% sugar, 0.3% pectin and 40% puree of pistachio hull, 60% sugar and without pectin) and in some samples, RMSE values were higher than 0.1. The Mizrahi–Berk model was not proper in most cases, because R^2 values were lower than 0.55 and RMSE values were out of range. The Casson model was not suitable for two samples containing 40% puree, 60% sugar, 0.3% pectin and 45% puree, 55% sugar, 0% pectin. The power-law, Bingham and Vocadlo models were totally suitable except for samples containing 40% puree of pistachio hull, 60% sugar and 0.4% pectin for the

TABLE 3.
THE RANGES OF STATISTICAL PARAMETERS OF THE RHEOLOGICAL MODELS DETERMINED FOR FLOW CURVES OF PISTACHIO GREEN HULL'S MARMALADE*

Pistachio hull (%)	Sugar (%)	Pectin (%)	Statistical parameters	Power law	Herschel–Bulkley	Casson	Bingham	Vocadlo	Mizrahi–Berk	Sisko
40	60	0	R^2	0.997–1.000	Not applicable	0.995–1.000	0.993–0.998	0.997–1.000	0.502–0.506	Not applicable
			RMSE	0.009–0.013	Not applicable	0.005–0.018	0.017–0.024	0.003–0.013	69.835–176.708	Not applicable
45	55	0	R^2	0.999–1.000	1.000	0.999	0.994–0.995	0.997–1.000	1.000	1.000
			RMSE	0.007–0.009	0.003	0.006–1.365	0.019–0.020	0.005–0.014	0.002–0.004	0.002
50	50	0	R^2	0.989–0.999	0.983–1.000	0.975–0.999	0.967–0.997	0.973–0.999	0.986–1.000	Not applicable
			RMSE	0.005–0.018	0.002–0.023	0.002–0.026	0.009–0.033	0.006–0.030	0.002–0.019	Not applicable
55	45	0	R^2	0.975–0.995	0.965–0.994	0.956–0.989	0.941–0.991	0.948–0.991	0.501–0.993	Not applicable
			RMSE	0.011–0.026	0.012–0.026	0.012–0.030	0.012–0.034	0.012–0.032	0.012–0.026	Not applicable
60	40	0	R^2	0.970–0.999	0.955–0.996	0.940–0.992	0.924–0.977	0.936–0.987	0.959–0.997	Not applicable
			RMSE	0.005–0.019	0.007–0.023	0.010–0.025	0.017–0.031	0.013–0.028	0.007–0.020	Not applicable
40	60	0.1	R^2	1.000	1.000	0.999–1.000	0.996–0.998	1.000	0.507–0.507	1.000
			RMSE	0.007–0.008	0.002–0.005	0.006–0.010	0.018–0.024	0.003–0.005	72.206–86.525	0.002–0.004
45	55	0.1	R^2	0.999	1.000	0.999–1.000	0.994–1.000	0.997–1.000	0.504–1.000	1.000
			RMSE	0.005–0.009	0.002–0.004	0.003–0.008	0.004–0.024	0.003–0.015	0.002–30.895	0.002–0.003
50	50	0.1	R^2	0.988–0.999	1.000	0.980–0.999	0.979–0.994	0.987–0.999	0.984–1.000	Not applicable
			RMSE	0.003–0.018	0.002–0.003	0.004–0.020	0.008–0.024	0.005–0.019	0.003–0.018	Not applicable
55	45	0.1	R^2	0.988–0.998	0.982–0.997	0.976–0.993	0.968–0.995	0.972–0.996	0.502–0.997	Not applicable
			RMSE	0.007–0.017	0.008–0.21	0.014–0.023	0.011–0.029	0.009–0.027	0.009–0.017	Not applicable
60	40	0.1	R^2	0.982–0.996	0.973–0.995	0.964–0.993	0.950–0.989	0.959–0.991	0.978–0.995	Not applicable
			RMSE	0.007–0.021	0.007–0.025	0.007–0.028	0.010–0.034	0.009–0.032	0.007–0.021	Not applicable
40	60	0.2	R^2	0.999–1.000	1.000	0.999–1.000	0.995–1.000	0.999–1.000	0.504–1.000	1.000
			RMSE	0.003–0.009	0.003–0.003	0.003–0.009	0.005–0.024	0.004–0.013	0.002–27.693	0.002–0.003
45	55	0.2	R^2	0.992–0.998	0.988–0.999	0.982–0.999	0.972–0.998	0.979–0.999	0.989–0.998	Not applicable
			RMSE	0.007–0.017	0.005–0.107	0.005–0.024	0.006–0.032	0.006–0.028	0.005–0.017	Not applicable
50	50	0.2	R^2	0.984–0.996	0.979–0.994	0.970–0.989	0.963–0.982	0.975–0.993	0.980–0.994	Not applicable
			RMSE	0.010–0.025	0.012–0.029	0.016–0.032	0.022–0.039	0.026–0.048	0.012–0.026	Not applicable

TABLE 3.
CONTINUED

Pistachio hull (%)	Sugar (%)	Pectin (%)	Statistical parameters	Power law	Herschel–Bulkley	Casson	Bingham	Vocadlo	Mizrahi–Berk	Sisko
55	45	0.2	R^2	0.995–0.999	0.988–0.998	0.985–0.996	0.975–0.986	0.988–0.991	0.992–0.997	Not applicable
			RMSE	0.056–0.058	0.059–0.062	0.061–0.063	0.067–0.070	0.063–0.065	0.058–0.060	Not applicable
60	40	0.2	R^2	0.997–0.999	0.996–0.997	0.989–0.997	0.980–0.983	0.988–0.990	0.996–0.999	Not applicable
			RMSE	0.003–0.006	0.005–0.008	0.008–0.011	0.014–0.017	0.011–0.013	0.005–0.008	Not applicable
40	60	0.3	R^2	0.999	Not applicable	0.603–1.000	0.999–1.000	0.554–1.000	0.503–1.000	0.999–1.000
			RMSE	0.006–0.011	Not applicable	0.004–0.572	0.004–0.025	0.003–13.333	0.003–83.547	0.003–0.011
45	55	0.3	R^2	0.984–0.996	0.902–0.994	0.971–0.988	0.964–0.981	0.973–0.987	0.980–0.994	Not applicable
			RMSE	0.016–0.026	0.018–0.029	0.025–0.033	0.032–0.060	0.027–0.035	0.017–0.027	Not applicable
50	50	0.3	R^2	0.993–0.998	0.988–0.994	0.983–0.991	0.975–0.982	0.979–0.991	0.966–0.993	Not applicable
			RMSE	0.007–0.014	0.011–0.019	0.012–0.021	0.020–0.027	0.013–0.025	0.010–0.015	Not applicable
55	45	0.3	R^2	0.981–0.997	0.981–0.996	0.976–0.992	0.971–0.985	0.975–0.990	0.980–0.997	Not applicable
			RMSE	0.005–0.012	0.006–0.012	0.008–0.013	0.013–0.022	0.011–0.014	0.007–0.012	Not applicable
60	40	0.3	R^2	0.995–0.998	0.993–0.999	0.991–0.997	0.906–0.988	0.987–0.992	0.994–0.998	Not applicable
			RMSE	0.046–0.007	0.005–0.009	0.007–0.010	0.013–0.016	0.010–0.013	0.005–0.008	Not applicable
40	60	0.4	R^2	0.990–0.995	0.987–0.992	0.980–0.987	0.975–0.982	0.981–0.987	0.935–0.992	Not applicable
			RMSE	0.019–0.230	0.044–0.226	0.023–0.035	0.034–0.231	0.027–0.034	0.020–0.142	Not applicable
45	55	0.4	R^2	0.974–0.995	0.971–0.994	0.957–0.989	0.946–0.985	0.962–0.993	0.968–0.992	Not applicable
			RMSE	0.014–0.032	0.015–0.034	0.018–0.040	0.024–0.045	0.016–0.039	0.015–0.034	Not applicable
50	50	0.4	R^2	0.995–0.996	0.992–0.994	0.983–0.991	0.980–0.982	0.991–0.993	0.992–0.995	Not applicable
			RMSE	0.010–0.012	0.012–0.016	0.016–0.018	0.022–0.025	0.014–0.018	0.012–0.013	Not applicable
55	45	0.4	R^2	0.985–0.998	0.980–0.999	0.972–0.998	0.962–0.992	0.970–0.995	0.983–0.999	Not applicable
			RMSE	0.004–0.030	0.005–0.027	0.006–0.030	0.012–0.037	0.010–0.033	0.004–0.024	Not applicable
60	40	0.4	R^2	0.980–0.999	0.964–0.998	0.960–0.996	0.936–0.980	0.948–0.993	0.975–0.993	Not applicable
			RMSE	0.004–0.011	0.006–0.015	0.007–0.015	0.020–0.087	0.011–0.018	0.005–0.012	Not applicable

* All data represent four determinations.
RMSE, root mean square error.

power-law (R^2 = 0.990–0.995, whereas RMSE = 0.019–0.230) and Bingham (R^2 = 0.975–0.982, whereas RMSE = 0.034–0.231) models, and 40% puree of pistachio hull, 60% sugar and 0.3% pectin for the Vocadlo model (R^2 = 0.554–1.000, and RMSE = 0.003–13.333). However, the obtained R^2 values were high for these samples, but the RMSE values were out of range. Perhaps, it can be concluded that R^2 is not always a suitable statistical parameter for estimation of the models ability. Among these three models, the Power law model was the one that best described the flow behavior of the marmalades in most cases, because the RMSE and R^2 values of different pistachio hull's marmalade samples ranged from 0.003 to 0.058, except for the sample mentioned earlier, and 0.970 to 1.000, respectively. The power law model reads as $\sigma = k\dot{\gamma}^n$, where k is the consistency coefficient and n the flow behavior index. Other workers also showed that the flow behavior of jams can be well described by time-independent rheological models, such the Herschel–Bulkley model for strawberry and apricot jams (Costell *et al.* 1987; Villarroel and Costell 1989), Casson and Herschel–Bulkley models for strawberry, peach, plum and apricot jam (Carbonell *et al.* 1991a,b), Casson for strawberry and peach jams (Costell *et al.* 1993), power-law model for strawberry jam (Grigelmo-Miguel and Martin-Belloso 1999), power-law and Herschel–Bulkley models for raspberry, strawberry, peach and prune jam (Maceiras *et al.* 2006).

Rheological Parameters

Table 2 gives the parameters of power-law model and the apparent viscosity of pistachio hull's marmalade at the shear rate of 40/s. As it is shown, the flow behavior index varied between 0.28 and 0.82 indicating a shear-thinning behavior, since the figures were smaller than one ($n < 1$). The flow behavior index (n) shows the degree of pseudoplasticity that is a measure of deviation from Newtonian behavior. As the flow behavior index (n) increases, the pseudoplasticity decreases (Grigelmo *et al.* 1999). The consistency coefficient and apparent viscosity of marmalade samples ranged from 1.9 to 121 ($Pa \cdot s^n$) and 0.67 to 0.8 ($Pa \cdot s$), respectively (Table 2). Increasing the pistachio hull concentration used in the formulation led to a higher consistency and pseudoplasticity of marmalade. Also the apparent viscosity increased when the percent of pistachio hull and pectin was increased in the marmalade formulation. However, the evolution of apparent viscosity values of the analyzed marmalades illustrated that the higher the pistachio hull content, the higher the viscosity variation observed in the marmalades. However, Fig. 1 shows that the apparent viscosity of marmalade with 0.3% pectin is lower than that of marmalade with 0.2%. On the other hand, data in Table 2 show that the total solids content in the product with 0.2% pectin is higher in comparison with the product with 0.3% pectin and that can be the reason for the increasing apparent viscosity.

Grigelmo-Miguel and Martin-Belloso (1999) studied the influence of fruit dietary fiber addition on rheological behavior of strawberry jam. Their results showed that increasing dietary fiber content increased the power law consistency coefficient, apparent viscosity and pseudoplasticity. The results obtained in this paper were in agreement with this paper. The reason for this behavior may be because of the fiber composition of pistachio hull.

Statistical analysis (ANOVA at 5% level of significance) indicated that the flow behavior index and consistency coefficient were significantly influenced by the concentration of pistachio hull and pectin ($P < 0.05$). The interaction between pistachio hull and pectin had no significant effect on the consistency coefficient ($P > 0.05$), but the flow behavior index was significantly influenced by the interaction between pistachio hull and pectin ($P < 0.05$).

Figures 2 and 3 show plots of the Power-law flow behavior index and consistency coefficient versus percent of pistachio hull. It can be seen that the flow behavior index decreased non-linearly with an increase in pistachio concentration (Fig. 2), whereas the consistency coefficient increased non-linearly (Fig. 3). The effect of pistachio hull on flow behavior index and

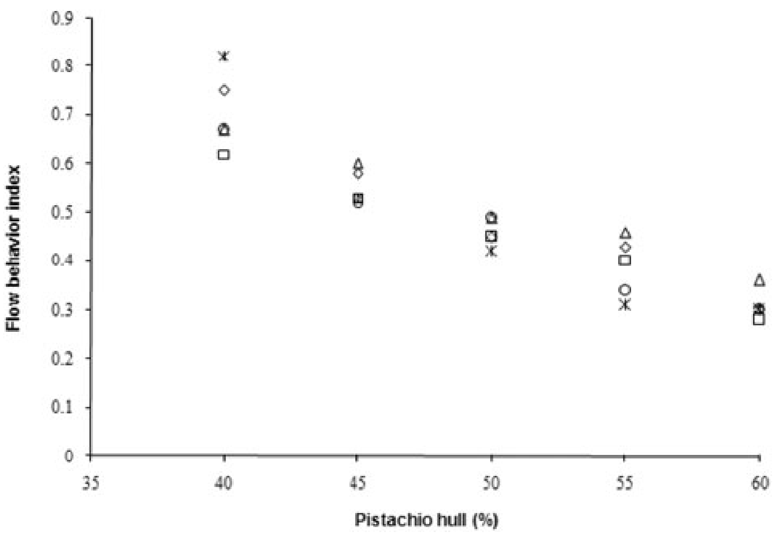

FIG. 2. EFFECT OF DIFFERENT CONCENTRATIONS OF PISTACHIO HULL ON FLOW BEHAVIOR INDEX OF PISTACHIO HULL'S MARMALADE (◇, 0% PECTIN; △, 0.1% PECTIN; ○, 0.2% PECTIN; ✳, 0.3% PECTIN; □, 0.4% PECTIN)

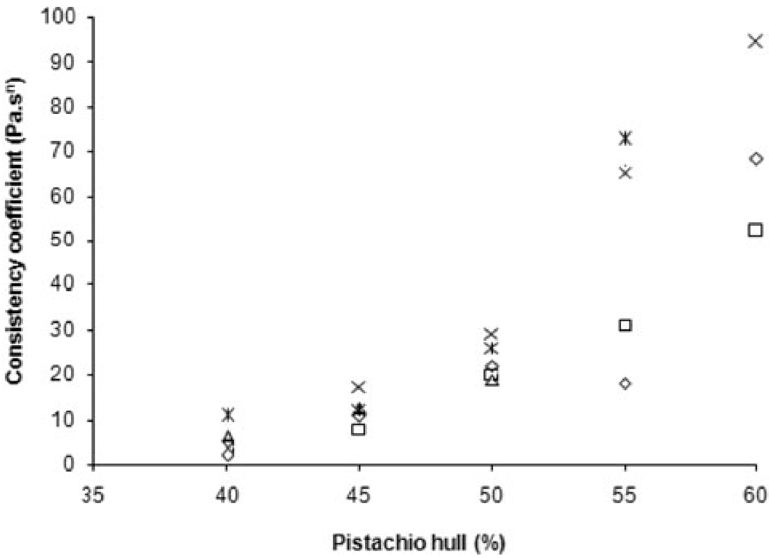

FIG. 3. EFFECT OF DIFFERENT CONCENTRATIONS OF PISTACHIO HULL ON CONSISTENCY COEFFICIENT OF PISTACHIO HULL'S MARMALADE (◇, 0% PECTIN; △, 0.1% PECTIN; ○, 0.2% PECTIN; ✳, 0.3% PECTIN; □, 0.4% PECTIN)

consistency coefficient was described by exponential (Eq. 4) and power (Eq. 5) functions (Rao 1999).

$$k = k_{c_1} \cdot e^{b_1 \times C} \tag{4}$$

$$k = k_{c_2} \cdot C^{b2} \tag{5}$$

In both equations, k_i and b_i are constants and C is the percent of pistachio hull used. These equations were plotted and corresponding model parameters are provided in Table 4. It seems that both exponential and power functions can be used to describe the relationship.

The results showed that the variation of flow behavior index and consistency coefficient with pectin concentration did not follow a descriptive trend (Figs. 4 and 5). The effect of pectin on flow behavior index and consistency coefficient was described by linear, exponential (Eq. 4) and power (Eq. 5) functions. The analysis of determination coefficients of models showed that a power law was not applicable to explain the effect of pectin on the flow behavior index and consistency coefficient. Meanwhile, the linear and

TABLE 4.
EFFECT OF PISTACHIO HULL ON THE POWER-LAW FLOW BEHAVIOR INDEX AND CONSISTENCY COEFFICIENT AT DIFFERENT PECTIN CONCENTRATIONS

% Pectin	Flow behavior index (*n*)						Consistency coefficient (*k*)					
	Exponential model (Eq. 4)			Power model (Eq. 5)			Exponential model (Eq. 4)			Power model (Eq. 5)		
	k_{c_1}	b_1	R^2	k_{c_2}	b_2	R^2	k_{c_1}	b_1	R^2	k_{c_2}	b_2	R^2
0	4.039	–0.043	0.963	1,741.70	–2.101	0.960	0.006	0.154	0.861	1×10^{-12}	7.670	0.880
0.1	2.278	–0.030	0.973	161.94	–1.479	0.961	0.019	0.135	0.979	8×10^{-11}	6.673	0.990
0.2	3.393	–0.041	0.963	1,084.60	–1.999	0.957	0.016	0.148	0.975	1×10^{-11}	7.257	0.967
0.3	5.653	–0.051	0.936	9,110.60	–2.546	0.960	0.009	0.159	0.932	9×10^{-13}	7.951	0.956
0.4	2.861	–0.037	0.956	548.11	–1.827	0.936	0.043	0.132	0.952	4×10^{-10}	6.445	0.932

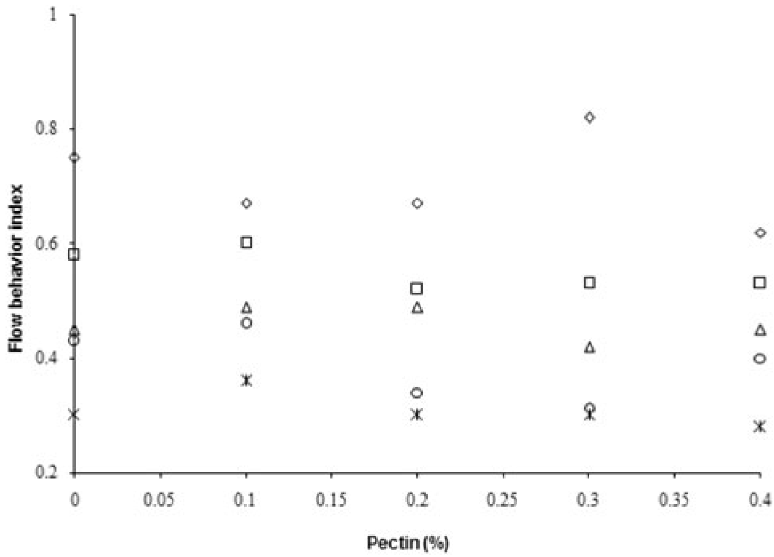

FIG. 4. EFFECT OF PECTIN ON FLOW BEHAVIOR INDEX OF PISTACHIO HULL'S MARMALADE AT DIFFERENT RATIO OF PISTACHIO HULL'S PUREE TO SUGAR USED (◇, 40–60; □, 45–55; △, 50–50; ○, 55–45; ⚹, 60–40)

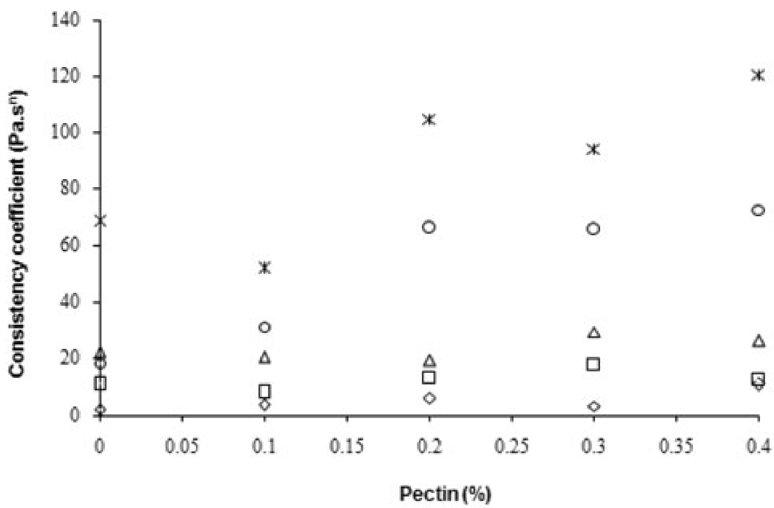

FIG. 5. EFFECT OF PECTIN ON CONSISTENCY COEFFICIENT OF PISTACHIO HULL'S MARMALADE AT DIFFERENT RATIO OF PISTACHIO HULL'S PUREE TO SUGAR USED (◇, 40–60; □, 45–55; △, 50–50; ○, 55–45; ⚹, 60–40)

exponential models were not be able to describe adequately the relationship between the percent of pectin and the flow behavior index and consistency coefficient (R^2 values were lower than 0.4 in most cases). This could be because of the differences in the composition of raw materials (Table 2).

CONCLUSION

Pistachio hull's marmalade is a semisolid gel that behaves as non-Newtonian pseudo-plastic material. To characterize the flow behavior of the samples, the power-law model was found the best to fit the data among the seven models tried in this study. The results showed that increasing the percent of pistachio hull increased the consistency coefficient and apparent viscosity, while decreased the flow behavior index. The change of flow behavior index and consistency coefficient with pectin concentration did not follow a clear trend.

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