Modeling the Time-Dependent Rheological Properties of Pistachio Butter

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Abstract

Pistachio butter (semi solid paste), which is made from roasted pistachio kernels, is an appropriate alternative to work on because of its high nutritional and economical values. In this study, time-dependent flow properties of pistachio butter were determined at two different temperatures (25˚C and 45˚C) for five different formulations (with different levels of emulsifying agents). Forward and backward flow curves were plotted and the amount of existing hysteresis loop was measured. Also, shear stress vs. time of shearing data were assessed using three models namely; Weltman, First-order shear stress decay with a zero equilibrium stress value, and First-order shear stress decay with a non-zero equilibrium stress value. To evaluate the ability of these models to predict the rheological characteristics of pistachio butter, three statistical parameters namely; R^2, RMSE, and MRDM were used and finally the Weltman model was found to be the most appropriate to fit the experimental data. The results showed that pistachio butter exhibits a thixotropic behavior and its apparent viscosity decreases with increasing the time of shearing.

Keywords: pistachio butter; rheology, thixotropy, modeling, weltman model, shear stress decay model.

Introduction

Pistachio butter, a semi-solid paste, is made from ground and roasted pistachio kernels with adding some proper flavorings and sweeteners. Because of the presence of high amount of unsaturated oil in such a product, it is also necessary to use proper amount of emulsifying and anti-oxidation agents in its formulation (Shaker *et al.*, 2005). Pistachio butter is of high nutritive value; for it is rich in lipids, proteins, carbohydrates, and vitamins and can be used in different food products such as cookies, ice creams, and cakes (Shaker *et al.*, 2005).

On the other hand, the characterization of time-dependent rheological properties of food systems is important to establish relationships between structure and flow (Abu-Jdayil, 2002) and to correlate physical parameters with sensory evaluation (Figoni and Sheomaker, 1983).

There is a number of published works on the rheological properties of semi-solid pastes such as mustard paste (Bhattacharya et al. 1999), peanut butter (Guillaume *et al.*, 2001) and sesame butter (Razavi, Habibi and Alaee 2007). Abu-Jdayil *et al.*, (2002) investigated rheological characteristics of milled sesame (tehineh) and it was found that tehineh exhibits a thixotropic behavior that increases with increasing shear rate and is mitigated by increasing temperature. Razavi and Habibi, (2006) investigated time-dependent flow behavior of reduced fat sesame paste/date syrup blends. They examined two models, known as Weltman model and first-order shear stress decay with a zero equilibrium stress, to predict the rheological behavior of samples and it was found that time-dependent behavior of samples was good fitted with these models. Taghizadeh and Razavi, (2009) studied the time-independent rheological properties of pistachio butter and it was found that pistachio butter behaves a non-Newtonian pseudo-plastic fluid with corresponding amount of yield stress. However, time-dependent rheological properties of pistachio butter, to the best of our knowledge, were not examined. A study regarding the chemical composition and sensory characteristics of pistachio butter was carried out by Shaker *et al.*, 2005. They found that to achieve the most emulsion stability, the best type of emulsifying agent is a combination of mono-diglyceride and lecithin. Generally, an understanding of time dependent rheological properties of food materials has a direct effect on the optimization of processing stages such as mixing, handling, storage, and final quality (Tabilo-Munizaga and Barbosa-Canovas, 2005).

The objectives of this work were (1) to investigate the time-dependent rheological properties of pistachio butter, (2) to determine the best model to fit the shear stress vs. time data in pistachio butter, and (3) to analyze the effect of different levels of emulsifying agents (mono-diglyceride and lecithin at five levels) on the time-dependent rheological characteristics of pistachio butter.

Materials and methods

Sample preparation

All samples studied in this research, were supplied from Pistachio Research Institute (PRI), Rafsanjan, Iran. The approximate composition (w/w%) of provided pistachio butter samples was as follows: Grounded and roasted pistachio kernels 84%, sweeteners such as sugar 10%, moisture content 3%, salt 1 -2%, and emulsifying agents 0-2%. There were five types of samples which were different in emulsifier's level. To facilitate the measurements, we named them as follows:

Type 1: blank sample or without any emulsifier,

Type 2: containing 0.5% of lecithin and mono-diglyceride.

Type 3: containing 1% of lecithin and mono-diglyceride.

Type 4: containing 1.5% of lecithin and mono-diglyceride.

Type 5: containing 2% of lecithin and mono-diglyceride.

Four samples were made from each type to be tested at two temperature levels (25˚C & 45˚C) with two repetitions. It has to be mentioned that according to previous study which was done on chemical and sensory evaluation of pistachio butter, it was found that pistachio butter type 3 has the most emulsion stability and the most homogenous texture (Shaker *et al.*, 2005).

Rheological measurements

Rheological properties of pistachio butter were measured with a Bohlin Visco 88 viscometer (Bohlin instrument, UK) equipped with a bob and a cup geometry (bob length = 60 mm; bob diameter = 14 mm; gap width = 1 mm) and a heating circulator (Julabo, Model F12-MC, Julabo Labortechnik, Germany). It should be pointed out that no surface slip was observed in this viscometer system. The software Bohlin v06.32 was used to generate shear stress-shear rate data. The instrument was equipped with a device that allows continuous speed variation of internal cylinder (bob). Shear rates ranging from 14 s^{-1} to 300 s^{-1} and from 300 s^{-1} to 14 s^{-1} were used to obtain forward (increasing shear rate) and backward (decreasing shear rate) curves, respectively. The period of experiment was about 8 min and the values of the shear rate and shear stress were recorded every 15 seconds. The resulting hysteresis loops were calculated by using Bohlin v06.32 software as an indication of the amount of time dependency.

In the second part of this work, the time-dependent rheological properties were investigated by shearing pistachio butter samples for 10 minutes at constant shear rate (150 s^{-1}). Then, the shear stress was measured as a function of shearing time. All measurements were done at two temperatures (25˚C & 45˚C) and a controlled temperature bath circulated water through the jacket surrounding the rotor and cup assembly to maintain the temperature.

Modeling time-dependent behavior

The shear stress vs. time of shearing data for all pistachio butter samples were fitted by following famous models (Steffe, 1996 and Rao, 1999):

1. Weltman, 1943:

$$\tau = A + B\ln(t) \qquad (1)$$

Where, τ is the shear stress, t is the shearing time, and A and B are constants that characterize a material's time dependent behavior.

2. First-order stress decay, with a zero equilibrium stress value:

$$\tau = \tau_0 e^{-kt} \qquad (2)$$

Where, τ_0 is the initial shear stress value, and k is the breakdown rate constant.

3. First-order stress decay, with a non-zero equilibrium stress value:

$$\tau = \tau_e + (\tau_0 - \tau_e)e^{-kt} \qquad (3)$$

Where, τ_{eq} is the equilibrium shear stress value.

Modeling evaluation

To select the most proper model for the prediction of time-dependent flow behavior in pistachio butter, three statistical parameters were used in this study as follow (Sokal & James, 1981):

1. Determination coefficient (R^2), which is obtained by:

$$R^2 = \frac{\sum_1^n \left(x_{pred} - \bar{x}\right)^2}{\sum_1^n \left(x_{\exp} - \bar{x}\right)^2} \qquad (4)$$

Where, n is the number of experimental data, $x_{\exp}$ is the value resulted from the experiment, x_{pred} is calculated value by the corresponding model, and $\bar{x}$ is the grand mean. The best value for R^2 must be close to 1.

2. Root Mean Square Error (RMSE), which is calculated as follow:

$$RMSE = \left[\frac{1}{n}\sum_1^n \left(x_{\exp} - x_{pred}\right)^2\right]^{\frac{1}{2}} \qquad (5)$$

The value resulted from equation above must be divided on the mean value of each treatment to achieve the final RMSE value. The optimized value for RMSE is in the range of 0 – 0.1.

3. Mean Relative Deviation Modulus (MRDM) or E%, which is calculated using the following relationship:

$$\%E = \frac{100}{n} \times \sum \left| \frac{x_{\exp} - x_{pred}}{x_{\exp}} \right| \qquad (6)$$

The optimized value for this parameter is in the range of 0 – 5.

Results and Discussion

Flow curves

Figs. 1-5 show the flow curves representing shear stress/shear rate relationship for pistachio butter samples of type 1, 2, 3, 4, and 5, respectively, obtained at 25˚C and 45˚C. The main characteristic of these rheograms were the development of a hysteresis loop, the higher the area below the curve, the higher the thixotropic effect (Holdsworth, 1993). The results showed that shear stress-shear rate relationship is non-linear and all samples behave as a non-Newtonian fluid, pseudoplastic type, with presence of thixotropy as result of structure breakdown (Figs. 1-5).

Table 1 shows the hysteresis values for all samples calculated by Bohlin v06.32 software. The high amount of hysteresis in all samples is an indication of the high shearing effect on the molecular structure of pistachio butter such that the apparent viscosity has decreased. In other words, there is an irreversible, shear induced, and permanent damage affecting the molecular structure of food biopolymers, namely fats.

Time-dependent flow properties

Pistachio butter samples were sheared at a constant shear rate (150 s^{-1}) for 10 minutes. Figs. 6 and 7 show the shear stress as a function of shearing time for five pistachio butter samples at 25˚C and 45˚C, respectively. The data obtained from these rheograms were fitted using three models, namely: Weltman (Eq. 1), the first-order shear stress decay, with a zero equilibrium stress value (Eq. 2), and the first-order shear stress decay, with a non-zero equilibrium stress value (Eq. 3). Table 2 shows the regression parameters obtained for these models. It can be found that although, in some cases, the first-order shear stress decay, with a non-zero equilibrium stress value shows satisfactory results, but the most appropriate model for all samples at both 25˚C and 45˚C is the Weltman model. In addition to, the first-order stress decay, with a zero equilibrium stress value, in most of the samples, shows low ability to fit the experimental data. Table 3 shows the parameters of the Weltman model evaluated at 25˚C and 45˚C. The A and B constants appeared in the range of 376.426 to 2213.493 Pa and 21.624 to 235.198 Pa, respectively. It can be understood that increasing the temperature has caused a great decrease in magnitude of A, which is an indication of resistance of the fluid against the flow, in all samples. Also, the most obtained value for parameter A is belonged to sample 3 at 25˚C which is considered as the optimized sample in the case of type and amount of emulsifying agent used in formulation. Furthermore, it can be observed that the extent of thixotropy embodied by the magnitude of B, decreases with increasing temperature, at the fixed shearing rate of 150 s^{-1}.

This means that the shearing effect is mitigated by increasing temperature, which could be explained in terms of extra flexibility and the resilience 3-D fat polymers gain such that they better align instead of breakdown with external applied shear stress. On the other hand, the highest amount of B constant is belonged to pistachio butter type 3 (the optimized sample), which could be interpreted in terms of high emulsion stability due to the proper and adequate amount of emulsifiers. These results are similar to findings reported by Abu-Jdayil, Al-Malah and Asoud, (2002) regarding milled sesame (tehineh). Both tehineh and pistachio butter are semi-solid foodstuffs (i.e. pastes) with high amount of fat in their chemical composition.

Conclusion

Pistachio butter is a semi-solid substance that behaves as non-Newtonian fluid. The presence of hysteresis in the forward and backward flow curves shows the high effect of time on the flow properties of pistachio butter samples. As far as the effect of steady shearing on the flow properties of pistachio butter is concerned, three models were used to predict the flow behavior, namely, Weltman, the first order stress decay with a zero equilibrium stress value and the first order stress decay with non-zero equilibrium stress value. It was found that pistachio butter exhibits a thixotropic behavior that is mitigated by increasing temperature and its apparent viscosity was decreased by increasing the time of shearing. Also, the Weltman model is appropriate to fit the time-dependency behavior of pistachio butter.

Acknowledgement

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Figures Caption

Fig. 1. Shear stress – shear rate relationship flow curves for pistachio butter type 1 at 25˚C and 45˚C

Fig. 2. Shear stress – shear rate relationship flow curves for pistachio butter type 2 at 25˚C and 45˚C

Fig. 3. Shear stress – shear rate relationship flow curves for pistachio butter type 3 at 25˚C and 45˚C

Fig. 4. Shear stress – shear rate relationship flow curves for pistachio butter type 4 at 25˚C and 45˚C

Fig. 5. Shear stress – shear rate relationship flow curves for pistachio butter type 5 at 25˚C and 45˚C

Fig. 6. Shear stress of pistachio butter at 25˚C as a function of shearing time

Fig. 7. Shear stress of pistachio butter at 25˚C as a function of shearing time

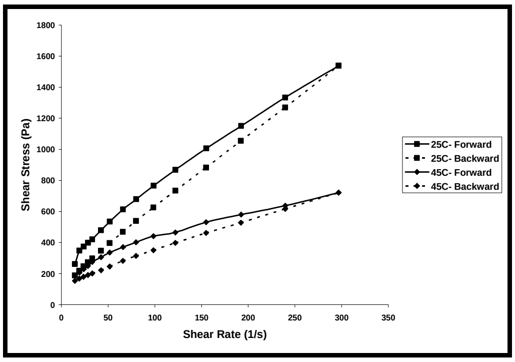

Fig. 1. Shear stress – shear rate relationship flow curves for pistachio butter type 1 at 25˚C and 45˚C

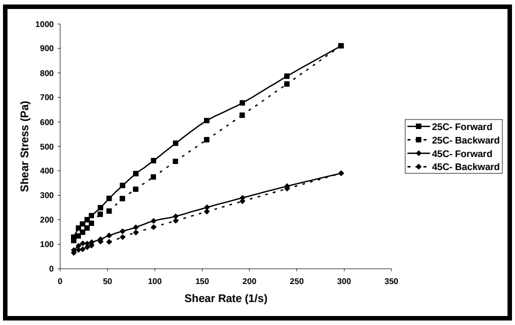

Fig. 2. Shear stress – shear rate relationship flow curves for pistachio butter type 2 at 25˚C and 45˚C

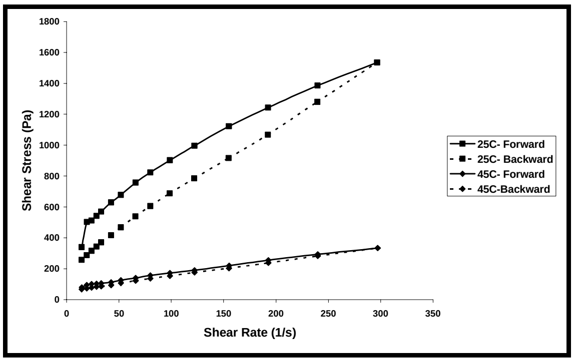

Fig. 3. Shear stress – shear rate relationship flow curves for pistachio butter type 3 at 25˚C and 45˚C

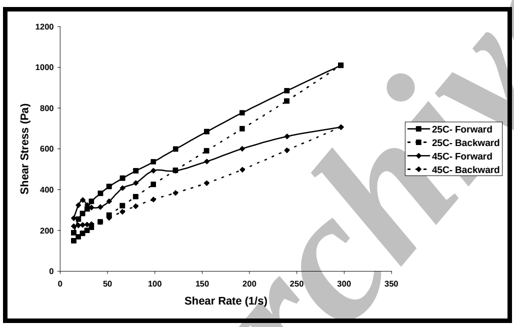

Fig. 4. Shear stress – shear rate relationship flow curves for pistachio butter type 4 at 25˚C and 45˚C

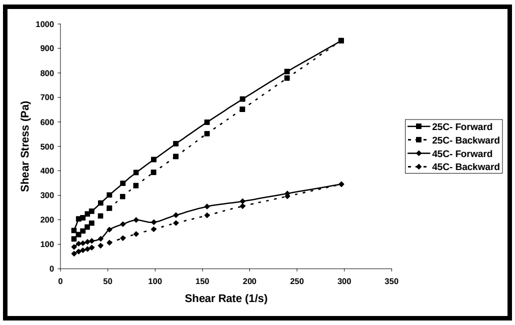

Fig. 5. Shear stress – shear rate relationship flow curves for pistachio butter type 5 at 25˚C and 45˚C

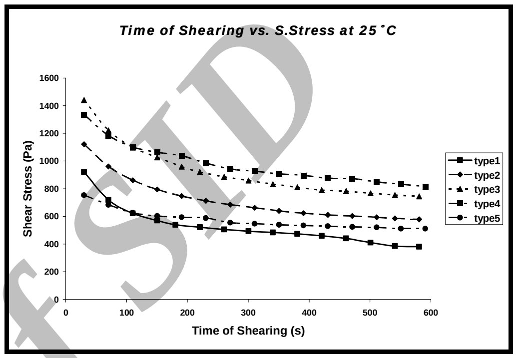

Fig. 6. Shear stress of pistachio butter at 25˚C as a function of shearing time

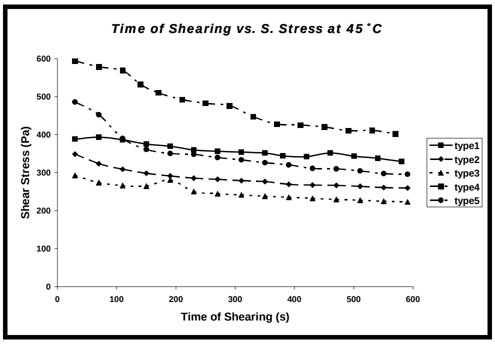

Fig. 7. Shear stress of pistachio butter at 25˚C as a function of shearing time

Table 1. Hysteresis values for pistachio butter samples at 25˚C and 45˚C

Sample	25˚C	45˚C
Type 1	23714	23719
Type 2	23687	23727
Type 3	23731	23748
Type 4	23712	23724
Type 5	23712	23701

Table 2. The regression parameters obtained for the three models fitted to shear stress - shearing time data

Sample	Model	25˚C			45˚C		
		R^2	*RMSE*	*E%*	R^2	*RMSE*	*E%*
Type 1	*Weltman*	0.967	0.050	3.662	0.935	0.013	0.857
	Frist order (zero stress value)	0.833	0.109	7.274	0.946	0.034	3.125
	Frist order (non-zero stress value)	0.960	0.051	4.996	___	___	___
Type 2	*Weltman*	0.992	0.017	1.680	0.997	0.004	0.362
	Frist order (zero stress value)	___	___	___	0.871	0.033	2.500
	Frist order (non-zero stress value)	___	___	___	0.988	0.225	22.275
Type 3	*Weltman*	0.992	0.018	1.652	0.985	0.009	0.701
	Frist order (zero stress value)	___	___	___	0.932	0.026	2.112
	Frist order (non-zero stress value)	___	___	___	0.988	0.009	0.621
Type 4	*Weltman*	0.933	0.093	8.366	0.996	0.009	0.634
	Frist order (zero stress value)	0.959	0.027	2.384	___	___	___
	Frist order (non-zero stress value)	0.984	0.016	1.229	___	___	___
Type 5	*Weltman*	0.986	0.013	1.141	0.971	9.196	1.709
	Frist order (zero stress value)	0.835	0.049	3.847	0.829	22.880	5.163
	Frist order (non-zero stress value)	0.984	0.014	1.017	0.975	8.409	2.044

Table 3. The parameters of Weltman model for a shearing period of 10 min, evaluated at 25˚C and 45˚C

Sample	25˚C		45˚C	
	A (Pa)	-B (Pa)	A (Pa)	-B (Pa)
Type 1	1373.374	153.351	477.771	21.624
Type 2	1735.620	185.336	449.416	29.882
Type 3	2213.493	235.198	376.426	23.705
Type 4	1918.806	171.844	891.593	75.921
Type 5	1020.187	81.159	703.344	64.659

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