Rheological Properties of Chocolate Pistachio

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Received: 21 August 2013 Accepted: 3 October 2013

Abstract
This research aimed to assess and determine rheological properties of chocolate pistachio produced from various volumes of monoglyceride (1% and 2%), date powders (34, 38 and 42%) and pistachio pastes. The analyses were performed at temperatures of 45 ºC, 65 ºC after 3 and 5 hours of processing. These products were found to exhibit non-Newtonian, pseudo-plastic behavior at all treatments. Apparent viscosities versus speed data were successfully fitted to a power law model. The flow behavior index, n, varied in the range of 0.8-0.94. The consistency index, k, was in the range 101.495-167.738 pa·s². According to statistical analysis, the exponential model was a better model to describe the effect of the soluble solids on the viscosity of chocolate pistachio containing varying percentages of date powder. The activation energy (Ea) was 446.2-41330 j/mol.

Keywords: Chocolate pistachio, Non-Newtonian, Pistachio paste, Power law, Pseudo plastic behavior.

Introduction
Pistachio is one of the most important horticultural plants grown in Iran. There are approximately 440,000 hectares of pistachio plantations in Iran. Chocolate is a multi-component system consisting of cocoa powder and sucrose (total solids of 65-75%) in a continuous fat phase, primarily composed of cocoa butter. To sweeten the product, date powder is used instead of sugar. Determination of rheological properties of chocolate is important in the manufacturing process for producing a high-quality product with a well-defined texture (Servais et al., 2004). Factors such as fat content, particle size distribution (PSD), moisture content, emulsifiers, mixing time, and temperature affect rheological properties, as well as production cost (Tscheuschner and Wunsche, 1979). The flow of molten chocolate is non-Newtonian, with an apparent yield stress, and can be described by a number of mathematical models, including the Bingham, Herschel–Bulkley and Casson models (Chevalley, 1999; Servais et al., 2004).

Pistachio butter, a semi-solid paste, is made from ground and roasted pistachio kernels with some sweeteners and flavors added. It exhibits a thixotropic behavior and its apparent viscosity is decreased with increasing the time of shearing (Shaker et al., 2010).

There are a number of published works on the rheological properties of semisolid pastes such as mustard paste (Bhattacharya et al., 1999), peanut butter (Guillaume et al., 2001) and sesame butter (Razavi et al., 2007). Akbulut et al. (2011) investigated the rheological characteristics of sesame pastes (tahini) blended with pine honey and found that tahini and Bozkir tahini exhibit a thixotropic behavior at all temperatures.

The rheological behavior of chocolate containing phyto-sterols was similar to that of standard chocolate (Akbulut et al., 2011). A substitute having a large particle size should be chosen to replace sucrose for improving rheological properties of chocolate, but the particle size should be small enough to obtain appropriate sensory properties (Sokmen et al., 2006). Increasing the solid concentration results in higher viscosity (Servais et al., 2004). High solid content, interactions of the suspended particles and their interfacial properties affect the rheological properties of chocolate (Bouzas and Brown, 1995). For stabilizing a paste an emulsifying agent such as a monoglyceride is required (Shaker et al., 2006). One of the most important parameters required for the design of a technological process in the food industry is viscosity. At the same time, viscosity has a significant effect on determining the overall quality and stability of a food system. Chocolate pistachio contains high levels of protein and dietary sugar, and when blended with date palm, it contains high levels of minerals, phenolic compounds, and antioxidants that might be a useful alternative food product in terms of nutrition and health for humans, specifically for children. Thus, this work was aimed at determining the emulsion stability and rheological characteristics of various blends and to evaluate the rheological characteristic of these blends as well as consumers’ acceptance of these blends.

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Materials and Methods

Materials

The product under study was manufactured in the Oghab halva factory (Tehran, Iran) in 2011. For the production of this product, pistachio paste was purchased from Fadak pistachio company of Sarvestan; the paste contained 60% fat. Dry milk was produced by the Kaleb Dairy Product Company and was packaged appropriately. Dry palm date powder was procured from the Razan Company, Hamadan, Iran. The monoglycerid employed, Myverol (E471), was obtained from the Danisco Company in Iran. The microbial and chemical properties of the pistachio paste, dry milk and dry palm date conformed to appropriate standards. Twenty four types of samples differing in emulsifier level, percentage of date palm powder, time of mixing and preparation temperature were used (Table 1). A ball mill made by the Aidingostar Company of Tabriz, Iran, was employed for the production of pistachio chocolate. The balls of the mill were made of steel and were 6 mm in diameter; of the mill had a capacity of 15 kilogram per experiment. The treated materials were then packaged appropriately and preserved at optimum temperature for analysis.

Table 1. Factors obtained in this search.

<table>
<thead>
<tr>
<th>Name of Product</th>
<th>Temperature of Production (°C)</th>
<th>Time of mixing (hour)</th>
<th>Emulsifier level</th>
<th>Percentage of dry palm date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chocolate Pistachio</td>
<td>45</td>
<td>3</td>
<td>1</td>
<td>34</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>38</td>
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<td></td>
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<td></td>
<td>3</td>
<td>42</td>
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<td></td>
<td></td>
<td></td>
<td>4</td>
<td>34</td>
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<td>5</td>
<td>38</td>
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<td>4</td>
<td>42</td>
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<tr>
<td>Chocolate pistachio</td>
<td>65</td>
<td>3</td>
<td>1</td>
<td>34</td>
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<td></td>
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<td>38</td>
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<td>3</td>
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<tr>
<td></td>
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<td></td>
<td>4</td>
<td>42</td>
</tr>
</tbody>
</table>

Rheometer

A controlled stress rheometer (model RVD, Germany), spindle SC-27, was utilized for determining the rheological properties of chocolate pistachio. The rheometer program, Rheocalc 32, was able to convert viscosity data into rheological information. All rheological measurements were conducted at 20 ± 1°C.

Results

Determination of flow behavior

The flow curves of chocolate pistachio samples were determined at 45 °C and 65 °C. The curves obtained were hysteresis loops, as seen in Figs. 1, 2, 3 and 4.
As can be seen in Figs. 1, 2, 3 and 4, the high shearing effect on the pistachio paste is such that the apparent viscosity decreased. In other words, there is an irreversible, shear-induced and permanent damage to the molecular structure of the food biopolymers, namely fats. These results are also in accordance with those of Arsenal et al., (2005), Razavi et al., (2007), Habibi–Najafi and Alaei (2006), Alpaslan and Hayta (2002). This is the result of shear inducing structural damage and deformation of structural biopolymers, especially fats. The particles may change direction and set in the direction of shear or may set in the flow direction with deformation that ultimately leads to a viscosity decrease (Abu-Jdayil et al., 2002).

The effect of research variables on the index of consistency and flow behavior

A power law model was employed for comparison of the samples with each other. Table 2 shows the consistency index ($k$) and the flow behavior index ($n$) of the samples. The magnitude of $k$ values and thixotropic areas decreased with an increase in temperature from 45 to 65°C. Abu-Jdayil et al., (2002) reported a similar temperature effect on flow properties for sesame paste. As per research results, the consistency index stood at $101.5-167.7$ pa.s$^n$. Analysis of variance in results indicated that all of variables, e.g. temperature and time of operation, the percentage of monoglyceride and palm date powder, affected the consistency index significantly. But of the treatments, temperature and time of operation are the most influential variables.
Table 2. Values of rheology index and consistence coefficient in the chocolate pistachio treatments

<table>
<thead>
<tr>
<th>Mixing Temp. (°C)</th>
<th>45</th>
<th>65</th>
<th>45</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Time (h)</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>%Mono</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>%date powder</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>K(µ.s⁻¹)</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>K(µ.s⁻¹)</td>
<td>n</td>
<td>n</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>R²</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>N.A</td>
<td>N.A</td>
<td>N.A</td>
<td>N.A</td>
<td>N.A</td>
</tr>
</tbody>
</table>

N.A: Not applicable

As shown in Table 2, the consistency index increased in all treatments by increasing the time of operation. The production operation was conducted in a ball mill of the rubbing type. As a result of rubbing and erosion, the particle size of constituents such as protein, date powder and fat globules decreased. The milling operation yielded a product with a uniform texture, organized emulsifying properties, and a higher consistency index. The changes of shear stress against shear rate in differential time are shown in Fig 5.

Fig. 5. Shear stress changes versus shear rate at various times in order to measure the products consistence coefficient

Temperature is an important agent that decreases the consistency index in the chocolate pistachio product. These results are similar to those obtained for sesame butter and milled sesame, and sesame paste and tahini blends (Abu-Jdayil et al., 2002), Arsalan et al., (2005) Habibi-Najafi and Alaei (2006), Alpaslan, Hayta (2002).

Rheological Traits Assessment Results

The observed curves (Figs. 1 and 2) for all forward (increase in shear rate) and backward (decrease in shear rate) treatments reveal the same hysteresis loop; and all samples show less viscosity in the backward stage than in the forward stage. Also, the obtained diagrams (Fig 1) reveal that increasing the shear rate increases the shear stress for all treatments in a non-linear way in the forward stages; on the other hand, it reduces the shear stress in backward stage (Fig. 2). The rheology index for all treatments was less than one (n<1); therefore, the fluid under testing is an attenuated non-Newtonian fluid with shear (Thixotropic behavior).

The effect of the research variables on consistency coefficient and rheology index

The well-known Power Model was used to study the effects of variables (the percentage of sweetening material, i.e. date powder; percentage of mono-glyceride; temperature and time) on the rheology
index and consistency coefficient. The data in Table 2 indicate consistency between the model and rheological data.

The effects of the research variables on activating energy

Arenas model was used to determine the activating energy of various treatments (Table 3). The activating energy values in chocolate pistachio treatments standing at a range of 17979- 41330 J/mol (Table 3).

<table>
<thead>
<tr>
<th>Mixing Time (h)</th>
<th>Mixing Temp. (°C)</th>
<th>45</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>%Mono</td>
<td>Ea (j/mol) R²</td>
<td>Ea (j/mol) R²</td>
</tr>
<tr>
<td>42</td>
<td>Date powder</td>
<td>-</td>
<td>N.A</td>
</tr>
<tr>
<td>34</td>
<td>33743</td>
<td>0.98</td>
<td>29421.6</td>
</tr>
<tr>
<td>38</td>
<td>29107</td>
<td>1.00</td>
<td>22904.3</td>
</tr>
<tr>
<td>42</td>
<td>N.A</td>
<td>-</td>
<td>N.A</td>
</tr>
<tr>
<td>34</td>
<td>41330.6</td>
<td>0.99</td>
<td>30840.6</td>
</tr>
<tr>
<td>38</td>
<td>446.22</td>
<td>0.98</td>
<td>31626</td>
</tr>
<tr>
<td>42</td>
<td>N.A</td>
<td>-</td>
<td>N.A</td>
</tr>
</tbody>
</table>

N.A: Not applicable

The effect of the research variables on the consistency coefficient

The values calculated for consistency coefficient were 101.5 - 167.7 Pa.s. Analysis of the observed variance reveals that all variables, including temperature and time of production processing, percentage of monoglycerides and percentage of sweetening material (date powder) had a significant effect on the consistency of the product (P< 0.05); however of the above variables, the process time and temperature were most important. As shown in the tables, an increase in processing time increases the consistency coefficient in all treatments. Therefore, the consistency coefficient increases in general. Fig. 5 shows that shear stress changes with shear rate at various times in order to measure the consistency coefficient of the product.

Discussion
Results of rheological evaluations

As mentioned earlier, the observed curves revealed the same hysteresis loop in all treatments and in both the forward and backward stages. Also, the apparent viscosity in backward stage was higher than that in the forward stage. The same results have been achieved by other research works conducted on the various materials including Arde-Shire (a meal made of grape and sesame) (Altay, 2005; Arslan et al., 2005; Ereifej and Karababa, 2005; Habibi-Najafi and Alaei, 2006).

This might be due to the effect of shear forces on the molecular structure of samples as well as the structural destruction of bio-polymers, especially fats; or they may be due to shear effects which improve the flow of fluids and reduce their viscosity. In the backward stage, the previous shear effects and regulation of particles reduce the friction, as a result of which the viscosity is reduced in the backward stage (Akbulut et al., 2011).

The figures also reveal that the changes in shear rate and shear stress increase in all treatments in a non-linear way both in the backward and forward stages.

Therefore, one may conclude that the fluid is non-Newtonian. The achieved value for the rheology index is less than one in all treatments; therefore the fluid is attenuated with (pseudo-plastic) shear. The finding is confirmed by other studies conducted on various emulsions. It has also been shown that members of this fluid group behave as pseudo-plastics and are close to Newtonian fluids (Marcotte et al., 2001).

Temperature is another basic factor that reduces the consistency coefficient of this Iranian product significantly (P<0.05), regardless of the processing time. These results are consistent with other studies on sesame butter product, including Arde (Tahini) and Arde Shire (mixing Tahini and Pekmez) (Akbulut et al., 2011; Altay, 2005; Ereifej and Karababa, 2005; Habibi-Najafi and Alaei, 2006).

In general, the viscosity of a fluid is affected considerably by temperature, so temperature control is necessary during processing of many foods. The effect of temperature on a fluid behavior can be described as follows:

Fluidity is affected by intermolecular forces such that the smaller the distance between molecules, the higher the intermolecular forces are. Thus, the movement of particles decreases and their viscosity increases; on the other hand, an increase in
temperature increases the heat energy of fluid molecules as well as their movement and as a result the distance between the particles increases. This leads to reduction in intermolecular forces and an increase in the final fluidity (Altay, 2005).

Apparently, on one hand, the temperature increase during the production of Iranian chocolate pistachio increases the movement of food particles, specifically in fatty phase, leading to a reduction in intermolecular forces and hence an increase in the final fluidity (Altay, 2005).

Also, in a study of mixtures of Arde and grape essence, an increase in the essence from 2 to 6 percent led to an increase in the mixture consistency coefficient (Ereifej and Karababa, 2005). An increase in the percentage of date powder to Iranian chocolate pistachio has again led to an increase in consistency coefficient of the product, resulting from an increase in the proportion of solid to non-solid (oil) phases in the product formulation. Furthermore, the proportion of the solid phase increases in the whole product as a result of viscosity increase. Other studies revealed that the proportion of solid compounds to non-solid compounds (such as oil and water) is of great importance in the consistency coefficient of the product, and since date powder is used in the formulation of the product, it is of less than 1 percent humidity. Therefore, the increase in viscosity and the consistency efficient in the final product is normal. In studies on the mixture of Arde and grape essence, an increase in the grape or date essence increases the amount of sugar materials; however, the mixtures have a humidity of higher than 25% and they can reduce the final consistency coefficient of the product, which can be increased by an increase in the percentage of essence brix as a result of humidity reduction and increase in sugars. Changes in shear stress vs. shear rate at various date percentages, determined with the aim of measuring the consistency coefficient, are shown in Fig. 7.
An increase in the percentage of glyceride increases the product consistency significantly, as well (P<0.05). A mixture of mono- and di-glyceride is used as an emulsifier and stabilizer in the formulation of similar products such as peanut and pistachio butter and halva to prevent them from separating into two phases and becoming over-oiled. The effect of glycerides’ increasing the chocolate pistachio consistency coefficient may be due to its emulsifying properties, which increase the connection between the product particles.

This increase in turn prevents the particles from moving and reduces fluidity as a result. On the other hand, the mono- and di-glyceride mixture creates a crystalline matrix in oil phase, which hardens the texture of the product and reduces its fluidity (Akbulut and Coklar, 2008). Changes in shear rate vs. shear stress for various percentages of mono- and di-glycerides and their effect on the consistency coefficient are shown in Fig. 8.

The effect of research variables on rheology index

The results presented in Table 2 reveal that the rheology index values for various treatments are 0.59 to 0.94, which indicate a pseudo–plastic behavior for all treatments. The closeness of the values to one indicates a more Newtonian behavior and their distance from one indicates a more thixotropic behavior.

The analysis shows that all the variables tested affect the rheological index significantly (P<0.05), but that temperature and percentage of mono- and di-glycerides are more important than other factors.

Increasing temperature reduces the rheological behavior in all treatments which is consistent with the findings of other investigations.

Apsellan and Hayta (2002) studied a mixture of Arde and grape essence and concluded that an increase in temperature reduces the rheological index value (Habibi-Najafi and Alaei, 2006). In another study on a mixture of Arde and date essence, the same results were obtained (Ereifej) and Karababa, 2005).

Yet another study on mixtures of Arde and date essence revealed that an increase in temperature reduces both the essence coefficient and rheological index (Abu-jayil et al., 2002).

Another effective factor on the rheological behavior of the product is the percentage of mono- and di-glycerides, such that an increase in the index reduces the thixotropic behavior and increases in the product. The reason is that an increase in emulsifying and stabilizing properties of the mono- and di-glycerides, which enhances the interaction between particles, increases the oil phase viscosity which in turn makes the product harder and its Newtonian characteristics change its behavior to that of a thixotropic one. A study of Arde oil has revealed that the complex exhibits Newtonian behavior; therefore, all factors increasing the oil phase viscosity induce more thixotropic behavior (Alpaslan and Hayta, 2002).

Time is another factor impacting the rheological index. An increase in processing time leads to an increase in rheological behavior index value to close to 1, i.e. more Newtonian behavior in the product.

Since an increase in the processing time reduces the diameter of particles and makes the product steadier, the fluid may become softer and exhibit a more Newtonian behavior.

Although the percentage of sweetening material affects the rheology significantly (p< 0.05), its effect is dramatically less than that of other variables. Our results show that an increase in the date powder as the sweetening material reduces the rheology index value slightly. This might be due to an increase in the percentage of solid material in proportion to the oil phase in the product as well as to an increase in the thixotropic behavior. Altay and Ak (2000) studied the rheology of Arde and concluded that its oil exhibits Newtonian behavior. The behavior is also observed when the solid material amounts to 20 percent, but in higher amounts the behavior changes from Newtonian to pseudo-plastic (Alpaslan and Hayta, 2002).

In another study, the effect of fat alternatives, including guar resin, xanthan gum and starch, on a mixture of Arde and date essence was studied. The result of this study showed that an increase in the density of each fat alternative reduced the rheology index value (Arslan et al., 2005).
The effect of research variables on activating energy

The result of variance analysis reveals that temperature and processing times and percentage of mono- and di-glycerides affect the activation energy significantly while, but that the percentage of sweetening material in the range studied (34-38 percent) does not have a significant effect on the activation energy. Temperature and the percentage of glycerides are more effective than other factors. An increase in the processing temperature reduces the activation energy. This indicates the higher dependency of treatment on temperature changes; in other words, treatments produced at lower temperatures (45°C) are more sensitive to temperature changes than those produced at higher temperatures (65°C).

The percentage of glycerides is also another factor impacting the activation energy, in that an increase leads to an increase in the activation energy temperature, i.e., a higher dependency of treatments on the percentage of the glycerides in proportion to temperature changes. Since the emulsifying and stabilizing characteristics of the glycerides are highly dependent on the mixture melting point, it seems that temperature changes can affect the applicable characteristics of the glycerides and, consequently, the product consistency coefficient.

An increase in the processing time leads to a reduction in the activation energy, but its effect is less than that of the other two factors. A longer processing time increases the viscosity of the particles and the firmness of the product; therefore, this is probably the reason for the lower dependency of the product on temperature changes.

Conclusion

It can be concluded that chocolate pistachio is attenuated with shear fluid which exhibits a thixotropic behavior for all the variables analyzed. Applying a higher temperature as well as a higher percentage of glycerides leads to the product having a more thixotropic behavior. However, an increase in the processing time results in the product having a more Newtonian behavior. The most important factors in the consistency coefficient of the product are temperature and processing time. They respectively increase and decrease the consistency coefficient and apparent viscosity. Of course, the percentage of glycerides is less effective than that of the other two factors. It also increases the consistency coefficient.

Dependancy of the final product consistency on temperature changes is makes more sense at lower temperatures than higher temperatures. However, an increase in the percentage of glycerides increases the dependency of product consistency coefficient on temperature changes. Time is less effective in this regard; Moreover, an increase in time reduces the dependency of the consistency coefficient on temperature changes.

References


