RHEOLOGICAL CHARACTERIZATION OF TAHIN/PEKMEZ (SESAME PASTE / CONCENTRATED GRAPE JUICE) BLENDS

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ABSTRACT

RHEOLOGICAL CHARACTERIZATION OF TAHIN/PEKMEZ (SESAME PASTE/CONCENTRATED GRAPE JUICE) BLENDS

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The aim of this study was to determine the rheological properties of tahin/pekmez blends at different tahin concentrations (20-32%) and temperatures (35-65 °C) by using a concentric cylinder rotational viscometer. Samples were sheared with seven different rotational speeds at an increasing order. The shear rates (0.75-63.9 s^{-1}) were calculated by the Power-law Approximation method. Tahin/pekmez blends were found to exhibit non-Newtonian, shear thinning behavior at all temperatures and tahin concentrations.

The experimental data of apparent viscosity versus shear rate were successfully described by the Power-law model. The model parameters; flow behavior index, **n** varied in the range of 0.7-0.85, whereas the values for the consistency coefficient, K, were in the range of 282-2547 mPa.s^n. Apparent viscosity and consistency coefficient of blends increased with increasing tahin concentration and decreasing temperature.

Temperature dependency of K was described by an Arrhenius-type equation. Activation energies (E_a) of the blends appeared in the range of 13376-28592 J/mol as the tahin concentration was increased from 20% to 32%. The effect of temperature on **n** was found to be significant but did not follow any descriptive trend. The relationship between K and tahin concentration was explained by exponential and power functions while tahin concentration had no significant effect on flow behavior index. Power function was found to be superior in explaining the variation of E_a with tahin concentration.

A mathematical model was formulated to determine the combined effect of temperature, tahin concentration and shear rate on apparent viscosity.

Keywords: Rheology, Tahin (Sesame Paste), Pekmez (Concentrated Grape Juice), Blend.

ÖZ

TAHİN/PEKMEZ KARIŞIMLARININ ÖZYAPISISININ İNCELENMESİ

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Bu çalışmanın amacı, tahin/pekmez karışımlarının degişik tahin derişimlerinde (20-32%) ve sıcaklıklardaki (35-65 °C) akma özelliklerinin çift silindirli döner özlülükölçer ile saptanmasıdır. Örnekler yedi değişik dönme hızında ve artan sıra ile incelenmiştir. Kayma hızları (0.75-63.9 s^{-1}) üs yasası yaklaşımı yöntemi ile hesaplanmıştır. Çalışılan tüm sıcaklık ve derişimlerde, tahin/pekmez karışımlarının Newtonsu olmayan, kaymayla incelen davranış gösterdiği tespit edilmiştir.

Görünür özlülüğün kayma hızıyla değişimine ilişkin deneysel bulgular üs yasası ile açıklanmıştır. Model koşullu değişmezleri olan, akış davranışı göstergesi, **n**, 0.7-0.85 aralığında, kıvam göstergesi, K ise 282-2547 $mPa.s^n$

aralığında değişmektedir. Karışımların görünür özlülüğü, μ_a, ve kıvam göstergesi, K artan derişim ve azalan sıcaklıkla artmaktadır.

K'nın sıcaklığa bağımlılığı, Arrhenius türü bir denklemle tanımlanmıştır. Karışımların etkinlik enerjileri tahin derişiminin %20'den % 32'ye artması ile 13376'den 28592 J/mol'a yükselmektedir. Akış davranış göstergesi sıcaklıktan etkilenmiş fakat belirgin bir değişim göstermemiştir. K ile tahin derişimi arasındaki ilişki logaritmik ve üssel fonksiyonlarla açıklanmış, bu arada tahin derişiminin akış davranış göstergesi üzerinde belirgin bir etkisi olmadığı anlaşılmıştır. Üssel ilişkinin E_a'nın tahin derişimi ile değişimini açıklamada daha iyi olduğu bulunmuştur.

Sıcaklık, tahin derişimi, ve kayma hızının görünür özlülüğe birlikte etkisi için bir matematik model çıkartılmıştır.

Anahtar sözcükler: Reoloji, Tahin, Pekmez, Karışım.

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LITERATURE SURVEY

1.1. Introduction

Tahin/pekmez blend is a traditional food product in Turkish breakfast. It has a wide usage especially in winter due to its high energy content. The product has high nutrition value arising from the constituents of tahin and pekmez. In the Turkish food market, tahin and pekmez are sold separately so the blends are prepared by the consumers. For blend preparation, the ratio of tahin to pekmez is determined by consumers according to their taste and preference.

Tahin is made from roasted dehulled sesame seeds. It is an ingredient for many other dishes such as halawah, chick peas (hommus), desserts, and bakery. The product is also popular in Middle Eastern countries (Alparslan & Hayta, 2002; Röbbelen, 1989). Pekmez is also a traditional grape product in Turkey. On the average, 20-25% of the grapes produced are used in the production of this traditional food product (TZOB, 2003). Pekmez is the concentrated form of grape juice with an extended shelf-life (Kaya & Belibağlı, 2002). It is regarded as a substitute product for jam and marmalade and has a wide usage in Turkish breakfast. It is also used for desserts such as Turkish aşure or can be mixed with tahin (Öztürk & Öner, 1999).

Knowledge on rheological properties is essential for design, process and quality control, sensory assessment, and consumer acceptance of a product (Abu-Jdayil et al., 2002). Consumer acceptance of tahin/pekmez blend is highly dependent on the ability to spread on another material such as bread. This has a direct relationship with viscosity and flow behavior (Alparslan & Hayta, 2002). In addition, production and maintenance of the product while providing proper consistency, stability and texture are the major concerns and require reliable rheological data (Abu-Jdayil et al., 2002).

Studies regarding the rheological characterization of pekmez, tahin, and tahin/pekmez blends are found in the literature. Kaya and Belibağlı (2002) studied the rheology of solid Gaziantep pekmez (82.1 °Brix) and its diluted samples (72.9-52.1°Brix). Abu-Jdayil, Kamah, and Asoud (2002) demonstrated time-dependent rheological behavior of tahin. The rheological and sensory properties of tahin/pekmez blends were studied by Alparslan & Hayta (2002) at pekmez concentration range of 2-6%.

In Turkey, tahin/pekmez blend as a single product (30 grams in a package) is produced by a few manufacturers (e.g. Tokgoz Gida San., Ankara). The blends are only sold to the Military Organization via auctions, and not to the domestic market. The military specifications for the product require 60% pekmez - 40% tahin. This figure can be granted as an average acceptability ratio, and obviously it is much different that the concentration range studied by Alparslan & Hayta (2002). Thus, further rheological information is required for tahin/pekmez blends.

1.1.1. Pekmez (Concentrated Grape Juice)

Pekmez is the concentrated form of grape juice. It is obtained by boiling the juice without addition of sugar or other food additives. The product can be considered to be a natural food containing natural sugars glucose, galactose and minerals. The aim of concentration or boiling is to pasteurize the grape juice and to extend the shelf-life by decreasing the water content (Kaya & Belibağlı, 2002).

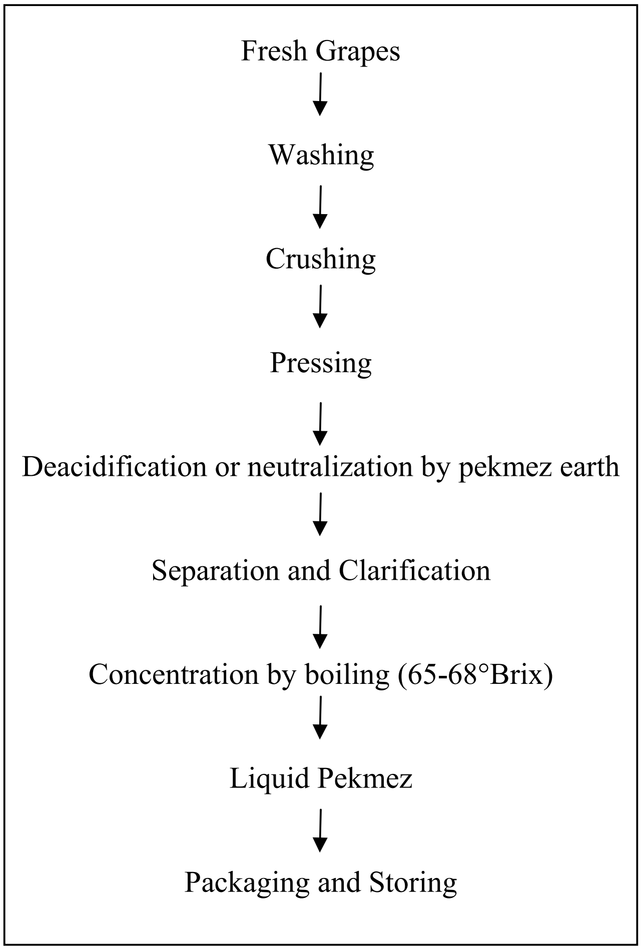

Figure 1.1. Steps in the production process of pekmez

In pekmez production, (Figure 1.1) the first step is washing and crushing the grapes. In order to obtain grape juice, washed grapes are processed with a pneumatical or mechanical press. The obtained grape juice is then treated with a calcareous soil known as 'pekmez earth'. The pekmez earth is composed of approximately 90% calcium carbonate. It causes naturally existing tartaric and malic acids to precipitate as calcium tartarate and calcium malate. Hence, the acidity is decreased and the juice is clarified by sedimentation. The clarified juice is then boiled in open vessels and rarely under vacuum to obtain a 65–68 °Brix solution (Kaya & Belibağlı, 2002).

Pekmez is a natural source of energy due to its high carbohydrate content (65-68%). It contains valuable minerals such as calcium (0.084-0.086%) and iron (0.005-0.01%). The high iron content makes the product a recommended treat for anemia (Öztürk & Öner, 1999). In addition, B1 and B2 vitamins add extra value to the product.

1.1.2. Tahin (Sesame Paste)

Tahin is produced from ground, dehulled, dry roasted sesame seeds. It has high nutritive value. It is rich in lipids (54-65%), proteins (17-27%), carbohydrates (6.4-21%). and dietary fiber (9.3%) It also contains important minerals and vitamins such as calcium (429mg/100g), phosphorous (732-840mg/100g), and iron (9g/100g), niacin (4.5-5.5 mg/100g), and thiamin (1.1 mg/100g) (USDA Database, 2003; Abu-Jdayil et al., 2002).

Sesame, *Sesamum indicum*, is the raw material of tahin. Tahin is a pure product of sesame without adding or removing any of its constituents (Alparslan & Hayta, 2002; Röbbelen, 1989). It has considerable antioxidant activity due to the major components of sesame oil. The antioxidants, sesamin and sesamolin, are effective chemicals to suppress the formation of free radicals thus act as anti-carcinogenic substances (Morris, 2002; Röbbelen, 1989). Moreover, sesame oil can resist oxidative deterioration and rancidity due to these antioxidants (Abu-Jdayil et al., 2002). Another benefit of sesame oil is to reduce cholesterol due to its high polyunsaturated fat content (Morris, 2002).

In Figure 1.2, typical flow chart for tahin production is illustrated. The sesame seeds are wetted and left overnight for dehulling operation. When the hulls are separated, the seeds are washed to remove any remaining undesired particles like stone and dirt. Prior to roasting, the seeds are centrifuged for water removal. The roasted seeds are milled to obtain the final product, tahin. It was found that 90% of the original antioxidant, sesamin, can be retained after roasting (Morris, 2002).

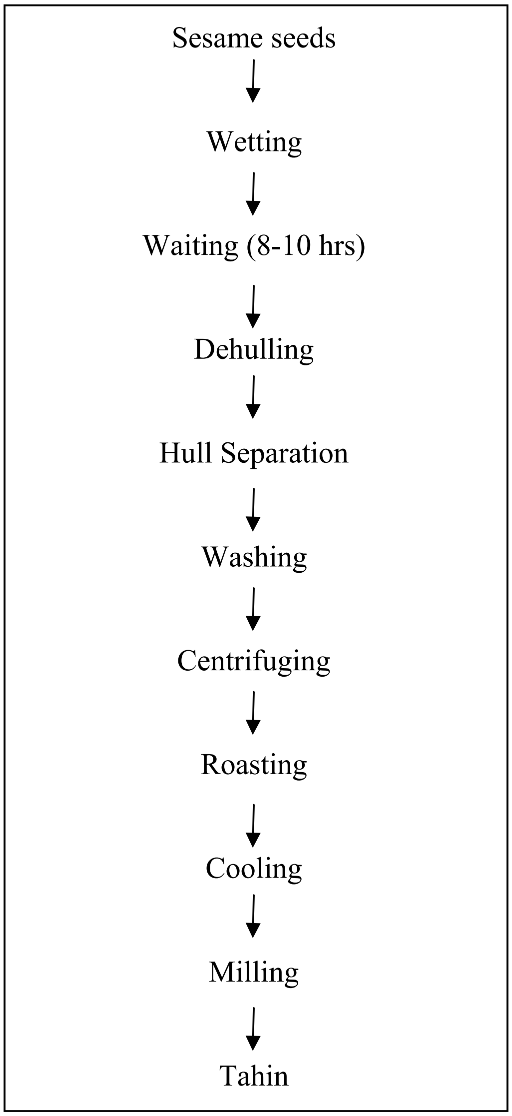

Figure 1.2. Flow chart for tahin production

1.1.3. Tahin/Pekmez Blends

There are many food products that exist in the form of emulsion, such as salad dressings, mayonnaise, milk, butter, and cream. Oil-in-water and water-in-oil are common types of emulsions in food systems. Tahin/pekmez blends can be regarded as an oil-in-water emulsion (Alparslan & Hayta, 2002). The two immiscible liquids; tahin and pekmez form a two-phase system. Tahin contains the oil phase (dispersed phase) and pekmez contains the water phase (continuous phase). Oil particles are suspended in water by the help of mechanical action.

The stability of an emulsion is dependent on the oil-water interface. Surfactants and proteins are the main classes of emulsifiers that stabilize an emulsion by surrounding the dispersed phase and stabilizing the droplets against coalescence (Wilde, 1998). The emulsifiers act as amphiphilic substances which interact with both hydrophilic and hydrophobic molecules (Wilde, 1998). In the case of tahin/pekmez blend, sesame proteins interact with lipids to form a stable emulsion (Alparslan & Hayta, 2002).

Tahin has a high protein and dietary fiber content. When enhanced with high mineral and vitamin containing pekmez, it offers a nutritious alternative to consumers (Alparslan & Hayta, 2002).

1.1.4. Objective of the Study

Tahin/pekmez blend is a common breakfast dish in Turkey. The components, tahin and pekmez are sold separately in the market. For customer convenience the blend can be offered as a single product to the domestic food market especially for use in catering (e.g. hotels, restaurants). Texture, sensory properties, and flow behavior determination require rheological characterization of the product. Temperature and concentration are variables that considerably affect the rheological properties.

The ratio of tahin to pekmez in the blends is an important determinant for consumer acceptance of the product. Rheological information about tahin/pekmez blends with an acceptable ratio of the components is missing in the literature. Therefore, the main objective of this study is to determine the rheological behavior of tahin/pekmez blends under the effect of tahin concentration (20- 32% (w/w)) and temperature (35-65°C).

The study was composed of mainly four sections. In the first section, the flow behavior of the blends at varying tahin concentrations and temperatures was studied by analyzing the behavior of shear stress and viscosity data against shear rate. Rheological parameters of the blends were calculated. In the second part, temperature dependency of the rheological parameters was studied. The effect of temperature was described by an Arrhenius type equation. Third section covered the effect of tahin concentration on the rheological properties. The relationship was explained by exponential and power functions. Finally, the combined effect of temperature, concentration and shear rate on apparent viscosity was investigated and a mathematical model equation was proposed.

1.2. Rheology

By definition, rheology is the study of the deformation and flow of matter. It is applicable to many industrial fields such as mining, geology, cosmetics, and polymers. Rheology of fluid foods provides good opportunities of study due to the biological nature of foods. Optimization of product development efforts, processing methodology and quality of food product requires careful investigation of the rheological properties (Rao, 1999; Steffe, 1996).

1.2.1. Significance in Food Industry

Rheological data are essential for several areas in food industry.

- Design of process equipments including heat exchangers, pipelines, mixers, extruders and pumps;
- Determining the functions of ingredients during product development;
- Intermediate or final product quality control;
- Shelf life testing;
- Evaluation of food texture and sensory assessment (Pelegrine et al., 2002; Rao, 1999; Manohar et al., 1998; Steffe, 1996).

1.3. Flow Models for Rheological Properties of Fluids

A flow model is considered to be a mathematical equation that describes rheological data such as shear rate and shear stress in a convenient manner. It is important to quantify how model parameters are affected by state variables such as temperature and concentration (Rao, 1999).

A fluid is distinguished from a solid by its behavior when subjected to a stress (force per unit area of application) or applied force. While an elastic solid deforms by an amount proportional to the applied stress, a fluid continues to deform under the similar applied stress. Shear stress, τ, is the stress component applied tangentially to the fluid with units expressed in Pa (N/m^2). Under the applied shear stress, a fluid flows at a velocity which increases with increasing stress. Shear rate, $\dot{\gamma}$, is the velocity gradient (rate of deformation) established in a fluid as a result of the applied shear stress. It is expressed in units of reciprocal seconds (s^{-1}). Viscosity is the resistance of the fluid to this stress. It is the property of a fluid which gives rise to forces that resist the relative movement of adjacent layers in the fluid. These viscous forces are caused by the forces existing between the molecules of the fluid (Rao, 1999; Geankoplis, 1993; Bourne, 1982).

For an ideal Newtonian fluid, the shear stress is linear function of the shear rate and the proportionality constant for the relationship, μ, is called the dynamic (or Newtonian) viscosity of the fluid. The relation is given by Newton's law of viscosity when the flow is laminar (Geankoplis, 1993; Barnes et al., 1989; Van Wazer & Lyons, 1966).

$$\tau = -\mu \cdot \dot{\gamma} \qquad (1)$$

where, τ is tangential shear stress, μ is the Newtonian viscosity and $\dot{\gamma}$ is the shear rate.

1.3.1. Newtonian Fluids

Fluids that obey Newton's law of viscosity (Eq.1) are called Newtonian fluids. For such a fluid, there is a linear relationship between shear stress (τ) and the shear rate ($\dot{\gamma}$) (Figure 1.3). This suggests that the viscosity, μ, is constant and it is independent of the rate of shear (Geankoplis, 1993). When shear rate is plotted against shear stress, the slope of the curve, μ, is constant and the plot begins at the origin. Using the units of N for force, m^2 for area, m for length, and finally m/s for velocity, gives viscosity as Pa s which is 1000 centipoise (1 Pa s = 1000 cP).

Typical Newtonian fluids contain low molecular weight compounds (e.g. sugars) and that do not include large concentrations of either dissolved polymers (e.g. protein, starch) or insoluble solids. Some examples of Newtonian foods are water, sugar syrups, edible oils, filtered juices, and milk (Rao, 1999). The following examples represent typical Newtonian viscosities at room temperature: water, 1cP; coffee cream 10 cP; vegetable oil, 100 cP; and honey 10000 cP (Steffe, 1996).

1.3.2. Non-Newtonian fluids

For non-Newtonian fluids, the relation between the shear stress (τ) and shear rate ($\dot{\gamma}$) is not linear and/or shear stress-shear rate plot does not begin at the origin. The fluid might exhibit time-dependent rheological behavior as a result of structural changes. Typical non-Newtonian materials are dispersions, emulsions, and polymer solutions. The viscosity is not constant but is a function of shear rate and may exhibit one of the two cases. Flow behavior may depend only on shear rate and not duration of shear (time-independent) or may depend on the duration of shear (time-dependent). Thus, non-Newtonian fluids can be divided into two broad categories as time- independent and time-dependent fluids. Various types of time independent behavior have been described in the literature (Rao, 1999; Barnes et al., 1989).

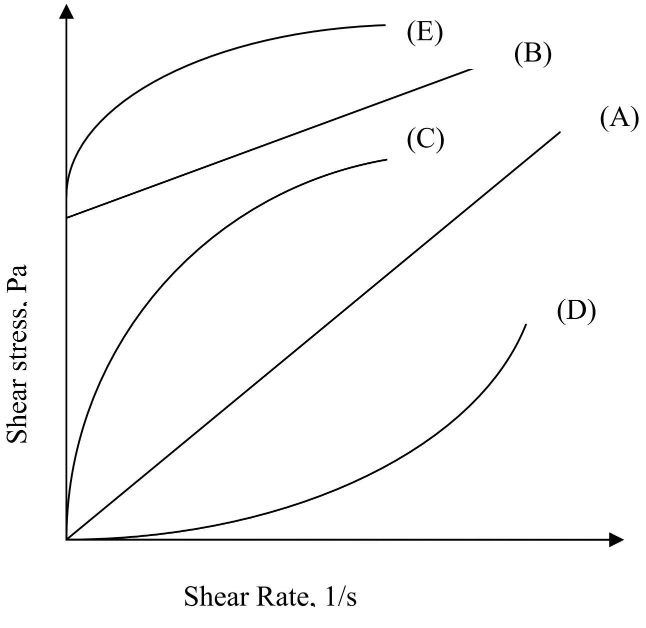

Figure 1.3. Flow curves for typical time-independent fluids. (A), Newtonian; (B), Bingham Plastic; (C), Shear thinning; (D), Shear thickening; (E), Hersley-Bulkley

1.4. Time-Independent Fluids

1.4.1. Bingham Plastic Fluids

This category is the simplest since the only difference from Newtonian behavior is that the linear relationship between shear stress and shear rate does not go through the origin (Figure 1.3) (Steffe, 1996).

$$\tau = \mu_{pl} \cdot \dot{\gamma} + \tau_0 \tag{2}$$

where, τ_0 is the yield stress and μ_{pl} is the plastic viscosity.

A finite stress so called yield stress (τ_0) is required to achieve flow. Below the yield stress, no flow occurs and the material exhibits solid like characteristics due to the stored energy (Steffe, 1996).

Toothpaste, tomato paste, margarine and chocolate mixtures are some examples of Bingham plastic fluids (Rao, 1999; Worlow, 1992).

1.4.2. Power-law Fluids

This type of non-Newtonian behavior can be explained by a power-law equation also called *Ostwald-de Waele* equation. This model has been used extensively to describe the non-Newtonian flow behavior both in theoretical analysis and in practical engineering calculations (Worlow, 1992; Bourne, 1982).

$$\tau = K \cdot \dot{\gamma}^n \tag{3}$$

where, K is the consistency coefficient (Pa. s^n) and **n** is the flow behavior index, (dimensionless). The consistency coefficient is an indicator of the viscous nature of a fluid.

Apparent viscosity, μ_a, is the ratio of shear stress to shear rate at a given rate of shear for shear dependent fluids. It represents the viscosity of a Newtonian fluid exhibiting the same resistance to flow at the chosen shear stress or shear rate (Van Wazer & Lyons, 1966).

The apparent viscosity, μ_a, for power-law fluids (Steffe, 1996) is,

$$\mu_a = f(\dot{\gamma}) = \frac{K \cdot \dot{\gamma}^n}{\dot{\gamma}} = K \cdot \dot{\gamma}^{n-1} \tag{4a}$$

of which the logarithmic form is used to determine the model parameters when experimental data are available as,

$$\ln \mu_a = \ln K + (n-1) \cdot \ln \dot{\gamma} \tag{4b}$$

According to the magnitude of the flow behavior index, **n**, power-law fluids are divided into two categories as shear thinning and shear thickening fluids.

1.4.2.1. Shear thinning Fluids

The majority of non-Newtonian fluids are covered in this category. With shear thinning (or pseudoplastic) fluids, the shear stress vs. shear rate curve begins at the origin but is concave upward (Figure 1.3). An increasing shear rate gives a less than a proportional increase in the shear stress. Applesauce, banana puree, orange juice concentrate, and many salad dressings are considered as shear thinning foods. While apparent viscosity is constant with Newtonian materials, it decreases with increasing shear rate in shear thinning fluids. Eq.3 applies to this type of behavior where, the flow behavior index is less than unity (**n**<1) (Rao, 1999; Steffe, 1996; Bourne, 1982).

1.4.2.2. Shear thickening Fluids

In shear thickening behavior, the shear stress vs. shear rate curve also go through the origin and it is concave downward; that is, an increasing shear stress gives a less proportional increase in shear rate (Figure 1.3). Apparent viscosity, the slope of the associated curve, increases with increasing shear rate. This type of flow is observed with gelatinized starch dispersions and corn flour-sugar solutions (Rao, 1999). Power-law model equation (Eq.3) is often applicable with the flow behavior index greater than unity (**n**>1).

1.4.3. Herschel-Bulkley Fluids

Herschel-Bulkley model is a general relationship to describe the behavior of non-Newtonian fluids (Figure 1.3).

$$\tau = K \cdot \dot{\gamma}^{n} + \tau_0 \tag{5}$$

It is a very convenient model since it reduces to Newtonian (**n** = 1) and to power-law behavior (**n** ≠ 1) as special cases ($\tau_0 = 0$). In addition, the model describes the Bingham Plastic Model where the yield stress is required (Steffe, 1996).

1.5. Time-Dependent Fluids

In some fluids, the apparent viscosity can either increase or decrease with time of shearing at a constant shear rate. Such changes can be reversible or irreversible. Time dependent fluids can be categorized into two classes as thixotropic and rheopectic fluids.

1.5.1. Thixotropic Fluids

Foods that exhibit time-dependent shear thinning behavior are said to be thixotropic fluids. Most of these fluids possess a heterogeneous system containing a fine dispersed phase. When at rest, particles and molecules in the food are linked together by weak forces. During shear the hydrodynamic forces are sufficiently high to break the interparticle linkages, resulting in a reduction in the size of structural units. Thus, a lower resistance to flow is detected during shear. This type of flow behavior is likely to occur with foods such as salad dressing and soft cheeses where the structural adjustments take place in the food until equilibrium is reached (Rao, 1999). The occurrence of thixotropy implies that the flow history must be taken into account when making predictions about the fluid behavior (Barnes et al., 1989).

Abu-Jdayil (2003) studied the thixotropic behavior of tahin. The structural breakdown of tahin at a constant shear rate was described by,

$$\left(\frac{\mu_a - \mu_{a\infty}}{\mu_{a0} - \mu_{a\infty}}\right)^{1-m} = (m-1)kt + 1 \qquad (6)$$

where, μ_{a0} is the initial apparent viscosity, $\mu_{a\infty}$ is the equilibrium apparent viscosity, m is the order of the structure breakdown reaction, k is the rate constant and t is time of measurement.

1.5.2. Rheopectic Fluids

Rheopexy (or antithixotropy) is associated with time dependent shear thickening behavior. These fluids are quite rare in occurrence. Viscosity of these fluids increases with time at a constant shear rate (Steffe 1996).

1.6. Variables Affecting Viscosity and Flow Behavior Parameters

It is critical to emphasize the way viscosity depends on variables like shear rate, temperature, pressure, time of shearing, and concentration. Fluids are subjected to high sensitivity due to changes in these variables. Time of shearing and variable shear rates affect viscosity due to the resulting structural changes in the fluid. However, for most practical purposes, the pressure effect is ignored. Temperature and concentration on the other hand, considerably affect rheological parameters (Barnes et al., 1989).

1.6.1. Effect of Temperature

There is usually an inverse relationship between viscosity and temperature. A wide range of temperatures are encountered during processing and storage of fluid foods, so the effect of temperature on rheological parameters is needed to be determined. While the flow behavior index, **n**, is assumed to be relatively constant with temperature, the effect of temperature on both apparent viscosity, μ_a and consistency coefficient, K of the power-law model is explained by an Arrhenius type relationship (Rao, 1999) as,

$$\mu_a = \mu_0 \cdot e^{\frac{E_a}{R.T}} \tag{7}$$

$$K = K_t \cdot e^{\frac{E_a}{R.T}} \tag{8}$$

where, μ_0 and K_t are the experimental constants, E_a is the activation energy (J/mol), R is the universal gas law constant (J/mol.K), and T is the absolute temperature (K). The quantity E_a, is the energy barrier that must be overcome before the elementary flow process can occur (Rao, 1999).

1.6.2. Effect of Concentration

There is usually a direct nonlinear relationship between concentration of a solute and viscosity at a constant temperature (Bourne, 1982). In most foods, it is often possible to identify the components that play an important role on the rheological properties. The effect of concentration, C, (soluble or insoluble solids) on apparent viscosity, μ_a, and the consistency index of the power-law model, K, is described by either exponential or power functions (Rao, 1999) as,

$$\mu_a = K_{c0} \cdot e^{b_0 \cdot C} \tag{9}$$

$$\mu_a = K_c \cdot C^b \tag{10}$$

$$K = K_{c1} \cdot e^{b_1 \cdot C} \tag{11}$$

$$K = K_{c2} \cdot C^{b_2} \tag{12}$$

where, K_c, K_{c0} K_{c1}, K_{c2}, b_0, b, b_1, and b_2 are experimental constants (Rao, 1999).

1.6.2.1. Effect of Concentration on Activation Energy

At a given temperature, activation energy for flow depends on the soluble solid content. The variation of activation energy with concentration is described by exponential and power functions as,

$$E_a = A_1 \cdot e^{d_1 \cdot C} \tag{13}$$

$$E_a = A_2 \cdot C^{d_2} \tag{14}$$

where, A_1, A_2, d_1, d_2, are experimental constants and C is the total soluble solid content (Kaya & Belibağlı, 2002).

1.6.3. Combined Effect of Concentration and Temperature

The increase in concentration and the decrease in temperature increase viscosity. The variables; temperature and concentration can be combined either with shear rate as,

$$\mu_a = f(T, C, \gamma) = K_{\dot{\gamma},T.C} \cdot \exp\left(\frac{E_a}{R \cdot T} + b \cdot C\right) \cdot \gamma^{\bar{n}-1} \tag{15}$$

or at a constant shear rate as,

$$\mu_a = f(T, C) = K_{T,C} \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \cdot C^{b} \tag{16}$$

where, $K_{\dot{\gamma},T,C}$, $K_{T,C}$, and b are experimental constants, and $\bar{n}$ is an average value for flow behavior index (Steffe, 1996).

In this study, an alternate relation is also investigated to express the combined effect of temperature, concentration and shear rate on apparent viscosity,

$$\mu_a = K_{\dot{\gamma},T,C} \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \cdot C^{b} \cdot \dot{\gamma}^{\bar{n}-1} \tag{17}$$

in which, only the parameter $\dot{\gamma}^{\bar{n}-1}$ is introduced to the right hand side of Eq.16.

1.7. Measurement of Flow

The study of the Newtonian and non-Newtonian flow behavior necessitates considerable care and instrumentation. Data from poorly designed instruments can be misleading. A viscometer must be capable of providing readings that are convertible to shear rate ($\dot{\gamma}$) and shear stress (τ). Further a well-designed instrument should provide recording of data in order to study time dependent behavior (Rao, 1999).

For viscometric measurements, the flow in the selected geometry should be steady, laminar, and fully developed. The temperature of the test fluid should be maintained uniform and constant for reliable measurement (Rao, 1999). Viscosity of fluids is highly temperature dependent. For instance, the viscosity of water at 20ºC changes 2.5% per 1ºC temperature change. Therefore, in all viscosity measurements it is essential that the temperature is closely controlled (Bourne, 1982). For Newtonian fluids, viscometers that operate at a single shear rate (eg. glass capillary) are acceptable. For non-Newtonian fluids, data should be obtained at several shear rates. Common viscometric flow geometries for rheological studies on foods are (1) concentric cylinder, (2) cone-plate, (3) parallel plate, (4) capillary/tube/pipe, and (5) slit flow (Rao, 1999).

For viscosity measurements laminar flow conditions are desired. Under conditions of turbulent flow of Newtonian fluids, the measured viscosity will be higher. However, since non-Newtonian fluids are generally viscous, usually laminar flows are encountered (Rao, 1999).

1.8. Rotational Viscometers

Traditional rotational viscometers comprise of cone and plate, parallel plate and concentric cylinder units operated under steady shear conditions (Steffe, 1996). The shear rate is derived from the rotational speed of a cylinder or a cone.

If the properties of flow behavior are required for the design of processes, it is recommended to use shear rates that cover the range that is expected to be used in the process (Rao, 1999).

1.8.1. Concentric Cylinder Viscometer

The concentric cylinder viscometer is a very common instrument that would operate in a moderate shear rate range. This function makes it a good choice for gathering data used in several engineering calculations (Steffe, 1996). It permits continuous measurements to be made under a given set of conditions and allows time-dependent effects to be studied. This is the most common type of viscometer that is used in the food industry (Bourne, 1982). In concentric cylinder geometry, a cylinder (bob) is placed coaxially inside a cup containing the selected volume of the test fluid (Rao, 1999). In Searle system concentric viscometer (Figure 1.4), the bob rotates and the cup is stationary. Couette-type systems are also available where the cup rotates and the bob is stationary (Rao, 1999). In Searle systems, the bob is rotated at a constant speed and the drag of the fluid on the bob is measured by means of a torque sensor. The measured figure is the torque (M) required to maintain a constant velocity of the bob (Ω). By changing the rotational speed, thus the shear rate and measuring the resulting shear stress, it is possible to obtain viscosity data over a wide range of shearing conditions (Steffe, 1996).

The following assumptions should be made in order to derive the mathematical relationships for the instrument performance (Steffe, 1996):

- Flow is laminar and steady,
- End effects are negligible,
- Test fluid is incompressible,
- Properties are not a function of pressure,
- Temperature is constant,

- There is no slip at the wall,
- Radial and axial velocity components are zero (Steffe, 1996).

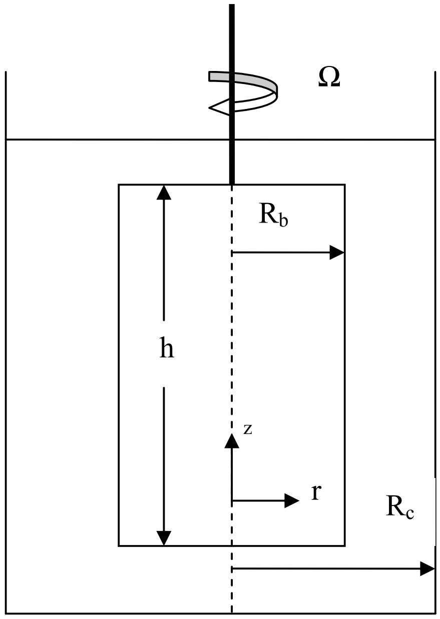

Figure 1.4. Concentric cylinder geometry.

Regarding the Searle type systems, the torque exerted on the bob by the fluid can be found by (Steffe, 1996),

$$M = 2\pi \cdot r^2 \cdot h \cdot \tau \tag{18}$$

where, r is location in the fluid ($R_b \leq r \leq R_c$), M is the torque, and h is the hight of bob. Solving Eq.18 for the shear stress at the bob, τ_b, ($r = R_b$) gives,

$$\tau_b = \frac{M}{2\pi \cdot h \cdot (R_b)^2} \tag{19}$$

For shear rate calculations, several techniques have been proposed such as simple shear approximation, Newtonian approximation, Power-law approximation and Krieger method (Steffe, 1996).

1.8.2. Shear Rate Approximation Techniques

1.8.2.1. Simple Shear Approximation

With a very narrow gap ($R_c - R_b \leq R_b$) the curvature of the walls is negligible. The system approaches simple shear i.e., couette flow. Assuming a uniform shear rate across the gap gives (Steffe, 1996);

$$\dot{\gamma}_b = \frac{\Omega \cdot R_b}{R_c - R_b} = \frac{\Omega}{\alpha - 1} \tag{20}$$

where, α is the ratio of cup radius, R_c to bob radius R_b, and Ω is the angular velocity (rad/s).

For the gap to be classed as narrow $1/\alpha$ must be greater than 0.97 (Barnes et al., 1989).

When calculating shear rates with this approximation corresponding average shear stress should be used (Steffe, 1996).

$$\tau_a = \frac{1}{2} \cdot (\tau_c + \tau_b) = \frac{M \cdot (1 + \alpha^2)}{4\pi \cdot h \cdot (R_c)^2} \tag{21}$$

where, τ_a is the average shear stress, τ_c is the shear stress at the cup,and τ_b is the shear stress at the bob.

1.8.2.2. Newtonian Approximation

For Newtonian fluids, the shear rate at the bob in a concentric geometry can be calculated from the following expression (Steffe, 1996; Whorlow, 1992) as,

$$\dot{\gamma}_b = 2 \cdot \Omega \cdot \left(\frac{\alpha^2}{\alpha^2 - 1} \right) \tag{22}$$

Commercial viscometers frequently use this equation to approximate the shear rate.

Newtonian shear rates need to be corrected for non-Newtonian behavior. The correction term depends on the extent of the deviation from Newtonian behavior and the size of the gap. In order to minimize errors in calculated shear rates it is advisable to work with concentric cylinders having a narrow gap (Rao, 1999). Yet, the difficulty of coping with suspensions containing large particules is an important limitation of narrow gaps. For this reason in many commercial viscometers $1/\alpha$ is less than 0.97 (Barnes et al., 1989).

1.8.2.3. Power-law Approximation

For a power-law fluid, the shear rate at the bob can be derived (Steffe, 1996) as,

$$\dot{\gamma}_b = \frac{2 \cdot \Omega}{n} \cdot \frac{\alpha^{(2/n)}}{\alpha^{(2/n)} - 1} \tag{23}$$

where, n is the consistency coefficient.

The flow behaviour index is calculated by evaluating the derivative of ln τ_b with respect to ln **Ω** (Steffe, 1996) as,

$$n = \frac{d(\ln \tau_b)}{d(\ln \Omega)} \tag{24}$$

For power-law fluids, **n** is the slope of the straight line of ln τ_b versus ln**Ω**. Once **n** is computed, Eq.23 can easily be evaluted (Steffe, 1996).

1.8.2.4. Krieger Method

In order to correct for non-Newtonian behavior of power-law fluids in a concentric cylinder geometry, an expression presented by Krieger and Elrod (Rao, 1999) has been extensively used:

$$\dot{\gamma}_b = \frac{\Omega}{\ln \alpha}\left[1 + \ln \alpha \frac{d(\ln \Omega)}{d(\ln \sigma_b)} + \frac{(\ln \alpha)^2 d^2 \Omega}{3\Omega d(\ln \sigma_b)^2}\right] \tag{25}$$

The Krieger solution is very close to Power-law approximation, but it is rather a complex method. When the flow behavior index, **n**, can be calculated at each τ_b, Power-law approximation solution provides excellent approximation for the shear rate at the bob (Steffe, 1996).

CHAPTER 2

MATERIALS AND METHODS

2.1. Sample Preparation

Commercial pekmez and tahin (Merter Helva San. ve Tic. A.Ş., Istanbul) were used in the experiments. Pekmez contained 66% total carbohydrate and 0.24 % sodium. The composition of tahin was 60.09% total fat, 10.5% carbohydrate, and 25.51% protein. The stated compositions of pekmez and tahin were provided by the manufacturer. Pekmez had an average total soluble solid content of 76 °Brix which was determined by using a hand refractometer (Tajiri Ind. Co., Japan) functioning in the range 58-90 °Brix.

2.1.1. Soluble Solid Content Adjustment

In order to work with standard samples, pekmez was diluted with distilled water and soluble solid content was adjusted to 70 °Brix by using the hand refractometer.

2.1.2. Vacuum Operation

For accurate viscosity measurement, the relevant samples should be free from entrapped air or air bubbles. For this purpose, both pekmez and tahin samples were vacuumed by using a vacuum pump (Vactorr 75, Precision Scientific, Chicago).

2.1.3. Preparation of Tahin/Pekmez Blends

After the vacuum operation, blends were prepared by mixing tahin with pekmez at the concentrations of 20%, 23%, 26%, 29%, and 32% (w/w). In order to attain a homogenous mixture, the blends were mixed evenly by a spatula. The blends were rested for about 2 minutes prior to the rheological measurements.

2.2. Rheological Analysis

2.2.1. Rotational Viscometer

Rheological properties of the tahin/pekmez blends were measured with a rotational viscometer (Visco Elite-R, Fungilab, Spain) equipped with the low viscosity adapter (LCP) which had a Searle-type concentric cylinder configuration (Figure 1.4) The concentric cylinder system had a bob length of 90.7 mm; bob radius of 12.545 mm; cup radius of 13.75 mm; and a gap width of 2.41 mm of which the dimensions were measured by using a digital caliper (Digimatic 500, Mitutoyo Corp., Japan). The ratio of cup radius to bob radius (α) was given as 1.0984 by the manufacturer. Sample volume of the cup was 18 ml. The equipment was a controlled shear rate device and operated at a wide rotor speed range. The rotor speeds of the LCP were in the range of 0.3-200 rpm with the corresponding viscosity range of 21333-32 cP. For each speed, there was a maximum viscosity value -full scale- that can be measured. The minimum viscosity reading was recommended as 15% of the full scale of the selected speed. The shear rate factor of the LCP adapter was supplied by the manufacturer assuming the sample is a Newtonian fluid,

$$\text{Shear rate}(1/s) = 1.2236 \cdot \text{rpm} \tag{26}$$

The equipment with LCP enabled rheograms to be constructed by providing apparent viscosity and shear stress data. The duration of the experiment and data collection increments could easily be set through the LCD screen. Datalogger software (Fungilab, Spain) enabled PC controlled analysis by transferring data to Microsoft Excel worksheet.

In order to maintain the system temperature constant during the measurements, the sample cell was placed into a thermostatically controlled water bath (Sub6, Grant, England). The temperature was set through the digital temperature display. The temperature setting range of the equipment was 15 ºC-99 ºC and the stability at 37 ºC had a precision of ± 0.1 ºC.

2.2.2. Rheological Measurements

The rheological measurements of tahin/pekmez blends with varying tahin contents of 20%, 23%, 26%, 29%, and 32% (w/w) were studied at temperatures 35 °C, 43 °C, 50 °C, 58 °C and 65°C. Prior to the measurements, the sample was loaded to the equipment and it was placed into the water bath to rest for 5 minutes in order to reach system temperature. This time was determined as sufficient to provide a maximum temperature difference of ± 0.5 °C between the selected temperature and the sample in each run. For each experiment, data collection was accomplished after 10 revolutions at a set rotational speed. Then for each successive revolution one point of viscosity and shear stress data at the set rotational speed were recorded up to 10 values. Each value was recorded at the completion of a revolution. The data were then transferred to Excel worksheet. Data calculations were carried out by using the averages of these 10 values.

For the associated temperature and concentration, the samples were sheared using seven different rotational speeds at an increasing order in order to study the non-Newtonian behavior. Rotational speeds (rpm) were selected according to the maximum and minimum readings of the full scale of the selected range. Thus each set of experiment required a different rpm range. On the overall, the rotational speed range was 0.6-50 rpm. In order to investigate the reproducibility of results two replicates were made and the average reproducibility was ±7%.

2.3. Statistical Analysis

Flow behavior and rheological properties of tahin/pekmez blends were determined by applying linear regression method via Microsoft Excel software. Model equations and coefficients of determination (R^2) were reported. Analysis of variance (ANOVA) test was applied to acknowledge any significant difference among rheological parameters; n and K under the effect of temperature and tahin concentration ($\alpha = 0.05$). Variables of temperature, concentration, and shear rate were combined into a single logarithmic model by using multiple linear regression method using Linest function in Microsoft Excel software.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Flow behavior determination

In order to determine the rheological characterization of tahin/pekmez blends at different tahin concentrations and temperatures, viscometric measurements were conducted by using a concentric cylinder type rotational viscometer. The blends contained tahin concentrations at the range of 20-32% (w/w). The temperature range was 35-65°C. For each set, seven different rotational speeds at an increasing order were used in order to investigate for non-Newtonian behavior.

It is necessary to convert rotational speed to shear rate data for accurate rheological analysis. Newtonian shear rates were computed by using Eq.26. In order to correct Newtonian shear rates for non-Newtonian behavior Power-law approximation method was employed. First, rotational speeds (rev/min) were converted to angular velocities (rad/s). From Eq.24 flow behavior indices were determined in order to apply Eq.23. The value of α was taken as 1.0984. This figure was calculated from Eq.26 which was supplied by the manufacturer for Newtonian approximation. The calculations resulted in a shear rate range of 0.75-63.9 (s^{-1}). The experimental data of shear stress, apparent viscosity and computed shear rates are given in Appendix A.

At all concentrations and temperatures, experimental results of the variation of shear stress with shear rate were found to be indicating a shear thinning non-Newtonian behavior. Figures 3.1 to 3.5 show the rheograms of blends at different tahin concentrations and temperatures. The Power-law model successfully described the relationship between shear stress and shear rate. Apparent viscosity of the blends decreased with increasing shear rate (Figures 3.6 to 3.10) indicating the shear thinning behavior.

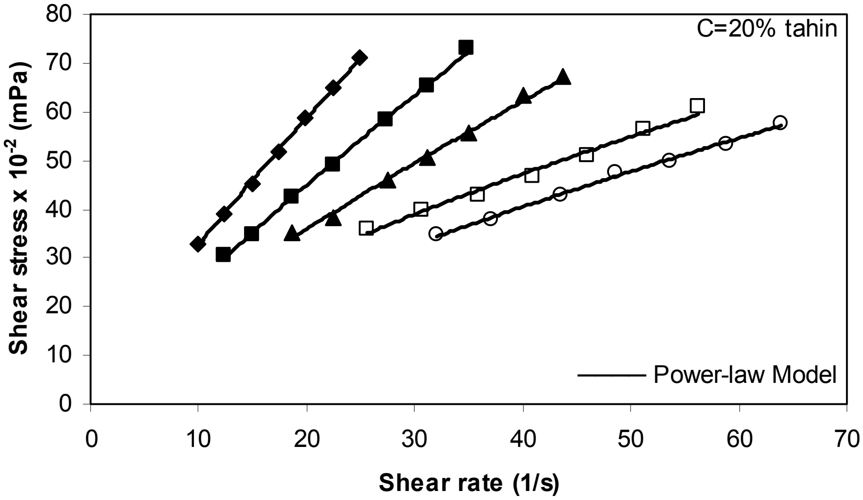

Figure 3.1. Rheograms for the blend containing 20% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲)50°C, (□)58°C, (○) 65°C.

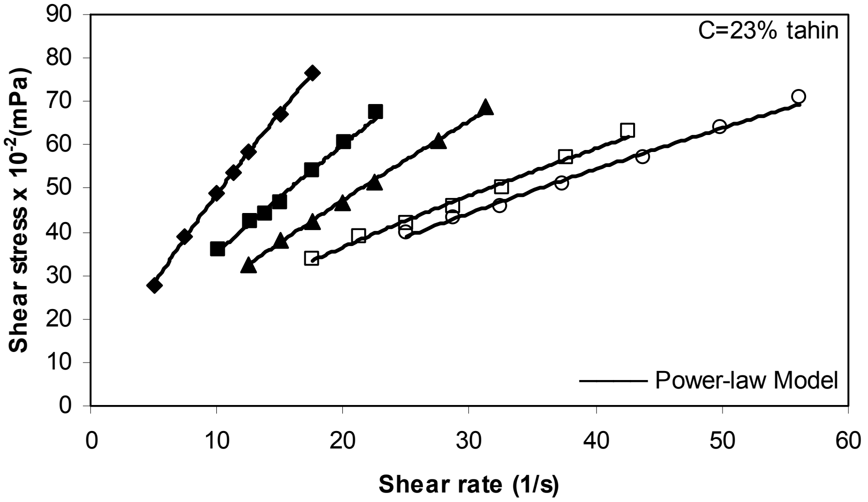

Figure 3.2. Rheograms for the blend containing 23% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲)50°C, (□)58°C, (○) 65°C.

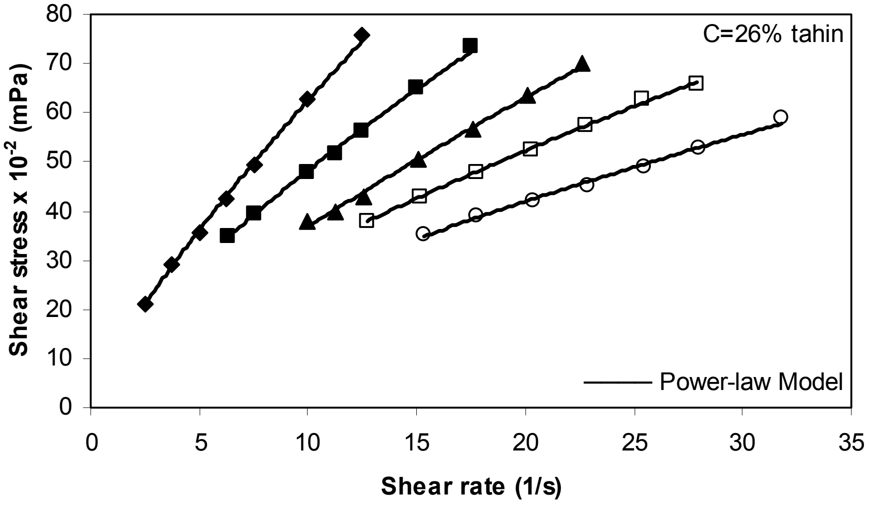

Figure 3.3. Rheograms for the blend containing 26% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲)50°C, (□)58°C, (○) 65°C.

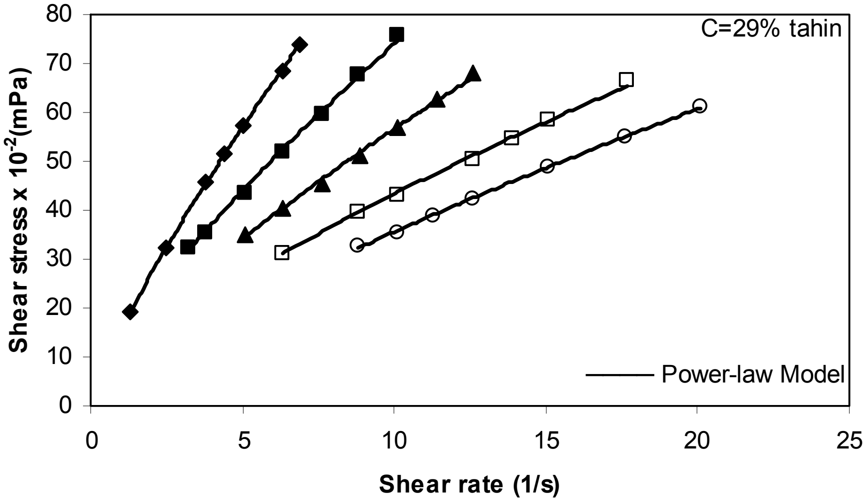

Figure 3.4. Rheograms for the blend containing 29% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲)50°C, (□)58°C, (○) 65°C.

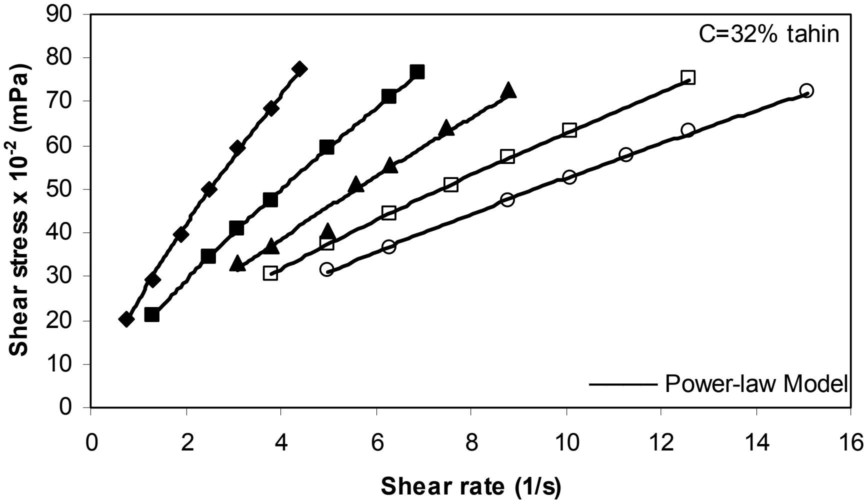

Figure 3.5. Rheograms for the blend containing 32% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲)50°C, (□)58°C, (○) 65°C.

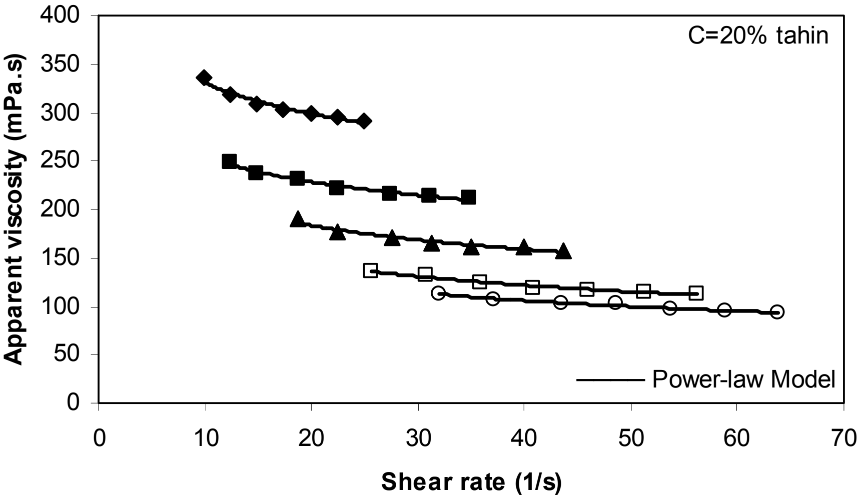

Figure 3.6. Apparent viscosity-shear rate relationship for the blend containing 20% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

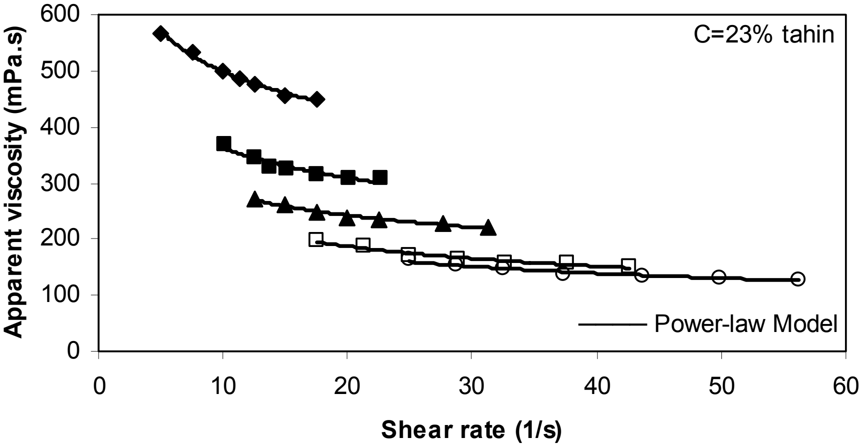

Figure 3.7. Apparent viscosity-shear rate relationship for the blend containing 23% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

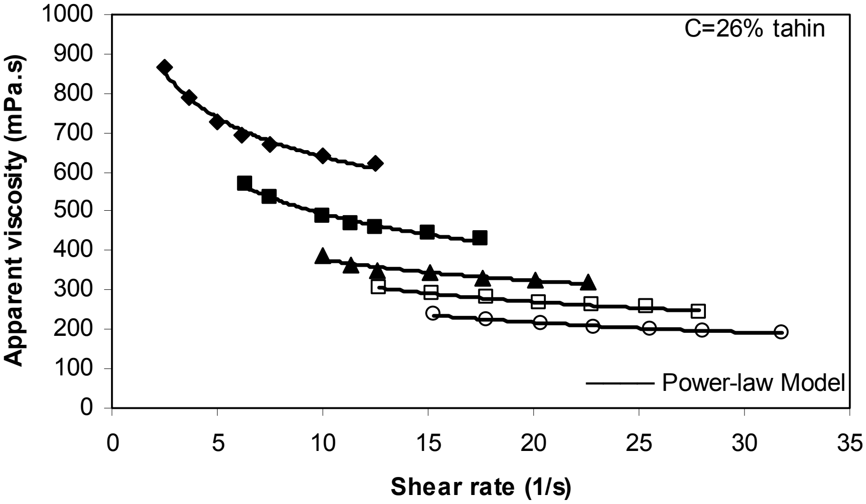

Figure 3.8. Apparent viscosity-shear rate relationship for the blend containing 26% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

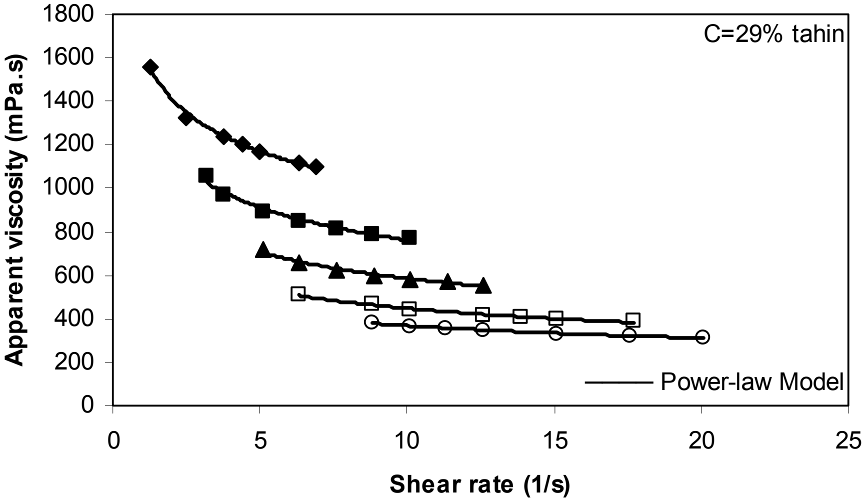

Figure 3.9. Apparent viscosity-shear rate relationship for the blend containing 29% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

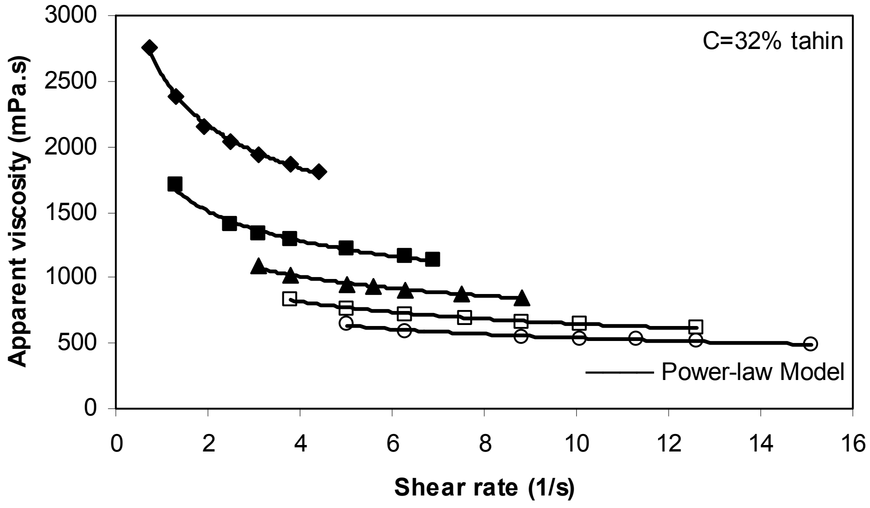

Figure 3.10. Apparent viscosity-shear rate relationship for the blend containing 32% tahin at different temperatures: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

In the light of these findings, the experimental data of apparent viscosity and shear rate were successfully fitted to Eq.4b to determine the model parameters; the flow behavior index, **n** and the consistency coefficient, K by regression analysis. From the slope of the regressed line, flow behavior index, **n**, and from the intercept, consistency coefficient, K was obtained. These values of **n**, K, and the coefficient of determination, R^2 at the studied concentrations and temperatures are summarized in Table 3.1.

Shear rate corrections to the experimental data were applied. Newtonian shear rates were corrected by using Power-law approximation method. The average correction achieved for the flow behavior index and consistency coefficient was found to be about 3% from the data. This value was also consistent with the theoretical percent error that would result by using Newtonian approximation instead of power-law approximation.

Table 3.1. Power-law parameters for blends at different concentrations and temperatures

	C (%TAHIN)														
	20			**23**			**26**			**29**			**32**		
T (°C)	**n**	**K(mPa.s^n)**	**R^2**	**n**	**K(mPa.s^n)**	**R^2**	**n**	**K(mPa.s^n)**	**R^2**	**n**	**K(mPa.s^n)**	**R^2**	**n**	**K(mPa.s^n)**	**R^2**
35	0.85	462	0.9677	0.80	783	0.9940	0.79	1034	0.9851	0.79	1630	0.9960	0.76	2547	0.9950
43	0.85	362	0.9753	0.77	611	0.9268	0.72	940	0.9824	0.74	1389	0.9736	0.77	1776	0.9877
50	0.79	341	0.9488	0.78	474	0.9743	0.78	626	0.9459	0.73	1087	0.9842	0.77	1388	0.9916
58	0.75	308	0.9732	0.70	465	0.9618	0.73	603	0.9936	0.73	834	0.9900	0.75	1157	0.9962
65	0.73	282	0.9810	0.71	409	0.9574	0.70	536	0.9738	0.76	640	0.9865	0.77	918	0.9889

$$\%\text{Error} = 1 - \frac{\dot{\gamma}_{\text{newtonian}}}{\dot{\gamma}_{\text{power}}} \tag{27}$$

Power-law model appeared to be suitable for describing the flow behavior of blends as proved by the level of coefficient of determination (R^2) which gave values ranging from 0.9268 to 0.9962 ($R^2 > 0.85$). The consistency coefficient, K, ranged from 282 to 2547 $mPa.s^n$. The values of flow behavior index, **n**, varied between 0.7 and 0.85 indicating shear-thinning (pseudoplastic) behavior since figures were smaller than unity (**n**<1). The degree of pseudoplasticity can be measured by the flow behavior index, **n**, which is a measure of deviation from Newtonian. As **n** increases, pseudoplasticity decreases. (Grigelmo et al., 1999).

The major constituents of pekmez are sugar and water whereas tahin is composed of mainly protein and oil. The fall in apparent viscosity with increasing shear rate can be explained by the structural breakdown of the blend due to the hydrodynamic forces generated and the increased alignment of these constituent molecules (Alparslan & Hayta, 2002; Rao, 1999). Shearing causes progressive deformation and disruption of oil droplets, resulting in less resistance to flow (Singh et al., 2003). Shear induced structural breakdown related to oil droplet deflocculation has also been reported for egg-yolk stabilized emulsions by Moros, Franco, and Gallegos (2002).

Abu-Jdayil, Malah, and Asoud (2002) showed that tahin is a non-Newtonian shear thinning fluid exhibiting thixotropic behavior. According to Eq. 6, and the model parameters provided by Abu-Jdayil (2003), apparent viscosity of tahin at T= 25 °C decreased by an amount of 4% in 5 minutes and 8% in 10 minutes at the shear rate of 15.2 s^{-1}.On the other hand, as reported by Kaya and Belibağlı (2002), pekmez samples with total solubles content in the range 52.1-72.9 °Brix possessed Newtonian fluid characteristics. Considering thixotropic tahin mixed with Newtonian pekmez at concentrations of 68-80% of the latter, the time dependency of tahin is probably highly cured by pekmez at the cost of losing its Newtonian behavior. Thus, the observed shear thinning behavior of the blends appears to be an intermediate behavior between these two distinct flow properties. This statement was supported by the experimental measurements of the apparent viscosity of tahin/pekmez blends at a constant shear rate which revealed no noticeable change with time.

The flow behavior of tahin/pekmez blends is in agreement with Alparslan and Hayta (2002). They reported that tahin/pekmez blends having pekmez concentration of 2-6% (w/w) behaved as shear thinning foodstuff at the temperature range of 30-75 °C. According to their results; the flow behavior index, **n**, was in the range of 0.43-0.58, while the consistency coefficient, K, varied from 9100 to 87200 mPa.s^n. In this present study, however, the values for flow behavior index appeared to be higher (0.7-0.85) which can be attributed to the higher pekmez concentration (68-80%) used in the blends causing less deviation from the Newtonian behavior. When shear rates cannot be evaluated in a given viscometer geometry, determination of fundamental rheological properties becomes very complex. Thus some viscometers can only generate comparative rather that absolute flow behavior data (Steffe, 1996). In the study of Alparslan and Hayta (2002), shear rates could not be computed, instead, rotational speed data were used for flow behavior analysis. With regard to this fact, it seems that comparison of the consistency coefficient values of these two studies in absolute terms would not be providing valid information.

3.2. Effect of Temperature on Flow Behavior

The effect of temperature on the rheological properties of tahin/pekmez blends were studied in the range of 35-65 °C. For the prepared samples the increase in temperature resulted in considerable decrease in viscosity values (Figures 3.6 to 3.10). This behavior can be explained by intermolecular forces restricting the molecular motion of the fluid. These forces, which determine the intermolecular spacing, are significantly affected by the change in temperature. As temperature increases, viscosity of the fluid decreases since thermal energy of the molecules increases and molecular distances develop due to reduction of intermolecular forces (Toğrul & Arslan, 2003; Hassan & Hobani, 1998).

Analysis of variance (ANOVA) (α = 0.05) showed that flow behavior index, **n** (Table B.1) and consistency coefficient, K (Table B.2) were significantly influenced by the change in temperature. As shown in Table 3.1, the values of both K and **n** decreased with increasing temperature except for the flow behavior index value of the blend containing 32% tahin. The decrease in the flow behavior index can be attributed to higher departure from Newtonian behavior.

While, there was not a descriptive trend for the flow behavior index, temperature sensitivity of the consistency coefficient was successfully described by an Arrhenius-type equation (Eq.8). Linear regression analysis was applied to the logarithmic form of Eq.8 (Figure 3.11) in order to determine the parameters of the relation (Table 3.2).

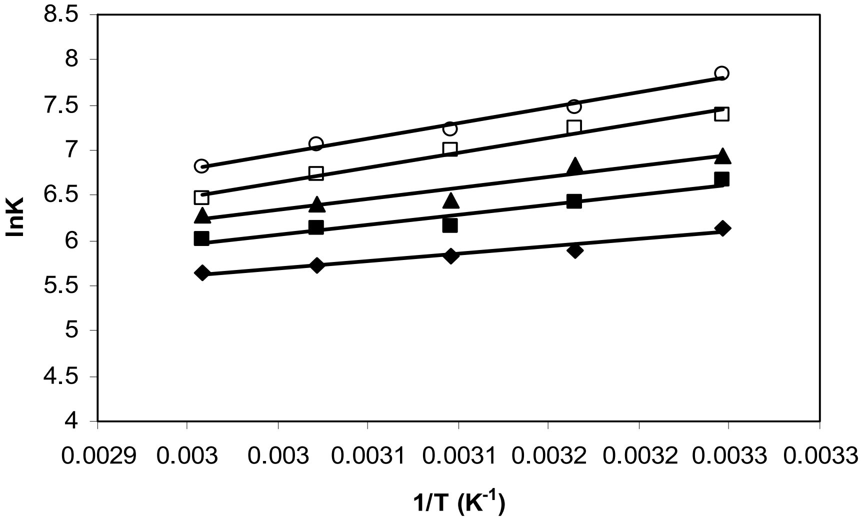

Figure 3.11. The effect of temperature on consistency coefficient of the blends at different tahin concentrations: (♦) 20%, (■) 23%, (▲) 26%, (□) 29%, (○) 32%.

Table 3.2. Parameters of the Arrhenius equation (Eq.8) for temperature dependency of consistency coefficient at different tahin concentrations.

C(%tahin)	K_t (mPa.s^n)	E_a(J/mol)	R^2
20	2.3705	13376	0.9513
23	0.5939	18253	0.9297
26	0.377	20288	0.9086
29	0.0398	27346	0.9835
32	0.0346	28592	0.9900

The activation energy, E_a, varied from 13376 to 28592 J/mol as the tahin concentration of blends varied from 20% to 32 %. Activation energy is a measure of temperature dependency for viscosity and consistency coefficient. As tahin concentration was increased, activation energy and temperature dependency of K was increased. It should be noted that the constant, K_t obtained by using the Arrhenius model decreased with increasing tahin concentration. Alparslan and Hayta (2002) also observed similar trends for activation energy, E_a and the experimental constant, K_t.

3.3. Effect of Concentration on Flow Behavior

In this part of the study, the effect of tahin concentration on flow behavior and rheological parameters were investigated. In the experiments tahin concentrations of the samples varied in the range 20% to 32%. At every temperature, the apparent viscosities of blends increased with increasing tahin concentrations (Appendix A). This behavior is illustrated in Figure 3.12 for T=50°C. Similar trends were observed at other temperatures.

Figure 3.12 also presents a comparison for the apparent viscosity of tahin, pekmez and tahin/pekmez blends. At 50 °C, pekmez (70 °Brix) exhibited Newtonian behavior (Table A.6), which is in line with the study of Kaya and

Belibağlı (2002). On the other hand, the apparent viscosity of tahin decreased with increasing shear rate (Table A.7). This result confirms the findings in the previous studies (Abu-Jdayil, 2003; Abu-Jdayil et al., 2002; Alparslan & Hayta, 2002). The apparent viscosity values of tahin/pekmez blends appeared within the range of tahin and pekmez viscosities as already discussed.

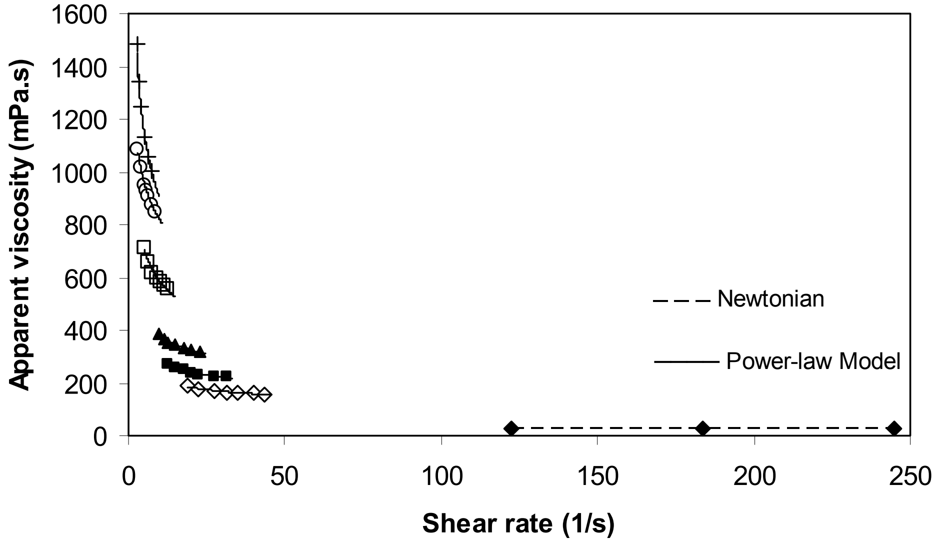

Figure 3.12. Apparent viscosity-shear rate relationships for pekmez, tahin/pekmez blends, and tahin at 50°C: (♦) pekmez, (◊) 20%, (■) 23%, (▲) 26%, (□) 29%, (○) 65%, (+) tahin.

Regarding the rheological data of tahin and pekmez in literature, comparisons in absolute terms do not provide useful information, possibly because of two main 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 (Steffe, 2002). Another reason could be the differences in the production or the source (raw material) of the product. Even very minor changes in composition or processing variables can dramatically influence the rheological properties.

Change in tahin concentrations significantly (α = 0.05) affected the consistency coefficients of the blends (Table B.2), while the effect on the flow behavior indices (Table B.1), were insignificant. Consistency coefficient, K, increased nonlinearly with concentration as shown in Figure 3.13.

The effect of tahin concentration on consistency coefficient was described by exponential and power functions. Linearized forms of Eq.11 and Eq.12 were plotted and corresponding model parameters are provided in Table 3.3.

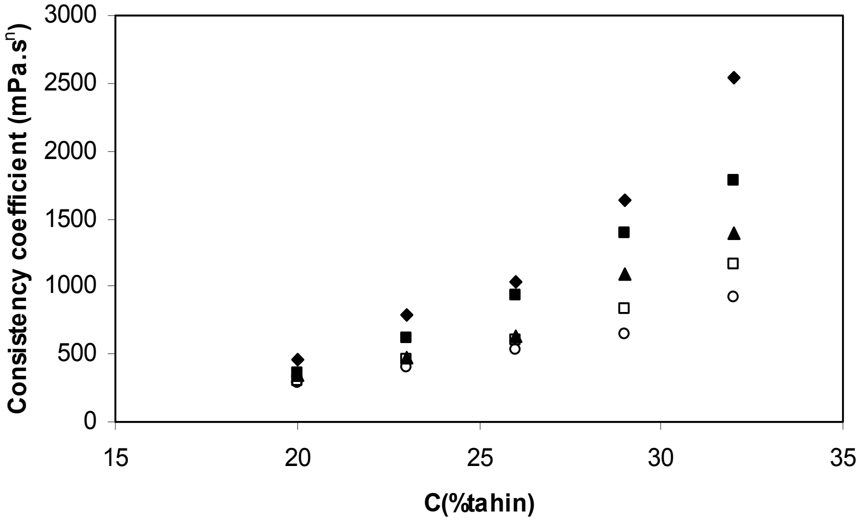

Figure 3.13. Effect of tahin concentration on consistency coefficients of the blends: (♦) 35°C, (■) 43°C, (▲) 50°C, (□) 58°C, (○) 65°C.

Table 3.3. Effect of tahin concentration on the consistency coefficient at different temperatures.

	Exponential Model (Eq.11)			Power Model (Eq.12)		
Temperature(°C)	b_1	K_{c1}	R^2	b_2	K_{c2}	R^2
35	0.1382	30.01	0.9935	3.5228	0.0119	0.9890
43	0.1334	27.26	0.9840	3.4284	0.0129	0.9963
50	0.1212	29.35	0.9858	3.0830	0.0311	0.9771
58	0.1077	36.98	0.9959	2.7501	0.0811	0.9954
65	0.0936	45.19	0.9874	2.3921	0.2195	0.9884

The analysis of correlation coefficients of models showed that both models successfully describe the relationship between concentration and consistency coefficient. For both models, the analysis of the experimental constants reveals that the effect of tahin concentration on the consistency coefficient was more pronounced at lower temperatures. This can be explained by the increase in viscosity thus the consistency coefficient of the blend due to the combined effect of increasing tahin concentration and decreasing temperature. High E_a values at higher tahin concentrations supports this conclusion where at a constant concentration, the change in K values is more significant for higher tahin concentrations as illustrated in Figure 3.13.

According to the findings in the literature, the rheological parameters and viscosity of emulsions increase with increasing dispersed phase (Abu-Jdayil, 2003; Moros et al., 2002). The increase of apparent viscosity and consistency coefficient, K, with increasing tahin (oil) concentration can be explained by oil droplet formation. As tahin content is increased, higher number of oil droplets is suspended in the blends. These droplets tend to agglomerate to form clusters. Cluster formation creates a volume fraction dependency on the viscosity of the emulsion. This means that as the volume fraction of an emulsion increases, the number of clusters formed will increase. These clusters disrupt streamlines and require more effort for the same flow rate thus subsequently increase the viscosity of the emulsion (Starov & Zhdanov, 2003). Increasing solid content with increasing tahin concentration can be another explanation to this phenomenon. As the solid content is increased, the interaction between particles and molecular movements increase, causing higher viscosity values for the fluid (Toğrul & Arslan, 2003; Alparslan & Hayta, 2002).

Moros, Franco, and Gallegos (2002) studied the effect of oil concentration on the rheological behavior of concentrated oil-in-water emulsions. They also reported that the apparent viscosities of the emulsions increased with an increasing oil concentration. In the study of Alparslan and Hayta (2002), however, increasing pekmez (decreasing tahin) concentration resulted in an increase of both viscosity and the consistency coefficient of the blends. Although the authors stated that the blends were oil-in-water emulsions, their results reveal water-in-oil type emulsion characteristics where, water, the dispersed phase, was introduced to the blends with the addition of pekmez causing an increase of the emulsion's viscosity.

3.3.1. Effect of concentration on Activation Energy, E_a

The variation of activation energy with tahin concentration was modeled by using exponential (Eq.13) and power (Eq.14) functions. The linearized forms of these two equations were used to determine the model constants as tabulated in Table 3.4.

Table 3.4. Influence of tahin concentration on activation energy

Exponential Model (Eq.13)			Power Model (Eq.14)		
A_1	d_1	R^2	A_2	d_2	R^2
3923	0.0641	0.9519	98.19	1.6504	0.9669

According to the values of the correlation coefficients, the relationship between E_a and tahin concentration was better described by the power model.

3.4. Combined Effect of Temperature, Concentration, and Shear Rate on Flow Behavior

A simple equation describing the combined effect of temperature and concentration on viscosity is a very useful tool for engineering applications (Kaya & Belibağlı, 2002). For this purpose, Eq.15 and 17 were applied to understand the combined effect of temperature, tahin concentration and shear rate on the apparent viscosity of tahin/pekmez blends. Multiple linear regression analyses were conducted on the linearized forms of the equations. The regression statistics of Eq. 15 and 17 including coefficients of the variables, standard errors for estimates and coefficient of determination are tabulated in Table C.1 and Table C.2, respectively. According to coefficient of determination values, both models adequately described the relationship. Yet Eq.15 provided a higher goodness of fit (0.9961) thus it can be recommended to be used as a single model,

$$\mu_a = 1.819 \cdot 10^{-3} \exp\left(3236.524\left(\frac{1}{T}\right) + 0.11151 \cdot C\right) \cdot \dot{\gamma}^{-0.2505} \qquad (28)$$

From the coefficients of Eq.28 the activation energy and average flow behavior index were determined to be 26910 J/mol and 0.7495, respectively.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

The flow characteristics of tahin/pekmez blends at five different tahin concentrations (20-32%) and temperatures (35-65 °C) were analyzed in the shear range of 0.75-63.9 s^{-1}.

At these temperatures and tahin concentrations, the blends exhibited non-Newtonian, shear thinning behavior. The apparent viscosity of the blends increased with increasing tahin concentration and decreasing temperature. Further, apparent viscosity-shear rate relationship of the blends can be successfully represented by the power- law model.

The model parameters: the flow behavior index, **n**, and the consistency coefficient are both significantly affected by temperature. The change of flow behavior index with temperature does not follow a descriptive trend, while consistency coefficient-temperature relationship can successfully be described by an Arrhenius-type equation. The effect of tahin concentration is significant only for K. It seems that both exponential and power functions can be used to acknowledge the relationship.

In order to observe the combined effect of temperature, tahin concentration and shear rate on apparent viscosity of the blends, a model equation was proposed with a high goodness of fit. The experimental data obtained in this study and the proposed model equations can be used in designing equipment for the blends, in quality control, process control applications and sensory evaluation of the product.

Further analysis can be conducted considering the blends' shelf-life, textural attributes, stability and sensory analysis in order to satisfy the end users.

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APPENDIX A

Table A.1. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ) and Apparent Viscosity (μ_a) at 20 %tahin concentrations and different temperatures (35-65 °C).

C (%tahin)	T (°C)	Ω (rpm)	$\dot{\gamma}$ (1/s)	τ x 10^{-2} (mPa)	μ_a (mPa.s)
20	35	8	9.9	32.8	335
		10	12.4	39	319
		12	14.9	45.2	308
		14	17.4	51.7	302
		16	19.9	58.7	300
		18	22.4	64.9	295
		20	24.9	71.2	291
	43	10	12.4	30.4	249
		12	14.9	34.8	237
		15	18.7	42.4	231
		18	22.4	48.9	222
		22	27.4	58.2	216
		25	31.1	65.4	214
		28	34.8	72.9	212
	50	15	18.7	35.2	190
		18	22.5	38.1	176
		22	27.5	45.8	170
		25	31.2	50.5	165
		28	35	55.6	162
		32	40	63.2	161
		35	43.7	67.2	157
	58	20	25.6	35.8	136
		24	30.7	39.7	132
		28	35.8	43	125
		32	40.9	46.7	119
		36	46	51.1	116
		40	51.2	56.3	115
		44	56.3	61	113
	65	25	32	34.6	113
		29	37.1	38	107
		34	43.5	42.8	103
		38	48.6	47.5	102
		42	53.7	49.9	97
		46	58.8	53.5	95
		50	63.9	57.5	94

Table A.2. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) at 23 % tahin concentrations and different temperatures (35-65 °C).

C (%tahin)	T (°C)	Ω (rpm)	$\dot{\gamma}$ (1/s)	$\tau \times 10^{-2}$ (mPa)	μ_a (mPa.s)
23	35	4	5	27.9	567
		6	7.5	39.1	533
		8	10	48.9	500
		9	11.3	53.6	487
		10	12.5	58.2	475
		12	15	67.1	457
		14	17.5	76.7	448
	43	8	10.1	36.1	369
		10	12.6	42.4	346
		11	13.8	44.1	328
		12	15.1	46.8	325
		14	17.6	54	315
		16	20.1	60.5	310
		18	22.6	67.6	307
	50	10	12.5	32.5	272
		12	15	38.1	260
		14	17.5	42.6	249
		16	20	46.6	238
		18	22.5	51.3	233
		22	27.6	61.1	227
		25	31.3	69	222
	58	14	17.5	33.7	197
		17	21.3	38.9	187
		20	25	41.8	172
		23	28.8	45.9	164
		26	32.6	50.3	158
		30	37.6	57.2	156
		34	42.6	63.3	152
	65	20	25	39.8	163
		23	28.7	43.3	154
		26	32.5	45.8	146
		30	37.4	51	139
		35	43.7	56.9	133
		40	49.9	64.2	131
		45	56.2	71	129

Table A.3. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) at 26 % tahin concentrations and different temperatures (35-65 °C).

C (%tahin)	T (°C)	Ω (rpm)	$\dot{\gamma}$ (1/s)	τ x 10^{-2} (mPa)	μ_a (mPa.s)
26	35	2	2.5	21.2	866
		3	3.7	28.9	789
		4	5	35.5	728
		5	6.2	42.4	692
		6	7.5	49.2	671
		8	10	62.8	642
		10	12.5	75.8	620
	43	5	6.3	34.9	571
		6	7.5	39.4	536
		8	10	47.7	487
		9	11.3	51.8	470
		10	12.5	56.2	460
		12	15	65	443
		14	17.5	73.6	430
	50	8	10	37.9	388
		9	11.3	40	363
		10	12.6	42.9	351
		12	15.1	50.5	344
		14	17.6	56.8	332
		16	20.1	63.4	324
		18	22.6	70.2	319
	58	10	12.7	37.9	305
		12	15.2	43	290
		14	17.8	47.9	280
		16	20.3	52.5	268
		18	22.8	57.5	261
		20	25.4	62.6	256
		22	27.9	65.9	245
	65	12	15.3	35.2	238
		14	17.8	39	227
		16	20.4	42.1	215
		18	22.9	45.2	205
		20	25.5	49.1	201
		22	28	52.7	196
		25	31.8	59.1	193

Table A.4. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) at 29 % tahin concentrations and different temperatures (35-65 °C).

C (%tahin)	**T (°C)**	**Ω (rpm)**	$\dot{\gamma}$ **(1/s)**	$\tau \times 10^{-2}$ **(mPa)**	μ_a **(mPa.s)**
29	35	1	1.3	19.1	1558
		2	2.5	32.4	1328
		3	3.8	45.7	1237
		3.5	4.4	51.5	1202
		4	5	57.3	1170
		5	6.3	68.4	1119
		5.5	6.9	73.8	1096
	43	2.5	3.2	32.3	1056
		3	3.8	35.5	969
		4	5.1	43.5	889
		5	6.3	51.8	847
		6	7.6	59.8	815
		7	8.8	67.7	791
		8	10.1	75.7	774
	50	4	5.1	34.9	714
		5	6.3	40.4	661
		6	7.6	45.5	620
		7	8.9	51.3	599
		8	10.1	57	582
		9	11.4	62.6	568
		10	12.6	67.9	555
	58	5	6.3	31.3	512
		7	8.8	39.8	465
		8	10.1	43	439
		10	12.6	50.2	419
		11	13.9	54.7	407
		12	15.1	58.6	399
		14	17.7	66.5	388
	65	7	8.8	32.7	385
		8	10.1	35.5	366
		9	11.3	39	354
		10	12.6	42.2	345
		12	15.1	48.9	333
		14	17.6	55.1	322
		16	20.1	61.2	313

Table A.5. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) at 32 % tahin concentrations and different temperatures (35-65 °C).

C (%tahin)	**T (°C)**	**Ω (rpm)**	**$\dot{\gamma}$ (1/s)**	**$\tau \times 10^{-2}$ (mPa)**	**μ_a (mPa.s)**
32	35	0.6	0.75	20.2	2756
		1	1.3	29.2	2389
		1.5	1.9	39.5	2154
		2	2.5	49.9	2038
		2.5	3.1	59.4	1941
		3	3.8	68.6	1870
		3.5	4.4	77.5	1810
	43	1	1.3	20.9	1706
		2	2.5	34.5	1408
		2.5	3.1	40.8	1334
		3	3.8	47.3	1289
		4	5	59.6	1218
		5	6.3	71.1	1162
		5.5	6.9	76.8	1141
	50	2.5	3.1	33.1	1084
		3	3.8	37.2	1015
		4	5	40.5	951
		4.5	5.6	51.3	932
		5	6.3	55.7	911
		6	7.5	64.1	874
		7	8.8	72.7	850
	58	3	3.8	30.6	835
		4	5	37.4	765
		5	6.3	44.3	724
		6	7.6	50.8	693
		7	8.8	57.2	667
		8	10.1	63.2	646
		10	12.6	75.2	615
	65	4	5	31.5	643
		5	6.3	36.4	594
		7	8.8	47.2	551
		8	10.1	52.5	537
		9	11.3	57.7	524
		10	12.6	63.1	516
		12	15.1	72.5	494

Table A.6. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) of pekmez at different temperatures (30-60 °C).

T (°C)	Ω (rpm)	$\dot{\gamma}$ (1/s)	$\tau \times 10^{-2}$ (mPa)	μ_a (mPa.s)
30	20	24.5	15.8	64.8
	30	36.7	24.0	65.6
	50	61.2	39.0	65
	60	73.4	48.3	65.8
40	60	78.4	28.0	38.2
	100	122.3	47.0	38.4
50	100	29.5	29.5	24.1
	150	183.5	Not available	24.2
	200	244.7	Not available	24.2
60	100	122.3	19.8	16.7
	200	244.7	40.8	16.2

Table A.7. Experimental Data of Shear Rate ($\dot{\gamma}$), Shear Stress (τ), and Apparent Viscosity (μ_a) of tahin at different temperatures (35-65 °C).

T (°C)	Ω (rpm)	$\dot{\gamma}$ (1/s)	$\tau \times 10^{-2}$ (mPa)	μ_a (mPa.s)
35	0.6	0.8	33	4533
	1	1.3	41	3371
	1.5	2	51	2767
	2	2.7	59	2429
	2.5	3.3	67	2189
	3	4	74	2019
43	2	2.6	46	1888
	2.5	3.2	52	1698
	3	3.9	58	1568
	4	5.2	69	1418
	5	6.5	81	1322
50	2	2.6	36	1482
	2.5	3.2	41	1339
	3	3.8	46	1248
	4	5.1	55	1133
	5	6.4	65	1055
	6	7.7	74	1002
58	2	2.6	28	1141
	2.5	3.2	32	1037
	3	3.9	36	968
	4	5.1	43	881
	5	6.4	50	822
	6	7.7	57	782
65	2	2.6	24	969
	2.5	3.3	27	883
	3	4	30	823
	4	5.3	37	748
	5	6.6	43	697
	6	7.9	49	662
	10	13.2	54	579

APPENDIX B

Table B.1. ANOVA results for the flow behavior index under the effect of temperature and concentration.

	C(%tahin)				
T (°C)	**20**	**23**	**26**	**29**	**32**
35	0.85	0.80	0.79	0.79	0.76
43	0.85	0.77	0.72	0.74	0.77
50	0.79	0.78	0.78	0.73	0.77
58	0.75	0.70	0.73	0.73	0.75
65	0.73	0.71	0.7	0.76	0.77

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	5	3.99	0.798	0.00107
Row 2	5	3.85	0.77	0.00245
Row 3	5	3.85	0.77	0.00055
Row 4	5	3.66	0.732	0.00042
Row 5	5	3.67	0.734	0.00093
Column 1	5	3.97	0.794	0.00308
Column 2	5	3.76	0.752	0.00197
Column 3	5	3.72	0.744	0.00153
Column 4	5	3.75	0.75	0.00065
Column 5	5	3.82	0.764	8E-05
ANOVA				

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.015504	4	0.003876	**4.5148515**	0.0124322	**3.0069174**
Columns	0.007944	4	0.001986	**2.3133372**	0.1020825	**3.0069174**
Error	0.013736	16	0.0008585			
Total	0.037184	24				

Table B.2. ANOVA results for the consistency coefficient under the effect of temperature and concentration.

	C(%tahin)				
T (°C)	**20**	**23**	**26**	**29**	**32**
35	462	783	1034	1630	2547
43	362	611	940	1389	1776
50	341	474	626	1087	1388
58	308	465	603	834	1157
65	282	409	536	640	918

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Row 1	5	6456	1291.2	675952.7
Row 2	5	5078	1015.6	328561.3
Row 3	5	3916	783.2	193483.7
Row 4	5	3367	673.4	110391.3
Row 5	5	2785	557	58795
Column 1	5	1755	351	4788
Column 2	5	2742	548.4	22719.8
Column 3	5	3739	747.8	49878.2
Column 4	5	5580	1116	161416.5
Column 5	5	7786	1557.2	406235.7

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1712941.8	4	428235.46	**7.9009234**	0.0010279	**3.0069174**
Columns	4601525	4	1150381.3	**21.224478**	3.091E-06	**3.0069174**
Error	867210.96	16	54200.685			
Total	7181677.8	24				

APPENDIX C

Table C.1. Regression statistics for linearized form of Eq.15

	E_a/ R	b	n-1	$\ln K_{\dot{\gamma},T,C}$
Estimated values	3236.524	0.11151	-0.2505	-6.3093
Standard errors (SE)	57.322	0.0017	0.01	0.2321
Coefficient of Determination (R^2)	0.9961			
Degrees of Freedom	171			
Regression sum of squares	105.7			
Residual sum of squares	0.413			

Table C.2. Regression statistics for linearized form of Eq.17

	E_a/ R	b	n-1	$\ln K_{\dot{\gamma},T,C}$
Estimated values	3110.594	2.72039	-0.2791	-11.774
Standard errors (SE)	84.2061	0.0238	0.0146	0.4623
Coefficient of Determination (R^2)	0.9914			
Degrees of Freedom	171			
Regression sum of squares	105.2			
Residual sum of squares	0.913			