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COLLOIDAL STABILITY AND SOME RHEOLOGICAL PROPERTIES OF TAHİN AND PEKMEZ-TAHİN BLEND

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BY
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Colloidal Stability and Some Rheological Properties of Tahin and Pekmez-Tahin Blend

M.Sc. Thesis
in
Food Engineering
University of Gaziantep

Supervisor
Prof. Dr. Sevim KAYA

by
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July 2008

Dedicated to my parents Fatma & Selahaddin and
my sister Laçin

ABSTRACT

COLLOIDAL STABILITY AND SOME RHEOLOGICAL PROPERTIES OF TAHİN AND PEKMEZ-TAHİN BLEND

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Particle size and temperature effects on the colloidal stability and rheological characteristics of tahin, which is a kind of protein-oil suspension, were investigated. Multimodal particle size distributions were determined using laser-scattering particle size analyzer. It was detected that colloidal stability of tahin was improved by decreasing particle size. A decrease in the storage temperature also caused the increase in the colloidal stability. Shear thinning and thixotropic behaviors were observed for tahin. Dynamic rheological tests showed that elastic structure of tahin changed regularly to viscous structure with decreasing particle size and the magnitudes of both storage (G′) and loss (G″) moduli increased with frequency. L-values, degree of darkness, increased with the reduction of particle size as a contrary of expected.

The effect of pekmez concentration on some physical properties of pekmez-tahin blend was also analyzed. Colloidal stability was improved with pekmez addition. According to the some quality parameters (appearance, taste, oiliness, adhesiveness, graininess, hardness and spreadability) detected with sensory analysis and rheological measurements, it could be stated that 15% pekmez containing tahin was the ideal blend in the studied range for production of spreadable pekmez-tahin.

Key words: Tahin, Particle size, Rheology, Colloidal stability, Color.

ÖZET

TAHİN VE PEKMEZ-TAHİN KARIŞIMININ KOLOİT DAYANIKLILIĞI VE BAZI REOLOJİK ÖZELLİKLERİ

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Bir çeşit protein-yağ süspansiyonu olan tahinin koloit dayanıklılığı ve reolojik özellikleri üzerine tane boyutu ve sıcaklığın etkileri araştırıldı. Lazer difraksiyon analiz cihazı ile incelenen tahinin, çoklu-model tane boyut dağılımı özelliğinde olduğu görüldü. Tane boyutunu düşürmekle koloit dayanıklılığın arttığı belirlendi. Aynı zamanda depolama sıcaklığının düşürülmesi de koloit dayanıklılığı arttırdı. Tahin için shear thinning ve tiksotropik akış özelliği gözlendi. Dinamik reolojik testler sonucunda tahinin azalan tane boyutu ile elastik yapıdan viskoz yapıya doğru değişime uğradığı ve saklama ve kayıp modül değerlerinin artan frekans değerleri ile arttığı belirlendi. Beklenenin aksine tane boyutunun azalması ile renk parametrelerinden koyuluk göstergesi L-değerinin arttığı anlaşıldı.

Pekmez konsantrasyonunun, pekmez-tahin karışımının bazı fiziksel özellikleri üzerine olan etkisi de analiz edildi. Koloit dayanıklılık pekmez ilavesi ile arttı. Bazı duyusal kalite parametrelerinin (görünüş, tat, yağlılık, yapışkanlık, tanelilik, sertlik ve sürülebilirlik) ve reolojik ölçümlerin sonucunda sürülebilir pekmez-tahin üretimi için çalışılan aralıkta ideal pekmez oranının %15 olduğu söylenebilir.

Anahtar kelimeler: Tahin, Tane boyutu, Reoloji, Koloit dayanıklılık, Renk.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS

τ	:	Shear stress
γ	:	Shear rate
μ	:	Viscosity
τ_o	:	Yield stress
G'	:	Storage modulus
G''	:	Loss modulus
ρ_s	:	Density of the solid particles
ρ_t	:	Density of tahin
ρ_o	:	Density of separated oil
ANOVA	:	Analysis of Variance
CS	:	Colloidal Stability
H_o	:	Height of oil phase in the test tube
H	:	Total height of tahin in the test tube
f	:	Frequency
K	:	Consistency coefficient
LDM	:	Laser Diffraction Method
n	:	Flow behavior index
Pa	:	Pascal
PSD	:	Particle Size Distribution
s	:	Second
SAOS	:	Small Amplitude Oscillatory Shear Measurements
t		Time
TPA	:	Texture Profile Analysis

CHAPTER I

INTRODUCTION

1.1 General Objective

The particle size analysis and rheological characterization of food products, especially for emulsions and suspensions, are important in their formulation, processing, transportation and storage. Tahin is a kind of colloidal suspension mainly composed of hydrophilic solids suspended in sesame oil (Abu-Jdayil, 2004; Altay and Ak, 2005). During production of tahin, the selected sesame seeds are mechanically dehulled, roasted and ground into paste (Kahyaoglu and Kaya, 2006). Sesame has a high nutritive value with respect to high amount of proteins, lipids and important minerals and vitamins (Abu-Jdayil et al., 2002). Antioxidant activity of sesamol and sesaminol in sesame also makes tahin shelf stable (Fukuda et al., 1987).

Although tahin is shelf stable with respect to chemical deteriorative reactions, colloidal instability is the main problem during storage of tahin (Isa, 2001). Sedimentation of solid particles causes negative effect on consumer acceptability on the market and also it is very difficult to redisperse the sediment cake for further processing. Due to the good health beneficial effects of tahin, there has been great interest for using it as an ingredient for creamy desserts and sauces. Thus, in order to use tahin properly as ingredient in foods or develop new spreadable products, it is important to improve its colloidal stability, understand rheological properties and their correlations with particle size. Consumer acceptance of tahin/pekmez blend which offers a promising nutritious and healthy alternative to consumers is highly dependent on spreadability on another material which requires information about rheological properties of the product (Alparslan and Hayta, 2002).

Recently much study has been reported about the rheological properties of tahin and its blends. Steady shear behavior of tahin and its blends were reported as pseudoplastic and thixotropic (Abu-Jdayil et al., 2002; Alpaslan and Hayta, 2002; Altay and Ak, 2005; Razavi et al., 2008). The rheological behaviors of many type of

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pekmez samples were studied by some researchers (Kaya and Belibağlı, 2002; Yoğurtçu and Kamışlı, 2006). Results indicated that pekmez samples were found to exhibit non-Newtonian behaviour. The consistency coefficient was found to decrease with the rise in temperature. As our knowledge no harmonious change of the flow behavior index as function of temperature was observed. None of these reports took into account the instrumentally measured particle size distribution that may play important role in rheological properties and colloidal stability of tahin. Since the instrument / process based on the laser diffraction principle has become standard tool for particle size analysis in food and allied industries (Singh et al., 2006), the exact data are required for particle size distribution of tahin. No size could be detected by the particle size analyzer in pekmez samples since most of its carbohydrate is in the form of monosaccharide (approximately 100% invert sugar) as glucose and fructose. However, it contains very small amount of sucrose and protein (Şengül et al., 2005). Dynamic shear rheological tests have been used to characterize the viscoelastic properties of macromolecular dispersions (Rao, 1999). Dynamic rheological properties of tahin and pekmez/tahin blends do not appear to have been studied.

Therefore, the objectives of this study were:

-To perform particle size analysis with a laser scattering instrument and determine the effect of particle size distribution on the colloidal stability, the steady and the viscoelastic behavior, and color of tahin.

-To prepare pekmez/tahin blends having different ratio and further analyze in terms of colloidal stability, viscoelastic properties and consumer acceptability of the blends to determine ideal ratio of spreadable pekmez/tahin product.

1.1 Manufacture of Tahin

Sesame, the scientific name of which is Sesamum indicum, is the raw material of tahin. In fact, tahin is 100% produced from sesame seeds. It is the product of milled seeds of sesame, which were de-hulled and roasted without adding or removing any of its constituents. Tahin is manufactured in specialized mills in Turkey and many of the Middle East Countries. Some are equipped with sophisticated machines, whereas others are still using the traditional method of manufacturing. However; basic principles followed are similar (Özcan and Akgül, 1994). The traditional tahin production steps are performed as follows (Figure 1.1):

Cleaning: Sifting the sesame seeds to remove all foreign materials (dust, stones, straw, etc…).

Soaking: Soaking the sesame seeds in fresh water for a period of (4-8) hours (depending of the sesame type and its absorption of water). This step will facilitate softening of the seed coats which become easy to separate.

Dehulling: Sesame is then transferred to dehulling machine which is basically composed of rotating drums which cause friction of seeds against the drums and against each other so that the hull are torn off.

Hull Separation: The seeds are then transferred to vats in which they are soaked in brine (14-18%). Depending on the difference of density of the seeds and its coats, the sesame seeds float on the surface while the coats sink to the bottom.

Washing: Seeds are then transferred to washing vats in which they are subjected to several washings with fresh water to get rid of salt residue.

Roasting: Seeds are then transferred to double jacketed semi-cylindrical roasters which are equipped with paddles to agitate the seeds during roasting ($100^{o}C/30min$). The moisture content of the seeds at the end of this step should not exceed 1%.

Sesame seed

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┌─────────────────────┐
│      Cleaning       │
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           │
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│      Soaking        │
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│     Dehulling       │
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│   Hull Separation   │
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│      Roasting       │
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│      Cleaning       │
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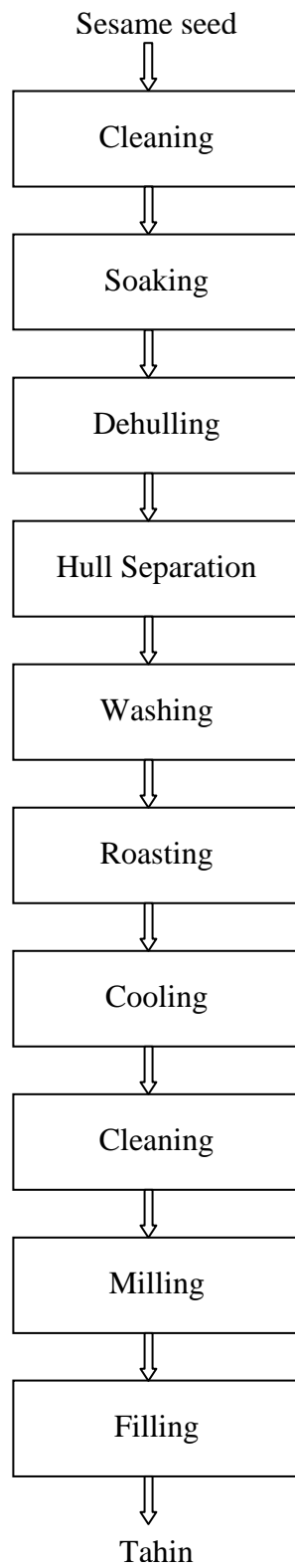
Tahin

Figure 1.1 Schematic representation of tahin production steps

Cooling: The roasted seeds are then cooled by spreading on wooden plates and manual agitation. Technicians in the mill test the sesame seeds for softness (which is essential property for the material flow during milling) before milling by rubbing the seeds between thumb and index fingers.

Cleaning: The seeds are sifted to remove any burnt impurities which are responsible for darkening of tahin.

Milling: The roasted seeds are crushed using a special stone mill to produce tahin. The temperature should not exceed $70^{o}C$.

Filling: Tahin is then filled in containers of various sizes and stored at room temperature.

Tahin can be made in one of two colors, white or reddish. Both white and reddish tahin are prepared from sesame. The reddish tahin gets its color from heating the sesame during roasting. The dehulled sesame is roasted at high temperature for 3-4 hours till they acquire an even brown color and suitable flavor; otherwise, the preparation procedure for both is the same.

1.3 The Chemical Composition and Nutritive Value of Tahin

Sesame seed is one of the world's important and the oldest oilseed crops known to man that also contains very good nutritional value (Sontag, 1981). Sesame plays an important role in human nutrition. Its seeds are used essentially for the production of oil, but also in the production of the paste (tahin) and in food formulations such as halaweh (helva), java beans and salads (Abou-Gharbia et al., 2000; Abu-Jdayil et al., 2002; Namiki, 1995).

The chemical composition of sesame shows that the seed is an important source of oil (44-60%) and protein (18-30%). It was also reported to have carbohydrate (13.5%) and ash (5.3%) moisture (5.2%) (Johnson et al., 1979; Kahyaoglu and Kaya, 2006).

Sesame is also a source of helpful biologically active components found in plant foods, such as phytochemicals and it is a functional food (Kanu et al., 2007). Seeds contain very useful phytochemical such as resveratrol, flavonoids, tocopherol, ethyl protocatechuate, phytosterols, lectins, sesamin, sesamolin and other phytochemicals which could be extracted for the purpose of the above to be utilized as functional ingredients. It could help in the prevention, control and management of diseases such as cancer, cardiovascular disease, osteoporosis, oxidative stress and other degenerative diseases. The combination of functional ingredients and rich nutritional composition of sesame makes it very unique and a very good functional food that could be developed as food for the children as well as for the aged.

1.3.1 Sesame oil

Sesame contains unique oil which is very easily digested and is stable to oxidative stress and for these reasons they are useful and healthy for consumption. Sesame not only contained an oil that has the ''good'' fat (monounsaturated fat), but they are also high in a variety of helpful antioxidants or chemicals that protects the human being from the damaging effects of free radicals when sesame oil is consumed because of the presence of sesamin and sesamolin in sesame seed.

Sesame oil is considered to be a health-promoting food because it contains a higher proportion of monounsaturated fatty acids (MUFA) than saturated fatty acids (SFAs) and it also contains bioactive compounds such as tocopherol and phytosterols (Yamashita et al., 1992). Sesame oil generally contains fatty acids, in the following percentages 45.3-49.4% oleic, 37.7-41.2% linoleic and 12-16% SFAs (Weiss, 1983). Sesame oil is composed of various fatty acids, as shown in Table 1.1 of which good percentages accounted for by only oleic and linoleic acids (LA) (Weiss, 1983). Oleic acid, with one double bond in its chain, belongs to the group of MUFAs while linoleic acid with two double bonds, belongs to the group of PUFAs (polyunsaturated fatty acids).

Table 1.1 Fatty acid composition of sesame oil (Weiss, 1983)

Fatty acid	Percentage
Oleic	45.3-49.4
Linoleic	37.7-41.2
Palmitic	7.8-9.1
Stearic	3.6-4.7
Arachidic	0.4-1.1
Hexadecanoic	0.0-0.5
Myristic	0.1
Saturated fatty acids	12-16

Several reports exist in the literature on chemical and nutritional properties of tahin and sesame oil (Damir, 1984; Sawaya et al., 1985; Unsal and Nas, 1995; El-Adawy and Mansour, 2002). The higher stability of sesame oil against oxidation as compared with other vegetable oils is well known (Namiki, 1995). This aspect facilitates the incorporation of sesame paste into spreadable products [e.g. peanut butter (Sumainah et al., 2000)] to extend their shelf life.

1.4 Colloidal Structure of Tahin

1.4.1 Definition of the colloidal system

Colloidal state can be defined as dispersion of one substance (dispersed phase) in another (dispersion medium) of such degree of subdivision as to possess properties different from those of the substance either in mass or in the solution. It is considered as mixtures that are intermediate between the solutions and suspensions (Graham, 1977; Jirgensons et al., 1964). Colloidal particles range in size from 1-100 µm. Particles less than 1µm are particles in true solution, and particles greater than 100 µm will form a coarse suspension (Rahman, 1995).

The accepted definition of colloidal system is confirmed by the properties of colloidal solutions. It is a heterogeneous system that strongly scatters light, possesses low diffusibility, is capable of dialysis and can be aggregatively unstable (labile) (Voyutsky, 1978).

There are at least two phases in a colloidal system, the colloidal material which is suspended or dispersed is known as dispersed phase, internal phase or micelles. These particles are discontinuous and are distributed throughout another medium known as the continuous phase, dispersion medium or intermiceller liquid (Aurand et al., 1973)

1.4.2 Stability of the Colloidal System

The stability of the colloidal system depends upon the magnitude of the potential barrier between the colloidal particles or macromolecules. This barrier can be electrical and/or mechanical dependent upon the particular system involved. In the absence of a barrier the colloid will coagulate or flocculate due to different forces (Graham, 1977).

There are two types of colloidal system, namely hydrophobic colloids and hydrophilic colloids. All colloids possess an electrical charge which may be either positive or negative (Aurand et al., 1973). For hydrophobic systems, the colloidal particles have no affinity for water and remain dispersed because of the electrical charge present; the barrier usually originates from the repulsion experienced by particles of like charge (Derjaguin, 1976). For hydrophilic systems, the colloidal particles have an affinity for water. Thus a hydration shield is found around the colloidal particles. This constitutes a mechanical barrier in addition to the electrical charge. Therefore, hydrophilic colloids are much more stable than hydrophobic colloids (Aurand et al., 1973). To increase the stability of the hydrophobic colloids protective colloids are used which are hydrophobic colloids added to hydrophobic to stabilize them by forming a protective layer around the particles. Proteins and gums are frequently used as protective colloids.

Temperature influences the stability of colloids since it alters the interfacial tension, adsorption of emulsifier, and viscosity of the system. Both viscosity and interfacial tension decrease with the rise of temperature. There is also some evidence that a large increase or decrease of temperature tends to coagulate the colloidal particles causing a destabilization of the system (Sherman, 1968).

Generally as storage temperature is decreased less fat separation occurred, possibly due to the increase in viscosity which slowed down the separation process (Ramsey and Swartzel, 1984). Ismail et al. (1983) also found that milk is much more stable during cold storage.

Helmer and Saffle (1963) found that meat emulsions breakdown did not occur at one specific temperature but took place over a wide range of temperatures. The exact temperature may be affected by processing conditions and type of meat. Higher temperature may actually aid breakdown by bringing the fat globules into contact with each other.

The stability of emulsions to extreme temperatures is of great practical importance, since commercial emulsions may be exposed to extremely high or extremely low temperature during processing. The increase in Brownian motion when raising the temperature will usually increase the rate of flocculation (Becher, 1965).

1.5 Particle Size Analysis

1.5.1 Significance of particle size

One of the most important defining characteristics of a particulate system is its particle size distribution (PSD). This parameter has a profound influence on the bulk flow properties, dispersability, and performance of the particles (Matsuyama and Yamamoto, 2004). PSD of a powder, or granular material, or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amounts of particles present, sorted according to size. PSD is also known as grain size distribution (Orhan and Özer, 2004). The method used to determine PSD is called particle size analysis, and the apparatus a particle size analyzer (Rawle, 1995). The PSD of a material can be important in understanding its physical and chemical properties. It affects the strength and load-bearing properties of rocks and soils. It affects the reactivity of solids participating in chemical reactions, and needs to be tightly controlled in many industrial products such as the manufacture of printer toner, cosmetics, etc. In the food industry -especially for emulsions and suspensions- the particle size of the food compounds is an important factor that affects the food

quality during processing, transportation and storage of foods. The determination of particle size is necessary to specify the formulation and storage conditions.

It is evident that particle size has an important influence on colloidal stability, and that small globules are much more stable to coalescence than large ones (Ivey et al., 1970). Homogenization achieves fat globules size reduction and increases the total surface area of the globules. The smaller fat globules remain evenly distributed throughout the system with fewer tendencies to coalescence which effectively controls the separation (Ramsey and Swartzel, 1984; Potter, 1986). Ramsey and Swartzel (1984) reported that particle size reduction and /or increase in viscosity must be utilized for separation to be kept to a minimum.

1.5.2 Definition of the particle

Particles are three-dimensional objects for which three parameters (the length, breadth and height) are required in order to provide a complete description. As such, it is not possible to describe a particle using a single number that equates to the particle size. In general, particle "diameter" implies a diameter of sphere, but for non-spherical particles, there is no unique diameter (Allen, 1996). Most sizing techniques, therefore, assume that the material being measured is spherical, as a sphere is the only shape that can be described by a single number (its diameter). This equivalent sphere approximation is useful in that it simplifies the way particle size distributions are represented (Malvern, 1993). In this case, in general, a certain basis (such as particle volume) will be defined and on that basis some reading relating to particle size will be measured. A diameter of a spherical particle with the same measurement will express the size as a dimension of length. This procedure gives the "equivalent diameter" (Matsuyama and Yamamato, 2004).

There are several ways of extending the above definition, so that a definition is obtained that also applies to non-spherical particles. Existing definitions are based on replacing a given particle with an imaginary sphere that has one of the properties identical with the particle.

Volume based particle size equals the diameter of the sphere that has same volume as a given particle; weight based particle size equals the diameter of the sphere that has same weight as a given particle; area based particle size equals the diameter of the sphere that has the same surface area as a given particle; hydrodynamic or aerodynamic particle size equals the diameter of the sphere that has the same drag coefficient as a given particle.

Definition of the particle size for an ensemble (collection) of particles presents a problem. Real systems are practically always polydisperse, which means that the particles in an ensemble have different sizes. The notion of particle size distribution reflects this polydispersity. There is often a need of a certain average particle size for the ensemble of particles. There are several different ways of defining such a particle size. There is an International Standard on presenting various characteristic particle sizes (ISO, 2004). This set of various average sizes includes: median size, geometric mean size, average size.

1.5.3 PSD measurement techniques

-Sieve method: This continues to be used for many measurements because of its simplicity, cheapness, and ease of interpretation. Methods may be simple shaking of the sample in sieves until the amount retained becomes more or less constant. Alternatively, the sample may be washed through with a non-reacting liquid (usually water) or blown through with an air current. The most obvious disadvantage is that the smallest practical sieve size is 20-40 µm, and many PSDs are concerned with much smaller sizes than this. A 20 µm sieve is exceedingly fragile, and it is very difficult to get material to pass through it. Another disadvantage is that the amount of energy used to sieve the sample is arbitrarily determined. Over-energetic sieving causes attrition of the particles and thus changes the PSD, while insufficient energy fails to break down loose agglomerates.

-Optical counting method: PSDs can be measured microscopically by sizing against a graticule and counting, but for a statistically valid analysis, millions of particles must be measured. This is impossibly arduous when done manually, but automated analysis of electron micrographs is now commercially available.

-Electrical counting method: An example of this is the Coulter counter, which measures the momentary changes in the conductivity of a liquid passing through an orifice that take place when individual non-conducting particles pass through. The particle count is obtained by counting pulses, and the size is dependent on the size of each pulse.

-Sedimentation method: These are based upon study of the terminal velocity acquired by particles suspended in a viscous liquid. Sedimentation time is longest for the finest particles, so this technique is useful for sizes below 10 μm, but sub-micrometer particles can't be reliably measured due to the effects of Brownian motion. Typical apparatus disperses the sample in liquid, and then measures the optical density of successive layers using visible light or x-rays.

-**Laser diffraction method:** The most popular method which is laser diffraction method (LDM) is an easy, rapid and reliable technique for the particle size analysis

1.5.4 Laser diffraction method

Laser diffraction has become one of the most widely used techniques for particle size analysis in many industries, with applications from product development through to production and quality control. It relies on the fact that particles passing through a laser beam will scatter light at an angle that is directly related to their size. As particle size decreases, the observed scattering angle increases logarithmically. Scattering intensity is also dependent on particle size, diminishing with particle volume. Large particles therefore scatter light at narrow angles with high intensity, whereas small particles scatter at wider angles but with low intensity (Plantz, 1981).

1.5.4.1 Particle size calculations in LDM

In laser diffraction, particle size distributions are calculated by comparing a sample's scattering pattern with an appropriate optical model. Traditionally, two different models are used: the Fraunhofer approximation and Mie Theory (Rhodes, 1998).

The Fraunhofer approximation was used in early diffraction instruments. It assumes that the particles being measured are opaque and scatter light at narrow angles. As a result, it is only applicable to large particles and will give an incorrect assessment of the fine particle fraction.

Mie Theory provides a more rigorous solution for the calculation of particle size distributions from light scattering data. It predicts scattering intensities for all particles, small or large, transparent or opaque. Mie Theory allows for primary scattering from the surface of the particle, with the intensity predicted by the refractive index difference between the particle and the dispersion medium. It also predicts the secondary scattering caused by light refraction within the particle. This is especially important for particles below 50 microns in diameter.

1.5.4.2 The advantages of laser diffraction method

Laser diffraction is a non-destructive, non-intrusive method that can be used for either dry or wet samples. As it derives particle size data using fundamental scientific principles, there is no need for external calibration; well-designed instruments are easy to set up and run, and require very little maintenance. Additionally, the technique offers the following advantages:

-*A wide dynamic measuring range*: Modern systems allow users to measure particles in the range from 0.02 micron to a few millimeters without changing the optical configuration, ensuring that both well dispersed and agglomerated particles are detected equally well.

-*Flexibility*: The technique is equally applicable to sprays, dry powders, suspensions and emulsions, allowing different product formulations to be compared in a realistic way.

-*Generation of volume-based particle size distributions:* This is normally equivalent to a weight distribution and is relevant to many processes as it indicates where most of the mass of material is located in terms of particle size.

-Rapid data acquisition: A single measurement across the entire dynamic range can be made in 0.4 milliseconds, allowing dynamic events to be studied.

-High repeatability: The ability to acquire data rapidly allows many thousands of measurements to be averaged when reporting a single result, providing repeatability. This, coupled with standardized operating procedures, ensures that the instrument to instrument variation is less than 1%, enabling direct comparison of data from different sites.

-Ease of Verification: As a first-principles technique, laser diffraction does not require calibration but can be easily verified using a variety of readily available standards.

The most important difference of the laser diffraction system compared to other methods in particle sizing is that it determines particle size distribution according to volumetric basis. By using the density of scattered laser light, the volumes of particles are calculated and the results are presented. In sieving and sedimentation techniques weight based calculations are used, it can be realized that the difference between the two techniques is great (Allen, 1996). The Laser diffraction technique utilized equivalent sphere theory for calculation of particle sizes (Malvern, 1993). If it is thought that the shape of clay particles is like sheet, needle or more complex, it can be understood why equivalent sphere technique is needed to determine particle sizes. The most important advantage of this technique is that it does not require the specific gravity and weight of particles (Rawle, 1995). By this way mistakes during the calculation of weight is avoided. It should also be realized that the sample includes various type of particles having different specific gravities. However the specific gravity test can only yield one average value. Because laser diffraction technique does not require the knowledge of specific gravity, there won't be such problems (Agrawal et al., 1991).

1.6 Basic Concepts of Rheology

There are numerous areas where rheological data are needed in the food industry:

-Process engineering calculations involving a wide range of equipment such as pipelines, pumps, extruders, mixers, coaters, heat exchangers, homogenizers calendars, and on-line viscometers;

-Determining ingredients functionality in product development;

-Intermediate or final product quality control;

-Shelf-life testing;

-Evaluation of food texture by correlation to sensory data;

-Analysis of rheological equations of state or constitutive equations.

The way of defining materials rheologically is by the terms *viscous*, *elastic* or *viscoelastic.* Gases and liquids are normally described as viscous fluids. An ideal viscous fluid is unable to store any deformation energy. Hence it is irreversibly deformed when subjected to stress; it flows and the deformation energy is dissipated as heat, resulting in a rise of temperature.

Solids, on the other hand, are normally described as elastic materials. Ideal elastic material stores all imposed deformation energy and will consequently recover totally upon release of stress. A viscous fluid can therefore be described as a fluid which resists the act of deformation rather than the state of deformation, while an elastic material resists the act as well as state of deformation.

A number of materials show viscous as well as elastic properties, i.e. they store some of the deformation energy in their structure while some is lost by flow. These materials are called viscoelastic; there are many examples among foodstuffs like cheese, pastes and gels.

1.6.1 Newtonian fluids

Newtonian fluids are those having a constant viscosity dependent on temperature but independent of the applied shear rate. One can also say that Newtonian fluids have direct proportionality between shear stress and shear rate in laminar flow.

$$\tau = \mu\gamma \qquad\qquad 1.1$$

where τ is shear stress, Pa; γ is shear rate, s^{-1}; μ is viscosity, $Pa.s^{-1}$.

The proportionality constant is thus equal to the viscosity of the material. The flow curve which is a plot of shear stress versus shear rate will therefore be a straight line with slope μ for a Newtonian fluid. A Newtonian fluid can therefore be defined by a single viscosity value at a specified temperature. Water, mineral and vegetable oils and pure sucrose solutions are examples of Newtonian fluids.

1.6.2 Non-Newtonian fluids

Materials which can not be determined by a single viscosity value at a specified temperature are called non-Newtonian. The viscosity of these materials must always be stated together with a corresponding temperature and shear rate. If the shear rate is changed the viscosity will also changed. Generally speaking, high concentration and low temperature induce or increase non-Newtonian behavior.

Apart from being shear rate dependent, the viscosity of non-Newtonian fluids may also be time dependent, in which case the viscosity is dependent not only of the magnitude of the shear rate but also of the duration in most cases of the frequency of successive applications of shear. Non-Newtonian materials that are time independent are defined as *shear thinning, shear thickening* or *plastic*. Non-Newtonian materials that are time dependent are defined as *thixotropic, rheopectic* or *anti-thixotropic*.

1.6.2.1 Non-Newtonian time independent fluids

*Shear thinning (pseudoplastic) flow behavior***:** The viscosity decreases with increased shear rate.

Examples: paint, shampoo, slurries, fruit juice concentrates, ketchup.

Shear thickening (dilatant) flow behavior: The viscosity increases with increased shear rate.

Examples: wet sand, concentrated starch suspensions.

Plastic flow behavior: It exhibits a so-called yield value, i.e. a certain shear stress must be applied before flow occurs.

Examples: quark, tomato paste, tooth paste, hand cream, some ketchups, grease.

1.6.2.2 Non-Newtonian time dependent fluids

Thixotropic flow behavior: Time thinning i.e. viscosity decreases with time; fluids are quite common in chemical as well as in food industry (yogurt, paint).

Rheopectic flow behavior: Time thickening i.e. viscosity increases with time; fluids are very rare (gypsum paste).

1.6.2.3 Flow behavior models

Several models are available for mathematical description of the flow behaviour of non-Newtonian systems (Figure 1.2). Examples of such models are *Ostwald, Herschel-Bulkley, Steiger-Ory, Bingham, Ellis* and *Erying*. These models relate the shear stress of a fluid to the shear rate, thus enabling the apparent viscosity to be calculated, as always as the ratio between shear stress and shear rates.
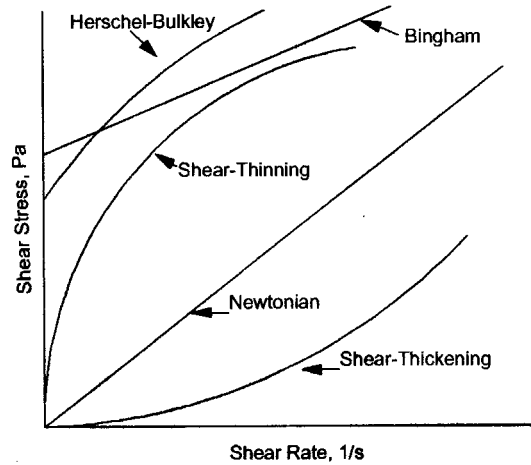
Figure 1.2 Flow curves are normally used for the graphical description of the flow behaviour

1.6.2.3.1 Power Law Equation

By far the most general model is the Herchel-Bulkley model also called the *generalised power law equation,* which in principle is an extended Ostwald model. The main benefit of the generalised power law equation is its applicability to a great number of non-Newtonian fluids over a wide range of shear rates. Furthermore the power law equation lends itself readily to mathematical treatment, for instance in pressure drop and heat transfer calculations.

The generalized power law equation applicable to plastic as well as shear thinning and shear thickening fluids according to the following:

$$(\tau-\tau_o)=K\,\gamma^{\,n} \hspace{4cm} 1.2$$

where τ is shear stress, Pa; τ_o is yield stress, Pa; K is consistency coefficient, $Pa.s^{n}$; γ is shear rate, s^{-1}; n is flow behavior index, dimensionless. Suitable modification of the generalized power law equation makes it possible to rewrite it to express each type of flow behavior.

For Newtonian fluids the power law equation looks like this: ($K=\mu$ and $n=1$):

$$\tau=K\,\gamma^{n}=\mu\,\gamma \hspace{4cm} 1.3$$

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For a plastic fluid the power law equation is used in the fully generalized form, with n<1 viscoplastic behavior and n=1 for Bingham plastic behavior.

For a shear thinning or a shear thickening fluid the power law equation becomes

$$\tau = K\,\gamma^{n} \hspace{4cm} 1.4$$

with n<1 and n>1, respectively.

For time-dependent fluids, which in practice mean thixotropic fluids, the mathematical models required for description of rheological behavior are generally far more complex than the models discussed so far. These fluids are therefore often described by time-independent process viscosities normally to the power law equation.

Abu-Jdayil et al. (2002) investigated the steady rheological properties (i.e., shear stress as a function of shear rate) of tahin and examined methods for characterizing time dependent rheological behavior under the effect of different temperatures and shearing conditions. Their results indicated that the steady shear behavior of tahin was pseudoplastic and the time-dependent behavior was thixotropic. Another study about rheological characterization of tahin was done by Altay and Ak (2005). They emphasized to determine the contributions of tahin oil and solid particles to the overall rheology of tahin. According to their results, the presence of solid particles (up to a relatively high level of 20%) simply increased the viscosity of the suspensions but did not introduce a deviation from Newtonian behaviour. Above this concentration, however, not only a significant increase in viscosity but also a shift to non-Newtonian (shear-thinning) behaviour was observed.

Abu-Jdayil (2004) studied the steady and time-dependent flow properties of halva (consist of tahin, sugar, citric acid and a small amount of saponin extract) in the temperature range between 25–45°C. He concluded that halva behaved like a shear thinning material and exhibited thixotropic behavior. On the other hand, the deviation from Newtonian behavior decreased with temperature.

1.6.3 Linear viscoelasticity

A viscoelastic material exhibits both elastic solid and viscous liquid behavior simultaneously under a wide range of conditions. An elastic solid stores mechanical energy during deformation and reverts to its original form (shape and size) upon removal of external forces; a viscous liquid dissipates such energy. Though no material is a "true solid" or a "true liquid", a steel spring or rubber band is a good example of an elastic solid, and water is an ubiquitous example of a viscous liquid. The simplest type of viscoelastic behavior is linear viscoelasticity, where the measured properties are independent of magnitude of the input variable (Ferry, 1980). This type of behavior is observed when the deformation is so small that the structure of a material is disturbed only to a negligible extent.

The small amplitude oscillatory shear (SAOS) measurements are commonly used to study the linear viscoelasticity of semi-solid foods. SAOS is a special subset of the dynamic mechanical analysis (DMA). DMA is used to measure mechanical properties of materials while that are subjected to an oscillating stress (or strain), usually applied sinusoidally. When DMA accounts for temperature effects, it is termed "dynamic mechanical thermal analysis" (DMTA). DMA and DMTA are extremely useful material characterization methods. The main feature of SAOS tests is that, due to small strain (and stress) used, they can be considered as objective and nondestructive tests suitable for probing material structure.

SAOS measurements allow determination of shear moduli, (I) storage modulus (or elastic modulus) and (ii) loss modulus (or viscous modulus) as a function of test frequency (f) in the linear viscoelastic (LVE) region of the test material. The material functions used to describe viscoelastic behavior are represented in Table 1.2. The storage modulus G' (f) is a measure of the energy stored and recovered per cycle, and the loss modulus G'' (f) is a measure of the energy dissipated or lost as heat per cycle of imposed deformation (Ferry, 1980). In addition, phase angle (or mechanical loss angle) δ and loss tangent tan δ, relative measures of the ratio of viscous to elastic component, can be determined.

Table 1.2 Material functions used to describe viscoelastic behavior

Material functions	Equation
Storage modulus	$G'=(\sigma_o/\gamma_o)\cos(\delta)$
Loss modulus	$G''=(\sigma_o/\gamma_o)\sin(\delta)$
Complex modulus	$G^*=(\sigma_o/\gamma_o)=(G'^2+G''^2)^{1/2}$
Complex viscosity	$\eta^*=G^*/\omega=(\eta'^2+\eta''^2)^{1/2}$
Dynamic viscosity	$\eta'=G''/\omega$
Complex compliance	$J^*=1/G^*$
Storage compliance	$J'=G'/(G')^2+(G'')^2$
Loss compliance	$J''=G''/(G')^2+(G'')^2$
Tangent delta	$\tan(\delta)=G''/G'$

In dynamic testing, a sample is subjected to an alternating strain, and the resulting stress is measured. Most often the form of the alternating strain is sinusoidal, and the deformation is usually in shear mode. In food rheology dynamic measurements are rarely made in compression mode (Weipert, 1997). The amplitude of strain is usually chosen to be small so that the stress response proportional to the input strain amplitude or, in other words, the response is in the LVE region. Then the material properties, G' (f), G'' (f), and tan δ are determined.

For a Hooken (ideal elastic) solid the loss angle $\delta=0$, so all the energy is stored (i.e., recoverable). For Newtonian (ideal viscous) liquid $\delta=\pi/2$, so all the energy is dissipated (i.e., lost) during deformation. The corresponding values for tan δ are 0 and ∞. For a viscoelastic material, $0<\delta<\pi/2$, and thus the relative amount of energy stored or dissipated is determined from the magnitude of phase angle.

An increase in tan δ indicates that the material is reacting to an external stress in a relatively more viscous and less elastic manner. For instance, tan δ is used as a measure of the dynamic character (life-time) of protein-protein bonds in rennet casein gels (Van Vliet, 1989). When, $G'=G''$, tan $\delta=1$ and the modulus value at this point is called the "crossover modulus". At tan $\delta=1$, the material is equally liquid and

solid. When tan δ<1, the material is more solid-like, and when signifies that the state of the material is crossing over from predominantly solid to liquid or vice versa.

1.6.3.1 Types of SAOS measurements

There are four major experimental variables in any dynamic test: strain (or stress), frequency, temperature and time. Thus, different types of dynamic tests can be set up changing one or more of these experimental variables. The commonly performed tests are: strain (or stress) sweep; frequency sweep; temperature sweep and time sweep. Each of these tests serves to fulfill a certain objective.

Depending on the input variable, two types of rheometers are commercially available: "controlled strain" with torque measurement and "controlled stress" with angular motion measurement. Bafna (1996) examined the precision of complex viscosity measurements in the constant stress and constant strain modes. One of the important findings of Bafna's work (1996) is that constant stress measurements provide improved precision at lower frequencies, whereas constant strain measurements are more precise at higher frequencies.

1.6.3.1.1 Strain (or stress) sweep test

In this type of oscillatory tests the moduli are measured as a function of increasing strain while frequency is fixed. Usually, the objective of a strain sweep test is to determine the critical point beyond which the dynamic shear moduli (G^*, G', G'') become dependent on the input variable, strain. In other words, it is carried out to determine the limits of linear viscoelasticity. The strain sweep test is the first step in dynamic mechanical analysis and always performed prior to a frequency sweep test in order to specify the strain level for frequency sweeps.

In case of controlled stress dynamic rheometers, a stress sweep is performed and serves the same purpose of identifying the limit of LVE region.

1.6.3.1.2 Frequency sweep test

The frequency sweep is probably the most versatile rheological test to characterize viscoelastic behavior of materials. In this test, a sinusoidal strain (or stress) of fixed amplitude is imposed on the material and dynamic moduli are determined over a wide range of frequencies. The resultant plot is also known as the "mechanical spectrum" of the material. The strain amplitude must be selected with care and, under all conditions, should be less than the strain limit of linear viscoelasticity. Contemporary rheometers are capable of measuring dynamic properties at a wide range of frequencies, typically from 0.01 Hz to 100 Hz. With advanced rheometers one can even conduct oscillatory measurements at frequencies as low as 10^{-5} Hz. With such instruments, the low frequency selection is dictated mainly by the stability of the sample and researcher's patience in performing long dynamic measurements. For instance it takes nearly 28 h to complete one oscillation cycle at 10^{-5} Hz. An efficient way to shorten the total experimental time is to use, whenever applicable, the time-temperature superposition (TTS) procedure. In the high frequency range, the measurements have been limited due to inertia effects. However performance improvements at high frequencies are reported for new rheometers (Eidam et al., 2001).

1.7 Pekmez

Fruit juice concentrate (Pekmez), a traditional Turkish food, is a concentrated and shelf-life extended form of mulberry or grape juice formed by boiling without the addition of sugar or other food additives (Gökçe and Çizmeci, 1965). Most of its carbohydrate is in the form of glucose and fructose; it easily passes into the blood without digestion. Since pekmez contains high amounts of sugar, mineral and organic acid, it is a very important food product in human nutrition (Üstün and Tosun, 1997). The production of pekmez has been continuously increasing because of nutritional importancy. It contains great amount of sugar and useful amounts of mineral elements such as K, Ca, Fe, P and Mg (Kayahan, 1982). The high iron content makes it a recommended treat for anemia (Öztürk and Öner, 1999). Pekmez has an important function in the working of the brain, in which glucose is an energy source. Furthermore, pekmez confers approximately 293 kcal/100 g of energy and

also has important organic acids and mineral materials. There are many publications about production, composition, standardization and health benefits of pekmez (Tekeli, 1965; Yazıcıoğlu, 1967; Kayahan, 1982; Batu, 1991a; Aksu and Nas, 1996; Üstün and Tosun, 1997 Demirözü et al., 2002; Kaya and Belibağlı, 2002; Şengül et al., 2005).

Fresh or dried grapes are particularly used in the production of pekmez, but apple, prune, watermelon, mulberry, apricot and sugar beet can also be used in pekmez production. The raw materials and processing conditions differ geographically. Pekmez is produced in all regions of Turkey, but varieties of grapes and processing techniques used in pekmez production are different. The most popular pekmez samples have been produced in different Anatolian cities such as Zile, Kastamonu, Sivrihisar, Afyon, Kahramanmaras, Gaziantep and Hatay in Turkey. These products are called with the names of produced regions, for example Gaziantep pekmez (Kaya and Belibağlı, 2002).

The first step in pekmez production is washing and crushing the grapes. Pressing the crushed grapes by a pneumatical or mechanical press provides us with a grape juice. Hot pressing is preferred so as to obtain the grape juice that has a high total solid and tannin content. The grape juice is then boiled with a calcareous substance called ''pekmez earth'' containing approximately 75-90% of calcium carbonate. The pekmez earth lowers the acidity caused by naturally existing tartaric and malic acids by precipitating them as calcium tartarate and calcium malate. Grape juice is concentrated usually in open vessels and rarely under vacuum to obtain 65–68 $^{\circ}$Brix; this product is called liquid pekmez (Figure 1.3). The liquid pekmez is mixed with 5–15% previously prepared crystal seed and stirred vigorously. It is then let to solidify and brighten the color for 2–3 days. The crystal seed is a previously mashed old solid pekmez. The added crystal seed causes nucleation on the concentrated liquid pekmez and results in crystallization of the sugar compound (Tekeli, 1965). The final product, called solid Gaziantep pekmez, is hard in texture and has a pasty form which can be easily spread on a slice of bread. It may be brown and yellow in color depending on the process (Kaya and Belibağlı, 2002)..
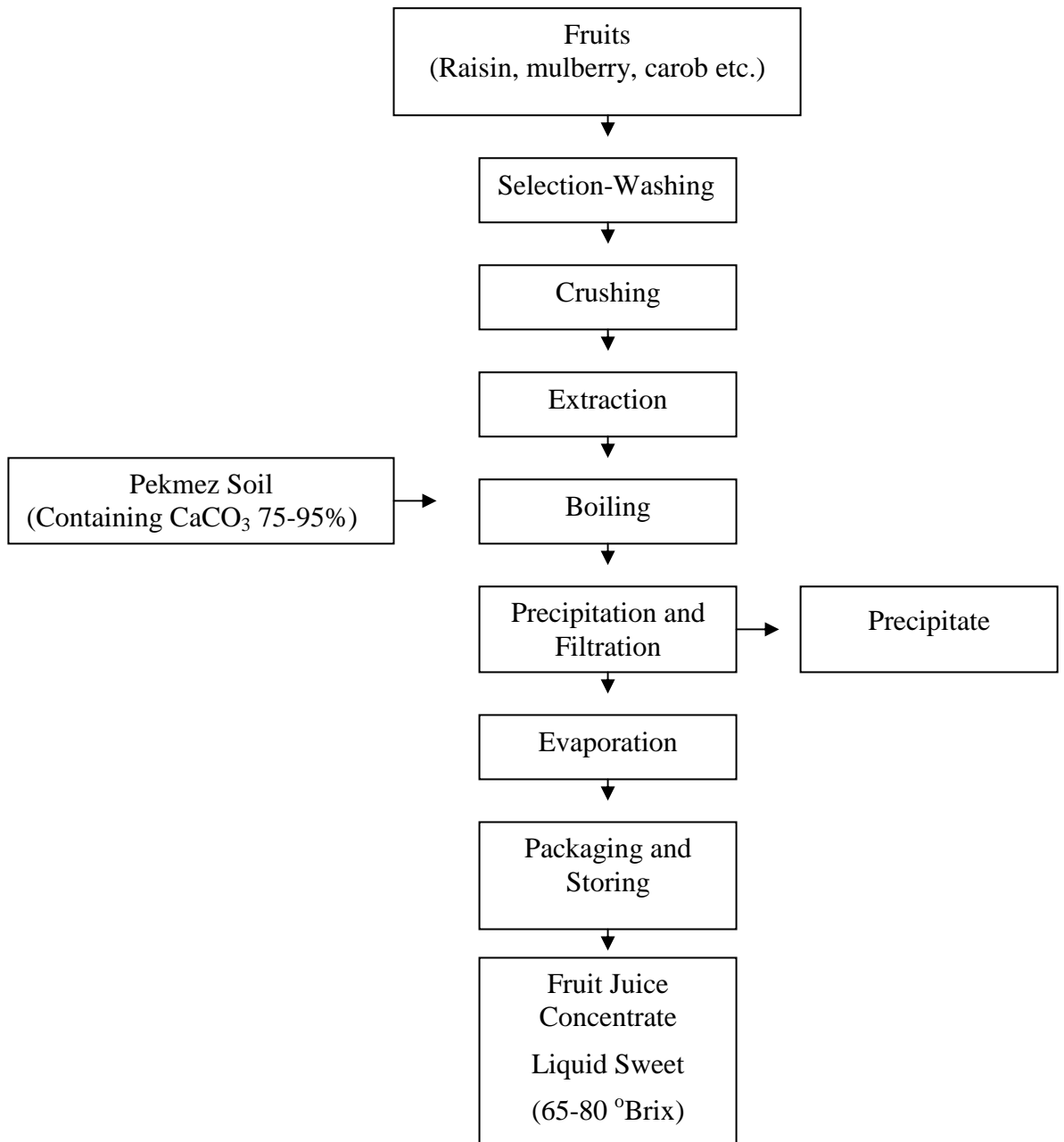
Figure 1.3 Manufacturing method for fruit juice concentrates (Pekmez)

The flowchart shows the following process:

Fruits (Raisin, mulberry, carob etc.) →

Selection-Washing →

Crushing →

Extraction →

Boiling (← Pekmez Soil (Containing $CaCO_3$ 75-95%)) →

Precipitation and Filtration (→ Precipitate) →

Evaporation →

Packaging and Storing →

Fruit Juice Concentrate Liquid Sweet (65-80 °Brix)

CHAPTER II

MATERIALS AND METHODS

2.1 Materials

The dehulled and roasted (150°C for 100 min) sesame seeds obtained from Özen Gıda A.Ş. were milled using a commercial miller (Gürmaksan, Co., Turkey) to produce tahin in our laboratory (Appendices, Figure B1). In this device, the sesame seeds pass into a narrow gap between a high speed rotating grooved disc and the stationary casing of the mill. Intense shearing action results in breakage of the feed. Tahin samples having different particle size were produced by manually controlling the gap between the discs.

Pekmez used in tahin-pekmez blends was supplied from a local producer in Gaziantep at spring harvest.

2.2 Pekmez/Tahin Blend Preparation

50 ml burettes containing 50 ± 0.5 grams of pekmez and tahin (the lowest sized sample: 3.86 μm) blends were prepared according to the varying pekmez proportions 6-40% (wt%) (Figure 2.1).

For colloidal stability measurements; 6, 8, 10, 15, 20, 25, 30, 35 and 40% pekmez containing blends were prepared and stored at 25°C for one month.

For rheological analysis; 10, 12, 15, 16, 17, 18, 19, 20, 30 and 40% pekmez containing blends were prepared and stored at 25°C for one month.

For sensory and texture analyses (mechanical hardness); 8, 10, 12, 15, 20% pekmez containing blends were prepared and stored at 25°C for one month.

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Pekmez-Tahin Blends (6-40% pekmez)

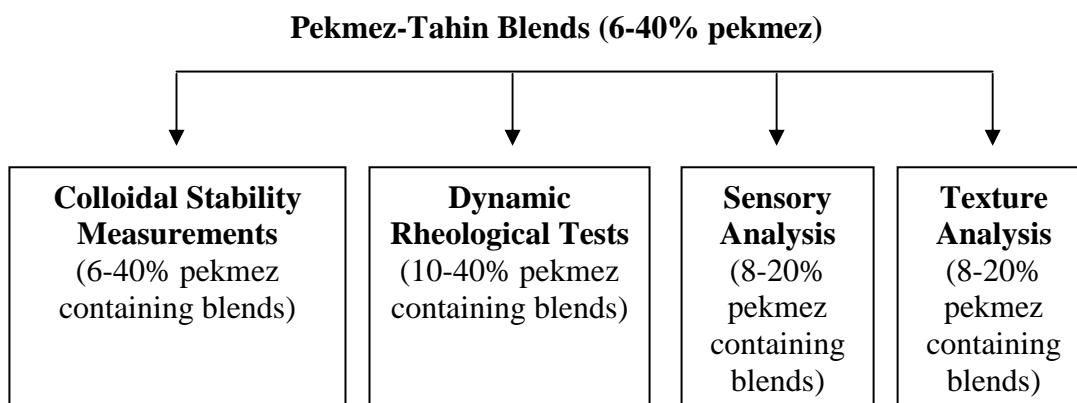| Colloidal Stability Measurements (6-40% pekmez containing blends)	Dynamic Rheological Tests (10-40% pekmez containing blends)	Sensory Analysis (8-20% pekmez containing blends)	Texture Analysis (8-20% pekmez containing blends)

Figure 2.1 Experimental design of pekmez-tahin blends

2.3 Chemical Analysis

Protein content of tahin was determined according to AOAC (AOAC, 1990) method. Kjeldahl method was used through digestion, distillation and titration steps. For digestion 2 g sample, 10 g potassium sulfate, 25 ml sulfuric acid, small amount of copper sulfate and boiling chips were put into the digestion tube and heated until digestion was completed (nearly 2 h). When the digestion was completed, clear light green color was observed. For distillation; 50 ml water, 50 ml of 50% sodium hydroxide and steam was used and distillate was collected into erlenmayer flask, which has 25 ml of 4% boric acid. For titration; methyl red was added as an indicator to the flask, which contains distillate and boric acid, and titration was done by 0.1 N hydrochloric acid. From the titration volume, the amount of $N-NH_4$ was calculated and protein was found by multiplying this value by 5.7.

The oil content of tahin was measured using oil extraction system (Velp Scientifica SER148, Italy) with hexane as solvent. It was performed for 6 h. Then, hexane was removed from oil by using rotary vacuum evaporator.

Moisture content of tahin was determined using method described in TSE 1201 EN ISO 1741. 25 g sample was weighed to yield a minimum of 5 mL water and recorded weight to nearest 1 mg, and transferred to 500 mL flask. Then, sufficient toluene was added to cover sample completely. Immediately it was filled receiving tube with toluene, pouring it through top of condenser and brought to boil and distilled slowly until most of the water passes over. It was distilled for 1hr to obtain clearing at the top of the condenser. When all water had apparently been distilled,

washed down condenser by pouring toluene in at top and continue distillation for 15 min to ensure all water is distilled. Receiving tube was allowed to come to room temperature and read volume of water in lower layer of receiver and record volume to nearest 0.01 mL.

Ash content of tahin was determined using method described in TSE 6399. 5 g sample was mixed with 2 ml ethanol and ignited at $900^{o}C$ until the cooled sample white or nearly white. From remaining sample ash content was calculated.

The refractive index of tahin and brix of pekmez were determined using automatic refractometer (Model PTR 46X, Index Instruments U.S., Inc.).

The density of tahin and its separated oil at room temperature ($25^{o}C$) was determined using a picnometer. The density of solid particles was calculated using the equation 2.1 (Rahman, 1995):

$$\rho_s = \frac{0.48}{\dfrac{1}{\rho_t} - \dfrac{0.52}{\rho_o}} \qquad\qquad 2.1$$

where ρ_s is the density of the solid particles, 0.48 is the mass fraction of solid particles, ρ_t is the density of tahin, ρ_o is the density of separated oil and 0.52 is the mass fraction of the oil.

2.4 Particle Size Analysis

The particle diameter and size distributions of tahin samples were measured using a laser scattering particle size distribution analyzer (LA-950, Horiba Ltd., France) (Appendices, Figure B2). The experiments were carried out using hexane to dilute the samples. The instrument was set at refractive indexes of 1.376 and 1.475 for hexane and sesame paste, respectively. The data were obtained and analyzed using the program; LA-950 for Windows (Horiba NextGen Project 2006 J.Y. Horiba) (Figures B3-B4). Particle size calculations were based on the Mie-Scattering theory. The mean, median, mode and diameter on cumulative (10 and 90%) were obtained. Unless otherwise stated, given particle size values were median values throughout

the study. Particle size analyses were applied for each sample five times and the average of them was given. The parameters obtained from particle size distribution graphs (a representative example in Appendices, Figure B4) are given below:

Mean: This is some arithmetic average of the data. There are a number of means that can be calculated for particles.

Median: This is the value of the particle size which divides the population exactly into two equal halves i.e. there is 50% of the distribution above this value and 50% below.

Mode: This is the most common value of the frequency distribution i.e. the highest point of the frequency curve.

$D_{V,10\%}$ and $D_{V,90\%}$: They indicate the coefficient of variation. It relates the width (breath) of the distribution to mean in percentage.

2.5 Colloidal Stability Measurement

Test tubes (1.5 cm diameter, 15 cm height) containing 16±0.5 grams of freshly prepared tahin samples were stored at 20, 30 and 40°C±1. 50 ml burettes containing 50±0.5 grams of pekmez-tahin blends were stored at 25°C±1. The height of formed free oil-phase (transparent) resulting from sedimentation of solid particles (Appendices, Figure B5) was measured periodically using a dial micrometer (Mitutoya, Japan). Percent colloidal stability (CS) was determined using the equation (Makri and Doxastakis, 2006) below:

$$CS\% = \frac{H_t - H_o}{H_t} * 100 \qquad\qquad 2.2$$

where H_o: height of oil phase and H_t: total height of tahin in the test tubes.

2.6 Color and Image Analyses

Color parameters (L-, a-, b-, and YI-values) of tahin samples and pekmez/tahin blends were determined using a HunterLab ColorFlex, A60-1010-615 model colorimeter (Hunter-Lab., Reston, VA) standardized each time with a white and a black ceramic plate. The color parameters were expressed as L-(whiteness or brightness/darkness), a-(redness/greenness), b-(blueness) and YI-(yellowness index) at any time, respectively.

For image analysis of tahin, a smear was prepared and evenly spread on a clean slide and covered by a cover slip. The samples were monitored under the polarized light microscope (Olympus BX51, Olympus Optical Co., Ltd., Tokyo, Japan) and photographed (20X objective) with a camera attached to the microscope. The pictures were analyzed with IMAQ vision builder (v.6.0, National Instruments Corp., Austin, Texas, USA) digital analyzing program.

2.7 Rheological Analyses

Rheological measurements were conducted using a rheometer (Haake Rheostress RS) coupled with a Peltier/Plate TCP/P temperature control unit and external DC 10 circulator (Haake GmbH, Karlshure) using cone and plate system (d: 35 mm, $\alpha = 2^{o}$). Data were analyzed using Rheowin Pro software (version 2.64, Haake).

2.7.1 Flow curves

The flow curves of tahin samples were measured at the temperatures of 15, 30 and $40^{o}C$. The samples were allowed to rest 5 min after loading, before measurement. The hysteresis loop was obtained by registering shear stress from 0.08 to 200 s^{-1} in 120 s and down in 120 s, samples were hold at 200 s^{-1} for one minute between two ramps. Areas under the upstream data points (A_{up}) and under the downstream data points (A_{down}) as well as the thixotropic area ($A_{up}-A_{down}$) were obtained.

The power law model which is the most frequently used for engineering application was applied to describe the steady shear flow data (Equation 1.4).

2.7.2 Oscillatory tests

The stress sweep test was carried out at $25^{o}C$ to determine the linear viscoelastic region of samples with appropriate stress value selected as 1 Pa. In frequency sweep test, viscoelastic parameters (G' and G'' moduli) were recorded versus frequency (f) between 0.01-50 Hz for fresh and stored tahin samples and pekmez/tahin blends.

2.8 Texture Profile Analysis

Texture profile analysis (TPA) of different proportions of pekmez containing (8, 10, 12, 15, 20%) pekmez/tahin blends were performed using a TA.XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY/Stable Microsystems, Godalming, UK). Test conditions were: P/25 aluminum cylinder probe (25 mm diameter); test speed 1 mm/s; pretest speed 1 mm/s, post test speed 1 mm/s; compression 25%; time pause, 5s. Data collection and calculation were done using the Texture Expert Exceed Version 2V3 (Stable Micro Systems, 1998).

2.9 Sensory Evaluation

Sensory analysis of different proportions of pekmez containing (8, 10, 12, 15, 20%) pekmez/tahin blends was carried out according to Gills and Resurreccion (2000), and Dubost et al. (2003) with slight modifications. Twenty panelists were chosen from Food Engineering Department of Gaziantep University. Ages ranged from 25 to 56. Eight of them were females. All panelists were non-smokers. Instructions were given in full to panelists beforehand. They evaluated the appearance (darkness), taste, oiliness, adhesiveness, graininess, hardness, spreadability and overall acceptability attributes (Appendices, Figure B6). The

blends were prepared 30 days in advance and stored at the room temperature (25°C). Each panelist received a rating form (5: most and 1: least), a slice of white bread, and a knife for each blend. Panelists cleansed their palates with water before rating each sample.

2.10 Statistical Analysis

The statistical analyses were done by the analysis of variance method (ANOVA) to determine the effect of particle size and storage temperature on colloidal stability, and rheological properties. The ANOVA tests were performed using SPSS 9.0 (SPSS Inc., Chicago, IL, USA). Duncan test was also applied to detect the differences of responses on colloidal stability of stored tahin samples. Sensory and texture analyses data were analyzed with Pearson correlation method (SPSS Inc., Chicago, IL, USA). The coefficient of determination (R^2) of regression analysis was determined by using commercial software (SigmaPlot 8.0, Jandel Scientific, San Francisco, USA). All measurements were carried out in triplicate, except particle size distribution measurements. The reproducibility was $\pm$ 5% on average. All statistical results were tabulated and given in Appendices for each test separately.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Composition

Chemical composition of tahin was determined as 52.2% oil, 27.2% protein, 0.3% moisture, 1.0% ash (carbohydrate content was not measured). The oil and protein content of tahin used were found within the range (50.0-65.0 and 17.0-27.0%, respectively) given in literature (Sawaya et al., 1985; Damir, 1994; Özcan and Akgül, 1994). However, compositional differences can exist owing to various factors such as the variety of sesame seed, its country of growth, the production techniques used, etc. The density values of tahin and its separated oil phase measured at room temperature was found as 1094 and 944 kg m^{-3}, respectively. The density of solid particles in tahin calculated using equation 2.1 was 1321 kg m^{-3}.

3.2. Particle Size Distributions

The mean, median, mode and diameter on cumulative (10 and 90%) of tahin samples were obtained and listed in Table 3.1. Using different milling rate during production of tahin resulted in the variations of the span and the height of the peaks, however all histograms represented multimodal particle size distributions with a breadth extent from 0.30 to 2000 μm. The presence of different and resolvable species in the sample caused multimodal histogram in the particle size distribution of sesame paste. Similar multimodal histograms were reported for peanut flour (Lima et al., 2000) and chocolate (Afoakwaa et al., 2007).

Table 3.1 Parameters of particle size distribution by laser scattering instrument of tahin samples

Sample Code	Median (µm)	Mean (µm)	Mode (µm)	$D_{V,10\%}$ (µm)	$D_{V,90\%}$ (µm)
S1	32.90	129.11	281.33±3	0.95	375.43
S2	26.13	101.82	245.68±5	1.06	309.67
S3	21.55	74.89	213.66±5	0.86	239.22
S4	8.83	34.77	3.64±0.05	0.73	110.96
S5	7.02	34.77	3.63±0.03	0.72	80.04
S6	5.76	19.04	3.64±0.04	0.25	50.80
S7	3.86	14.23	0.31±0.01	0.25	26.14

The samples with the highest and the lowest median values are shown in Figure 3.1. The obtained histograms showed that all samples had tetramodal distributions except S7 sample that gave trimodal distribution. The highest diameter value and cumulative volume percentage of each peak of the histograms are given over the peaks in the Figure 3.1. 50.4% of size distribution of S1 sample having 32.9 µm median values was greater than 83.7 µm with a maximum 661 µm while 43.3% of S7 were lower than 1.3 µm. Main peaks (50.4% and 43.3%) represented mesokurtic distribution and the others tended to platykurtic for samples S1 and S7. Distribution is more important than mean particle size and if more than one peak was identified, a mean value should not be used (Lima et al., 2000). Since nearly all histograms had similar multimodal distributions the median values could be used to describe the particle size of the systems (Malbos et al., 2007). Thus the median values were used to differentiate the samples from each other in this study.
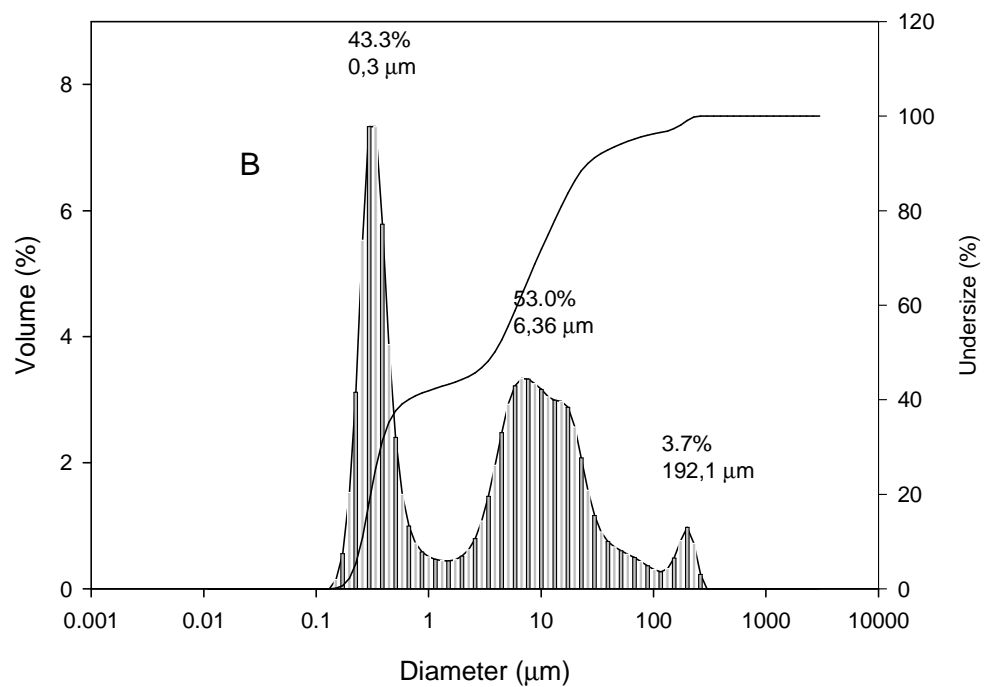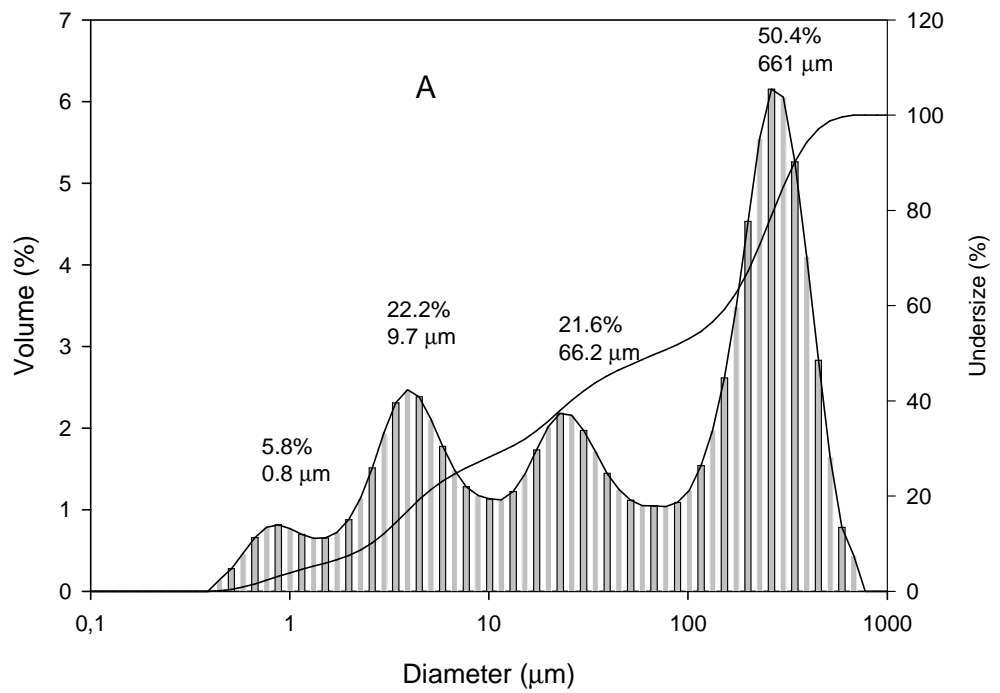
Figure 3.1 Frequency histogram with the right ordinate and cumulative undersize distribution with the left ordinate for samples having median values S1: 32.9 μm (A), S7: 3.86 μm (B)

3.3 Colloidal Stability

The variations in colloidal stability of tahin stored at 20, 30 and 40°C were tabulated in Table 3.2. It was clear that decreasing particle size improved the colloidal stability. This could be explained with declining particle size improves dispersion of the solid phase in oil phase and interaction of solid and oil phases and increasing cohesiveness (Barnes et al., 1989).

Table 3.2 Colloidal stability values of tahin having different particle size stored for 26 days at different temperature

Sample Code	Colloidal Stability (CS %)		
	20°C	30°C	40°C
S1	88.56[a*]	84.66[a]	83.96[e]
S2	92.98[b]	87.06[c]	82.67[c]
S3	94.42[c]	86.51[b]	80.9[b]
S4	96.52[d]	86.81[d]	80.55[a]
S5	95.9[e]	86.7[d]	82.96[d]
S6	96.66[f]	89.68[e]	85.32[f]
S7	97.12[g]	94.42[f]	92.84[g]

[*]Numbers followed by different letters in a column are significantly different ($p<0.05$)

Actually, from Figure 3.2, it is understood that higher particle sized samples lost the stability at a higher rate than the smaller ones. From the Stoke's Law (Equation 3.1), the sedimentation velocity values of S1 and S7 were calculated as 8.95 and 0.12 mm h^{-1}.

$$V_g = \frac{d^2(\rho_p - \rho_f)}{18\eta}g \qquad\qquad 3.1$$

where Vg: sedimentation velocity (m s^{-1}); d: particle diameter (m); ρ_f and ρ_p: solid and continuous (oil) phases density (kg m^{-3}), respectively; η: continuous phase viscosity (0.0895 Pa.s at 20°C), and g: acceleration of gravity (9.81 m s^{-2}).

Stoke's law is clearly predicated on a number of basic assumptions: all particles have the same density and spherical shape. The results of colloidal stability measurements and Stoke's law calculations correlated to each other, but calculated sediment velocities (Stoke's law) were found higher than measured ones (colloidal stability). This was probably due to the structural properties of solids in tahin (surface area, density and shape differences of particles).
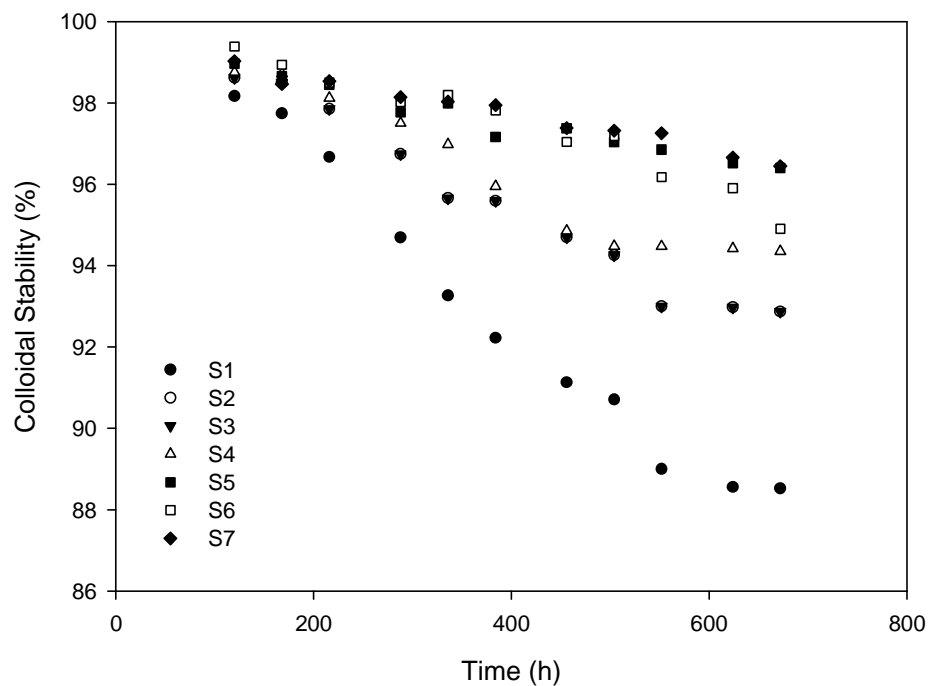

Figure 3.2 Effect of particle size on colloidal stability of tahin samples at 20°C (S1-S7 are the codes of samples given in Table 3.1)

As the storage temperature increased, the colloidal stability of the samples decreased. This reduction probably is due to the low viscosities of oil at high temperature. It was found that although effect of both parameters (particle size and storage temperature) on tahin stability was found as significant (p<0.05), but the temperature had more pronounced effect on the colloidal stability of tahin with respect to the highest F value (Appendices, Table A1) especially for the samples having particle size greater than 5 μm. Two samples with having different particle

size were selected to show the effect of storage temperature in Figure 3.3. There was a linear relationship between particle size and colloidal stability at 20°C, however with increasing temperature this trend has changed, almost lost.
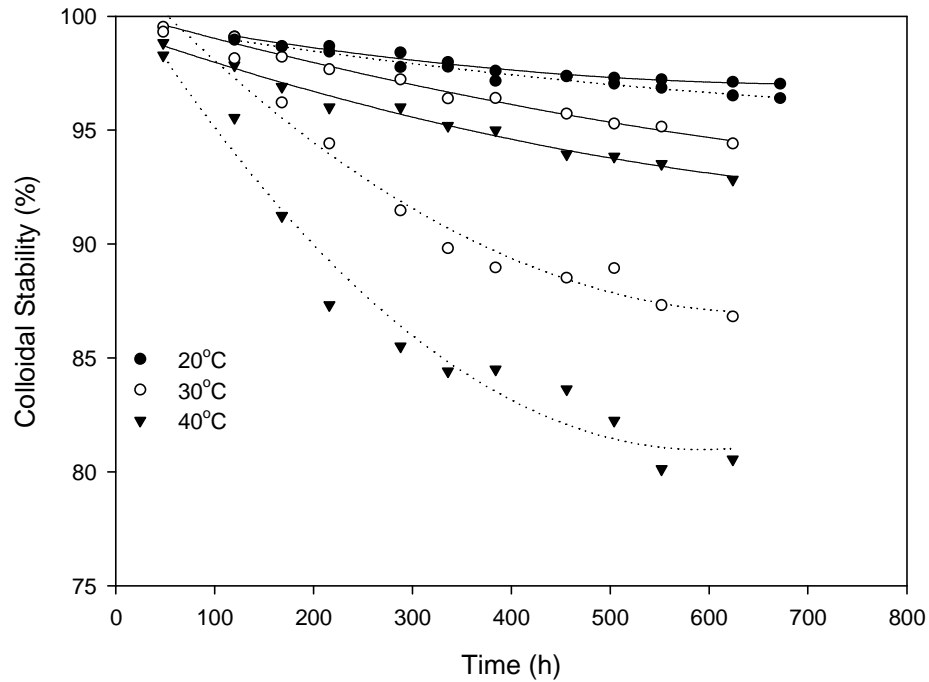

Figure 3.3 Effect of storage temperature on colloidal stability of tahin samples; S5: 7.02 μm (dotted curves) and S7: 3.86 μm (line curves)

The protein analysis of the separated oil from tahin and its solid phase proved that separated oil phase did not contain protein but around 50% of the oil was present in sediment cake. The single datum in literature was in a good agreement with our result. Al Yamani (1996) reported that oil separation of tahin almost reached equilibrium within 2 months with the values 11.2 and 13.7% at 25 and 35°C. There was not any information about particle size of his sample, and at the same time the author applied centrifugation at 4000 rpm for 2 hours and suggested that maximum oil separation was only around 50% (called as free oil) and the rest of the oil has been found as bound oil making a complex with the protein part of the tahin. Under centrifugation conditions, the sediment density of tahin, namely proteins, increases and releases a larger volume of free oil. After sedimentation, the redispersion of sediment into the oil phase was very difficult.

3.4 Image and Color Analyses

The image analyses of some tahin samples having different particle size are shown in Figure 3.4. They show the system in tahin composed of a suspension of solid particles in a continuous oil phase. The solid particles represent essentially proteins and other constituents of the sesame seeds. From here, it can be concluded that the colloidal state of tahin is solid in oil suspension. A flowery structure can be seen in detail around the protein. It is predicted that this structure facilitates flocculation of the collapsed proteins each other to form more solid like constitution and release of free oil to the upper surface.
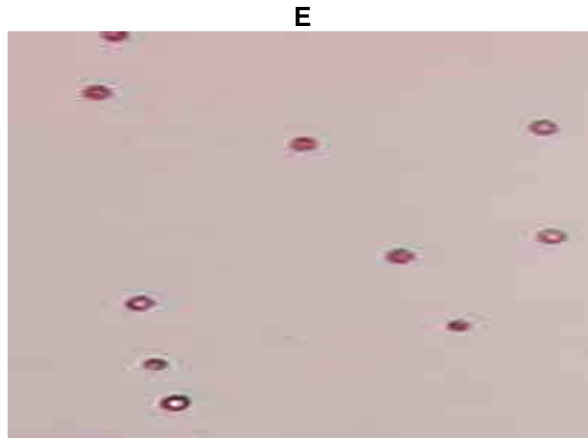
E
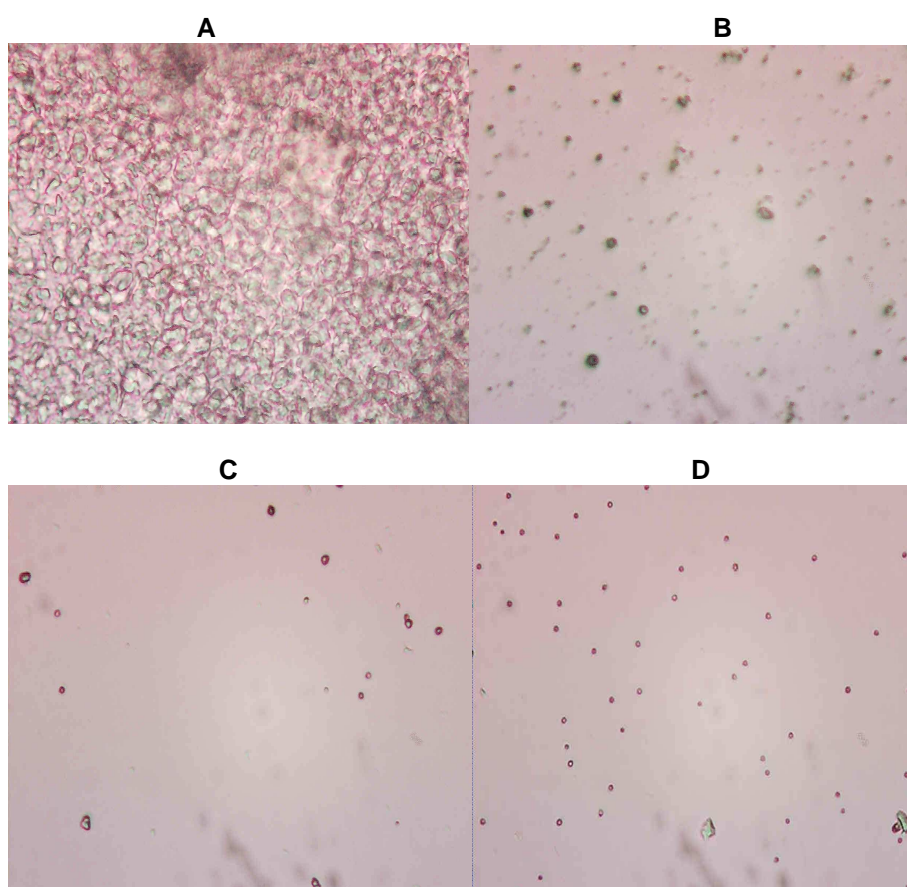
Figure 3.4 Image analyses of some tahin samples (A shows direct image of sample having 32.9 μm particle size; B, C, D shows the image (after wiping gently on lamel) of samples having 32.9, 21.55 and 7.02 μm particle size respectively; E shows the enlarged section cutted from Figure D

It was found that L-values of tahin decreased with the reduction of particle size (Figure 3.5). The color of tahin influenced by main composition and by the presence of colorants, like carotene, green pigments, chlorophyll etc., which their effect on color increased with the roasting and dehulling processes (Elleuch et al., 2007). The overall appearance of a food is therefore determined by a combination of light scattering and absorption phenomena (Chantrapornchai et al., 1999). Scattering is largely responsible for the turbidity, opacity or lightness of an emulsion, whereas absorption is largely responsible for the chromaticness (blueness, greenness, redness, etc.). The degree of scattering by an emulsion/ colloid system depends on the concentration, size and refractive index of any particles (Chanamai and McClements, 2001) whereas the degree of absorption depends on the concentration and type of chromophores present (McClements, 2002).
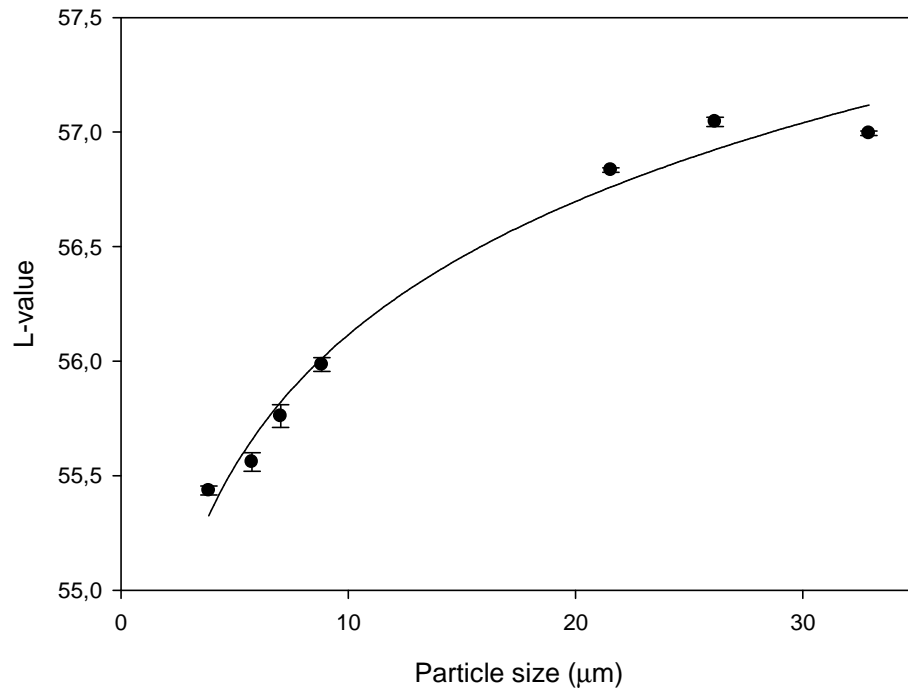
Figure 3.5 Changes in L-value of tahin with particle size

Probably, high amount of small and free particles in the low sized tahin samples increased absorption of light. Besides of this, high shear intensity during milling caused heating that accelerates browning reactions. It was reported that tahin includes carbohydrates between 6.4-21.0 wt% and browning reaction is detected in tahin (Afoakwaa et al., 2007). The second order equation (Equation 3.2) described adequately (R^2: 0.9967) the relationship between L-value and median particle size values (Figure 3.5).

$$L\text{-value} = 54.87 + 0.14(PS) - 0.0024(PS)^2 \qquad 3.2$$

where PS: median particle size.

3.5 Rheological Measurements

3.5.1 Flow behavior

Figure 3.6 shows that the tahin samples having different particle size exhibits shear-thinning (pseudoplastic) behavior since the apparent viscosity decreases with shear rate. It is shown that the reduction of particle size has an obvious effect on apparent viscosity of tahin. The fall in apparent viscosity with shear rate seems to be as a result of the disruption of three dimensional structures through the breaking of primary and secondary bonds (Davis, 1973). This result confirms the results of previous studies on flow behavior of tahin (Abu-Jdayil, 2002; Abu-Jdayil et al., 2004). It is evident from Figure 3.6 that the apparent viscosity at any given shear rate increases by increasing particle size. Barnes (1989) also demonstrated that the viscosity of a suspension increases when the particles form flocs that enclose and immobilise some of the continuous phase. It was reported that at processing viscosities, moving from monomodal to multimodal distributions has significant effect on the relative viscosity; but the benefit of increasing greater trimodal distributions is small (Servais et al., 2002). On the other hand, all tahin samples represented distributions greater than trimodal, their rheological properties became different. This was probably due to the differences in the particle size of samples.
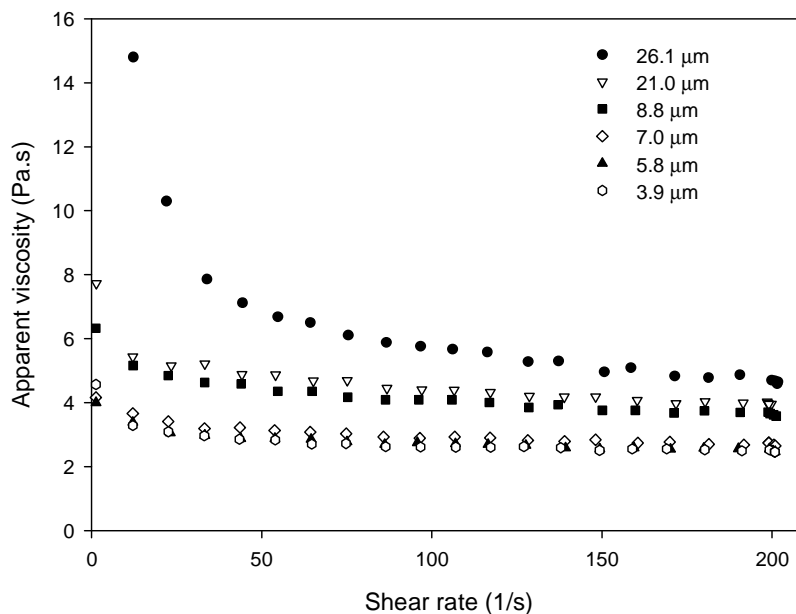
Figure 3.6 Apparent viscosity of different sized tahin samples as a function of shear rate at 15°C

The flow curves of tahin samples having different particle size were determined at 15, 30 and 40°C (Figures 3.7-3.9) both in the forward (increasing shear rate) and backward (decreasing shear rate) directions. Decreasing particle size caused important deviations from non-Newtonian behavior. The presence of hysterises loops is an indication of thixotropic behavior. The formation of loops was explained by Altay and Ak (2005) as shearing caused a gradual breakdown of aggregate structures in tahin during the first forward ramp and this resulted in a decrease in shear stress.

Figure 3.7 Effect of particle size on flow curves of tahin samples at 15°C

Figure 3.8 Effect of particle size on flow curves of tahin samples at 30°C

Figure 3.9 Effect of particle size on flow curves of tahin samples at 40°C
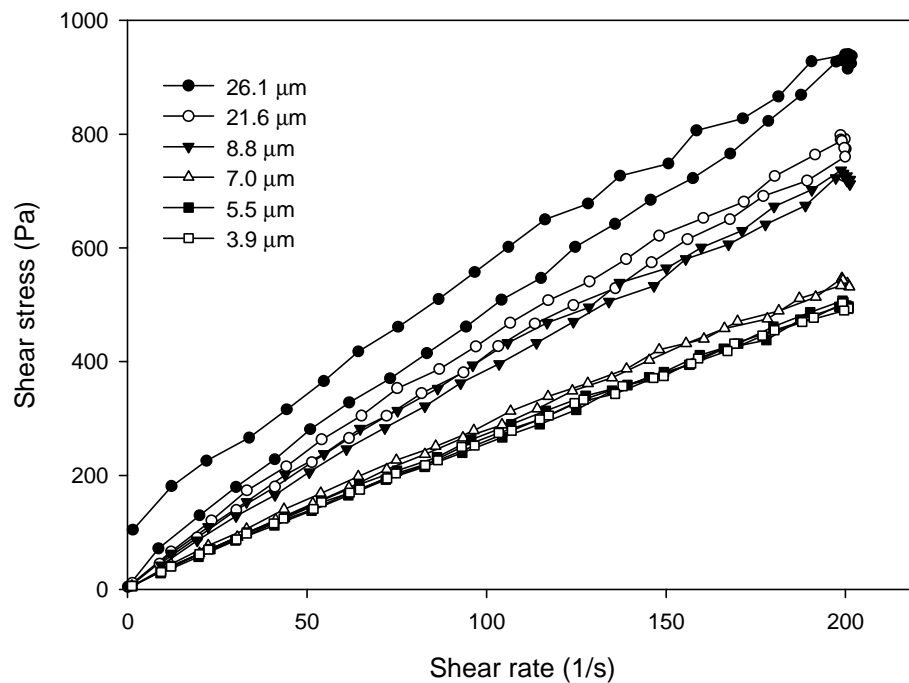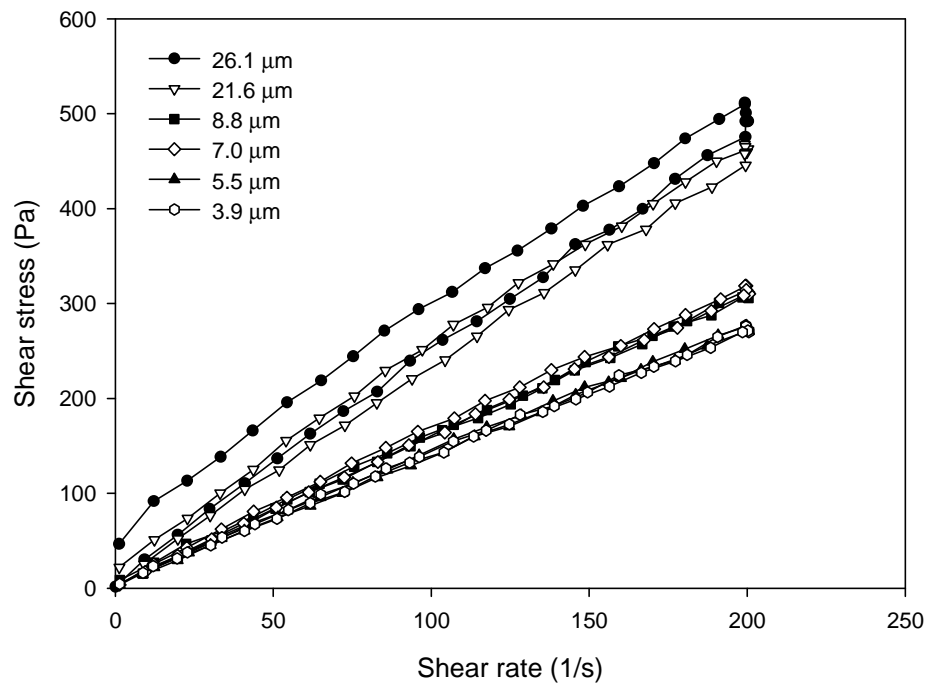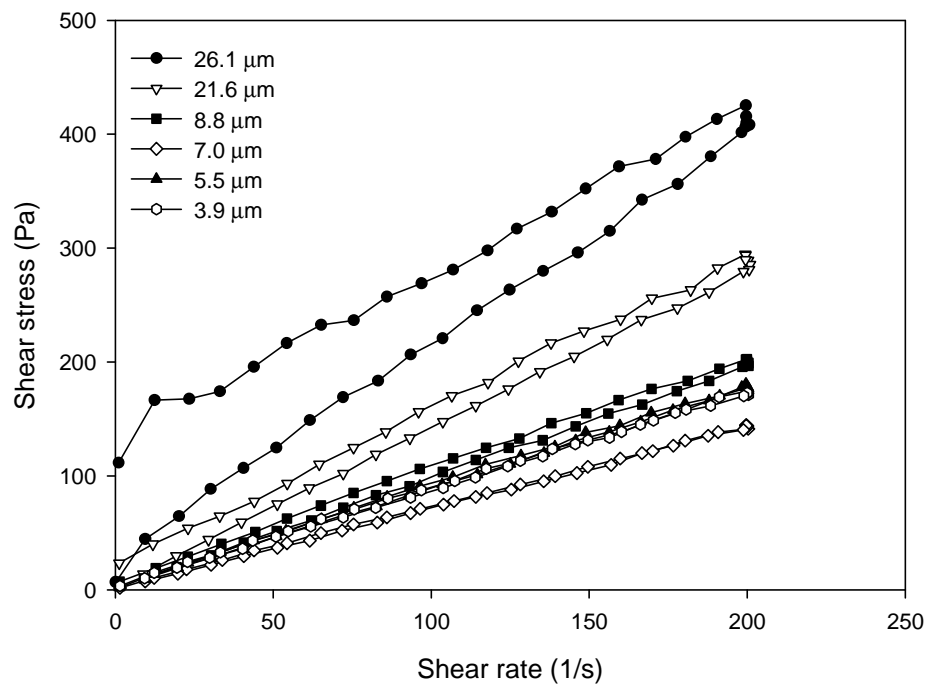
In order to evaluate the flow behavior characterization of tahin samples, Power law model was selected (Equation 1.4) (Çiftçi et al., 2008). Thixotropic area was calculated to complete the comparison within the samples (Table 3.3). The size of thixotropic area decreased with the reduction particle size of tahin samples. The consistency coefficient (K) and flow behavior index (n) of the samples were also represented in Table 3.3. The magnitudes of K values decreased but n values increased by decreasing particle size.

Table 3.3 Effect of particle size and temperature on flow parameters of tahin samples

Particle size (μm)	K (Pa.s)			n			A_t		
	15^oC	30^oC	40^oC	15^oC	30^oC	40^oC	15^oC	30^oC	40^oC
S1	UD	UD	UD	UD	UD	UD	126300	77230	74570
S2	24.29	15.20	10.38	0.68	0.72	0.78	17040	62380	9114
S3	8.79	5.38	3.36	0.85	0.84	0.84	5099	4470	3473
S4	7.68	2.62	1.76	0.86	0.92	0.89	4465	1205	1868
S5	4.82	2.34	0.92	0.89	0.93	0.93	2209	1264	971
S6	4.15	2.02	1.28	0.91	0.93	0.93	939	1371	800
S7	3.81	2.07	1.28	0.92	0.92	0.93	134	999	714

K, n, and A_t are the consistency coefficient, flow behavior index and thixotropic area, respectively. UD: undetectable.

Abu-Jdayil et al. (2002) reported similar temperature effect on flow properties of tahin. They suggested that there was an irreversible, shear induced, and permanent damage affecting the molecular structure of food biopolymers, namely fats. However, in this study it was detected that protein was the most effective constituent on the structural damage because separated sesame oil phase had Newtonian characteristics with viscosity values as 0.0995, 0.0696, and 0.0499 Pa.s determined at 15, 30 and 40^oC, respectively, while solid parts (mainly protein) exerted solid like characteristics. The effect of measurement temperature on the steady shear flow behavior of tahin sample S5 (median size: 7.02 μm) is shown in Figure 3.10. The extent of hysterises loops decreased as the temperature increased from 15 to 40^oC

(Figure 3.10). The increased motions of solid particles and continuous phase at higher temperatures probably hinder flocculation or help disrupt aggregate structures when the shear is applied (Altay and Ak, 2005).
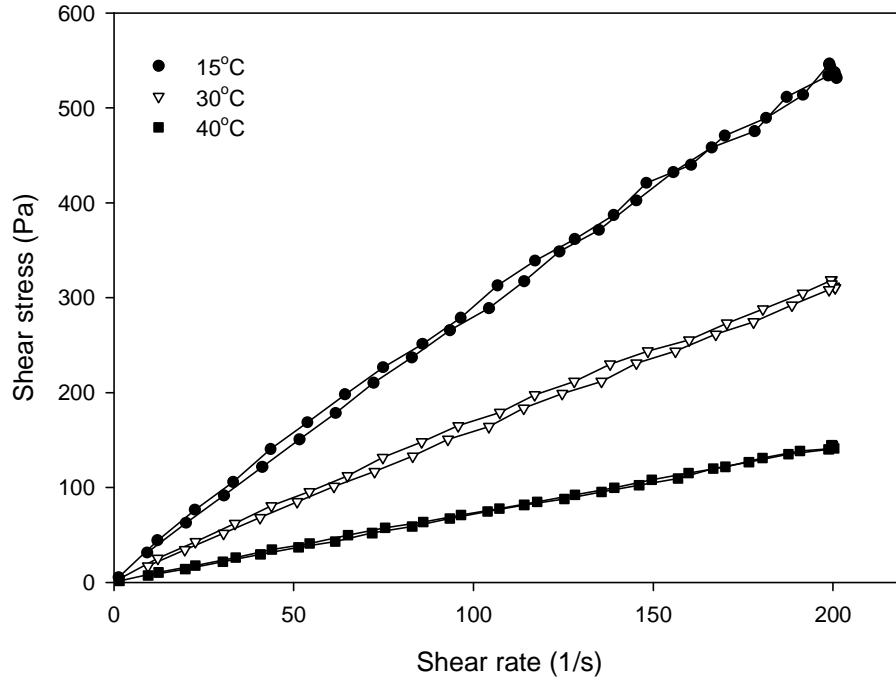
Figure 3.10 Effect of temperature on flow curves of tahin (S5:7.02 μm)

For determining relationship between particle size, temperature and power law parameters (K and n), it was found that three parameter exponential growth model (Equation 3.3) was sufficient for K value (R^2=0.9136); and an empiric relation (Equation 3.4) was good for n value (R^2=0.9486).

$$K= 9.47 - 0.233T + 0.0025*\exp (0.33PS) \qquad 3.3$$

$$n= [(0.908 - 0.031*PS + 0.0005T) / (1 - 0.033*PS)] \qquad 3.4$$

where PS: median particle size, and T: temperature (^{o}C).

3.5.1.2 Storage effect

Further rheological tests were done to observe the changes in the structure of tahin during storage were more likely to depend on physical (rather than enzymatic or chemical) events such as flocculation or coagulation of particles. For these investigations separated oil was removed, and the samples were taken from the surface of the precipitated solid part. The samples were stored even one month; this storage caused very important structural deformation which detected experimentally and visually. During storage of tahin, sedimentation of solid particles resulted in two phases, one was free oil over the paste and second sticky agglomerate solid structure, further it became very hard to mention about any flow behavior of the solid phase, especially having higher particle size than 5 μm. It was observed that stored tahin still showed the pseudoplastic behavior (Figures 3.11 and 3.12) which can be concluded that it is a characteristic of tahin regardless of the storage temperature and time.

It was determined that the apparent viscosity increases with increasing storage temperature (Figure 3.13). The increase in viscosity of tahin indicates more interactions in the tahin structure occurred during storage, resulting in a further development of the coagulation of protein. It was predicted that that rearrangement of the protein network is responsible for the increase in the apparent viscosity.

Increase in storage temperature enlarged the structural breakdown. However, analyzing effects of particle size and storage temperature on flow behavior of tahin statistically showed that both parameters have significant effect ($p < 0.05$) but the most important parameter was the particle size with respect to F value (Appendices, Table A2).
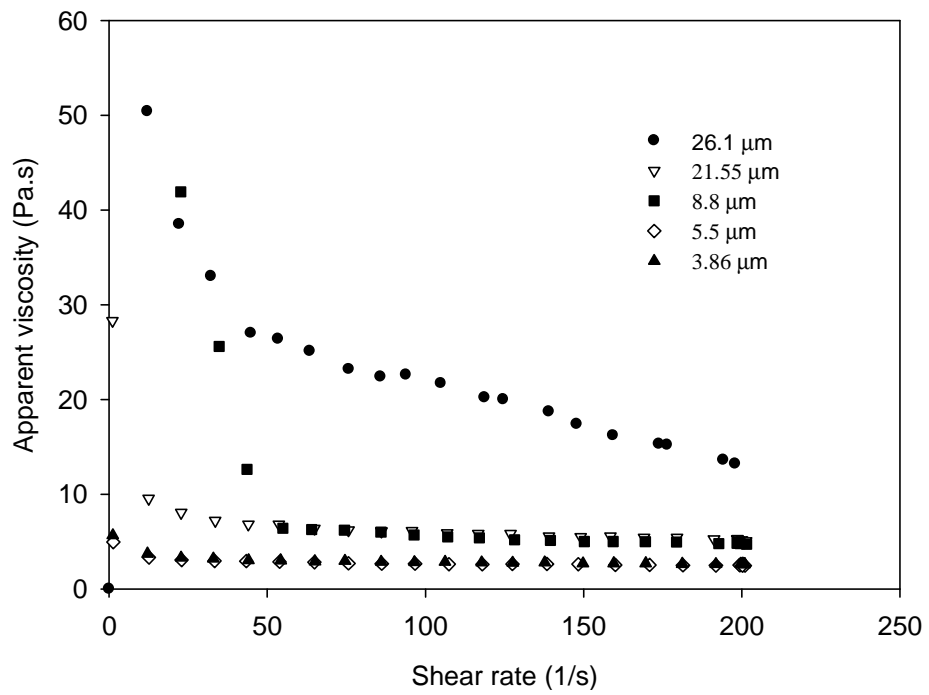
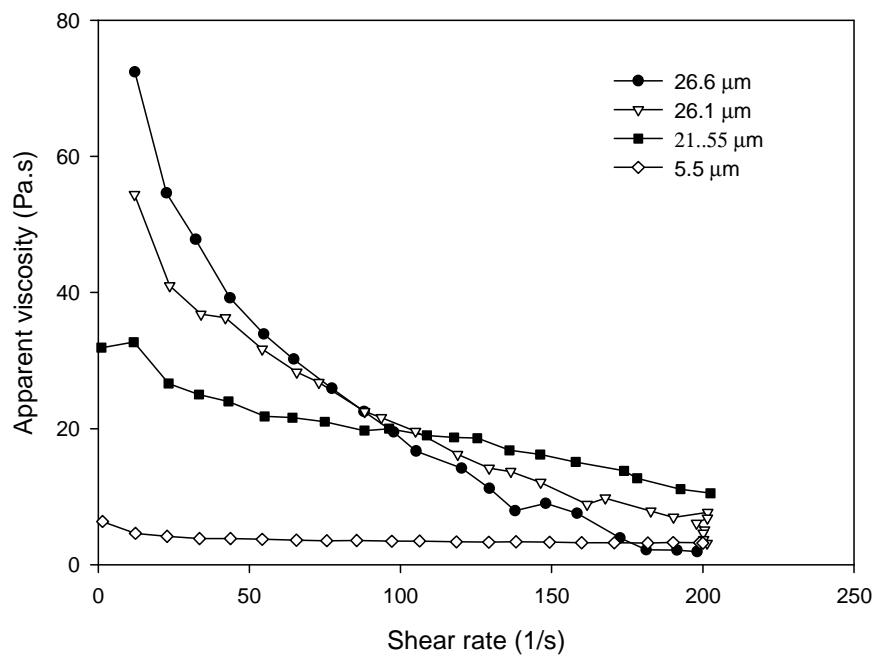Figure 3.11 Effect of particle size on apparent viscosity of stored tahin at 20°C

Figure 3.12 Effect of particle size on apparent viscosity of stored tahin at 40°C
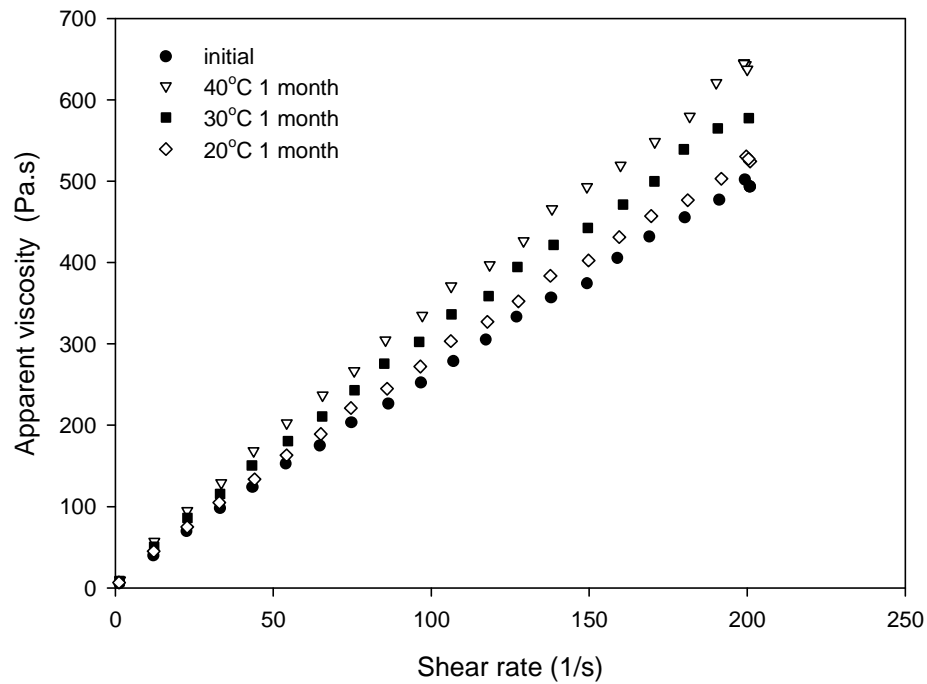
Figure 3.13 Effect of storage on the finest sized tahin sample (3.86 µm)

3.5.2 Dynamic oscillatory testing

Dynamic oscillatory testing, designed to measure structure without deformation, was another method applied to measure structural changes in tahin with particle size variation. The changes in storage (G′, which is related with elastic character) and loss (G″, which is related with viscous character) moduli of S1-S3 as a function of the frequency for different particle sized tahin samples were studied at 25°C. In tahin samples having coarse particles (S1-S3), G′ values were higher than G″ values for all frequencies; Figure 3.14 represents the modulus values of S3, as an example. The larger value of storage modulus is indicative of strong particle–particle interactions and/or the network type structure in a stabilized form (Carreau et al., 2002). Decreasing the particle size resulted in increase of tendency from elastic to viscous character of tahin (Figure 3.15). In fine particle sized samples (S4-S7), loss modulus G″ values were higher than storage modulus values showing liquid-like behavior. It was found that the magnitudes of both G′ and G″ increased with frequency. On the other hand, G′ curves of the samples observed a sudden increase

phenomenon around 10 Hz frequencies; at higher frequency, since deformation process occurs very fast so sample showed solid-like character. This phenomenon is best explained by Deborah number (Rao, 1999), which quantifies the notion that all material tend to exhibit increasingly solid-like characteristics over shorter experimental time scale (high frequency) (Everett and McLeod, 2005).

A dilute solution, a concentrated solution and a gel show distinctive behavior when food material is subjected to a frequency sweep (Steffe, 1996). In this study, the fine particle sized samples (S4-S7) showed similar characteristics with dilute polymer solutions for that G″ is larger than G′ over the entire range, but at higher frequencies they approached to each other (Cho et al., 2006). Such trend was also reported for corn starch-locust bean gum mixtures (Alloncle and Doublier, 1991). In this type behavior G′ and G″ curves intersect (G′=G″) at higher frequencies and showing a clear tendency for more elastic behavior. On the other hand, coarse particle sized samples showed strong gel like properties with independence of frequency.
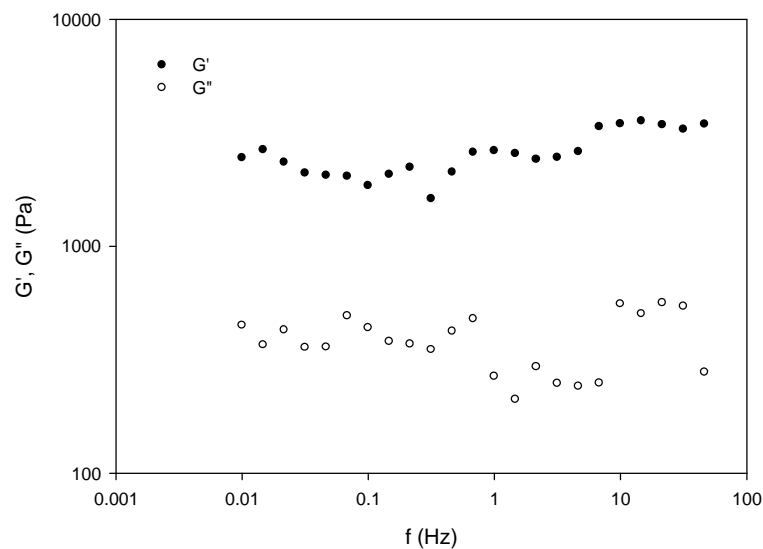

Figure 3.14 Effect of frequency on storage (G′) and loss moduli (G″) for tahin S3 (median particle size: 21.55 μm)
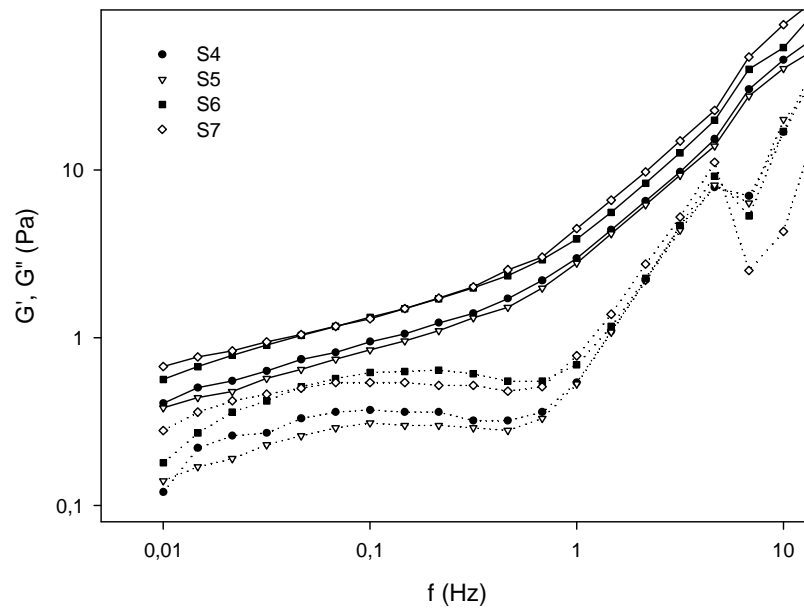
Figure 3.15 Effect of frequency on storage (G′, dotted line) and loss moduli (G″, solid line) for tahin having different particle size

In general, at low frequencies, the flow behavior is controlled by transitional motion of macromolecules, and G″ is usually higher than G′ (Da Silva and Rao, 1992). At high frequencies, on the other hand, the value of G′ increases due to macromolecular distortion and it is higher than G″ value.

Statistically, particle size, storage temperature and time were analyzed using analysis of variance (ANOVA) method. It was found that particle size is the most important parameter affecting viscoelastic behavior of tahin with respect to F value (Appendices, Table A3). Similarly, the effects of storage temperature and particle size on storage stability of peanut butter were studied and importance of particle size was also demonstrated (Citerne et al., 2001).

The changes in viscoelastic parameters can be described by the nature of sesame paste that is not physically stable and prone to oil separation (Isa, 2001). The oil separation resulted in increasing protein concentration of sample that improves elastic behavior. By the same manner, Avanza et al. (2005) reported that the storage modulus (G′) of gels increased with increasing protein concentration. Since oil separation occurs less in coarse particle sized samples than fine sized, increasing of storage modulus appeared markedly.

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3.6 Some Physical Properties of Pekmez/Tahin Blends

In the Turkish food market, tahin and pekmez are sold separately and for blend preparation, the ratio of tahin to pekmez is determined according to consumer preference. However, it is difficult to adjust this ratio due to structural changes which occur during storage. In this study, some physical properties of the samples containing 6-40% pekmez were analyzed to observe the structural changes in tahin with pekmez addition, and to find ideal ratio of spreadable pekmez/tahin blend..

3.6.1 Colloidal stability

Tahin samples (S7, the most stable sample) containing different proportions of pekmez (6-40%) and control tahin sample were stored at $25^{o}C$ for one month to measure colloidal stability. The addition of pekmez improved the colloidal stability of the blends. Phase separation was not observed in pekmez containing samples (a negligible separation which was lower than 1% occurred in 6-8% pekmez containing tahin). Firstly, this may be attributed to sesame proteins acting as emulsifier at the oil–water interface (Dickinson and Golding, 1997). The protein is adsorbed at the interface between oil and the aqueous phase to lower surface tension and slightly increases the density of oil droplets, and consequently decreases and/or prevents the oil separation (Dickinson and Golding, 1997; Hemar et al., 2001; Paraskevopoulou et al., 2007). Secondly, pekmez inhibits the coalescence of oil droplets into larger oil droplets, which have a tendency to separate from the blend. This is consistent with observations on sunflower oil water emulsions studied by Maskan and Göğüş (2000) which showed that the addition of sugar increased the stability of emulsions.

3.6.2 Rheological measurements

The rheological properties were analyzed to find an ideal pekmez-tahin blend for production of spreadable chocolate cream type product. In literature, some rheological properties of tahin/pekmez blends at different concentrations were studied but viscoelastic properties were not investigated. Arslan et al. (2005) determined the flow behavior of tahin/pekmez blends at 20–32% tahin

concentrations that tahin/pekmez blends were found to exhibit non-Newtonian, shear thinning behavior at all tahin concentrations. It was reported that n increased (0.7-0.85) with increasing pekmez concentration and approached to Newtonian behavior. In the other study made by Alpaslan and Hayta (2002) with using 2-6% pekmez concentration, all blends exhibited pseudoplastic behavior. In the same manner n was found to be inversely related with the tahin concentration and temperature. It was reported that solid pekmez exhibited non-Newtonian behavior (Kaya and Belibağlı, 2002; Yoğurtçu and Kamışlı, 2006).

Figure 3.16 shows the effect of pekmez concentration (10-40%) on viscoelastic parameters storage modulus (G′) and loss modulus (G″) at 25°C. The magnitudes of both G′ and G″ were increased with increasing pekmez concentration. At control and 10%, samples, moduli values show higher frequency dependence and viscous (liquid-like) behavior that is G″ was greater than G′. On the other hand, frequency dependency decreased with 20% and greater pekmez concentration; elastic (solid-like) character became dominant since G′ was greater than G″.
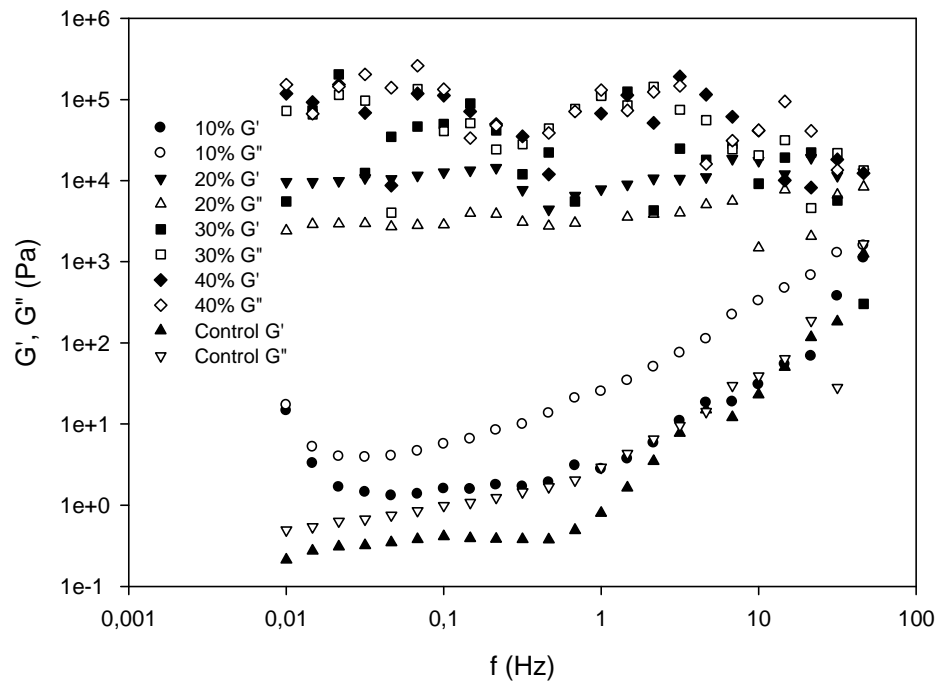
Figure 3.16 Effect of pekmez concentration on viscoelastic moduli of pekmez-tahin blends (10-40%) at 25°C

As shown here, in order to observe the changeover from viscous to elastic structure and to see the effect of storage on viscoelasticity, it is necessary to investigate samples with a pekmez concentration between 10 and 20%. Therefore, 10, 12, 15, 16, 17, 18, 19 and 20% of pekmez containing samples were prepared and analyzed in terms of viscoelasticity after storing for 30 days at 25°C.

After storage period, samples (Figures 3.17 and 3.18) showed liquid-like behavior up to 15% pekmez concentration that G′ and G″ increased with frequency and G″ was greater than G′ in the entire range of frequency. After 15% concentration, the dominant behavior changed to elastic structure. Similar trends were observed for the samples containing 16-19% pekmez, as it was observed for over 20% concentration. Based on the observations, the samples with higher pekmez concentration have more compact and solid-like structure with higher values of storage modulus.
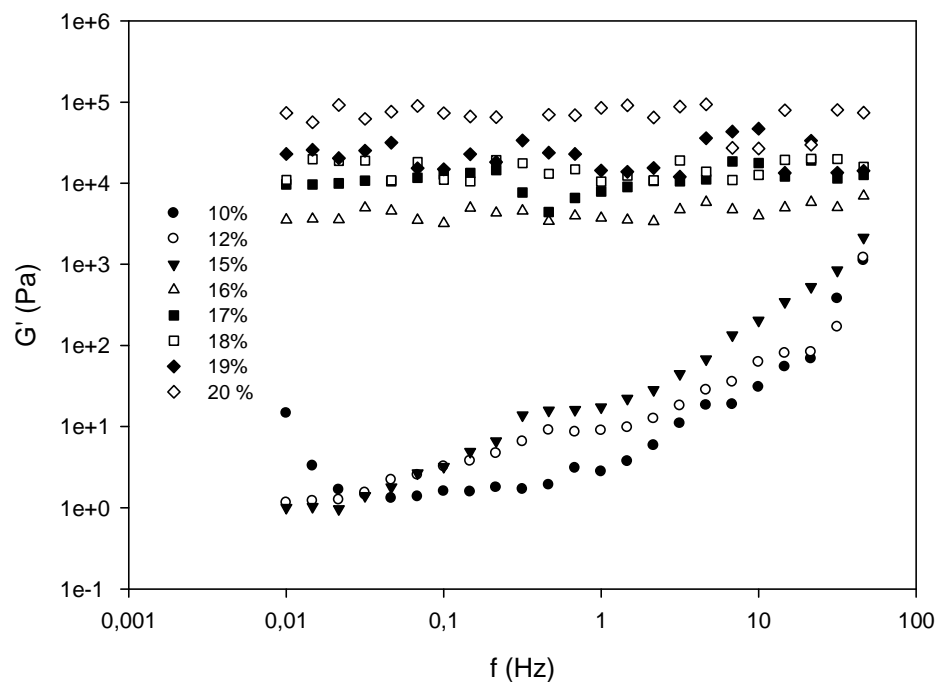
Figure 3.17 Effect of concentration on storage modulus of pekmez-tahin blends (10-20%) at 25°C
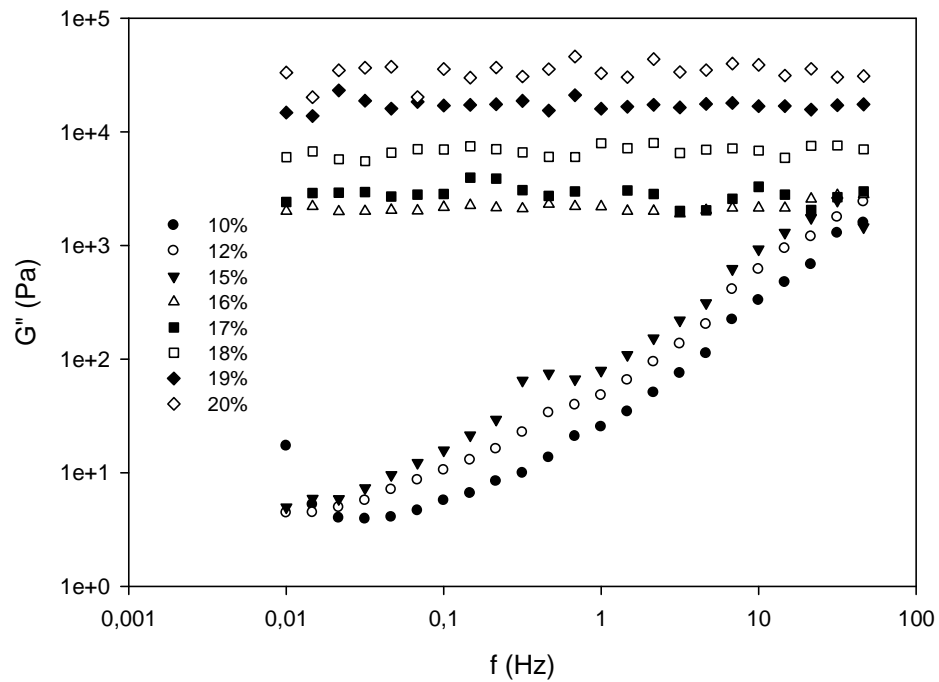
Figure 3.18 Effect of concentration on loss modulus of pekmez-tahin blends (10-20%) at 25°C

3.6.3 Color of pekmez/tahin blends

Color parameters changed with increasing pekmez concentration as seen in Figure 3.19. This was the possible result that the alterations in the physical state and structure of a food product can alter the color of a system (Alpaslan and Hayta, 2002). The lightness (L) value decreased with increasing concentration of pekmez in blends whereas redness (a) value showed a reverse trend affecting from color of pekmez. Similarly, the addition of sugar resulted in a decrease in whiteness value of surfactant stabilized oil-in-water emulsions as reported by Weiss and Liao (2000). It has been suggested that sugar changed the optical properties of the water phase in such a way that scattering and absorption of light is strongly reduced. YI- value (yellowness index) went up rise like a- value. No appreciable changes in b-value (blueness) were observed.
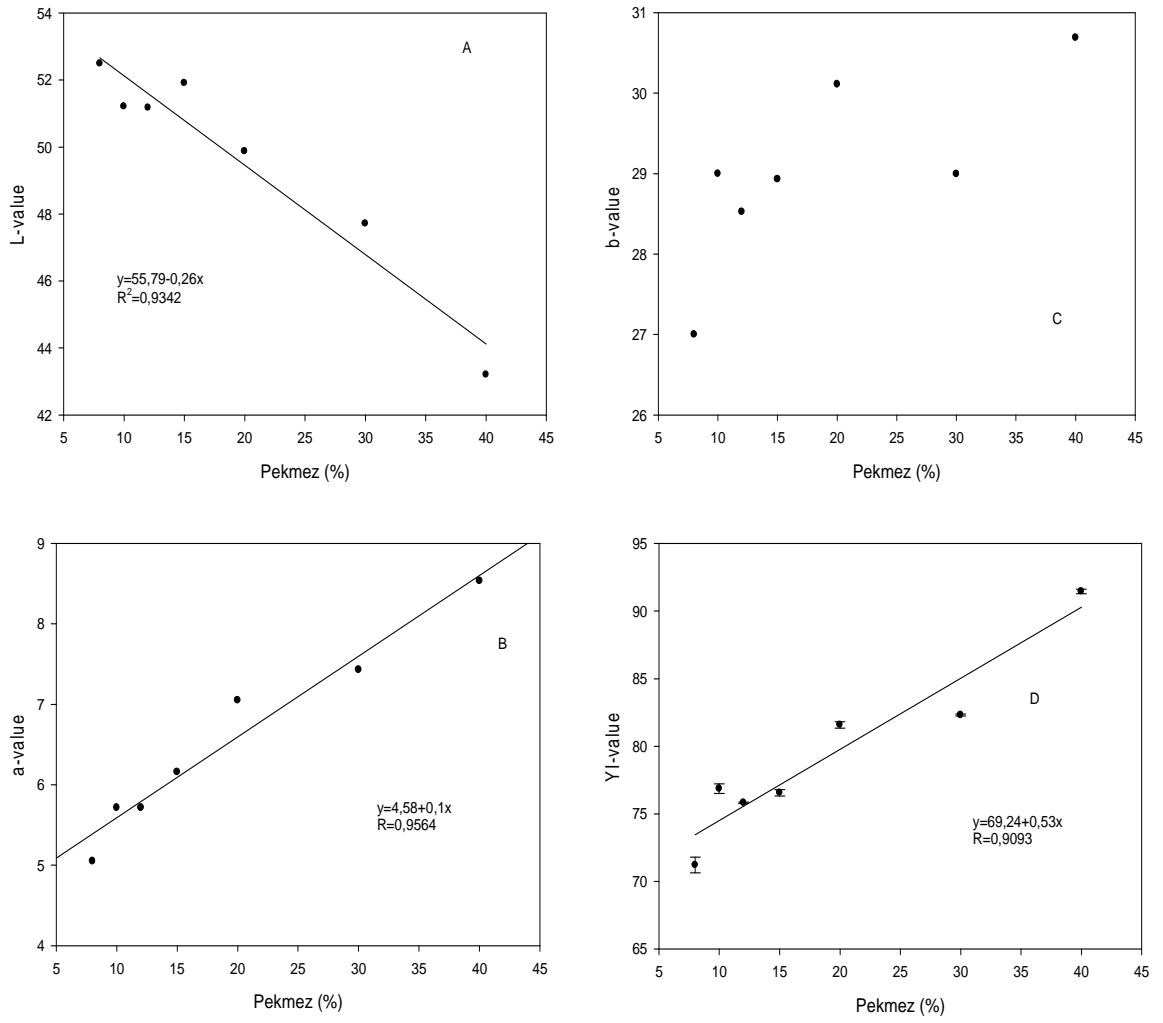
Figure 3.19 Effect of pekmez concentration on color parameters (A: L-value; B: a-value, C: b- value; D: YI- value) of pekmez-tahin blends (8-40% pekmez)

3.6.4 Sensory analysis of pekmez/tahin blends

Significant differences were determined statistically for appearance (darkness), taste, oiliness, adhesiveness, graininess, hardness, spreadability and overall acceptability with changing proportion of pekmez in tahin samples ($p < 0.05$ and $p < 0.01$) (Appendices, Table A4).

Interaction of these properties provided from sensory analysis results with pekmez concentration is indicated in Figure 3.20. The highest overall acceptance score was given to the blend containing 15% pekmez compared to the blends with 8%, 10%, 12% and 20% pekmez.
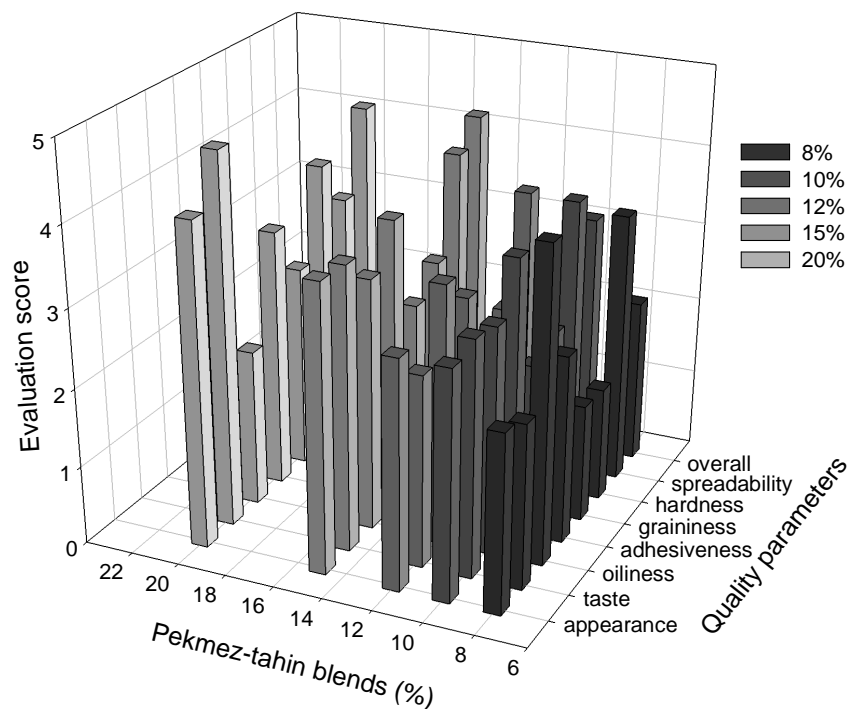
Figure 3.20 Effect of concentration on sensory properties of pekmez/tahin blends (8-20%)

Figure 3.21 shows the comparison of sensorial appearance (darkness) and L-value (brightness). As expected, they displayed opposite trends reflecting their opposite meanings. Sensorial judgement correlated well with instrumental measurement result that color of blends darkening with increasing pekmez concentration.
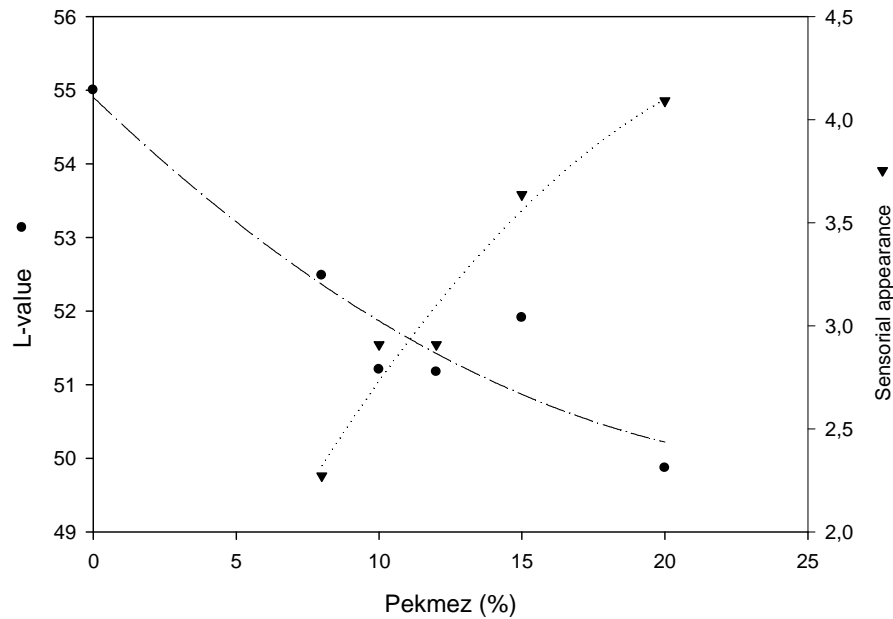
Figure 3.21 Correlation of L-value and sensorial appearance for pekmez-tahin blends at different concentrations (8-20%)

It can be seen from the Figure 3.22 that sensorial spreadability was in accordance with oiliness of blends. Pearson correlation result confirmed that oiliness showed positive correlation with spreadability (r= 0.935, p<0.05) (Appendices, Table A4). Spreadability increased to certain amount of oil content but decreased at more than 15% pekmez containing blends. This may be attributed to increasing of mechanical and sensorial hardness values of blends. Pearson results revealed that oiliness was negatively correlated with sensorial hardness (r= -0.911, p<0.05) (Appendices, Table A4). It is also possible that the reduced spreadability was caused by formation of aggregates of emulsion droplets. Aggregation reduces the area of oil or protein layer in contact with the water interface thereby reducing the chance of breaking of the protein layer (Schokker et al., 2002).
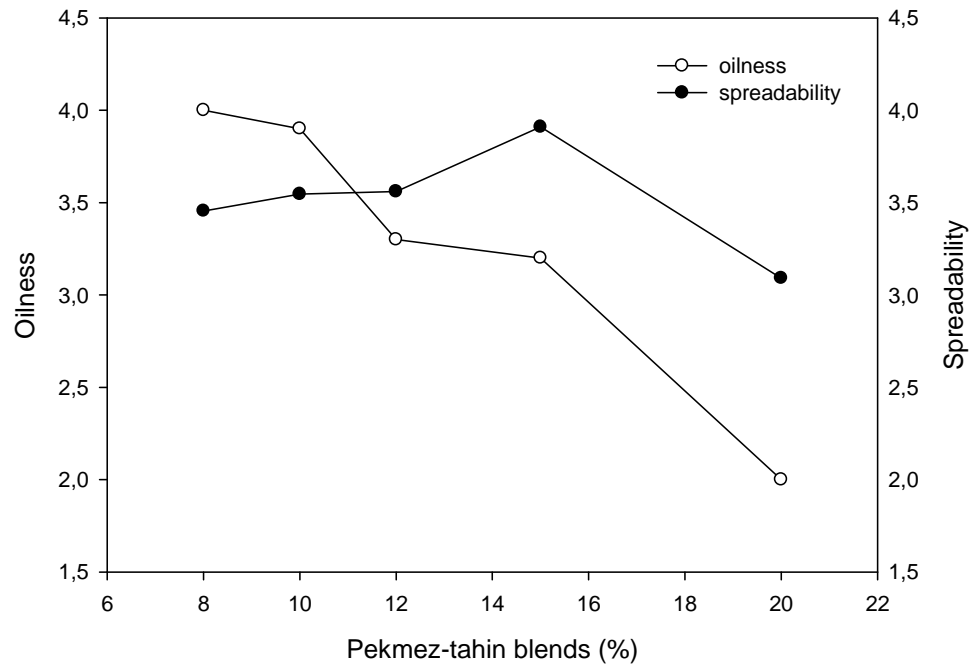
Figure 3.22 Correlation between oiliness and spreadability of pekmez-tahin blends at different concentrations (8-20%)

It was determined that the result of the sensorial judgement of hardness was directly proportional to the hardness of the network as measured by texture analyzer for five different proportions of samples (Figure 3.23). Statistically strong positive correlation was also found with pearson correlation between sensorial and instrumental hardness results (r= 0.942, p<0.05) (Appendices, Table A5).
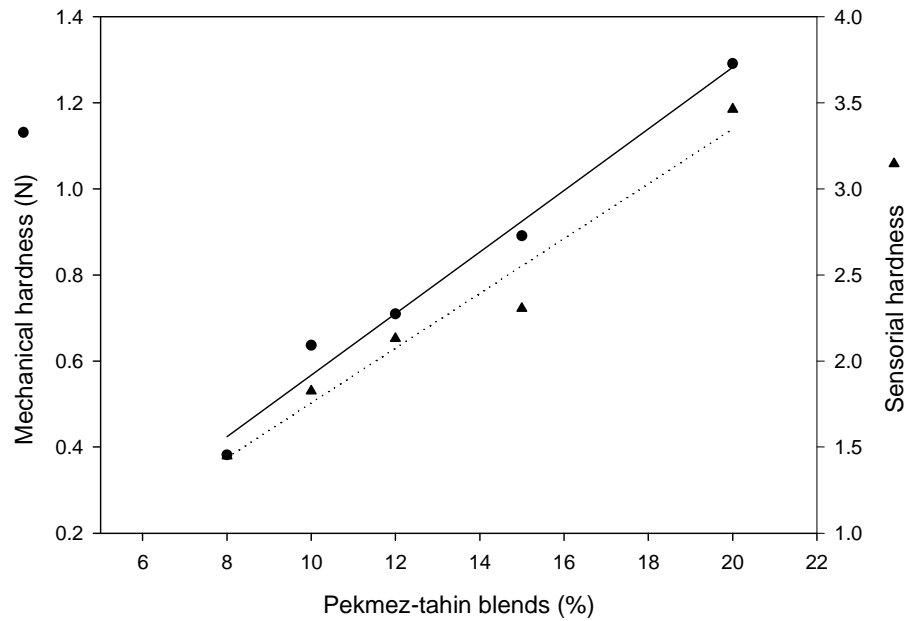
Figure 3.23 Correlation between mechanical and sensorial hardness of pekmez-tahin blends at different concentrations (8-20%)

Figure 3.24 shows the relationship between sensorial spreadability and storage modulus. There was a directly proportional increase with pekmez concentration up to 15% but sudden decrease is shown after this point. This may arise from reducing spreadability due to more solid-like structure from 15 to 20% blend. So, this was the expected result that spreadability property decreased with increasing hardness. It was reported that many of the sensorial properties mainly spreadability related with crystal structure in products like chocolate, butter and ice-cream by Narine and Marangoni (1999). They determined that the shear elastic moduli of fat crystal networks were directly proportional to the hardness of the network as measured by cone penetrometry, for some eight different fat systems. In the same manner, it was revealed that mechanical hardness values of pekmez-tahin blends positively correlated with storage modulus (r= 0.967, p<0.01) (Appendices, Table A5).
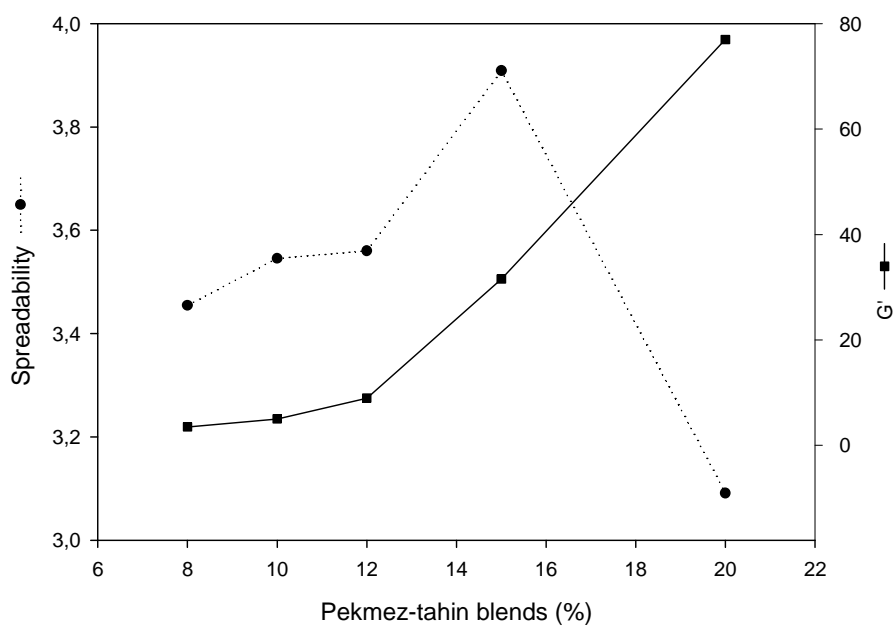
Figure 3.24 Correlation of sensorial spreadability and elastic modulus for pekmez-tahin blends at different concentrations (8-20%)

Additionally, the correlation of sensorial hardness with graininess was positive ($r = 0.929$, $p < 0.05$) (Appendices, Table A5). No significant correlations were found for adhesiveness of blends. Besides spreadability, 15% pekmez containing blend became the most suitable in terms of all sensorial properties.

CONCLUSIONS

Tahin is a colloidal suspension and particle size distribution plays an important role in its stability. Tahin had multi modal distribution and reducing particle size increased the colloidal stability. The results were in a good agreement with the rheological data.

The pseudoplastic and thixotropic characteristics were observed for all size of tahin samples. The magnitudes of thixotropic area decreased exponentially with the decreasing particle size of tahin samples. During storage, sedimentation of solid particles resulted in two phases, one was free oil over the paste and second sticky agglomerate solid structure, further it became very hard to mention about any flow behavior of the solid phase, especially having higher particle size than 5 μm. Stored samples still showed the pseudoplastic behavior which can be concluded that it is a characteristic of tahin regardless of the storage temperature and time.

Dynamic rheological tests showed that decreasing particle size resulted in increase of tendency from elastic to viscous character of tahin. Fine particle sized samples showed similar characteristics with dilute polymer solutions, whereas coarse particle sized samples showed strong gel-like properties with independence of frequency. Color of tahin was getting darker with decreasing particle size.

The addition of pekmez improved the colloidal stability of the pekmez-tahin blends. Based on the observations on viscoelastic parameters of blends, the samples with higher pekmez concentration had more compact and solid-like structure with higher values of storage modulus. 15% concentration was the changeover point for the transition from viscous to elastic structure. The lightness (L) value decreased with increasing concentration of pekmez in blends whereas redness (a) value showed a reverse trend affecting from color of pekmez. According to the parameters (appearance, taste, oiliness, adhesiveness, graininess, hardness and spreadability) detected with sensory analysis and rheological measurements, it could be concluded that 15% pekmez containing tahin was the ideal blend for production of spreadable pekmez-tahin.

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APPENDICES

Table A1. ANOVA (three-way) table for colloidal stability of different sized tahin samples by particle size, storage temperature and time

Source	Type III Sum of Squares	df	Mean Square	F
Corrected model	15862,9[a]	299	53,0	2×10^7
Intercept	33735,4	1	33735,4	2×10^{10}
Particle size	2238,1	9	248,7	1×10^8
Temperature	5454,5	2	2727,3	1×10^9
Time	4835,4	9	537,3	2×10^8
Particle size*Temperature	1008,1	18	56,0	3×10^7
Particle size*Time	631,5	81	7,8	3595350
Temperaure* Time	688,7	18	38,3	2×10^7
P.Size*Temperature*Time	1006,6	162	6,2	2865253
Error	0,001	300	$2,2 \times 10^{-6}$	
Total	49598,4	600		
Corrected Total	15862,9	599		

$a = R^2 = 1.000$ (R^2 adjusted to 1.000)

Table A2. ANOVA (two-way) table for flow behavior of different sized tahin samples by particle size and storage temperature

Source	Dependent variable	Type III Sum of Squares	df	Mean Square	F
Corrected model	K	$3891,80^a$	23	173,12	8×10^9
	n	$0,595^b$	23	0,026	124,17
	Thixotropic Area	$8,8 \times 10^{9a}$	23	$3,8 \times 10^7$	2×10^8
Intercept	K	1917,97	1	1917,9	9×10^{10}
	n	35,5	1	35,5	170397
	Thixotropic Area	$1,5 \times 10^9$	1	$1,5 \times 10^9$	7×10^8
Particle size	K	2797,3	7	399,6	2×10^{10}
	n	0,470	7	0,067	322,3
	Thixotropic Area	$4,6 \times 10^9$	7	$6,6 \times 10^8$	3×10^8
Temperature	K	153,5	2	76,7	4×10^9
	n	0,012	2	0,006	29,7
	Thixotropic Area	$5,3 \times 10^8$	2	$2,6 \times 10^8$	1×10^8
Particle size * Temperature	K	1031,0	14	73,6	4×10^9
	n	0,113	14	0,008	38,6
	Thixotropic Area	$3,6 \times 10^9$	14	$2,6 \times 10^8$	1×10^8
Error	K	5×10^{-7}	24	2×10^{-8}	
	n	0,005	24	0,000	
	Thixotropic Area	50	24	2,083	
Total	K	5899,8	48		
	n	36,1	48		
	Alan	1×10^{10}	48		
Corrected Total	K	3981,8	47		
	n	0,600	47		
	Thixotropic Area	$8,8 \times 10^9$	47		

$a = R^2 = 1.000$ (R^2 adjusted to 1.000), $b = R^2 = 0.992$ (R^2 adjusted to 0.992)

Table A3. ANOVA (two-way) table for viscoelastic parameters of different sized tahin samples by particle size and temperature

Source	Type III Sum of Squares	df	Mean Square	F
Corrected model	$1,4 \times 10^{10a}$	14	$9,8 \times 10^8$	2×10^7
Intercept	$2,1 \times 10^9$	1	$2,1 \times 10^9$	2×10^{10}
Particle size	$8,2 \times 10^9$	4	$2,1 \times 10^8$	1×10^8
Temperature	$1,1 \times 10^9$	2	$5,5 \times 10^8$	1×10^9
Particle size * Temperature	$4,4 \times 10^9$	8	$5,5 \times 10^8$	3×10^7
Error	5×10^{-5}	15	$3,3 \times 10^{-6}$	
Total	$1,6 \times 10^{10}$	30		
Corrected Total	$1,4 \times 10^{10}$	29		

$a = R^2 = 1.000$ (R^2 adjusted to 1.000), $b = R^2 = 0.992$ (R^2 adjusted to 0.992)

Table A4. Pearson correlations of sensory analysis parameters of pekmez-tahin blends with concentration

	Conc.	Appear.	Taste	Oil.	Adhes.	Grain.	Hard.	Spread.	Overall
Conc.	1	.971(**)	.941(*)	-.852	.525	.927(*)	.991(**)	-.367	.829
Appear.	.971(**)	1	.963(**)	-.863	.710	.980(**)	.976(**)	-.208	.928(*)
Taste	.941(*)	.963(**)	1	-.909(*)	.653	.971(**)	.957(*)	-.377	.910(*)
Oil.	-.852	-.863	-.909(*)	1	-.601	-.819	-.911(*)	.935(*)	-.727
Adhes.	.525	.710	.653	-.601	1	.751	.576	.327	.845
Grain.	.927(*)	.980(**)	.971(**)	-.819	.751	1	.929(*)	-.152	.976(**)
Hard.	.991(**)	.976(**)	.957(*)	-.911(*)	.576	.929(*)	1	-.396	.834
Spread.	-.367	-.208	-.377	.935(*)	.327	-.152	-.396	1	.035
Overall	.829	.928(*)	.910(*)	-.727	.845	.976(**)	.834	.035	1

** Correlation is significant at the 0.01 level (2-tailed).
 * Correlation is significant at the 0.05 level (2-tailed).

(Con. : Concentration, Appear. : Appearance, Oil. : Oiliness, Adhes. : Adhesiveness, Hard. : Hardness, Spread. : Spreadability).

Table A5. Pearson correlations of storage modulus (G'), hardness and mechanical hardness values of pekmez-tahin blends with spreadability

	Spreadability	Hardness	Mechanical Hardness	G'
Spreadability	1	-.396	-.602	-.779
Hardness	-.396	1	.942(*)	.860
Mechanical Hardness	-.602	.942(*)	1	.967(**)
G'	-.779	.860	.967(**)	1

** Correlation is significant at the 0.01 level (2-tailed).
 * Correlation is significant at the 0.05 level (2-tailed).

Figure B1. Milling machine used in this study
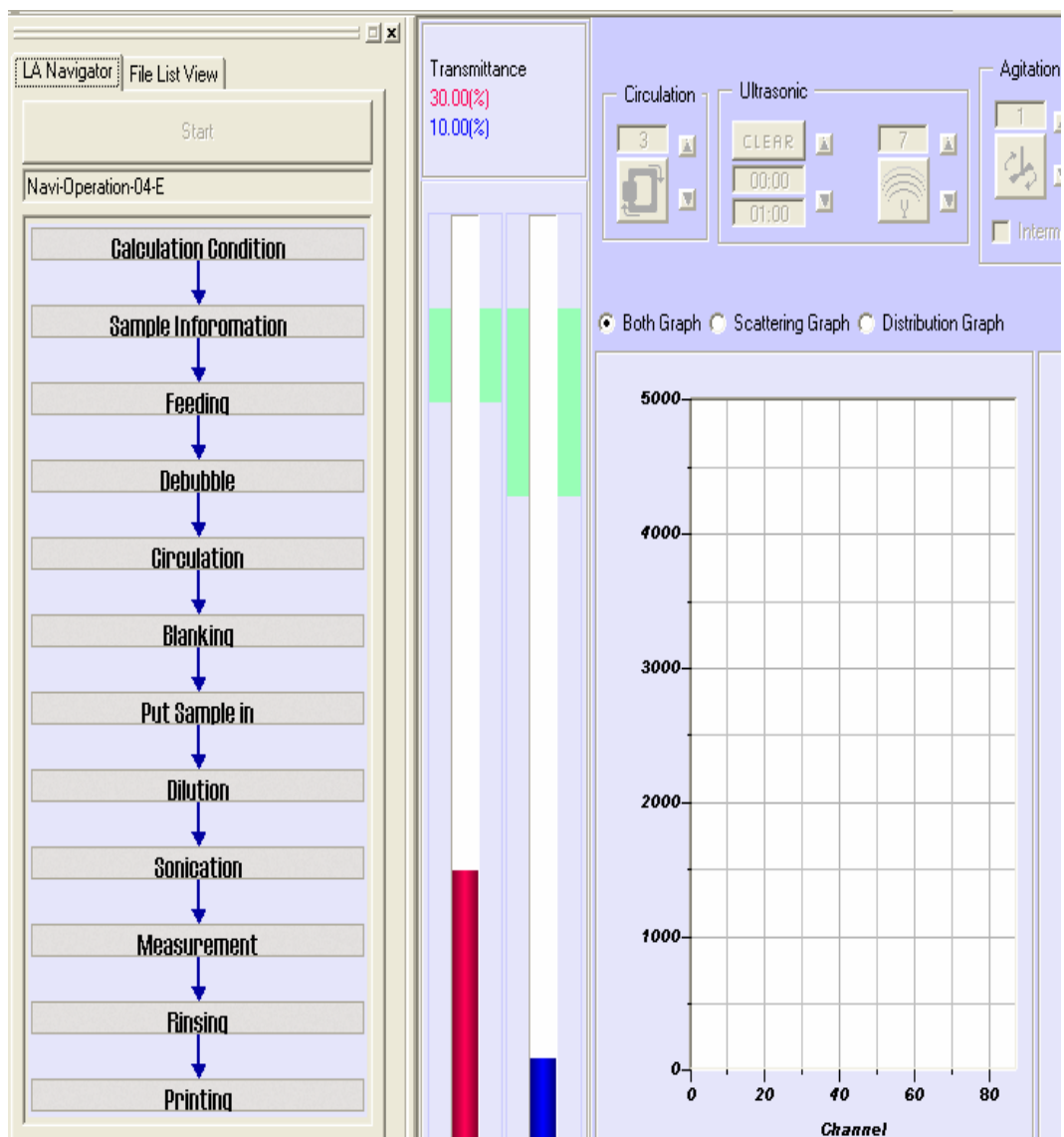
Figure B2. Particle size analyzer

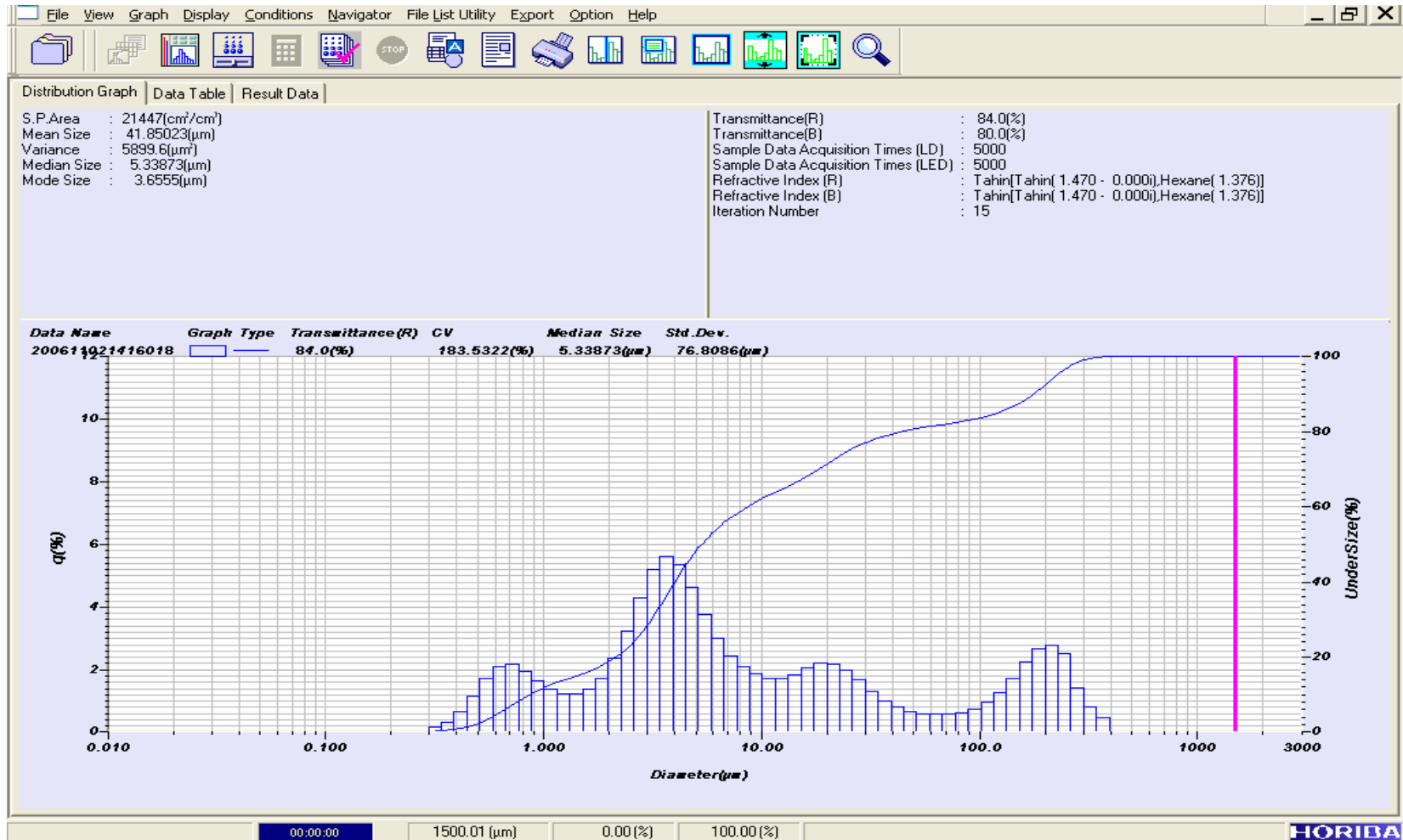Figure B3. Programme used in particle size measurement

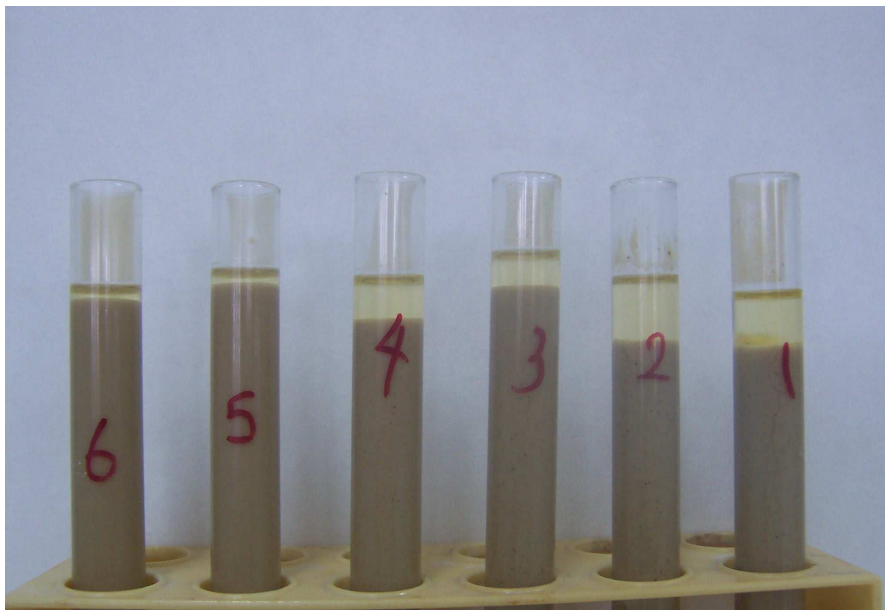Figure B4. A representative example of particle size measurement result

Figure B5. Representative example of some tahin samples indicating phase separation during storage at 20^oC (A: initial, B: after 20 days)

You are given 5 samples containing different proportions of tahin and pekmez. Please rank the samples according to the given attributes using the ranking order.

Thank you for your kind attendance.

Terms used in sensory analysis

Appearance: Degree of darkness on external show.

Taste: Degree of liking when eaten.

Oiliness: Amount of oil perceived in mouth after the sample is expectorated.

Adhesiveness: The degree to which sample adheres to lips.

Graininess: The amount of particles present in sample.

Hardness: The force required to compress the sample between the tongue and palate.

Spreadability: Ease of spread of sample on a bread.

Ranking order

```
1                          5
|——————————————————————————|
Least                    Most
```

Attribute	Sample Code				
	A	**B**	**C**	**D**	**E**
Appearance (Darkness)					
Taste					
Oiliness					
Adhesiveness					
Graininess					
Hardness					
Spreadability					
Overall Acceptability					

Figure B6. The survey used in the sensory analysis