INVESTIGATION OF CENTRIFUGAL AND RHEOLOGICAL TECHNIQUES TO PREDICT STABILITY OF PEANUT BUTTER

by

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(Under The Direction of Manjeet S. Chinnan)

ABSTRACT

Oil separation has been a major problem in peanut butter, which is prevented by incorporating stabilizers. This additive forms a network structure at low temperatures, which entraps the oil thereby, preventing its separation. The structure also imparts a viscoelastic property to peanut butter. The objective of the study was to 1) develop a rapid testing method based on centrifugation, and 2) characterize the viscoelastic properties of peanut butter using controlled stress rheometry**.** Centrifugation technique helped in predicting the shelf life of stabilized peanut butter as 1-2 yr at 21-24 °C storage. Creep recovery and time sweep tests performed using advanced rheometer were useful in monitoring the deterioration of peanut butter during the three-month storage at 35 °C.

INDEX WORDS: Peanut butter, Centrifugation, Oil separation, Structural Strength, Accelerated storage, Controlled stress rheology, Creep, Oscillatory tests, viscoelastic properties

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To

Mummy, Papa

Geetu- Rajesh

Kavi-Raja

Bitu

& Dristi

I would not have reached this far if it weren't for the love, support, encouragement and their blessings.

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CHAPTER 1

INTRODUCTION

Peanuts *(Arachis hypogaea L.)* are one of the most nutritious foods nature has provided to mankind. It contains about 25-27% protein, 48-50% fat, and 12-16% carbohydrates and is a good source of water-soluble B vitamins. It is believed that peanuts were first domesticated in the South American countries of Paraguay and Peru. Today, this legume is grown mainly in the tropical and temperature regions of more than 50 countries and is one of the important oil bearing commercial crops in the world. India, China and the United states are the world's major peanut producers. Limited production coupled with inadequate storage facilities for peanuts and its products, has restricted the utilization of peanuts. They are a major source of edible oil. In the United States, peanuts are primarily in manufacturing value-added -products such as, peanut butter, salted peanut snacks and candy.

Peanut butter is a wholesome and highly nutritious food obtained from grinding of mature, shelled, washed and blanched (roasted and deskinned) peanuts. For a product to be labeled as peanut butter, it is mandatory that it contain 90% peanuts, a requirement that renders it a very good source of protein and certain essential fatty acids making it an excellent food for children. However, that also makes it rich in peanut oil, which is released from peanut cells while they are converted to fine textured peanut butter. There exists a difference in the density of peanut oil and solid meal, which enables the oil to migrate to the surface of peanut butter when allowed to stand at room temperature for a considerable time. This results in the formation of two immiscible layers of oil and solid meal. The oil separation has been a major problem in peanut butter since it is associated with old rancid peanut butter by the majority of consumers. Oil separation is prevented by the addition of a stabilizer. Stabilizers are normally hydrogenated oil or their blends,

which possess the ability to crystallize at low temperatures and form crystals that are capable of trapping oil. This principle is used in the manufacture of stabilized peanut butter. The formation of crystal network serves the dual purpose of holding oil and providing a smooth spreadable texture to the butter. Citrene and his coworkers reported the presence of 'soft-solid gel like behavior' in stabilized peanut butter. In this study, the terms 'crystal network structure' of peanut butter and 'weak gel like structure' have been used interchangeably. A well-formed crystal network does not permit migration of oil into the product over a long time; hence, it is the strength of this network, which holds the key to the prediction of product shelf life with regards to oil separation.

Currently, most of the quality assurance testing conducted on peanut butter is with respect to texture, color, salt content and particle size. The consistency of product texture is determined by using only a cone peneterometer after a 48 h time lag following product manufacture. There is however, no quick test available to determine how long the butter will remain stable without exhibiting any oil separation (shelf life). Therefore, research needs to focus on developing a method, which can provide reliable and timely information about the shelf life of peanut butter in the shortest time possible after its manufacture. Oil separation in peanut butter occurs due to the action of gravitational forces over a considerable time period. This phenomenon in peanut butter can be artificially simulated by the use of centrifugation. The centrifugal force can destabilize the matrix of peanut butter to produce an oil layer. If a correlation could be established between the oil separation due to centrifugal and natural forces acting on peanut butter, we would be able to predict the shelf life of the product in the shortest time interval.

Peanut butter is a viscoelastic food product. A material is said to be viscoelastic when it exhibits both solid and liquid-like behavior. These viscoelastic properties are not inherent in the butter but imparted by the network structure formed by the addition of a stabilizer. The oil separation in peanut butter is critically depended on the matrix of crystals formed by the stabilizer, which is also responsible for the viscoelastic nature of the butter. Formation of the crystal network could be considered similar to the formation of gel network in foods and non-food materials. Dynamic rheological experiments have been employed to monitor the process of gelation in many biopolymers and to understand the gel/food structure. These techniques are known to be non-destructive and non-interfering with respect to gel formation or softening and provide the added advantage of expressing the results in fundamental terms, which can be further related to gel structure. Therefore, an evaluation of the strength of network structure formed in peanut butter using rheological techniques may reveal valuable information regarding the overall process of network formation. The primary objectives of the project were:

1) To develop a rapid method of determining the shelf life of peanut butter, with respect to oil separation based on centrifugation.
2) To investigate the viscoelastic properties of peanut butter by employing the technique of controlled stress rheometry using two types of measurements-oscillatory tests (time and torque sweep) and creep-recovery tests.
3) To monitor the impact of stabilizer levels and storage conditions on the texture and viscosity of peanut butter.

CHAPTER 2

LITERATURE REVIEW

Definition

Peanut butter is a nutritious snack prepared by grinding shelled and blanched (roasted and deskinned) peanuts. Salt, sweetners, stabilizing and emulsifying agents are often incorporated to improve the quality of product with respect to taste, texture and shelf life. The unique flavor and nutritional value makes peanut butter one of the most favorite American snacks and is considered by many as a staple along with bread and milk (APC 2002).

Statistics

The amount of edible peanut crop produced in the year 2000 was 1,480 million pounds of which 796 million pounds were used to manufacture peanut butter. (NASS 2001). Peanut butter industry consumes fifty percent of the edible grade peanut crop in the United States, which accounts for around 10% of the world crop (Virginia-Carolina Peanut Promotions 2000).

Standard of Identity

A product to be labeled as peanut butter must contain at least 90% peanuts; the remainder may comprise other additives like stabilizers, and sweeteners. Peanut products containing more than 10% of non-peanut ingredients are referred to as peanut spreads or imitation peanut butter (U.S. FDA 2002). The total oil content of peanut butter must not exceed 55% by weight, with the exception of reduced fat peanut butter, which contains up to 25% less fat. The maximum acceptable levels for optional ingredients such as salt, stabilizer and dextrose are 1.6, 4 and 6%, respectively. Aflatoxin content of the product

should not be greater than 15 ppb (AMS 2002). Vitamin fortification and the addition of artificial colors, flavors, sweeteners, and preservatives are not permitted (Weiss 1970).

Peanut butter variety

Various kinds of peanut butter available in the market can be placed into four distinct categories:

1. ***Texture*** (a) Smooth or creamy peanut butter, which comprises of a very fine and an even textured product, where the grainy peanut particles are not detectable. (b) Medium textured peanut butter, which contains detectable peanut particles of less than 1/16 inch dimension. (c) Chunky or crunchy textured peanut butter, which contains peanut particles that are a size larger than 1/16 inch dimension.
2. ***Types*** (a) Stabilized peanut butter, which contains a stabilizer as an added ingredient to prevent any free oil separation in the product. (b) Non-stabilized peanut butter, also referred to as "natural" or "organic" (McWatters and Young 1978) peanut butter, which consists of ground peanuts only and may contain salt as a seasoning.
3. ***Styles*** (a) Regular pack, stabilized peanut butter in which the outer skin of peanuts has been removed prior to grinding and may contain salt and some nutritive sweeteners. (b) Specialty pack peanut butter, which is obtained from ground peanuts that have not been blanched and may contain salt and other nutritive sweeteners.
4. ***Grades*** (a) Grade A peanut butter, which has a uniform dispersion of the added ingredients, free from defects and scores 90 points or above for factors like color,

flavor, and aroma. (b) .Grade B peanut butter, which has a reasonably good dispersion of the added ingredients and scores above 80 points. (c) Peanut butter that does not satisfy the criteria required for Grade A and B is referred to as substandard (Woodroof 1983).

Proximate composition and nutritional value of peanut butter

Composition The proximate composition of peanut butter containing only crushed roasted peanuts and salt is given in Table I below (El-Shimi 1992).

Table 1: Proximate composition of Peanut butter

Components	**%**
Moisture	1.60
Protein	26.50
Fat	48.91
Carbohydrate	16.69
Fiber	2.40
Ash	3.92

Many researchers have reported on the compositions of different types of peanut butter available in the market (McWatters and Young 1978; Smith and other 1962; Roberson and others 1965). In a study conducted on stabilized, non-stabilized and imitation peanut butter by McWatters and Young (1978), it was found that the protein content in peanut butter was significantly higher (23 to 25%) than for peanut spread

(16%). The fat content of peanut butter was in the range of 54 to 47%; stabilized butter showed the least variation in oil content when compared to that of non-stabilized samples. Average oil content of spreads was reported to be below 50%. Moisture content of stabilized, non-stabilized and imitation peanut butter was 2.01, 0.74 and 1.63%, respectively.

Nutritional value Peanuts are considered as one of the major sources of plant protein and vegetable oil. Peanuts are normally preferred over other plant proteins in the preparation of food supplements on the basis of color, bland flavor and content of flatulence producing carbohydrates (Resurreccion 1988). They are rich in vitamins (A,, E, B6), thiamin (B1), riboflavin, niacin, folic acid, phosphorus, iodine, manganese, zinc, copper and iron (Galvao and others 1976). Since peanut butter consists of 90% peanuts, this makes it an excellent source of protein, carbohydrates, certain essential fatty acids, vitamins and minerals. Its food value was reported to be higher than a beef steak, which contains 20% protein and no carbohydrates (Thompson 1920). However, the protein quality of peanuts as gauged by the protein efficiency ratio (PER), the plant protein (PER=1.7) was found to be inferior to casein (PER=2.5) by 32%. An improvement in the quality of this low cost protein source is normally achieved by the supplementation of skim milk protein (McWatters and Young 1978). A study on fortification of peanut butter was recently done (Yeh 2001).

The fat present in peanuts is mainly composed of glycerides of fatty acids, 80% of which are unsaturated (Lenth 1939). The major fatty acids present in peanuts are: oleic, linoleic, palmitic and stearic. Traces of behenic, arachidic palmitic and lignoceric are also present (Roberson and other 1965). Presence of high amount of polyunsaturated

fatty acids (PUFA) makes the raw material extremely vulnerable to fat peroxidation and reduce its shelf life (Shewfelt and Young 1977). On the other hand, the unsaturated fat content renders peanuts and its products as versatile and healthy foods with good flavor making them an obvious choice to be included in weight loss and diabetic diets (APC 2002). Dr. Richard Mattes at Purdue University has conducted numerous studies relating to peanut consumption with reference to the satiety factor as well as cardiovascular diseases. He and his coworker (Alper and Mattes, 2002) have reported that, "Despite being energy dense, peanuts have a high satiety value and chronic ingestion evokes strong dietary compensation and little change in energy balance." Spanish variety of peanuts is richer in polyunsaturated fatty acids compared to Virginia and runner type, which have a higher percentage of monounsaturated fatty acids (Woodroof 1983).

Brief History of Peanut Butter

The first commercial production of peanut butter in the Unites States was undertaken by a physician in St.Louis Missouri in 1890, as a health food for the invalids (Woodroof 1983). Also during that period, Dr. John Harvey Kellogg patented the process of manufacturing peanut butter, which was used for patients at his Battle Creek Sanitarium, a health food retreat in Michigan (Virginia-Carolina Peanut Promotions 2000). Unfortunately, it was priced too high due to the unavailability of appropriate equipment for its manufacture. At the end of World War I, the farmers who sought to expand the peanut crop felt the need for a peanut butter type product, while the consumers needed a stable wholesome and nutritious food made directly from the field crop. Consequently, peanut butter came to be manufactured commercially by individual

shopkeepers, depending upon the anticipation of sales and sold in folded paperboard-cartons or boats. This type of peanut butter is available even today under the label of 'old fashioned'. There have been several changes adopted since to make it feasible for the manufacturer to produce and distribute peanut butter on a large scale (Weiss 1970). These include development of proper processing techniques of roasting peanuts and incorporating them into peanut butter products, extension of shelf life by the use of appropriate emulsifiers and stabilizers to prevent oil separation, use of antioxidants to prevent rancidity and inclusion of various additives to increase the palatability of the product.

Manufacture of peanut butter

Originally, peanut butter consisted of only ground-roasted peanuts to which a small amount of salt was added as a flavoring and the product had a shelf life of a few days (Weiss 1970). In the past, when peanut butter was made in small batches as needed for sale, its preparation was more of an art of roasting, blanching and grinding (Woodroof 1983). The increased consumer acceptance of peanut butter as a staple item of diet led to the expansion of the peanut butter industry over the years (Vincent and Szabo 1947). The volume of peanuts being processed today is much larger and the manufacture of peanut butter now has become a science of temperature controls, scanning of raw materials, electronic sorting and grading, aflatoxins determination, adhering to rigid specifications, and vacuum packaging to provide a high quality end product (Woodroof 1983).

Ingredients

Peanuts

There are four main varieties of peanuts grown in the U.S, namely: Virginia, Runner, Spanish and Valencia. The former three varieties are normally used in the making of peanut butter. Peanut butter manufacturers purchase their peanuts from cleaning and shelling factories that provide cleaned, shelled and graded peanuts. Only the U. S grade No.1 peanuts are used in the processing of peanut butter (Weiss 1970). Any variety of peanuts can be used in making the product, but the most desirable consistency for this product is obtained by processing two parts of Spanish or runner peanuts and one part of Virginia peanuts (Woodroof 1983). The most commonly used are the Runner type, which are the cheapest. Also the oil from Virginia and runner types consist of less of linoleic acid along with high amounts of natural antioxidant tocopherol making it more stable than the Spanish peanuts. Virginia peanuts are too low in oil content in comparison to Spanish and runner, which produce a softer and oilier peanut butter (Woodroof 1945).

Salt

Salt is the main flavoring ingredient added to the peanut butter, and the amount added is between 1.5 to 2.0% by weight (Weiss 1970). Concentration of this additive has a significant effect on the crystalline structure and ease of swallowing of the product. Crystallinity for the butter increases with higher salt levels. During consumption, salt like sucrose, has the ability to draw saliva into the peanut butter causing a decrease in its viscosity, which makes it easier to swallow. Crippen and others (1989) studied the effect

of salt on peanut butter texture; they found that consumers preferred peanut butter texture with higher salt concentration of 1.2% in comparison to 0.6%. However, salt along with sweeteners results in the problem of grittiness in the product. In the presence of solutes like sugar, dextrose, salt or corn syrup solids, the moisture present in the butter is unable to maintain them in a solution state and thus, a super-saturated sugar-salt solution is formed during heating, which gives rise to sugar-salt crystals on cooling causing grittiness in the product. The crystals formed thus are usually much larger than their original size in the seasoning ingredients. It was then thought that by using pulverized salt the problem might be reduced but since salt was found to be partially responsible, the usage of expensive grade of salt was discontinued (Woodroof 1983).

Sweeteners

Different manufacturers use a variety of sweeteners in the processing of peanut butter. A regular peanut butter formula consists of 6.0 to 6.9% of dextrose or corn syrup solids. The sweetness capability of corn syrup solids depends upon the extent of hydrolysis of the parent compound-cornstarch. The sweetness level can be identified by the dextrose equivalent (DE) since 100% hydrolysis of cornstarch will yield dextrose. Sucrose and honey (in conjunction with sucrose) are also some of the preferred sweeteners. The sugar present in honey is invert sugar, a mixture of fructose and dextrose, which is sweetener than sucrose. Sugar also aids in decreasing the adhesiveness of peanut butter, making it easier to swallow. Added sugar acts as nuclei for fat crystallization, which reduces the stickiness in the butter (Crippen and others 1989).

Stabilizers and Emulsifiers

Stabilizers are compounds, which are added to peanut butter to reduce or eliminate the problem of natural oil separation in peanut butter. Stabilizers mainly used in peanut butter manufacture are: hydrogenated (hardened) peanut oil, a blend of cottonseed and rapeseed oil (Fix-X), a blend of mono, di or tri glycerides of vegetable oil. The regular peanut butter formulation contains about 2.0% stabilizer (Weiss 1970), but levels as high as 5.5% are also encountered (Woodroof 1983). Stabilizers and their role are discussed in more detail later in this chapter.

Unit operations

Peanut butter manufacture involves seven basic steps: roasting, cooling, blanching, sorting and grading, grinding, deaeration and packaging (Weiss 1970).

The Stock

Most of the peanut industries purchase cleaned and shelled peanuts from the supplier. A few manufacturers prefer to do the cleaning themselves for economic reasons, however, it is undesirable since it can lead to contamination of the product with the dirt. Hence, cleaning is conducted in a separate building.

Roasting

The first step in the manufacture of peanut butter is the dry roasting of raw peanuts. It involves application of heat to generate the heavy roasted color and flavor,

eliminating the raw peanut flavor to improve the palatability of the product (Willich and others 1954). The application of heat first results in marked reduction in the moisture content followed by the appearance of oily translucent spots on the surface of the cotyledons due to the free oil migration from the cytoplasm. This free oil deposits over the cell wall and skins of nuts lead to change in color referred to as white roast. It is during the final stage of roasting when the peanuts develop the dark roast color (Woodroof 1983). The brown color in roasted peanuts is the result of sugar-amino acid reactions that produce melanin. Increasing the temperature or time of roasting can further intensify the golden brown color of melanin (Patte 1991).

Peanuts can be dry roasted by different methods either in a batch or continuous cycle. For instance, in a batch process, peanuts may be heated to 320 °F in a revolving oven. The retention time of the peanuts inside the oven may vary depending upon the batch size, variety, the roast level, and uniformity desired. Batch processes provide the advantage of roasting each variety separately, manipulating the conditions of the process depending upon the moisture content of the starting material and also gives the flexibility of controlling the number of roasters operating to meet the variations in the production. The batch processes however have the disadvantage of being labor intensive, and due to loading and unloading of roasters result in the spillage of precious raw material. Therefore, manufacturers normally prefer continuous roasters as they have the added advantage of providing uniform roast and smoother operations (Woodroof 1983). The process conditions for continuous roasting have to be well controlled since over roasted nuts impart an undesirable dark brown color along with burnt flavor, where as under roasted peanuts lack the flavor and color of adequately roasted peanuts (Woodroof 1983).

Cooling

After the peanuts are "brown roasted", they are immediately cooled to arrest further roasting or darkening. Roasted peanuts are transferred into a bin in which cold air is discharged with the help of suction fans to reduce the temperature of the product evenly (Weiss 1970). It is important to process the roasted peanuts into finished product as quickly as possible since holding them may result in the loss of its volatile fresh roasted flavor imparting a 'stale' note to peanut butter (Weiss 1970).

Blanching

The next process in the manufacture of peanut butter is blanching which involves mechanical removal of the skins, or seed coats. This is achieved by rubbing of nuts between brushes or ribbed rubber belting. This process also results in peanut splits therefore leading to loosening of the germ or the "heart". Removal of skins and hearts is done by passing the peanuts over a screen and in front of a fan, which blows away the light seed coats and allow the germ to pass through the holes in the screen. Skins if not removed properly tend to appear as dark specks in the finished product, while the presence of germ, gives a rancid taste to the butter and expedites the rancidity of the product (Woodroof 1983).

Grading and sorting

This step removes the immature, damaged, discolored peanuts and those infected with molds. The removal of immature and mold infected kernels is done by using graders and sorters which are basically revolving shakers with sized screens. The under

developed or immature kernel, which on an average are smaller than mature kernels, go through the screen where as the mold infected unsplit kernels are retained by the large screens (Weiss 1970). Removal of discolored and damaged peanut kernels is done using the electronic eye; and magnets remove the metal, foreign material contamination in the blanched peanuts (Woodroof 1983).

Grinding

In this unit operation, the dry roasted, blanched and sorted peanuts are converted to uniform, homogenous paste by passing it through a grinding mill. Various manufacturers, depending upon requirement of the end product use different types of mill such as attrition mills, comminuters, homogenizers, disintegrators or colloidal type (Woodroof 1983). Stone and steel plate mills comprise of a built-in rotor revolving against stator, normally set at a clearance of 3-5 mils (25 to 75 μm) (Weiss 1970). Grinding of peanuts to fine texture butter is achieved in a two step grinding operation: (i) Primary grind involving crushing of roasted nuts along with the additional recipe ingredients such as salt, sweeteners, stabilizers, emulsifiers fed to the mill to obtain a peanut paste of coarse or medium grind. (ii) Secondary grind includes the conversion of the intermediate paste to a smooth, textured peanut butter. A coarse or a fine grind is obtained by the manipulation the clearance or the width of the processing gaps through which the mixture is allowed to pass when the same mill is employed for both the stages of grinding. Commonly, two mills are used in series for the each stages of grinding. This increases the throughput of the mills and also lowers the output temperature of product to140-170 ˚F (Weiss 1970). Temperature of the mill is maintained 10 to 15 ˚F above the

melting point of the stabilizer (140- 160 ˚F) so as to achieve a uniform mixing of the additive through out the product (Woodroof 1983). In cases when only a single mill is used the temperature of the exiting product may reach to 180 ˚F.

Deaeration

Hot peanut butter is deaerated to remove unwanted air, which gets incorporated during the grinding process. Non-deaerated peanut butter shows the presence of concave surfaces due to contraction from variable distribution of air, this results into streaking of peanut butter in the container in which it is packaged (Woodroof 1983). These defects are eliminated by pumping of hot peanut butter on to the top of a large tank kept under vacuum. The product is allowed to flow down the tank walls to expose maximum surface area, which allows escape of trapped air; at this stage the product is ready to be cooled (Weiss 1970).

Cooling

It is essential to remove the heat generated during the process of grinding as soon the product exits the deaerator, to induce the fat crystallization. The efficacy of the stabilizer is largely dependent on the manner in which peanut butter is cooled. Shock chilling of peanut butter produces large amount of crystal of small sizes, which are allowed to grow by slow tempering of peanut butter without disturbing it. The temperature of product is allowed to drop from 170 to 120 ˚F or lower (80 °F) by passing through votators or surface scraped heat exchangers (Woodroof 1983; Karn 2001).

Packaging

Chilled peanut butter is then filled in appropriate jars. It may be pressure filled or by gravity. This mainly depends upon the amount of the stabilizer added and filling temperature. Higher temperature in the range 110-130 ˚F permit the gravity filling of the peanut butter but if the temperature is allowed to drop further, below to 95-100 ˚F, the product requires pressure filling. Peanut butter is then deposited in appropriate jar under vacuum to remove the air present in the headspace of the jar in order to shield the product from going rancid (Woodroof 1983). Peanut butter can be packaged in 12/18 ounce PET (Polyethylene tetraphtalate) jars. Peanut butter is often packaged in 12/18 ounce glass jars. For larger requirements of a snack or candy factory, peanut butter can be supplied in 6/5# plastic tubs, 35 lb re-sealable plastic pails, 50 lb poly-lined "bag in the box" or 450 lb fiber poly-lined drums. (Groebfarms 2002).

Shelf Life of Peanut Butter

Peanut butter is a low moisture content food containing not more than 55% fat, the majority of which is unsaturated. This makes the product semi-perishable since it is highly resistant to spoilage by microorganisms; however the high unsaturation makes it susceptible to rancidity in the presence of air or moisture (Woodroof 1983). The spoilage reactions in peanut butter are disintegration of the protein fraction in the presence of bacteria and darkening of peanut butter caused by the reaction of sugar and protein. Both reactions involving protein fraction are rare occurrences since they require high amounts of moisture than is present in product and are therefore most often an indication of moisture contamination. The incidence of salmnellosis caused by *Salmonlella*

Mbbandaka were reported in Australia. *Salmonella* Senftenberg was also found to be present in the peanut butter (Burnett and other 2000). Burnett and others (2000) studied the survival of *Salmonella* in peanut butter and peanut spreads. It was found that the microorganism was able to survive in the peanut butters and spreads for 24 weeks at 5 °C and possibly at 21 °C, and also was found to be dependant on the product formulation.

At the time of harvest, the moisture content in peanuts is between 18-25%, which is then reduced to 10% by mechanical drying to prevent mold growth on the raw material. The relative humidity maintained during storage is 65-70% where the kernels are allowed to equilibrate to the moisture content of 7% (Shewfelt and Young 1977). Roasting of peanuts further decreases the moisture to 0.5-1.0% depending upon the conditions applied (Woodroof 1983). Salt added to peanut butter acts as a preservative. It dissolves in water droplets thereby increasing its concentration by as much as 7-fold in the solution. At this level, salt inhibits growth of harmful bacteria in water droplets (El-Shimi 1992).

Rancidity can be defined as the changes in odor and flavor of lipids associated with fat deterioration. Rancidity can occur due the hydrolysis of ester due to enzyme action, heat or moisture, resulting in the liberation of fatty acids which are mainly responsible for rancid flavor. Degradation of oils involving reaction with molecular oxygen via autoxidation mechanism is referred oxidative rancidity. The ends products of oxidative rancidity are generally acids and aldehydes (Nawar 1996). .

In a study conducted by Willich and others (1954) on oil stability in product as affected by processing and storage, it was discovered that oils were highly resistant to autoxidation during the manufacture, whereas reduction in the oil quality was observed

during storage for 2 years at 80˚ F in the absence of light. Stability of oil was to be found to independent of factors such as salts, mixture of salts, hydrogenation vegetable oil and the extent of roasting if the peanut butter is properly sealed. They also found that the air present in the headspace could acutely affect the stability of fats within a short period of time, but once the entire supply of oxygen is utilized, no further deterioration was observed. Peanut butter is therefore, packaged in airtight container, under vacuum or nitrogen flush to retard incidence of rancidity.

Enzyme catalyzed autoxidation can occur in raw peanuts. This however, is rare in roasted peanuts since the external heat applied to the material deactivates the lipoxygenase responsible for inducing rancidity in peanuts. Roasting also results in loss of natural antioxidants present in raw peanuts which is compensated by the addition the artificial antioxidants. Butylated hydroxyanisole (0.01%), synergized with propyl gallate-citric acid mixture in propylene glycol, was found to maintain the freshness for peanut butter samples for which the jar seals were broken; in comparison to peanut butter with unbroken seals containing no additives (Cecil and Woodroof 1951). El-shimi (1992) also studied the oxidative stability of five different formulations of peanut butter where additives such as salt, casein, sucrose and lecithin were varied. The extent of rancidity was determined by thiobarbituric acid method. It was also reported that the presence of casein and lecithin delayed the onset of rancidity in peanut butter, which was partly due to the presence of phosphoric acid group in lecithin that strengthens the activity of phenolic antioxidants.

Oil separation in peanut butter and its prevention

Peanut butter is a dispersion of solid material released due to grinding of roasted peanuts suspended in liquid oil. There exists a difference in the specific gravity of oil and solid meal phase, which causes the lighter oil phase to migrate to the surface of the product when allowed to stand at ambient temperature conditions for an extended time period. This result in the formation of two separate layers in the jar: 1) a top layer of free oil that undergoes autoxidation imparting a rancid flavor to the peanut butter, and 2) a layer of dry compact mass found at the bottom of the jar which is extremely difficult to spread and too hard to be palatable (Aryana and others 2002). This defect can be corrected by the incorporation of a stabilizer, which reduces the density difference between the two phases. Stabilizers are partially hydrogenated vegetable oil, mono, di or triglycerides of vegetable oils or their combination (Woodroof 1983). They crystallize at low temperatures to form a network that can trap oil within itself, which is exploited in the manufacture of stabilized peanut butter. These hard fatty compounds behave similar to plasticizers in shortenings (Weiss 1970). Grinding of peanut paste to obtain the final product raises the temperature to 77 ˚C (170 ˚F), which melts the stabilizer thereby uniformly dispersing it through out the product. The product is then shock chilled to 49 ˚C (120 ˚F) (Woodroof 1983). The drop in temperature initiates the process of crystallization of the stabilizer leading to trapping of oil and thus preventing its migration to the surface over a period of time. According to Citrene and others (2000), stabilized peanut butter exhibits 'soft-solid gel like behavior'. In this report the terms 'crystal network structure' of peanut butter and 'weak gel like structure' have been used interchangeably. This crystal network formed by stabilizer requires freshly prepared

peanut butter to be left undisturbed for 48 h at 26 °C (78 °F) (Karn 2001). Following this tempering period, manufacturers conduct a quality control test to determine the consistency of the product by using a cone peneterometer, which is not a very precise testing method. In the past, much of the work conducted on peanut butter was with respect to identifying an appropriate stabilizer to eliminate the problem of oil separation and examine its effect on the textural properties of peanut butter (Aryana and others 2002; Gills and Resurreccion 1998; Hinds and others 1994; Lenth 1939; Woodroof 1983).

Stockton in 1921 patented the manufacturing process of stabilized peanut butter using hydrogenated peanut oil. The stabilizer used in the study was a blend of 85% natural peanut oil and 15% fully hydrogenated oil (m.p 58-60 °C) (Woodroof 1983). It was reported that the hardened fat in the mixture was responsible for the resistance of the product towards oil separation. The stabilizing ingredient used in peanut butter formulation leads to the trapping of oil. Hydrogenation is a process of decreasing the degree of unsaturation of oils by the addition of hydrogen atoms across the double bond in the presence of a catalyst. The primary objective here is to alter the melting profile of the final product, which has a direct impact on its physical properties, thereby, rendering a fat more suitable for the application where the original fat was inappropriate (Rajah 1994). Natural oil does not crystallize due to high degree of unsaturation, however, upon its hydrogenation, it hardens and its melting point is elevated to form a solid state at room temperatures. The crystallization of the fat occurs almost instantaneously throughout the freshly prepared butter upon cooling, well before the oil-meal dispersion can separate. Rapid cooling is desirable since fats then crystallize into the lower melting form,

producing large numbers of finely divided crystals, which have the maximum potential to stabilize the peanut butter (Freeman and Singleton 1954).

Proctor and Gamble introduced 'Fix' stabilizer in the year 1950 and patented the process of manufacturing of stabilized peanut butter. Fix was a blend of hydrogenated peanut oil and salt in peanut oil. Since the salt was inherent in its recipe, it improved the flavor of the end product. The product was a white semi-solid substance having the same consistency as the soft shortening used in the preparation of bakery products. The commercial stabilizer used in the manufacture of peanut butter was Fix-X™ (Proctor and Gamble, Cincinnati, OH). It is a mix of hydrogenated rapeseed oil and cottonseed oil containing 33-37% behenic acid ($C_{22:0}$), which is a primary active component of the mixture imparting stabilizing properties to the blend. Fix-X ™ was used in various studies to stabilize peanut paste (Muego and others 1992) and as a control to compare the effectiveness of palm oil as a stabilizer (Hinds and others1994; Gills and Resurreccion 2000). A variety of stabilizing agents are being used by manufacturers and vendors in the peanut butter industry but for propitiatory reasons that information is not available.

Unhydrogenated palm oil was investigated as a potential stabilizer for peanut butter, since oil did not have the disadvantage of being a probable source of trans fatty acids, which is generated during the hydrogenation of oil. Hinds and others (1994), reported palm oil could successfully hold oil in the dispersion when added in the range of 2-2.5% for over a period of one year at 21-24 °C. The criteria for judging the stability was a maximum of 0.5% oil separation at 30-35 °C after two weeks, based on the USDA regulation of 0.5 ml free oil/jar for a freshly prepared product after 24 hour of storage at 30 °C (Woodroof 1983). However, an extensive study conducted to investigate the

sensory and physical characteristics of peanut butter stabilized with palm oil demonstrated that it was unable to keep the oil from separation for one year. It was reported that regardless of the amount of stabilizer present, oil separation was observed in the samples that were stored at 21, 30 and 45 °C, higher temperature showed more oil separation. The shelf life of peanut butter with 2.5% palm oil at 30 and 45 °C was 113 days (Gills and Resurreccion 2000).

Texture

The production of peanut butter has been commercialized since the early 1900s in the United States and the product has since been one of the favorite snack items with its market demands steadily increasing. This provided an incentive to conduct extensive research on various aspects affecting the quality of the end product such as: impact of raw material, processing techniques, prevention of oil separation by the addition of suitable stabilizer, texture characteristics and sensory studies have been conducted on the peanut butter. An appropriately tempered stabilized peanut butter exhibits improved texture, appearance, spreadable characteristics, decreased stickiness and better fluid consistency over a wide range of temperature (10 to 37 ˚C), providing a "good melt-in-the mouth properties" and high resistance to oil migration of oil (Rajah 1994).

Cone penetrometry has been a routine technique in evaluating physical texture of the spreads (Moran 1994). It is a standard quality control test, and is used by many researchers as a reliable method along with other advanced instruments to gauge the strength of the food product (Ahmed and Ali 1986; Muego and others 1990; Vincent and Szabi 1947). The strength of the solid fat is gauged depending upon the depth to which

the cone attached to the vertical shaft, travels through various layers in the product. The yield value can be estimated by the formula, for determination of the hardness of the solid fat:

$$C = KW/p^{1.6}$$

Where C is yield value; K is cone penetration constant (depends on the cone angle); W is the total weight of the cone plus shaft assembly including the additional weight placed on the cone; and P is the depth of penetration in mm as recorded in the dial (Bourne 1982).

The standard conditions used by the majority of researchers were set to allow the cone to penetrate through peanut butter for 5 s with varying weights for the cone and shaft. The results are reported in millimeters (distance traveled by the cone). Ahmed and Ali (1986) investigated the effect of oil content and peanut seed on the texture of peanut butter and found that higher oil content produced a softer product, leading to increased penetration of the cone through the sample. Muego and others (1990) compared the firmness of peanut paste to that of the experimental and market samples of peanut butter. The paste was found to be firmer, followed by the experimental and the market sample respectively. Vincent and Szabo (1947) also used the cone penetrometry technique to characterize firmness using experimental and commercial peanut butter or paste samples. Their conditions differed slightly from the standard protocol, in that the cone was allowed to sink into the sample for 1min instead of 5 s. They observed that the peanut butter with greater fluid consistency had yielded greater depth of penetration followed by samples

with fine grinds and commercial samples. Peanut butter with the lowest spreadability registered least penetration depth. They, however, did not mention the details regarding preparation of laboratory samples.

Instron

This instrument is primarily used to investigate the stress-strain relationship of materials by performing standard tests in tension, compression, or bending; as well as advanced tests involving stress relaxation, stress recovery, energy of deformation and rupture. It was originally designed for testing engineering materials (metals, wood, plastics, and fibers) and since then has been adapted to new applications in food research. One of the most important applications using Instron has been in performing texture profile analysis for various food products.

The instrumental texture profile analysis test was pioneered by the General Food's technical corporation center. It involved the compression of bite-sized food particle twice, in reciprocating motion so as to mimic the action of the jaw. The response was recorded as force time curve from which a number of textural parameters were calculated to give good correlation with textural sensory attributes (Bourne 1982). The origins can be traced back to the bite tenderometer developed by VolodKevich, as an attempt to create the conditions the food particles are subjected to when they are consumed. It was first described in 1938. The instrument measured the force of biting of a food particle as a function of deformation and total energy involved in the process. The idea led to the development of MIT tenderometer in the 1950s, an assembly of complete set of human dentures with a mechanized chewing system with variable motions. This

assembly simulates the denture surfaces and food mastication process encounters in human mouth. (Szczesniak 1963). The next development in this area after a decade was the General Food (G.F.) texturometer that employed a plunger instead of dentures to compress a bite-size sample twice in a reciprocating motion duplicating the actions of human oral cavity. The observation was recorded as the force time curves from which seven textural parameters were determined namely: factorability, hardness, cohesiveness, adhesiveness, springiness, gumminess and chewiness. These parameters were found to provide high correlations with the sensory ratings. Instron Universal testing is therefore the fourth generation instrument in this series.

Bourne (1968) adapted the Instron machine to perform the G. F. texture profile to understand the textural changes occurring during pear ripening. Since then, numerous researchers have conducted texture studies on a variety of food materials using this instrument (Henry and others 1971; Collins and Sanchez 1979; Ahmed and Ali 1986; Muego and others 1990; Hinds 1994).

Collins and Sanchez (1979) used this instrument to study the firmness of the prepared samples of peanut butter containing peanut shell flour and commercial samples by allowing the probe to penetrate 2 cm into the sample at crosshead speed of 10 cm/min. In the study, peanut shell flour was used as an additive to reduce the amount of stabilizer added for the prevention of oil separation. They investigated the effects of the flour on the texture and sensory profile of the butter from which they concluded that the peanut shell could be a potential additive. They however did not conduct any stability studies with regards to oil separation.

Ahmed and Ali (1986) investigated the adhesiveness of peanut butter by penetrating a stainless steel plunger to a depth of 0.4 cm. From this depth, the plunger was then withdrawn at the same speed at which it was allowed to penetrate (0.5 cm/min). During the backward movement, a small amount of butter was still attached to the probe, which stretched initially before breaking. They expressed results in terms of the index of adhesiveness for the sample as the force (N) needed to detach the material from the plunger. Adhesiveness of a sample is defined, as the force required in dislodging material that adheres to the palate during mastication.

Muego and others (1990) further extended the approach to analyze the textural characteristics of peanut paste and butter samples by obtaining the force deformation curves to calculate the adhesiveness of samples. He also conducted a modified texture profile analysis on the samples. In a modified TPA, the sample (2.5 g) was compressed between two plates until the clearance between the plates was 2 mm, followed by reversal of the crosshead causing sample decompression. From the force deformation curves the seven main characteristics of the samples were then calculated. The authors found the texture profile analysis to be a superior and more objective method for testing adhesiveness for the sample in comparison to cone penetrometry.

Microscopic studies

Young and Schadel (1990) proposed a unique method using scanning electron microscopy (SEM) to determine the extent of homogenization in peanut butter. This method examined the arrangement of the microstructure features of stabilized peanut butter. The method was originally employed for examining damaged peanut seed tissue.

Three commercial peanut butter samples observed under a scanning electron microscope exhibited difference in the spatial arrangement of protein bodies. The technique of light microscopy was also used to understand the impact of three different types of grinding processes used in the preparation of non-stabilized peanut butter (Young and Schadel 1991). Coupling of two grinding processes in a sequence was found to improve the spatial relationship of the cellular material such as the protein bodies, starch grains and cell and tissue fragment. Aryana and others (2000) further adapted the method of SEM to gauge the effectiveness of palm oil as a stabilizer by comparing the microstructure of palm oil stabilized peanut butter with non - stabilized peanut butter and that prepared with a commercial stabilizer. Peanut butter stabilized with the hydrogenated oil (commercial stabilizer) did not show any presence of clusters of protein bodies, cell wall fragments; where as in the case of palm oil as an alternate stabilizer, small clusters of protein were observed with cell fragments. The criterion of gauging the effectiveness of stabilization or stability of peanut butter was the absence of cell wall fragment and protein bodies. Clusters of protein bodies and cell wall fragments were present in the non-stabilized sample; peanut butter containing palm oil exhibited the presence of smaller clusters whereas, the hydrogenated vegetable oil stabilized sample was superior than the palm oil stabilized samples. However, both kinds of micro structural bodies were absent in the samples after 130 days of storage at high temperature of 45 °C. No difference was found in the microstructure arrangement for all samples kept at 0 °C.

Rheological study

Rheology is a branch of physics defined as the study of flow and deformation of matter, and the mechanical properties of solid, semi-solids and fluids (Rao 1999). The previous studies conducted on peanut butter were restricted to texture and firmness evaluations to judge the product's structural strength and understand its sensory characteristics. The terminology, in the case of texture profile analysis for individual product type is based on the underlying rheological properties as mentioned in the early texture profile publications (Meilgaard and others 1987). Lately, researchers have focused their attention on understanding the rheological properties of peanut butter using advanced rheological techniques. Campanella and Peleg (1987) described peanut butter as the power law fluid. index (n) of 0.5-0.7 using the squeeze flow viscometry. This technique involves the compression of the fluid between two parallel plates. The peanut butter were allowed to relax for a few minutes after loading, following which it was subjected to constant strain (deformation) using Instron and creep tests using a creep tester (constant stress). A Power law fluid can be defined by the empirical relationship

$$\tau = K\dot{\gamma}^{n}$$

where, τ is the shear stress (Pa), $\dot{\gamma}$ is shear rate (1/s)K is the consistency index (Pa s^n), and the exponent 'n' is the flow behavior index (dimensionless) that indicates the extent of deviation from the Newtonian flow for the fluid. For a Newtonian fluid n=1; n>1 for dilatant fluid and for pseudoplastic fluid n <1 (Bourne 2002).

Campanella and Peleg (1987) also demonstrated the presence of viscoelastic behavior in peanut butter since force deformation of the samples started from the point of origin and not from a non-zero value as for liquids. For the creep tests, however the presence of viscoelastic nature was only noted in the initial stages of the application of a constant stress that later resulted in a rapid dissipation as the butter starts to flow under the applied stress. In this case, creep tests were applied to understand the flow characteristic. However, authors made no mention of samples recovery from stress removal in the creep tests.

Citrene and others (2000) also conducted an extensive study on the rheological properties of stabilized and non-stabilized peanut butter under constant stress and strain conditions. It was found that the transition stress values for stabilized and non-stabilized peanut butter were 250 and 10 Pa respectively, applied during creep tests. For oscillatory strain sweeps, stabilized samples displayed the presence of a weak gel for which the storage modulus (G′) was higher than that of the non-stabilized suspensions. Storage modulus (G´) represents the amount of stored energy in the system and is the most sensitive indicator of changes occurring in the viscoelasticity of the material. The stabilizer incorporated enrobes the surface of the solid particles giving rise to repulsive forces similar to the steric stabilization of colloidal suspensions in polymers, resulting in the formation of weak gel-network. Due to the gel-network formed the sample exhibits an apparent yield stress and thixotropic behavior.

Viscoelasticity

Classical theories of elasticity and hydrodynamics deal with the mechanical properties of solids and viscous liquids, respectively. According to these theories, stress in solids is directly proportional to the applied strain (Hooke's law), whereas for liquids, stress is proportional to the strain rate (Newton's law). Certain materials, which are not perfect solids, may not exhibit a constant deformation on application of constant stress but deform slowly with time or creep, and the strain developed on the sample will gradually reach an equilibrium value. Materials that deviate from liquid-like behavior, under same conditions, may store a part of the energy input and dissipate the rest as heat and after stress removal may partially recovery (Ferry 1970). Such characteristics are referred to as viscoelastic behavior. To sum up, viscoelasticity is the intrinsic property of material that displays both as solid-like and liquid-like behaviors. They are both elastic as well as viscous food materials, and the fundamental rheological measurements are basically designed to establish their viscous and elastic properties.

Rheology helps in characterizing the physical properties of liquids and soft solids such as yield stress, stress-strain relationship and viscoelasticity. There are two important approaches for conducting rheological measurements: controlled rate and controlled stress. In the former, the rate of strain is controlled and resulting shear stress is measured. Many of the earlier viscometers were designed to operate on this principle. In the latter, torque is the independent variable and the resulting displacement is measured as the rate of strain. This is a relatively new technique pioneered by Carri-Med PLC and has proven to be a useful tool in understanding the processes such as sedimentation, extrusion and stabilization (AR 1000 TA instruments manual 2000).

The controlled stress rheometer has been used in measuring the viscoelasticity of food products as well as inorganic products. Munoz and Sherman (1990) employed this technique to determine the dynamic viscoelastic properties of commercial salad dressings, mayonnaise, reduced calorie mayonnaise and salad creams using oscillatory stress and frequency sweeps. Their primary objective was to characterize viscoelastic properties of commercial salad dressings using small amplitude oscillatory experiments where the responses were related to their respective structures. Munoz and Sherman (1990) determined the linear viscoelastic range (LVR) for all the samples using the oscillatory stress sweeps and conducted the frequency sweep tests on them within their LVR. All standard mayonnaise samples displayed larger values of LVR for the maximum stress amplitude in comparison to the reduced fat samples followed by salad creams. Such values were due to the presence of intermolecular forces within the protein molecules which are of greater significance in mayonnaise than in salad dressings. The elastic properties of the salad dressings were found to be inferior as they showed significantly lower G′ and higher G″/G′ values.

Rosalina and Bhattacharya (2001) investigated the effect of modification of starches and their concentration on the rheological behavior of starch water dispersions using controlled rate and controlled stress techniques. Steady shear time dependent flow properties of viscoelastic starch gels were investigated by conducting stress relaxation, creep, and steady stress sweep tests. The viscosity of the starch gels determined as the function of shear rate obeyed the power law model except at very low stresses. Stress relaxation tests were used to measure the decay in stressed sample subjected to a constant magnitude of strain (Rao 1999). Cross-linking of starch was shown to increase relaxation

modulus; however, an increase in starch modification was found to lower the modulus. Creep tests were carried on the starches to understand the effect of modification on the viscoelasticity. It was found that increasing concentration of the starch improved the viscoelastic nature of the sample, and the steady state flow was attained within a short interval, which is typical of a viscoelastic fluid. Cross-linking in starches occurs at random and therefore the network strength is not uniform throughout. This results in larger deformations due to breakdown of weaker cross links followed by rupture of strong cross links.

Creep Recovery test

Creep recovery tests are conducted to evaluate the strength of material, within its LVR, to gain a better insight of the viscoelastic behavior. The material is subjected to a constant stress, instantaneously at the outset (t = 0) and the strain developed on the material is then measured. The stress is maintained constant for a time interval t, following which it is removed and the sample is allowed to recover (Recovery). The LVR of a material can be determined by either conducting a torque sweep, which involves subjecting the samples to increasing amplitudes of stress at a constant frequency or by frequency sweep in which the frequency applied on the sample varied. Within the linear viscoelastic region, creep curves obtained at the different stresses should overlay on each other. The response of a material subjected to creep tests is reported as compliance (J), which is the ratio of shear strain (γ) to constant shear stress (σ_c) and is a measure of the amount of sample deformation. The data is represented in terms of creep compliance and is expressed as (Rao 1999):

$$J(t, \sigma_c) = \gamma/\sigma_c$$

A typical illustration of creep curve for a viscoelastic solid is divided into three main regions (Rao 1999):

1. The region A-B corresponds to instantaneous compliance (J_o). In this region, the bonds of the material are stretched elastically so as to allow complete recovery. If stress is discontinued beyond this region, the material will exhibit a complete recovery. The instantaneous compliance indicates the presence of an undisturbed network (Gladwell and others 1985).

$$J_o = 1/G_o \qquad (1)$$

where G_o is the instantaneous elastic modulus (Rao 1999).

2. The region B-C refers to the time dependent retarded compliance (J_R), which is associated with retarded elastic modulus, viscosity ($\eta_{R)}$ and retardation time (τ_R). In this region of retarded elasticity, the elastic capacity of the material deteriorates due constant breaking and reforming of bonds, which do not occur at the same rate. The equation representing the retarded elastic region using mean values of retarded elastic compliance variables (Shama and Sherman 1966):

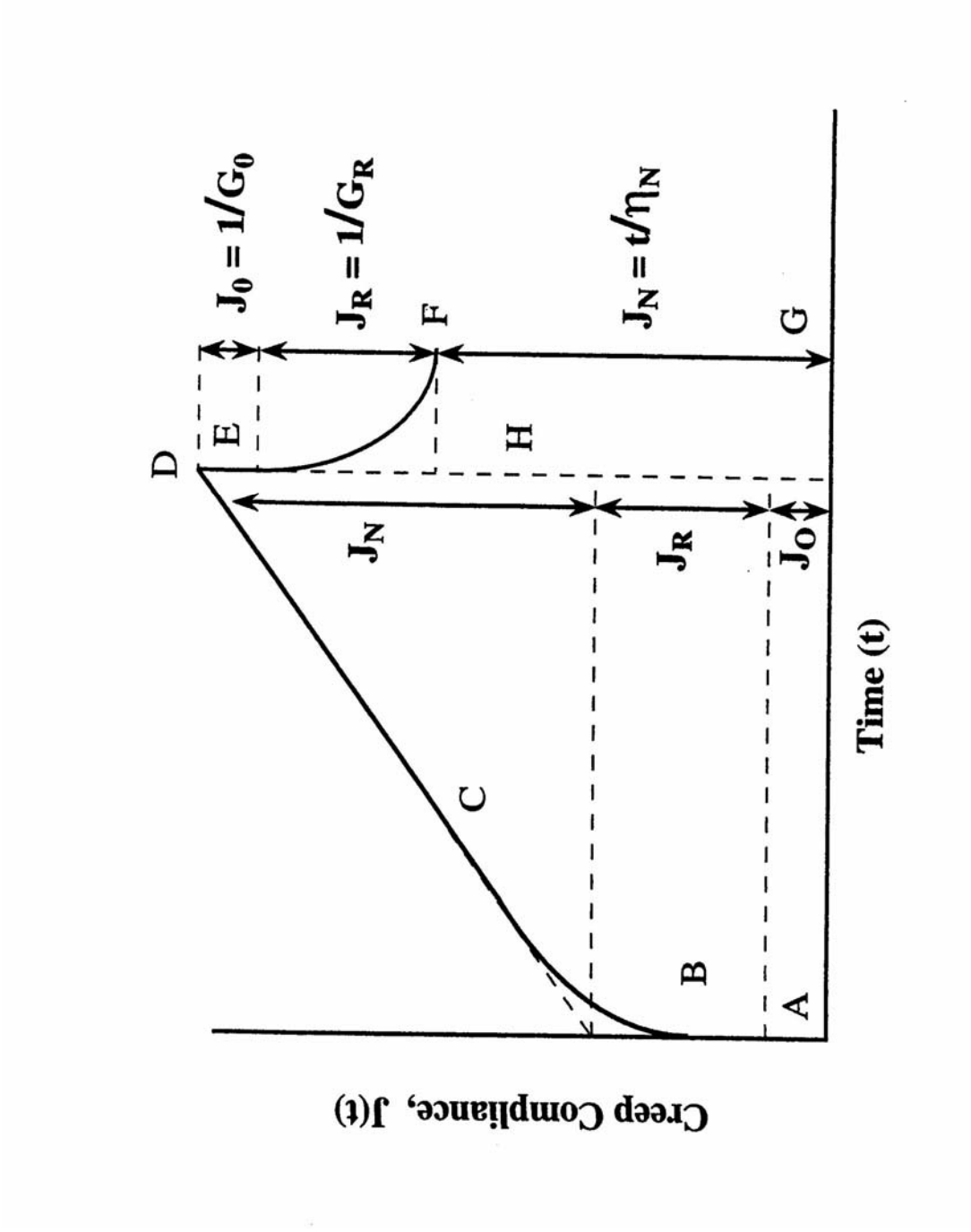

Figure 2.1: Schematic representation of Creep compliance curve for a viscoelastic material (Rao 1999)

$$J_R = J_m [1- \exp (-t/\tau_m] \quad (2)$$

J_m- mean compliance representing all the bonds

τ_m- mean retardation time = J_m x η_m

η_m- mean viscosity

Since all changes with bond breaking and reformation occur at a different rate, the term τ is replaced by series of retardation times (τ_1, τ_2, τ_3... τ_i). Accordingly, J_m and η_m can be replaced by their respective series of retarded elastic moduli (J_1, J_2, J_3...J_i) and associated viscosities (η_1, η_2, η_3....η_i) (Shama and Sherman 1966).

$$J_R = \Sigma i \, Ji \, [1-\exp (-t/\tau i)] \quad (3)$$

3. Region C-D represents the linear region of the Newtonian compliance (J_N) in which the restructuring of ruptured bonds takes longer than the test period and the structural units flow past one another (Sherman 1966). The newtonian compliance is given as

$$J_N = t/\eta_N \quad (4)$$

Therefore, the overall creep compliance for a viscoelastic material is given as:

$$J(t) = J_o + J_R + J_N$$

$$= J_o + \Sigma_i \, Ji \, [1-\exp (-t/\tau_i)] + t/\eta_N \quad (5)$$

Several studies have been conducted to investigate viscoelastic properties of food products using creep compliance techniques (Rosalina and others 2001; Citrene and others 2000; Chronakis 1996; Katsuta and others 1990; Munoz and others 1990 Gladwell and others 1985; Sherman 1966; Shama and Sherman 1966). The results are described in terms of mechanical models usually containing two retardation compliances terms (J_1 and J_2) and the model parameters are related to the structural characteristics of samples. However, with the introduction of dynamic rheological tests, which have gained importance over the years, the focus has shifted towards interpretation of the results in terms of the structure and composition of the material over data analysis using mechanical models (Rao 1999). The mechanical models are used to understand viscoelastic response of the material which is explained in terms of G', G'', J_o and J_i. These parameters are described in detail at the end of this chapter under the glossary of terms. The mechanical model consists of an elastic spring and dashpot which represents Newtonian viscosity η. A dashpot is an assembly of cylinder, filled with high viscosity fluid, with a loosely fitted plunger. The series arrangement of the elastic spring element and the dashpot is referred to Maxwell model and parallel arrangement is known as the Kelvin-Voigt model (Rao 1999). Sherman (1966) determined the creep behavior of frozen, melted and ice cream mix. The creep compliance behavior for the frozen as well as the ice cream prepared from a mix was represented by the inclusion of two retarded compliances (J_1, J_2); where as for the melted ice cream only one of the terms (J_1) was included.

$$J(t) = J_o + J_1 (1-e^{-(-t/\tau_1)}) + J_2 (1-e^{-(-t/\tau_2)}) + t/\eta_n \qquad (6)$$

Gladwell and others (1985) used creep tests to investigate the influence of disperse phase (oil) concentration on the viscoelastic properties of oil-water emulsions. The viscoelastic behavior of the emulsions was explained by the presence of two elastic retardation terms (Eq. 6). The changes in the viscoelastic properties were monitored by measuring the instantaneous compliance (J_o), and the two retardation compliances (J_1 and J_2). A reduction in Jo, J_1 and J_2 was observed with increase in oil concentration. This was due to formation of a strong undisturbed network with oil, thereby increasing the contribution of instantaneous elastic shear modulus G_o (= 1/ J_o). An increase in the elastic behavior of a material reduced the contribution of the viscous component, which was represented by decreasing first and second retardation compliances (J_1 and J_2).

Oscillatory test

Viscoelastic behavior of fluid foods can also be studied using dynamic rheological experiments, which are referred to as Small Amplitude Oscillatory Shear (SAOS) tests. The material is kept under oscillatory stress or strain maintaining a constant frequency ω, and phase difference between the two is measured. An oscillatory strain or deformation produces two types of stress components in viscoelastic materials: elastic component (in phase with the strain) and viscous component (90° out of phase with strain). Response of the sample, expressed as the stress generated as a consequence of the applied strain is calculated by:

$$\sigma_o = G'\gamma_o \sin(\omega t) + G''\gamma_o \cos(\omega t) \qquad (7)$$

Where G′ is storage modulus, which is measure of the stored energy in a substance; G″ is loss or viscous modulus that is measure of the energy dissipated by the substance; σ_o is stress amplitude; γ_o is strain amplitude

Therefore, in viscoelastic substances oscillatory stress lags behind the applied strain by an angle δ. δ falls in the range of 0 to π/2 depending upon the contribution of the viscous and elastic components.

$$\sigma (t) = \sigma_o \sin (\omega t + \delta) \quad (8)$$

Hence the loss tangent is given by

$$\text{Tan } \delta = G''/G' \quad (9)$$

When G′ >> G″, the material behaves like a solid and shows complete recovery from deformation. However, when G″ is greater (G″ >> G′), the viscous component dominates resulting in dissipation of applied energy because the material deforms displaying a liquid-like characteristic (Rao 1999).

Time sweeps are oscillatory experiments which involve the application of small amounts of strain to a sample to monitor G′ as a function of time. They are used to evaluate the thixotropic recovery of the sample subjected to loading and sampling (Groh 2000). Time required for G′ to attain an equilibrium value is identified as the time period required for the structure to re-build itself.

The linear viscoelastic region of a sample is usually determined by oscillatory stress sweeps or torque sweeps. In this test, the material is subjected to increasing amplitude of oscillatory stress at constant frequency and temperature. The storage modulus (G´) is plotted against the applied stress. The range of stress over which the storage modulus (G´) is independent of the applied stress is defined as the linear viscoelastic region. In the linear region, the material structure is unbroken. Beyond a value of applied stress, the storage modulus (G´) is unable to withstand the applied stress and the structure breaks. The value of stress is referred to critical stress (σ_c) and corresponding storage modulus value is G'_C. Higher the value of the critical stress (σ_c), stronger is the strength of the material under investigation (Groh 2000).

Peanut butter has been the subject of various studies primarily directed towards improvement in texture and shelf life of products. In previous studies, researchers had measured the natural oil separation as an indicator of shelf life of product simply by decanting and weighing the top oil layer. This is a time consuming process since the oil to separate in stabilized peanut butter requires at least two weeks of storage at 30 °C. Oil separates in peanut butter under the influence of gravity. Increasing the magnitude of force experienced by peanut butter by centrifugation would result in rapid oil separation, which may be accurately measured. However, to validate the use of centrifugation as a shelf life predicting technique for peanut butter, it is necessary to perform extensive centrifugation tests on the product with different stabilizer levels. Also it would require establishing a correlation between the oil separated by the centrifugal force and under the influence of natural gravity. Previous rheological investigations of peanut butter have been conducted with the aim of understanding the viscoelasticity and yield stress. The

evaluation of the weak gel-network of peanut butter in terms of the rheological parameters has never been conducted. Therefore, the primary objectives of this study were to outline a test based on centrifugation–based to estimate shelf-life of peanut butter dispersion (time for which peanut butter exhibits no oil separation) and to apply control stress rheometry as a tool to measure the structural strength of network formed in peanut butter.

Glossary

1. **Creep: Its** the increase in deformation (strain) on the sample as a function of time when sample is kept under constant stress.
2. **Creep recovery test**: It is used to evaluate the strength of material usually within its linear viscoelastic range, to gain a better insight of the viscoelastic behavior. The material is subjected to instantaneous stress (t = 0) and resulting strain developed on the material is measured as the response. The stress is maintained constant for a time interval t, following which it is removed and the sample is allowed to recover (Recovery).
3. **Creep compliance (J(t), m^2/N):** Its the ratio of shear strain (γ) to shear stress (σ_c) and is a measure of the extent of deformation in the sample during creep testing. Creep compliance can be expressed as:

$$J(t,\sigma_c) = \gamma/\sigma_c$$

4. **Complex modulus (G*, Pa)**: It is the difference between storage modulus (G′) and loss modulus (G″):

$$G^* = G' - \ddot{\imath}G''$$

$$|G^*| = [(G')^2 + (G'')^2]^{1/2}$$

5. **Complex viscosity (η^*, Pa s):** It is related to complex modulus and represents the angle between viscous stress and shear stress. Complex viscosity is the difference between storage viscosity (η'') and loss viscosity(η''):

$$\eta^* = \eta' - \ddot{\imath}\eta''$$

It can also be represented as:

$$|\eta^*| = [(\eta')^2 + (\eta'')^2]^{1/2}$$

6. **Instantaneous elastic shear modulus (J_o, m^2/N):** It is a reciprocal of elastic shear modulus ($J_o = 1/G_o$). It is a measure of the strength of unperturbed network structure present in viscoelastic material, in a creep recovery test.
7. **Gap (microns):** The term "gap" denotes the physical distance maintained between peltier plate and attachment of the rheometer.
8. **Kelvin-Voigt model:** It consists of parallel arrangement of spring element and dashpot (also see mechanical model).
9. **Linear viscoelastic range (LVR): Its** the region in which the properties of material are independent of applied deformations (stress or strain) and are only time dependent.
10. **Loss modulus (G″, Pa**): It represents the magnitude of energy lost as viscous dissipation per cycle of deformation.
11. **Loss viscosity (η′, Pa s):** It is the ratio of the loss modulus (G″) to angular frequency (ω) and is real part of complex viscosity.

$$\eta' = G'' / \omega$$

12. **Loss tangent (tan δ):** It is the ratio of the energy dissipated to that of stored per cycle (see phase lag):

$$\text{Tan } \delta = G'' / G'$$

13. **Maxwell element**: It consists of a spring and a dashpot placed in a series of positions (see mechanical model).

14. **Mechanical model:** It facilitates in visualizing the different patterns of viscoelastic behavior. The model consists of two key elements: 1) A spring element, which represents a perfectly elastic solid 2) A dashpot, piston and cylinder, which represents movement of a Newtonian fluid
15. **Non-linear viscoelastic range: Its** the region in which properties of material are a function of applied deformation (stress or strain) and time.
16. **Oscillatory frequency sweep:** In this test, a material is subjected to increasing frequency at a constant stress.
17. **Oscillatory stress sweep:** In this test, a material is subjected to increasing amplitudes of oscillatory stress at a constant frequency.
18. **Oscillatory time sweep:** In this test, a material is kept under constant strain, and the time required for storage modulus to stabilize to an equilibrium value is monitored.
19. **Phase lag (δ, degrees):** In a small amplitude oscillatory experiment, depending upon the nature of test sample, a lag occurs between the applied controlled variable and response variable. This lag is referred to as phase lag or loss angle. For a perfectly elastic solid, if the controlled variable is stress, strain (response) is in phase with the applied oscillatory stress ($\delta = 0$ º); whereas in case of perfectly viscous fluid, strain lags behind applied oscillatory stress by an angle of 90º. Material which generates a phase lag between 0 and 90 ($0 < \delta < 90$º) is referred to as viscoelastic in nature. For illustration of this concept see Figs. 2.2 to 2.4.

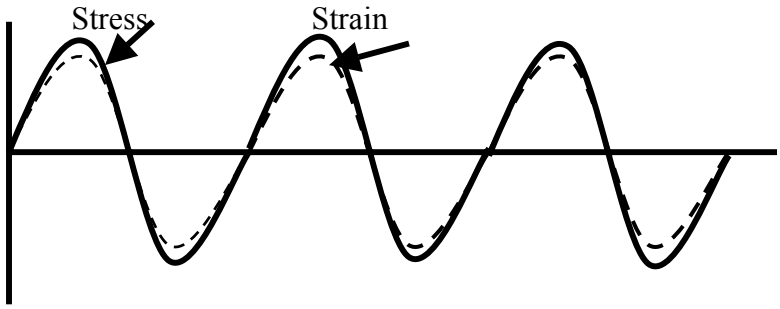

Figure 2.2: Stress versus strain response for a perfectly elastic solid ($\delta = 0^{o}$)

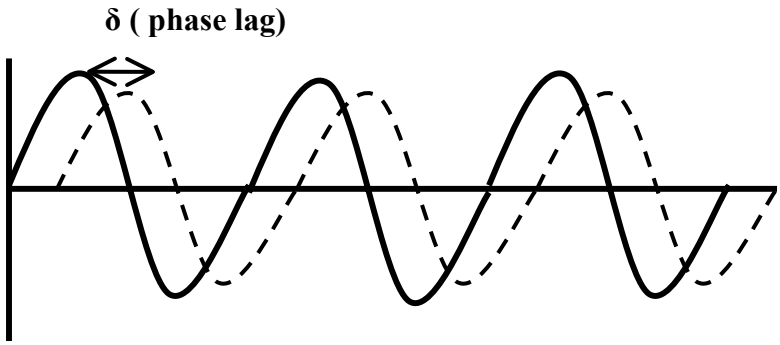

Figure 2.3: Stress versus strain response of perfectly viscous material ($\delta = 90^{o}$)

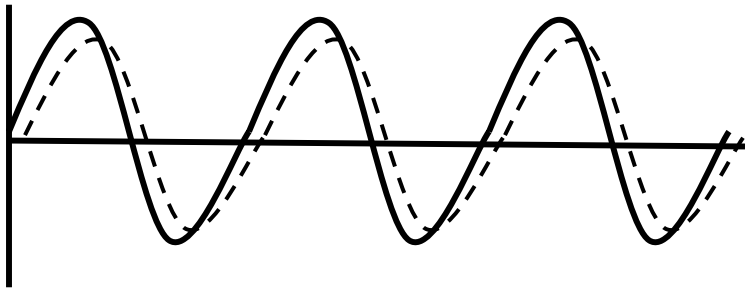

Figure 2.4: Stress versus strain response of a viscoelastic material ($0^{o} < \delta < 90^{o}$)

20. **Retardation elastic compliance (J_R, m^2/N):** This term represents the region of retardation elasticity in creep compliance curve. This region involves a breaking and reformation of bonds when the material is under constant stress.

21. **Small amplitude oscillatory shear:** The principle of these tests is to subject a sample to oscillatory stress or strain amplitudes and subsequently measuring the resulting deformation developed in the sample**.**

22. **Storage modulus (G′ , Pa**): It represents the magnitude of energy that is stored or recoverable per cycle of deformation in dynamic oscillatory test.

23. **Storage viscosity (η″, Pa s):** It is defined as the ratio of storage modulus to angular frequency and is the imaginary part of complex viscosity.

$$\eta'' = G'/\omega$$

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CHAPTER 3

DEVELOPMENT OF A RAPID METHOD BASED ON CENTRIFUGATION TO PREDICT OIL SEPARATION IN PEANUT BUTTER[1]

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ABSTRACT

Centrifugation studies were conducted on commercial and experimental samples for identifying the optimum condition (10,035 m/s^2 -10 min) for simulating oil separation in peanut butter. Oil separation under the influence of natural gravitational force was also studied in samples under accelerated storage condition of 35 °C for three months. The response of fresh samples was correlated with that of stored samples to predict product shelf life of peanut butter. Control samples with no added stabilizer (0.0 %) were found to have a shelf life (time for which product exhibits no oil separation) of less than 15 d; whereas stabilized samples were predicted to be shelf stable for 1 yr at 21-24 °C storage.

Key words: Peanut butter, oil separation, centrifugation

INTRODUCTION

Peanut butter is a dispersion of solid material suspended in liquid oil. Due to the density difference which exists between the oil and solid particulates phase, the lighter phase oil tends to migrate to the surface of the container when the product is stored at ambient temperature (Freeman and Singleton 1952). The breakdown of dispersion results in the formation of two separate layers: 1) A free oil layer which is prone to autoxidation and imparts the stale and rancid odor to the product; 2) A dry compacted layer formed at the bottom of the jar due to settling of heavy particles under gravitational influence, which is unpalatable and too firm to spread evenly (Aryana 2002). Oil separation in peanut butter is prevented by the addition of stabilizers. Stabilizers are partially hydrogenated vegetable oil, mono, di or tri glycerides or their combination (Woodroof 1983). The primary function of a stabilizer is to entrap oil and prevent its upward migration. They have the ability to crystallize into finely divided crystals at low temperatures, which on tempering form a network structure. Citrene and others (2000) showed the presence of 'soft solid gel like behavior' in stabilized peanut butter. In our study we are using 'crystal network structure' and weak gel interchangeably. This network structure then serves a dual purpose of holding the oil and providing a smooth spreadable texture to the butter. A well-formed crystal network prevents migration of oil in the product over a period; hence, it is the strength of this network, which holds the key in predicting a product's shelf life. At present, Cone penetrometry is generally the quality assurance test conducted to evaluate the product texture, an indicator of network strength. This test is performed on peanut butter samples, which have been tempered at

26 °C over a period of 48 h. Therefore, there is a need to develop a method which can provide pertinent information on the shelf stability of peanut butter in a shortest possible time after its manufacture.

Many studies have been reported which focused on developing a suitable stabilizer for peanut butter and have a favorable influence on product texture and shelf life (Hinds and others 1994; Gill and Resurreccion 2000). Stabilizer efficacy was judged by the measurement of oil separation after the peanut butter had been stored for more than 24 h. In both the studies, it took a minimum of 15 days under accelerated storage conditions at elevated temperature of 35 °C to judge the suitability of the stabilizer.

Oil separation in peanut butter occurs under the influence of gravitational force, which is a slow and natural process. This process can be expedited by increasing the gravitational pull over the particles by the application of centrifugal force. The technique of centrifugation has been extensively employed to achieve instantaneous breakdown of emulsions in order to separate two immiscible phases. The standardized method of determining the percent fat present in milk is a prime example illustrating the importance of this technique. Totlani and others (2000) conducted preliminary studies on determining the feasibility of using centrifugation technique as a tool to predict the shelf life of peanut butter (time for which the product exhibits no oil separation); they reported this technique has an excellent potential as a rapid testing method. Objective of this study was to conduct a comprehensive investigation for employing centrifugation as a rapid testing method for predicting the shelf-life stability of peanut butter.

MATERIALS AND METHODS

Commercial samples

An initial set of experiments was conducted on commercial samples of peanut butter: Kroger Creamy ® (stabilized) and Kroger Krema® (non-stabilized), supplied by Tara foods (Albany, GA). The samples were subjected to twenty five different combinations of centrifugal speed and time (Table 3.1). The purpose was to select a smaller number of optimum centrifugation treatments for a follow up study involving a broad range of stabilizer levels.

Experimental samples

This study included measurements of oil separation under the influence of gravitational force and applied centrifugal force on laboratory prepared samples of peanut butter containing five different levels of a commercial stabilizer. Samples were prepared in our pilot plant by incorporating a commercial stabilizer - Fix-X™ into Kroger Krema® peanut butter. Kroger Krema® was the base material in preparing all the batches of samples. Stabilizer Fix-X™ (m.p. = 65.5 °C), a blend of fully hydrogenated cottonseed and rapeseed oil, and was obtained from Proctor & Gamble, Cincinnati, OH. Peanut butter samples containing five different stabilizer levels (0.0, 0.5, 1.0, 1.5 & 2.0%) were prepared by blending Krema® with pre-melted stabilizer, Fix-X™ in a modified colloidal mill (model M-MS-3, Morehouse industries, Los Angeles, CA). Prior to grinding, the base material was warmed in a steam jacketed kettle and appropriate amount of stabilizer was added. The clearance between the mill stones was kept at 5 microns (0.125 mm).

The mill temperature was maintained at 70 ± 2 ˚C. . The product temperature exiting the mill was found to be in range of 88–95 ˚C, which was subsequently lowered to approximately 37-41 °C by passing a material over a specially designed heat exchanger cold plate (42 cm x 50 cm), kept at 5 ± 1 ˚C (figure3.1). Cooling facilitated the shock chilling of the product, initiating crystallization of the stabilizer. Based on the visual determination of product as it thickened upon contact with cold plate, it was scraped into a collection trough fixed to the cold plate. It was then transferred to a collection pail.

Peanut butter with 0.0% stabilizer was referred to as "control". However, "control" batches were also subjected to preheating, grinding and chilling process as the others with various levels of stabilizer. Upon completion of the preparation process, samples (500 g) of the cooled product was transferred into labeled glass jars (6.6 cm i.d.). Another set of peanut butter samples were drawn into 60 ml plastic syringes for monitoring the oil separation occurring in peanut butter due to natural gravitational force.

Experimental samples were grouped into two categories: "Fresh" and "Stored". The samples analyzed on the same day (0 d) and within 24 h (1 d) and 48 h (2 d) of their manufacture were referred to as "fresh" samples. All peanut butter samples, with the exception of 0 d were allowed to cool in an ice bath for about 4 h prior to holding them in a tempering chamber (Environmental Growth Chamber, Chagrin Falls, OH) maintained at 26 ˚C ± 2. "Fresh" samples were further divided into two sub groups, where one set was analyzed at 26 °C and the other at 35 °C. Samples for oil separation study following tempering for 48 h at 26 °C were transferred to a secondary chamber that was maintained at 35 ± 2 ˚C, for an extended accelerated storage study for 3 mo and these samples were

referred to as "stored" samples. Product tempering at 26 °C for 48 h is a standard practice employed by the manufacturers to allow completion of network formation.

Estimation of come-up time

Come-up time was measured for various centrifugal speeds using Beckman induction drive centrifuge (model J-2-21M centrifuge, rotor type JS-13.1, Palo Alto, CA). Measurements of the come-up time for each of the five rpm settings (Table 3.1) were done in triplicate. Centrifuge tubes containing tap water- equivalent to the mass of peanut butter- were used in the tests. Come-up time was recorded using the digital display of centrifuge and was reported in minutes.

Oil separation

Centrifugation

Commercial samples

Peanut butter samples were subjected to 25 combinations of centrifugal speed and time (Table 1) using Beckman induction drive centrifuge (Model J-2-21M, rotor type JS-13.1, Palo Alto, CA) with temperature maintained at 26 ˚C. Peanut butter samples (5 g ± 0.2) were weighed into 50 ml transparent, polycarbonate centrifuge tubes (Nalge Co, Rochester, NY). Samples were transferred into the tubes with the help of a peanut butter dispenser, modified from a hand held paste extruder(Anjali Stainless Steel Works, Mumbai, India) (figure 2). This arrangement enabled the deposition of required amount of peanut butter into the centrifuge tube with minimum incorporation of air. Each

treatment was replicated four times and each replicate consisted of duplicate measurements.

Experimental samples

Fresh samples analyzed at 26 ℃

Peanut butter samples (5 g) were centrifuged using Beckman induction drive centrifuge (Model J-2-21M, rotor type JS-13.1 Palo Alto, CA). The samples were centrifuged at five short-listed treatment combinations obtained from the commercial sample study. These treatments were: 12,000 rpm (g = 22,579 m/s^2) and 10,000 rpm (g = 15,680 m/s^2) for 8 and 10 min, and 8,000 rpm (g = 10,035 m/s^2) for 10 min. The oil separation measurements were conducted in accordance to the method followed in the commercial sample study.

Fresh samples analyzed at 35 ℃

Centrifugation tests were performed according to the procedures detailed above with the exception of the sample temperature, which was maintained at 35 ˚C instead of 26 °C. Peanut butter samples were first tempered in a conventional air oven (Lindberg /blue M, Asheville, NC) at 38 ˚C for 1 hr after which they were subjected to rheology tests for a study reported later. Upon completion of the two measurements, sample jar was returned to the oven for a period of 1 hr (this was done to compensate the temperature drop occurring in the sample while it was subjected to rheological testing),

and subsequently subjected to centrifugal oil separation studies at 10,035 m/s^2 for 10 min at 35 ˚C.

Measurement of separated oil

Centrifuged peanut butter samples were placed on metal racks at an angle of 8° for 15 min to allow drainage of separated liquid oil. This enabled the oil to accumulate at the shoulder and not at the neck of the centrifuge tube for easy yet thorough removal. The separated oil was in two step process. First a collection swab (Face secret™, cotton rounds, Esthetician Services Inc., Los Angeles, CA, USA) attached to a wooden skewer was used (figure 3.3). Kimwipes™ EX-L (Kimberly-Clark Corporation, Roswell, GA, USA) tissue wrapped around a wooden skewer was used. Both the cotton swabs and kim wipes were weighed before and after tare. The results were reported as % oil separated (w/w):

$$\% \text{ Oil separated} = \frac{\text{Weight of oil separated (g)}}{\text{Weight of peanut butter (g)}} \times 100$$

Natural Gravitational Force

This test was conducted only on stored samples held at elevated temperature of 35 ˚C in accelerated storage conditions for 3 mo. A specially designed syringe-pipette configuration (figure 3.4) was used to observe the oil separation occurring in peanut butter under the influence of natural gravitational force. Peanut butter (60 ml) was first

drawn into the large syringe following which the pipette was attached using thermo set glue. The syringes (60 ml) were bored to the same internal diameter (i.d. =5.25 mm) as the affixed pipette (5 ml). This allowed the oil from the peanut butter sample in the syringe to migrate unobstructed to the attached pipette enabling accurate measurement of the separated oil layer. The plunger of the syringe allowed meniscus adjustment for oil in the pipette. Four replicates were prepared for each sample. The oil separation was monitored at 15 d intervals.

Analysis of data

The standard errors for mean oil separation for commercial samples were calculated using Microsoft® Excel program. Analysis of variance (ANOVA) and Duncan's multiple range tests were performed to evaluate the significance of the treatments on oil separation data obtained from centrifugation. Centrifugation data in fresh (analyzed at 26 °C) and stored samples was analyzed using randomized complete block design with factorial layout, where replication was the block factor. The sources of variation taken in the statistical model were: stabilizer, treatments, replication, day, stabilizer x treatments, day x treatment, day x stabilizer, replicate x day. Data collected from natural gravitational force tests was subjected to regression analysis using the Microsoft® Excel.

RESULTS AND DISCUSSIONS

Centrifugation

Come-up time

In centrifugation, it takes a finite amount of time for a rotor to achieve the desired rpm value, which is referred to as the 'come-up time'. Come-up time, if not taken into account, can add up to a sizable difference leading to inconsistencies in studies involving centrifugation. For example, the rotor JS 13.1 takes 2.7 min to attain 12,000 rpm; if not taken into account, it will reduce the actual run time for a sample by 2.7 min. For rotor type JS 13.1, the come-up times for various rpm settings are presented in Table 2. The centrifugation time for sample runs in the current study reflect the adjustment for come-up time.

Commercial samples

The percentage of oil separation for two commercial peanut butter samples at various centrifugation treatments (stabilized and non-stabilized peanut butter) are presented in Tables 3 and 4. The % oil separation, as expected, increased with higher centrifugal force and time. This increasing trend in oil separation was gradual in non-stabilized samples in comparison to the stabilized ones. Non-stabilized butter (Kroger Krema®) exhibited an average oil separation of 9.24% and 13.59% when centrifuged at 2,508 m/s^2 -2 min and at 22,579 m/s^2 -10 min, respectively, for an overall 1.5 fold increase. For the same test conditions, the stabilized samples (Kroger Creamy ®) exhibited a 22-fold increase in oil separation. Non-stabilized butter yielded higher oil

separation than stabilized samples for all centrifugation time at two lower g values (2508 and 5,644 m/s^2) and for 10,035 m/s^2 -2 min. The stabilized samples gave higher oil separation in all conditions more severe than 10035 m/s^2 -4 min. This may be attributed to the fact that stabilized peanut butter has a smooth, uniform texture, where peanuts have to undergo fine grinding process with the addition of a stabilizer. Fine grinding results in the liberation of higher quantities of peanut oil from the roasted and blanched kernels in comparison to coarse grinding (Freeman and Singleton 1952). On the contrary, non-stabilized samples are obtained by coarse grinding of roasted and blanched peanuts. The separated oil in non-stabilized sample was basically free oil capable of migration to the surface even at room temperature conditions without any applied force. For stabilized sample, on the other hand the oil is released by the breakdown of the crystal network under applied centrifugal force.

Centrifugal force of 2,508 m/s^2 for all the time periods was not adequate enough to displace the oil from the matrix in stabilized sample. A substantial increase in oil separation was observed at 5,644 m/s^2-6 min and 10,035 m/s^2-4 min. The latter condition was of importance since the oil separation of stabilized samples henceforth, was consistently higher than that of the non-stabilized sample. However, incremental increase in the oil separation for more rigorous conditions was gradual. Therefore, it may be concluded that the destruction of the weak gel structure due to the applied force have occurred at 10,035 m/s^2-4 min, as noted by the accelerated increase in oil separation at this condition. Furthermore, at higher settings of centrifugation speed and time, oil separation reached equilibrium. This was true only for non-stabilized samples at 26 °C.

For samples having a stronger crystal network due to greater percentage stabilizer might require higher settings of centrifugation force and time. Experimental variations were attributed to the presence of the extremely fine particles that adhered to centrifuge tube walls following centrifugation. These particles adhere to the collection swab at the time of sampling of the separated oil. The following are the two proposed reasons which might have been responsible for the presence of fine particles causing excessive variability:

1. The sample weights in the experiments were within the range of 5.0 -5.2g, and since it was not possible to deposit exactly 5g of peanut butter using the peanut butter dispenser (figure 3.2). The tare sample weight was regulated by removing excess sample with a stainless steel spatula. In this process a few particles may have adhered to the centrifuge tubes walls.
2. The overall readings were consistently high in treatments with higher settings of time (8 and 10 min) of centrifugation. It was possible that particles experiencing the force for a longer time interval may have subsequently detached from wall and since are heavier than the oil fell into the residual mass of peanut butter. As a result these particles then did not get absorbed in the collection swap for giving a false reading.

Selection of five optimum conditions

The criteria for short listing the five optimum conditions were:

Criterion 1: The separated oil obtained from the test condition should be clear and free from the any suspensions of peanut butter particles in the supernatant.

Criterion 2: The separated oil should be adequate enough to be measurable.

Criterion 3: The results should be reproducible giving a small standard error.

During selection, greater emphasis was given to the results obtained from stabilized sample since non-stabilized sample gave a clear oil separation for all test conditions with the exception of 2,508 m/s^2-2 and -4 min and 5,644 m/s^2 -2 min. Four treatments: 5,644 m/s^2 -4 min; 10,035 m/s^2 -2 min, 15,680 m/s^2-2 min, and 22,579 m/s^2 - 2 min were discarded based on criterion 1 (particle suspension in oil). Criterion 2 (inadequate oil separation) was used to drop these six conditions: 2,508 m/s^2 at all time periods; 5,644 m/s^2 -2 min. Nine treatments - 5,644 m/s^2 -6, -8 and -10 min; 10,035 m/s^2 -6 and -8 min; 15,680 m/s^2-4 and -6 min; 22,579 m/s^2 –4 and -6 min were not considered due to criterion 3 (high standard error). Following six combinations remained after deleting above treatments from the set of 25 treatments (Table 1): 10,035 m/s^2-4 and 10mins; 15,680 m/s^2-8 and 10 min; and 22,579 m/s^2-8 and -10 min. Out of the six conditions the five combinations with maximum time and centrifugal speed values were short listed for further investigation (Table 5).

Experimental samples

Fresh samples analyzed at 26 ℃

Determination of the optimum centrifugation condition

The oil separation was found to be significantly dependent on centrifugation conditions and stabilizer levels in samples. Tempering time (s), day (s) - (time after product manufacture) - did not affect the oil separation significantly ($p > 0.05$) (figure

3.5). The average oil separation in peanut butter samples for 0, 1 and 2 d sampling intervals, at five centrifugal treatments for various stabilizer levels is illustrated in figure 3.6. Oil separation decreased with increase in stabilizer levels as evidenced in combinations with higher centrifugal speed and time interval. There was a significant drop (18%) in the amount of oil separation recorded for treatment-I (10,035 m/s^2 -10 min) when the stabilizer level increased from 0.0 to 2.0%; for rest of the treatments however, the decline in percentage oil separation was in the range of 12 to 14 % with increase in the additive levels.

The oil separation increased gradually with increases in the stabilizer levels from treatment-I (10,035 m/s^2 -10 min) to treatment-II (15,680 m/s^2 -8 min) and from treatment-I (10,035 m/s^2 -10 min)to treatment- IV (22,759 m/s^2 -8 min) (figure 3.6). There were no significant differences in the oil separation occurring in peanut butter in treatments-II and III (15,680 m/s^2 -8 and -10 min) (figure 3.6). Similarly there was no significant difference in the oil separation between treatments-IV and V (22,759 m/s^2 -8 min and -10 min). Statistically, the oil separation decreased with increase in stabilizer level. However, there were no significant differences in oil separation in peanut butter blended with 1.0, 1.5 and 2.0% stabilizer levels. These results are indicative of the destructive nature of the centrifugation technique on the matrix formed by stabilizer in peanut butter. Since the centrifugal speed and time combinations may be severe enough to break up the matrix in all the samples to the same extent so as to release similar quantities of oil that is not significantly different. Therefore, the centrifugation technique for samples analyzed at 26 °C was unable to differentiate once the stabilizer levels was

greater than 1.0%. In all the treatment combination, the oil separation obtained was clear and oil separation for 10,035 m/s^2 - 10 min was significantly different from the rest of the four treatments. Therefore it was short listed as the optimum combination for investigations conducted in fresh samples at elevated temperature of 35 °C.

Fresh samples analyzed at 35 °C

The oil separation in peanut butter samples for various stabilizer levels at single optimum centrifugation treatment of 10,035 m/s^2 -10 min is shown in figure 3.7. The oil separation was found to be independent of the day it was centrifuged but was significantly affected by the amount of stabilizer present. The oil separation in stored samples decreased by 24% with the increase in the stabilizer levels from to 0.0 to 2.0%. Percent oil separated was significantly different for all the five levels of stabilizer, when samples were centrifuged at the optimum condition. Comparison of oil separation at 26 and 35 °C, showed only a marginal increase when centrifuged at high temperature. This indicated that the damage to weak gel structure caused by the external centrifugal force applied did not differ due to the temperature of analysis (figure 3.8).

Natural Gravitational Force.

Effect on oil separation in peanut butter samples placed in 60 ml syringes and held at 35 ˚C is shown in figures 3.9 and 3.10. The amount of stabilizer present in the sample had a direct impact on free oil separation. As the stabilizer percentage increased the oil separation decreased sharply. In the absence of stabilizer, 0.0% sample showed a 16.3%

oil separation at the end of the three-month storage period; where as, peanut butter containing 2.0% stabilizer level showed no oil separation under accelerated storage conditions.

A quadratic equation of second order was fitted on the data obtained from samples containing 0.0% and 1.0% stabilizer levels which explained 99.7% ($R^2 = 0.997$) and 98.1%variability in dependent variable- oil separation ($R^2 = 0.981$), respectively. For samples containing 0.5 and 1.5% stabilizer levels, linear model was able to explain 98.3% and 77.1% of variability, respectively. The model equations for various levels of stabilizer are given below:

$$y_0 = -0.4017x^2 + 5.6856x - 3.2326 \qquad (R^2 = 0.997)$$

$$y_{0.5} = 0.5203x - 0.3484 \qquad (R^2 = 0.981)$$

$$y_1 = 0.0077x^2 - 0.0102x - 0.0069 \qquad (R^2 = 0.983)$$

$$y_{1.5} = 0.0214x - 0.0333 \qquad (R^2 = 0.771)$$

where, y_z is the oil separation for stabilizer level, z, and x is the storage time in days

Statistical analysis conducted on the data showed that both stabilizer and time and their interaction had significant effect on the amount of oil separation in peanut butter placed under accelerated storage conditions. The oil separation of 0.0% stabilizer level for all time intervals was significantly different than the rest of the samples. For 30 d, the oil separation of peanut butter with 0.5% stabilizer level was found to be significantly different. However, for the other storage periods (>30 d), oil separation

values for samples with stabilizer percentage ranging between 0.5 to 2.0% were not found to be significantly different.

Hinds and coworkers suggested a criterion of predicating long term stability of peanut butter based on 1.0% of oil separation under gravitational forces of a sample placed at 35 °C for two weeks (Hinds and other 1994). They established a cut-off limit of 0.5% oil separation in peanut butter for 2 week storage at 35 °C. Based on these criteria, they predicted the samples containing stabilizer palm oil (2-2.5% level) to be stable for more than one year when kept at 21-24 °C. The same criterion was adopted in our study to correlate oil separation from centrifugation and natural gravitation force studies. The oil separation above 0.5% was obtained only in the case of 0.0% sample; where as, 0.5% stabilized sample showed 0.17% oil separation which was well below the cut off limit. The average percentage of oil separation of peanut butter centrifuged at 35 °C was 14.81, 14.06, 12.81, 12.56 and 11.94% for 0.0, 0.5, 1.0, 1.5 and 2.0% stabilizer levels, respectively. Therefore, for peanut butter samples showing oil separation using centrifugation technique in the range of 14.81 ± 0.072 will not be stable for one year at 21-24 °C. Samples with higher percentage of stabilizer and oil separation in the range of 11.94 to 14.06 from centrifugation should remain stable for period of more than 1 year when stored at 21-24 °C.

CONCLUSIONS

Centrifugation of peanut butter samples at the optimum combination of 10,035 m/s^2-10 min was most successful in illustrating differences amongst samples with five

stabilizer levels. Therefore it has the highest potential for use in a rapid method to predict the shelf life of peanut butter with regards to oil separation. However, the correlation between the amount of oil separated in stored samples, naturally versus samples subjected to centrifugation, could only be established based on the criterion of 0.5% separation for storage time of 15 d at 35 °C. It is important to have a criterion to evaluate oil separation for stored samples for each and every storage interval. Since the criterion of 0.5% was not valid for all the storage intervals, samples kept at 35 °C for 30 d would have had much higher oil separation than the samples evaluated at 15 d intervals. Therefore, if the cut-off limit of 0.5% oil separation after 2 wk storage at 35 ° C is used, certain stabilizer level samples may fail to meet this criterion. And hence would be referred to as unstable samples or samples with reduced shelf life, which might not be true. The criterion established by Hinds and others (1994), was based on the data obtained from studying commercial samples under accelerated storage conditions, which was 1.0% at the end of 15 days. However, information on the history of the sample or the amount of stabilizer present was not provided. In this study the sample containing 0.5% stabilizer showed 1.0% oil separation only at the end of 45d. And therefore, based on our analysis, the samples of peanut butter used in the study conducted by Hinds and others (1994) would contain stabilizer level less than 0.5%, which is relatively low level of stabilizer in peanut butter required to prevent oil separation.

FUTURE WORK

The correlation on the basis of amounts of the oil separation between samples subjected to centrifugation and stored samples could be explored under one storage interval. Also, deterioration of the samples was studied only at one single temperature of 35 °C. Kinetic modeling can be used for evaluating the rate constants for degradation in peanut butter at different temperatures (4, 25 and 35 °C) to determine the Arrhenius equation constant (k_A) and activation energy (E_A) involved in the reaction. In addition these constants can be used to calculate the ratio of reaction rates at two different temperatures (Labuza 2002). The data may then be correlated with oil separation obtained by centrifugation of freshly prepared peanut butter samples. Alternately, a market sample with a known history and stabilizer can be placed along with an experimental sample, under identical storage conditions for each storage interval. This will enable in establishing a criterion for cut off limit of oil separation for any time period.

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Table 1: Twenty five treatment combinations used in generating oil separation in commercial samples

Centrifugal speed (rpm)	**Centrifugal force *g* (m/s^2)**	**Time intervals (min)**
4,000	2,508	2, 4, 6, 8, 10
6,000	5,644	2, 4, 6, 8, 10
8,000	10,035	2, 4, 6, 8, 10
10,000	15,680	2, 4, 6, 8, 10
12,000	22,579	2, 4, 6, 8, 10

Table 2: Come–up time values for various centrifuge settings

Centrifugal speed (rpm)	**Centrifugal force *g* (m/s^2)**	**Come up time (min)**
4,000	2,508	0.7
6,000	5,644	1.0
8,000	10,035	1.2
10,000	15,680	1.6
12,000	22,579	2.7

Table 3: Percentage of oil separation, mean (standard error of mean), in stabilized peanut butter at various centrifugation treatments

Centrifugation Speed (rpm)	*g* value (m/s^2)	Centrifugation time (min) 2	4	6	8	10
4,000	2,508	0.70†	1.78 †	2.41 †	3.92 †	4.38 †
		(0.03)	(0.14)	(0.20)	(0.52)	(0.42)
6,000	5,644	1.85 †	3.71††	6.53	8.36	8.74
		(0.28)	(0.12)	(0.45)	(0.67)	(0.41)
8,000	10,035	7.99 ††	11.34	12.38	12.76	13.17
		(0.42)	(0.05)	(0.22)	(0.32)	(0.11)
10,000	15,680	11.70 ††	12.18	12.89	13.56	13.65
		(0.28)	(0.18)	(0.23)	(0.12)	(0.12)
12,000	22,579	13.67 ††	14.49	14.51	14.97	15.99
		(0.73)	(0.42)	(0.41)	(0.15)	(0.15)

† Oil separation not very substantial (<5%)

†† Suspension present in the oil separated

Table 4: Percentage of oil separation, mean (standard error of mean), in non-stabilized peanut butter at various centrifugation treatments

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Centrifugation speed (rpm)	*g* value (m/s^2)	Centrifugation time (min)				
		2	**4**	**6**	**8**	**10**
4,000	2,508	9.24 ††	9.66 ††	9.62	9.68	9.69
		(0.12)	(0.13)	(0.17)	(0.05)	(0.18)
6,000	5,644	10.53††	10.31	10.41	10.43	10.56
		(0.03)	(0.29)	(0.13)	(0.03)	(0.08)
8,000	10,035	10.86	11.35	11.42	11.41	11.47
		(0.26)	(0.05)	(0.16)	(0.21)	(0.07)
10,000	15,680	11.68	11.81	12.17	12.38	12.48
		(0.24)	(0.16)	(0.32)	(0.10)	(0.09)
12,000	22,579	12.82	13.15	13.18	13.28	13.59
		(0.09)	(0.06)	(0.07)	(0.12)	(0.11)

†† Suspension present in the oil separated

Table 5: Five short listed treatments used in generating oil separation in experimental samples- "fresh" samples at 26 °C

Treatment	Centrifugal speed (rpm)	Centrifugal force g (m/s^2)	Time intervals (min)
I	8,000	10,035	10
II	10,000	15,680	8
III	10,000	15,680	10
IV	12,000	22,579	8
V	12,000	22,579	10

Figure legend.

Figure 3.1: Schematic of a modified Morehouse mill used in the manufacture of experimental samples

Figure 3.2: Schematic of a modified peanut butter dispenser

Figure 3.3: Technique of absorbing the oil separated by centrifugal force from the centrifuge tube

Figure 3.4: A syringe-pipette configuration used in measurement of separated oil in natural gravitational force test

Figure 3.5: Effect of tempering on the percentage oil separation in experimental samples for treatments described in Table 5

Figure 3.6: Effect of stabilizer level on the percentage oil separation in fresh samples analyzed at 26 °C by centrifugation at five centrifugation treatments (treatments described in Table 5)

Figure 3.7: Percentage oil separation in fresh peanut butter samples centrifuged at 10,035 m/s^2 -10 min and 35 °C

Figure 3.8: Comparison of oil separation due to centrifugation at optimum condition (10035m/s^2 -10 min) at 26 and 35 °C

Figure 3.9: Percent oil separation in 0.0 and 0.5% stabilizer levels stored for three months at 35 °C by natural gravitational force

Figure 3.10: Percent oil separation in 1.0 and 1.5% stabilizer levels stored for three months at 35 °C by natural gravitational force

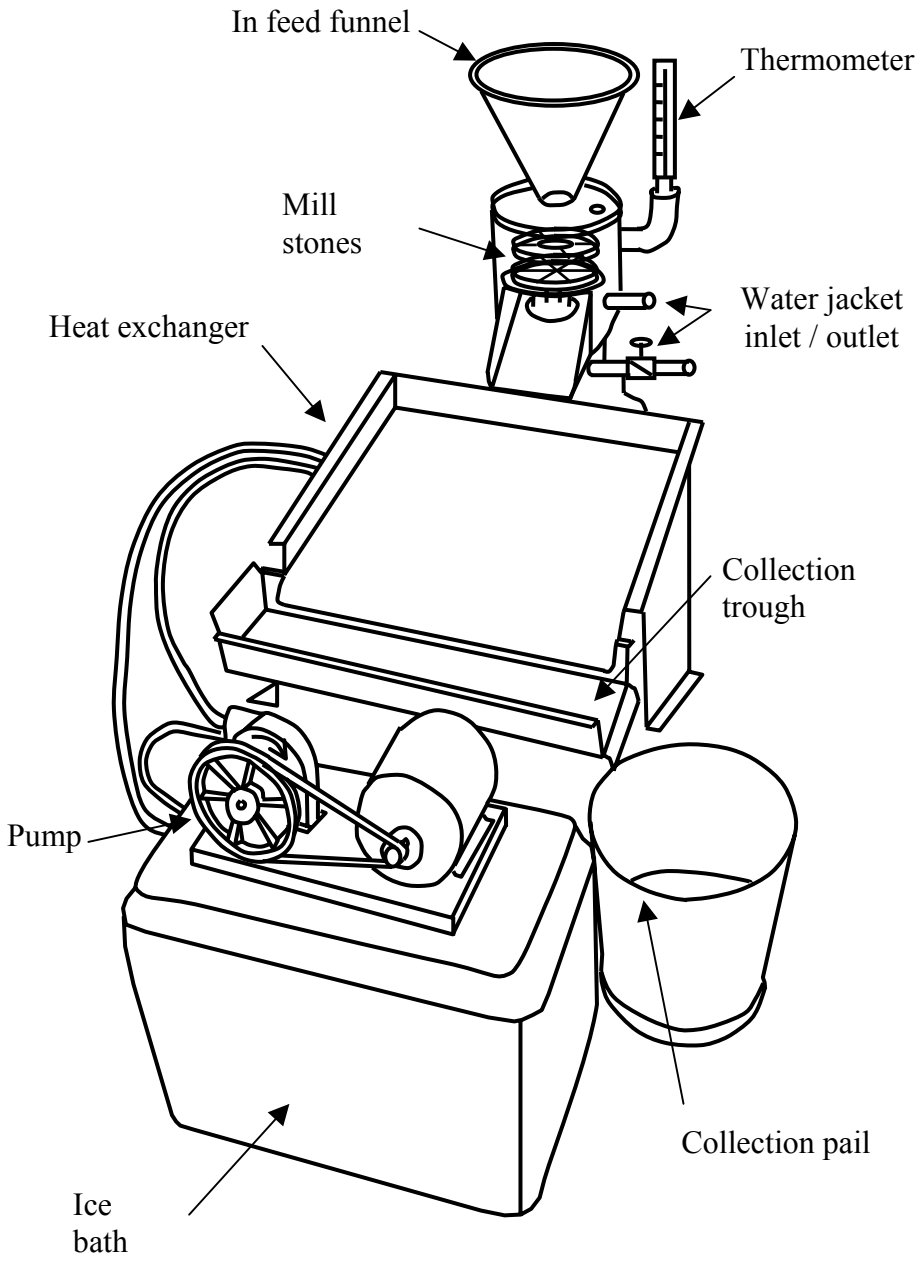
In feed funnel
Thermometer
Mill
stones
Water jacket
inlet / outlet
Heat exchanger
Collection
trough
Pump
Collection pail
Ice
bath

Figure 3.1

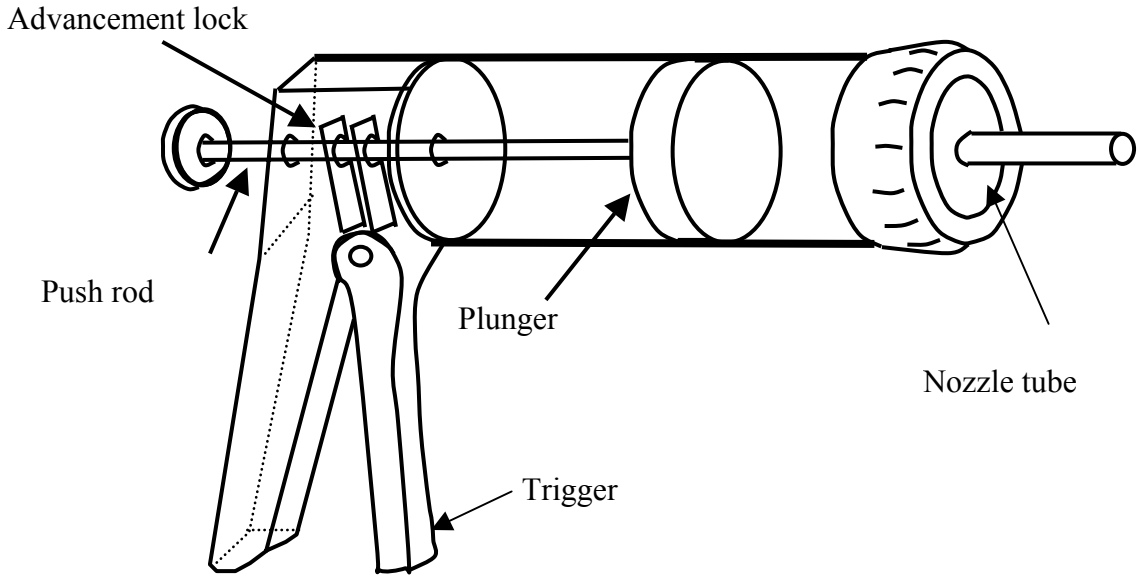

Figure 3.2

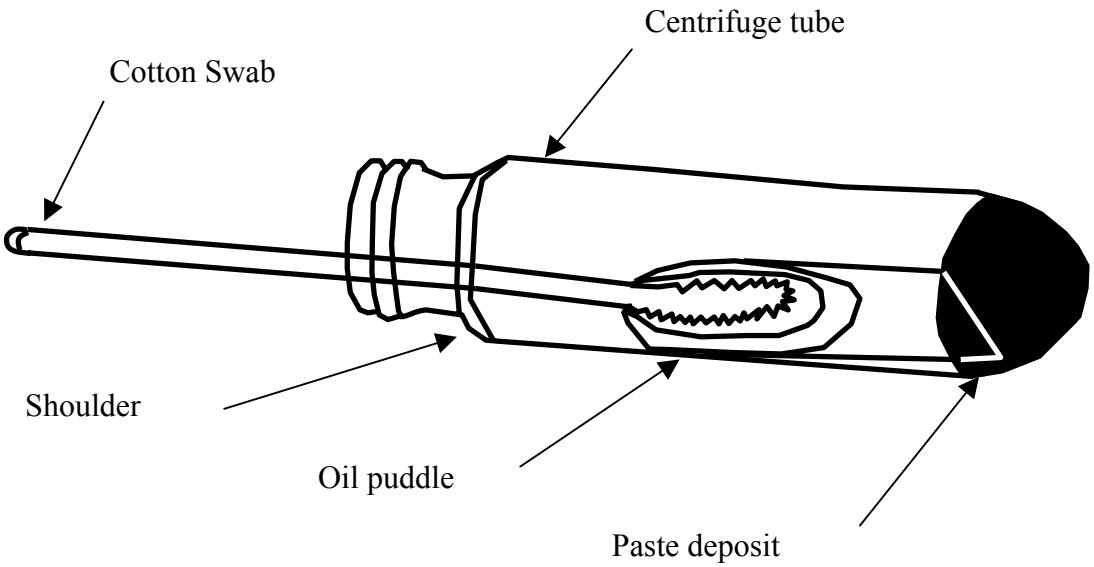
Centrifuge tube
Cotton Swab
Shoulder
Oil puddle
Paste deposit

Figure 3.3

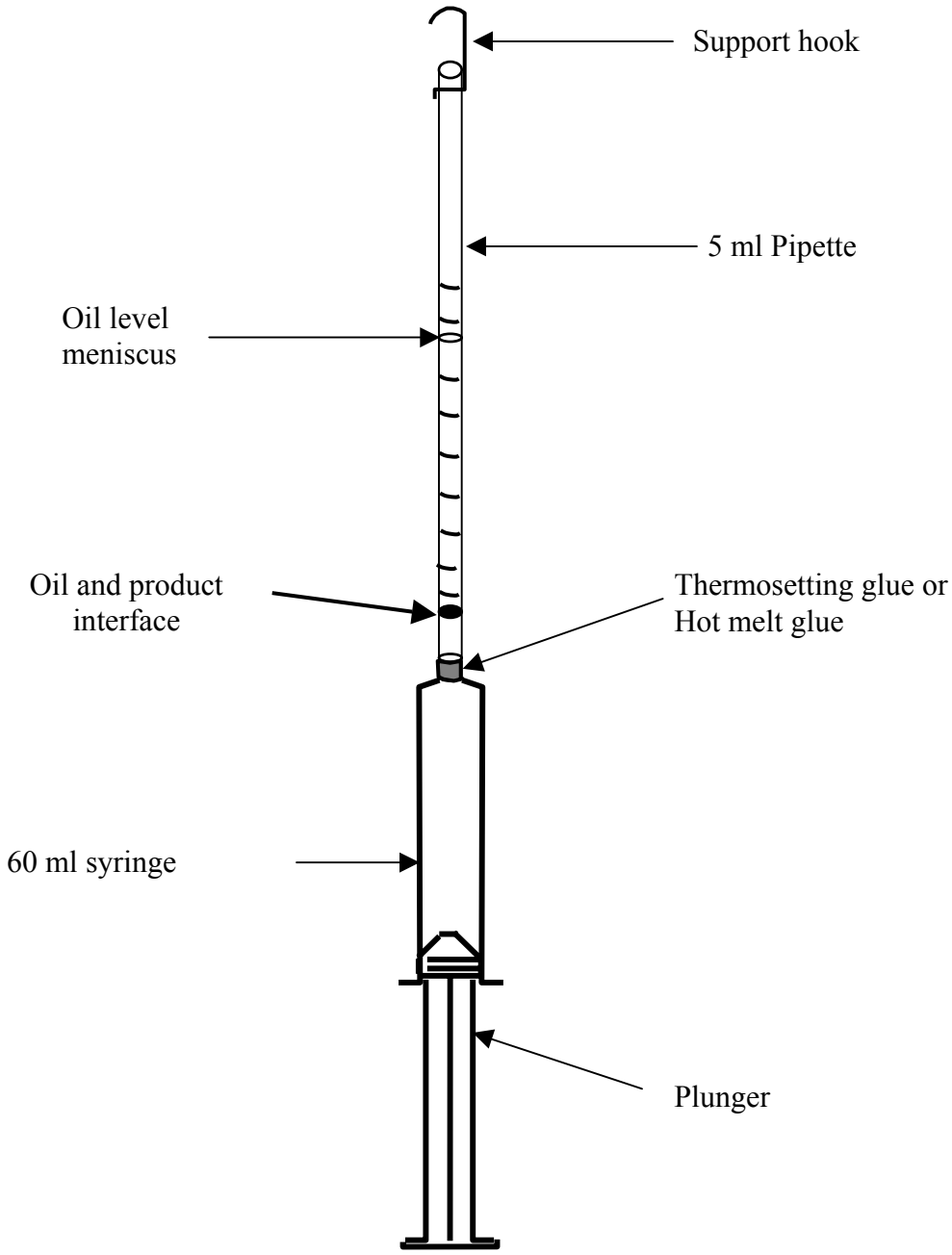
Support hook
5 ml Pipette
Oil level
meniscus
Oil and product
interface
Thermosetting glue or
Hot melt glue
60 ml syringe
Plunger

Figure 3.4

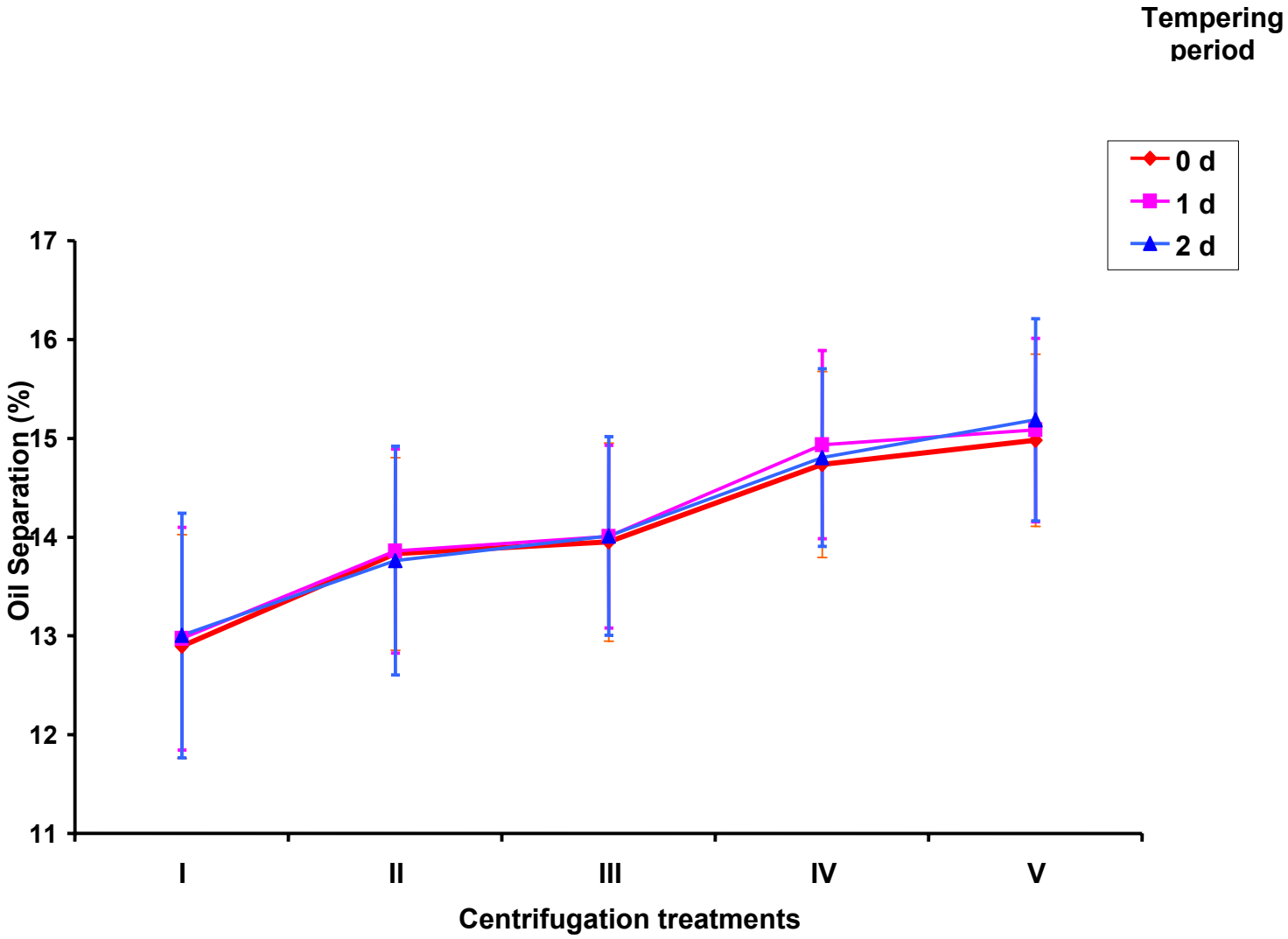
Tempering period
0 d
1 d
2 d
17
16
15
14
13
12
11
Oil Separation (%)
I
II
III
IV
V
Centrifugation treatments

Figure 3.5

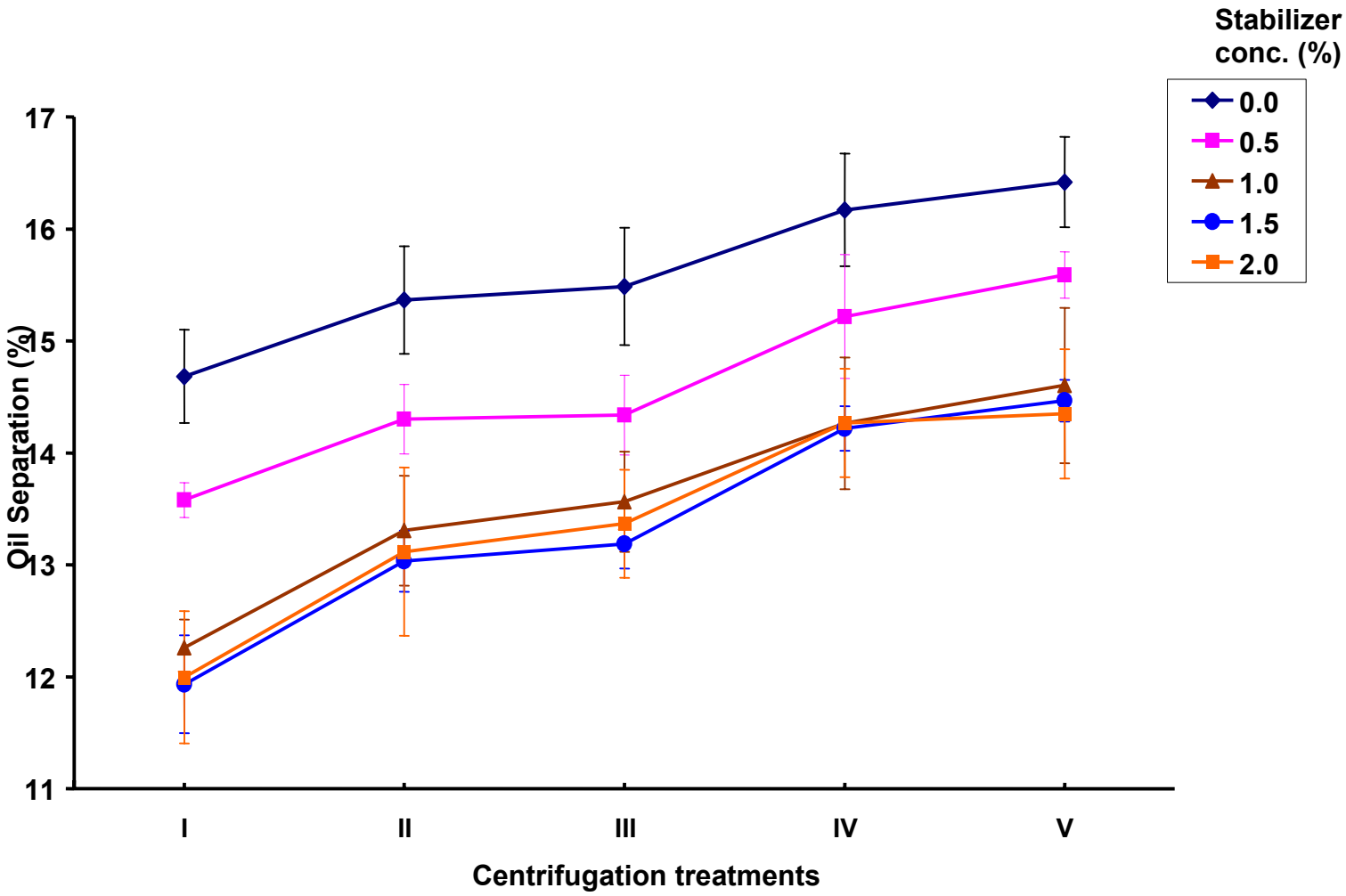
Stabilizer conc. (%)
0.0
0.5
1.0
1.5
2.0
Oil Separation (%)
17
16
15
14
13
12
11
I
II
III
IV
V
Centrifugation treatments

Figure 3.6

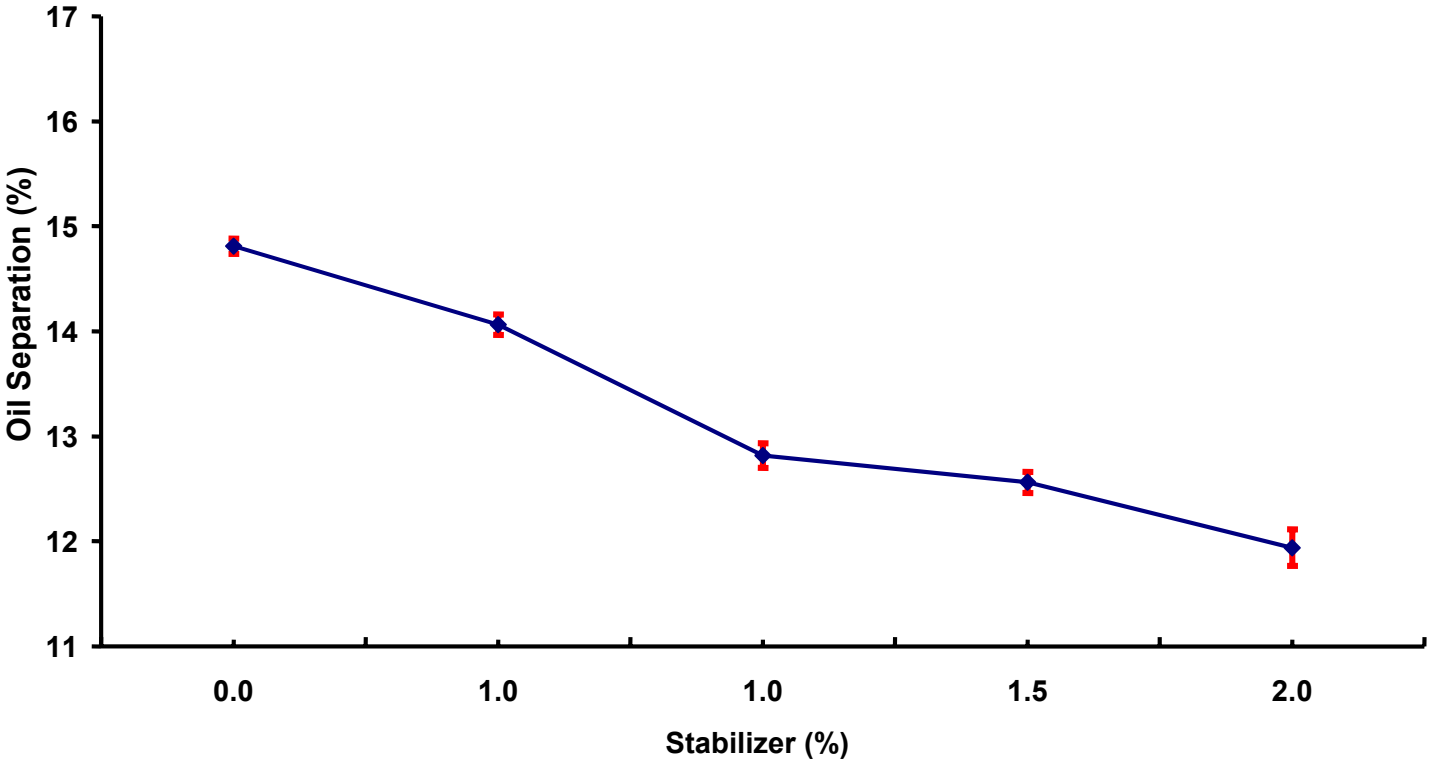

Figure 3.7

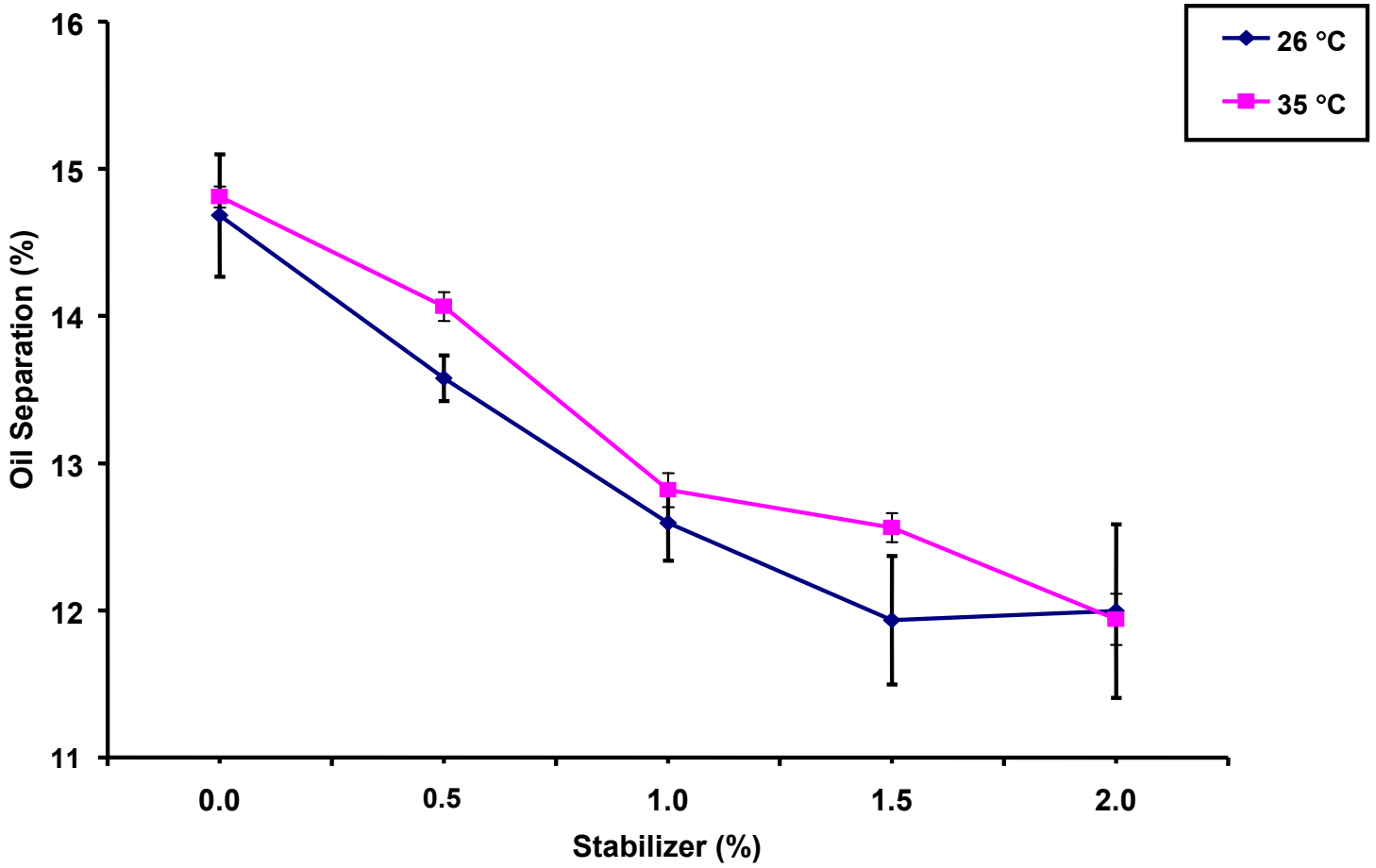
26 °C
35 °C
Oil Separation (%)
16
15
14
13
12
11
0.0
0.5
1.0
1.5
2.0
Stabilizer (%)

Figure 3.8

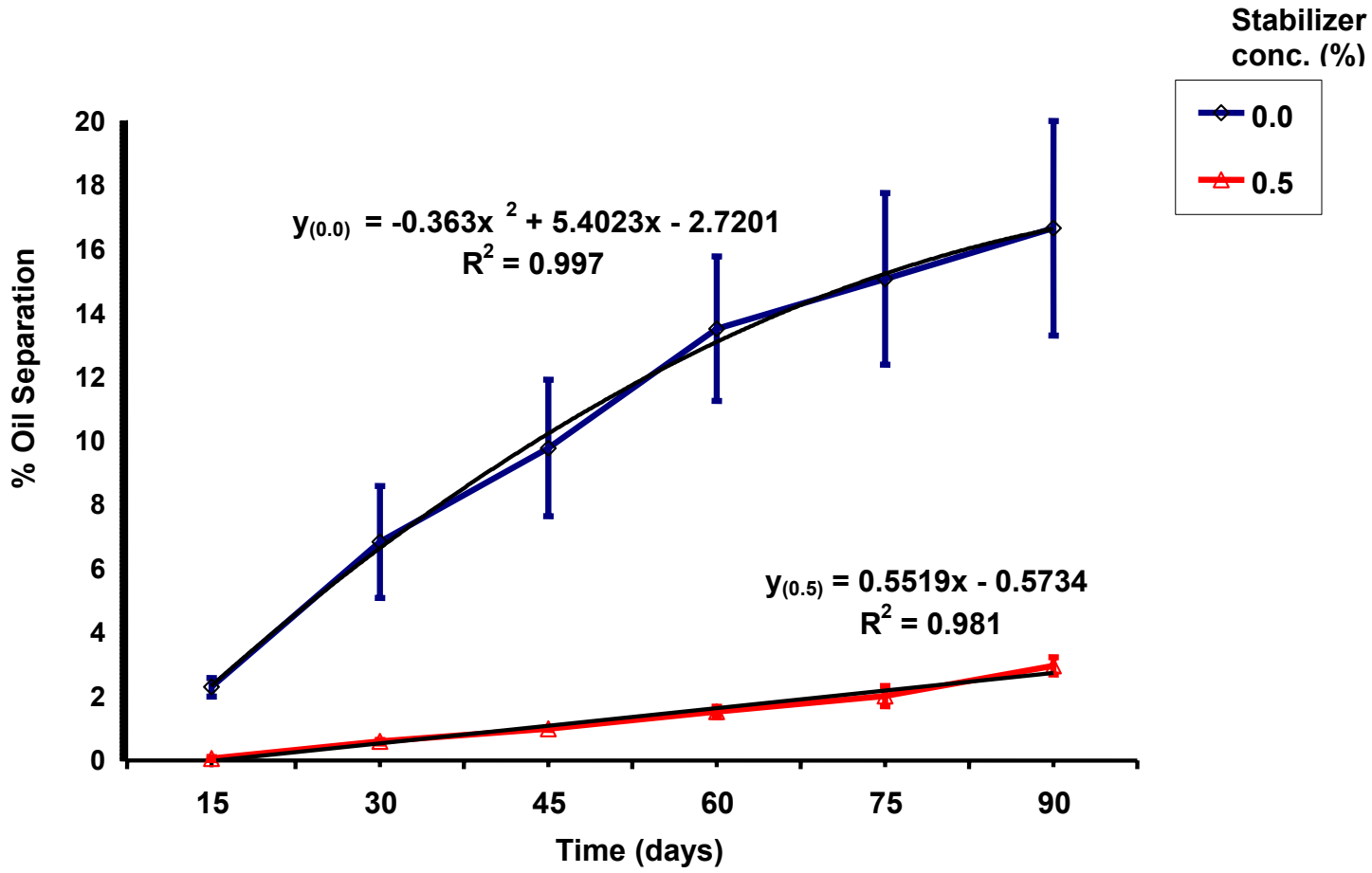
Stabilizer conc. (%)
0.0
0.5
$y_{(0.0)} = -0.363x^2 + 5.4023x - 2.7201$
$R^2 = 0.997$
$y_{(0.5)} = 0.5519x - 0.5734$
$R^2 = 0.981$
% Oil Separation
0
2
4
6
8
10
12
14
16
18
20
15
30
45
60
75
90
Time (days)

Figure 3.9

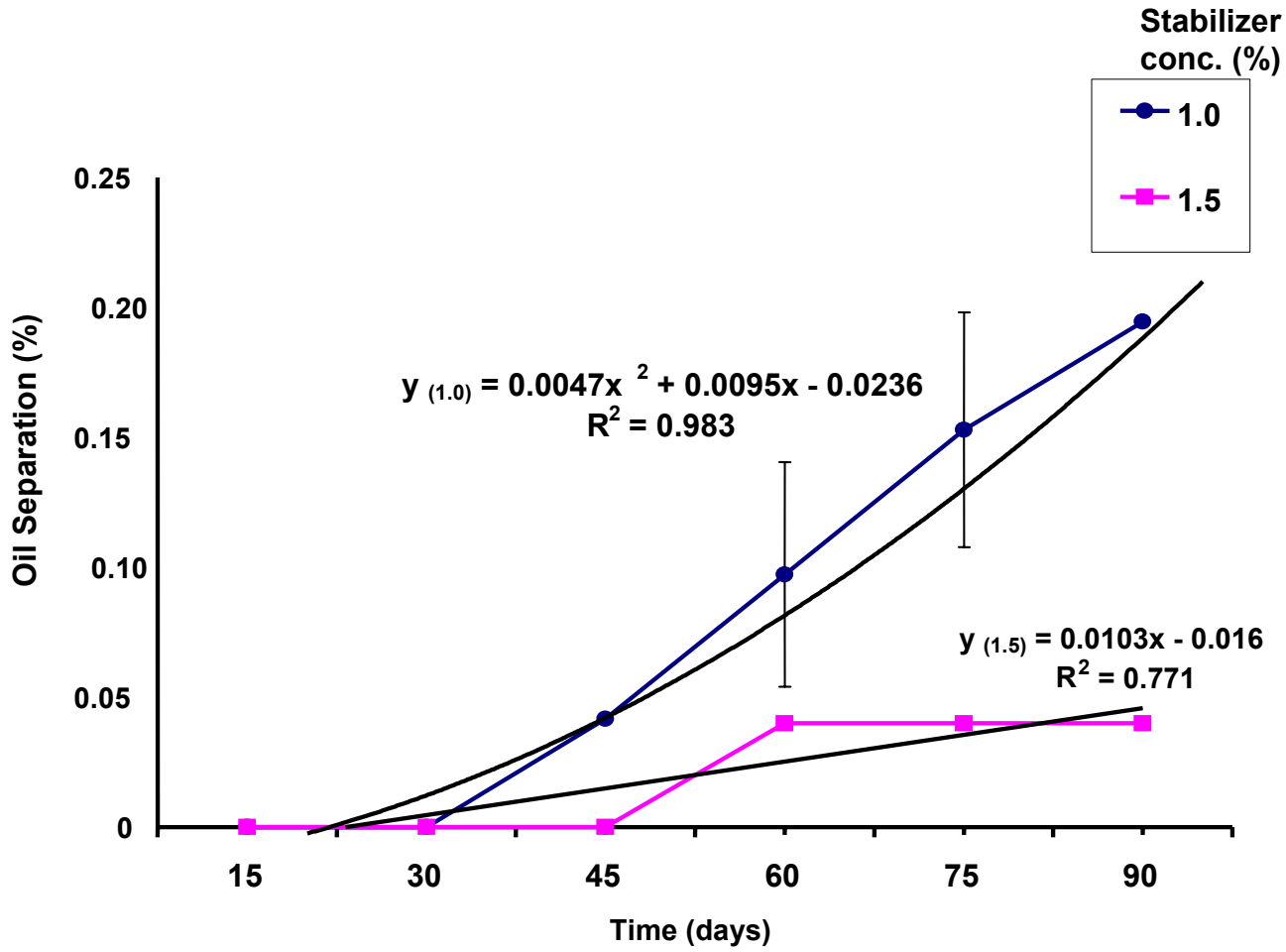
Stabilizer conc. (%)
1.0
1.5
0.25
0.20
0.15
0.10
0.05
0
Oil Separation (%)
y (1.0) = 0.0047x 2 + 0.0095x - 0.0236
R2 = 0.983
y (1.5) = 0.0103x - 0.016
R2 = 0.771
15
30
45
60
75
90
Time (days)

Figure 3.10

CHAPTER 4

EFFECT OF STABILIZER LEVELS AND STORAGE CONDITIONS ON THE TEXTURE AND VISCOSITY OF PEANUT BUTTER[1]

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To be Submitted to The Journal of Food Science

ABSTRACT

Peanut butter samples containing various levels of stabilizer (0.0 to 2.0%) in fresh and stored conditions were subjected to texture and viscosity tests using Instron Universal Testing machine and Brookfield viscometer, respectively. In both tests, only the stabilizer level was found to significantly affect the texture and viscosity of peanut butter. The two tests were unable to track the subtle changes that occurred in fresh peanut butter samples during the period of network formation at 26 °C. However, pre-warming of the fresh sample to 35 °C resulted in increased sensitivity in texture analysis. It was observed in samples stored at 35 °C for 3 mos that the stabilizer level as low as 1.0% proved adequate in stabilizing peanut butter.

Key words: Peanut butter, stabilizer, texture, viscosity

INTRODUCTION

Peanut butter is a dispersion of peanut oil in peanut solids released due to grinding of roasted mature, shelled, washed, and blanched peanuts. For a product to be labeled as peanut butter, it is a mandatory requirement that it contain 90% peanuts and the remainder comprise of sweeteners, seasonings, emulsifiers and/or stabilizers (USFDA 2002). Peanuts contain 48-50% fat which is composed of glycerides of fatty acids, 80% of which are unsaturated (Lenth 1939). Unsaturated fat due to the presence of double bonds is able to exist in liquid form at room temperature. Peanut butter dispersion, if allowed to stand at ambient temperature conditions for extended period tends to break down in two layers with peanut oil rising to the surface and dry compact layer of peanut solids deposited at the bottom of the package (Aryana and others 2002).

Oil separation is prevented by the addition of stabilizers. Stabilizers are partially hydrogenated vegetable oil, mono-, di-, or tri-glycerides of vegetable oils or their combination (Woodroof 1983). These compounds are able to crystallize at low temperature. These crystals are further allowed to develop a network structure by tempering of the fresh product. Tempering of the freshly prepared stabilized peanut butter for a period of 48 h is a general practice employed by the peanut butter manufacturers. This permits the crystals form a matrix or a weak gel which immobilizes the free oil (Karn 2001). Hence, prevents its migration. During the network formation period of 48 h, changes occur in the texture and viscosity of peanut butter samples. According to Citrene and others (2000), stabilized peanut butter presents a 'soft solid gel like behavior'. In our study we are using 'weak gel' and 'crystal network structure' interchangeably. Many studies have used these changes as an indicator to determine the

effect of different treatments in which the manufacture and shelf-stability of samples of peanut butter are subjected to. Changes in texture firmness of the samples are evaluated by two main techniques: First is the Cone penetrometry; it is a standard quality control test, and is used by many researchers as a reliable method along with other advanced instruments to gauge the strength of the food product (Ahmed and Ali 1986; Muego and others 1990; Vincent and Szabi 1947). The strength of the solid fat is gauged depending upon the depth to which the cone attached to a vertical shaft travels through various layers in the product. One of the disadvantages of cone peneterometry is the large sample size that is needed to perform the test. The second technique involves the use of Instron Universal testing machine. This device has been extensively used in determining hardness, cohesiveness and adhesiveness of peanut butter samples affected by stabilizer levels or storage intervals (Aryana and others 2002, Hinds and others 1994; Ahmed and Ali 1986). Texture profile analysis (TPA) on peanut butter has also been extensively conducted using the Instron machine (Muego and others 1990). Seven textural parameters associated with the TPA method or its modification have been reported to correlate well with the sensory attributes.

The objective of this study was to examine viscosity and textural changes in peanut butter samples prepared with various levels of stabilizer, during tempering period of 48 h and when subjected to accelerated storage condition of 35 °C for three months.

MATERIAL AND METHODS

Peanut butter preparation

This study involved measurements of texture and viscosity of laboratory prepared samples of peanut butter containing five different levels of a commercial stabilizer. Samples were prepared in the pilot plant by incorporating the commercial stabilizer - Fix-X™ into Kroger Krema® peanut butter. Kroger Krema® was the base material in preparing all the batches of samples. Stabilizer Fix-X™ (m.p. = 65.5 °C), a blend of fully hydrogenated cottonseed and rapeseed oil, was obtained from Proctor & Gamble, Cincinnati, OH. Peanut butter samples containing five different stabilizer levels (0.0, 0.5, 1.0, 1.5 and 2.0%) were prepared by dispersing pre-melted stabilizer Fix-X™ into Krema® in a steam jacketed vessel. This mixture was then subjected to thorough blending in a modified colloidal mill (Model M-MS-3, Morehouse industries, Los Angeles, CA). The base material was warmed in the steam jacketed kettle prior to the addition of a predetermined amount of stabilizer. The clearance between the mill stones was kept at 5 microns (0.125 mm). The mill temperature was maintained at 70 ˚C $\pm$2. The product temperature exiting the mill was found to be in the range of 88-95 ˚C, which was subsequently lowered to approximately 37-41 °C by passing the material over a specially designed heat exchanger cold plate (42 x 50 cm^2) maintained at 5 ± 1 ˚C as described in chapter 3. Cooling facilitated the shock chilling of product, initiating crystallization of the stabilizer.

Peanut butter with 0.0% stabilizer was referred to as “control”. However, “control” batches were also subjected to preheating, grinding and chilling like the other

batches with various stabilizer levels. Upon completion of the formulation process, the cooled product was distributed into 500 g glass jars (6.6 cm i.d).

Experimental samples were grouped into two categories: "Fresh" and "Stored". The samples analyzed on the day of manufacture (0 d) and at 24 (1 d) and 48 h (2 d) were referred to as "fresh" samples. All peanut butter samples, with the exception of 0 d samples were allowed to cool in an ice bath for 4 h prior to holding them in a tempering chamber (Environmental Growth Chamber, Chagrin Falls, OH) maintained at 26 ˚C ± 2. Fresh samples were further divided into two sub groups, where one subgroup was analyzed at 26 °C and the other at 35 °C. Fresh samples at 26 °C were analyzed for texture and viscosity at room temperature. For "fresh" samples at 35 °C, the samples were brought to 35 °C by first tempering it in an oven at 38˚C for 1 h, following which Instron and Brookfield measurements were done. Following the tempering of 48 h at 26 °C, a separate set of peanut butter samples were transferred to a secondary chamber that was maintained at 35 $\pm$ 2 ˚C, for an extended accelerated storage study for 3 mos; and these samples were referred to as "stored" samples. For stored samples, in case of any visible oil separation, the texture and viscosity values were determined after neatly decanting the oil from the jar and measurements were conducted on undisturbed layer of peanut butter beneath the oil. Product tempering at 26 °C for 48 h is a standard practice employed by the manufacturers to allow the completion of network formation.

Rheological tests

Each sample jar (500 g) was used for both texture and viscosity determinations. Care was taken to begin each sample analysis first with the texture measurements at

precisely five distinct locations on the surface of peanut butter leaving the layer below undisturbed for viscosity analysis.

Texture

Instron Universal Testing instrument (Model 5544, Instron Corporation, Canton, MA, USA) fitted with 10N cell was used to evaluate the firmness characteristics of peanut butter samples. The probe used was a miniature penetration cone (10.90 mm long, and 16.15 mm diameter at the base, and 45˚ angle) (figure 4.1). The assembled cone and the attached aluminum rod (23.5 cm long) weighing 93 g were programmed to penetrate the samples with precision to a depth of 9 mm at the rate of 20 mm/s at five distinct locations. Energy required by the cone to penetrate into the samples was recorded using Merlin software provided by the Instron Corporation.

Apparent viscosity

Apparent viscosity (Pa s) measurements were conducted on peanut butter samples (500 g) using the Brookfield Digital viscometer (Brookfield Engineering Laboratories, Stoughton, MA) equipped with T spindles (A–E) mounted on a helipath stand. The shear rates selected ranged from 0.5 to 100 rpm. A maximum of four spindles were used for measuring viscosity of fresh samples; and a minimum of 2 spindles were used for stored samples.

Analysis of data

Analysis of variance (ANOVA) and Duncan's multiple range tests using General Linear Models (GLM) were used to evaluate the significance of the treatments on the responses using the SAS procedures (1990). The response variable for texture tests and viscosity were energy (mJ) and viscosity (Pa s), respectively. The experimental design fresh (analyzed at 26 °C) and stored samples was analyzed was randomized complete block design with factorial layout, where replication was the block factor. The sources of variation taken in the statistical model were: stabilizer, day, replication, day x stabilizer, replicate x day, replicate x stabilizer. The data for texture as well as viscosity analysis was sorted by stabilizer and day.

RESULTS AND DISCUSSIONS

Texture

Fresh samples at 26 °C

Peanut butter samples containing stabilizer levels from 0.5, 1.0, 1.5 and 2.0% showed an improvement in texture firmness when left undisturbed for 0, 1 and 2 d (figure 4.2). The amount of energy required for the cone to penetrate peanut butter sample was found to depend on the stabilizer level and the period of network formation. There was significant interaction between the two independent variables ($p<0.05$). Higher the stabilizer percentage and tempering duration, greater was the energy expended by the cone to travel through each peanut butter sample. After sorting the data by stabilizer, day (period of network formation) was found to be significant for 1.0% stabilized peanut butter. For samples containing 1.0% stabilizer, the firmness was significantly higher on

the 2nd day. In all the other stabilizer levels, day was insignificant ($p > 0.05$). Increase in the firmness of the sample was a consequence of the strengthening of the crystal network formed by the stabilizer. For 1 and 2 d , sample containing 2.0% stabilizer level was found to have a significantly higher firmness than all the other peanut butter samples. This was due to the presence of a stronger network in the case of a higher stabilizer level, and hence the probe required greater energy to penetrate.

Stored samples

The effect of stabilizer and storage conditions on the texture of peanut butter samples are presented in figure 4.3. Stabilizer was found to be a significant variable affecting the firmness of peanut butter samples. Day was found to be significant ($p < 0.05$) only for 0.0 and 2.0% stabilized samples. In all the other stabilizer levels (0.5, 1.0 and 1.5%) day was not significant ($p > 0.05$). There was no visible oil separation observed in the peanut butter samples jars containing 1.0, 1.5 and 2.0% stabilizer levels, unlike those for samples with 0.0 and 0.5% stabilizer levels.

The texture for 0.0% stabilized peanut butter initially declined (15 to30 d) and then gradually increased up to 75 d storage (figure 4.3A). The increased firmness for the non-stabilized peanut butter was attributed to the presence of a hard compact layer at the bottom of the jar. This hard layer was formed due to natural oil separation which occurred in the sample over storage. For 0.5% stabilizer level, a U-shaped response curve was noted for this stabilizer level (figure 4.3B). The initial decrease in the firmness was due to the degrading sample structure caused by the slow breakdown of the dispersion. Unlike in 0.0% sample, where hardening of the sample occurred after 30 d

storage time, for samples with 0.5% stabilizer level, the additive present in the system delayed the formation of the hard layer by two months. In samples containing 1.0 and 1.5% stabilizer, there was no significant change in texture firmness values when stored at 35 °C for three months (figure 4.3C and 4.3D). In sample containing 2.0% stabilizer, the firmness at 60 d storage time was significantly higher than that at 30 d storage time (figure 4.3E). This was a consequence of an improved network structure when samples were allowed to stand undisturbed. For 1.0, 1.5 and 2.0% stabilized samples, high level of the additive resulted in the formation of a stronger network of crystal. This enabled the samples to withstand the harsh storage condition longer than other samples. Stabilizer level of 0.5% was found to be inadequate in preventing oil separation in peanut butter, occurring under the influence of natural forces.

Fresh samples at 35 °C

The effect of stabilizer and period of network formation on the texture of peanut butter samples analyzed at 35 °C are presented in figure 4.4. The firmness of peanut butter samples was found to be dependent on stabilizer level and day. There was a strong interaction between independent variables -stabilizer level and day-which necessitated the sorting by day before further analysis. There was no significant difference in the firmness of all peanut butter samples for 0 and 1 d. On 2 d, responses of all samples, with exception of 0.0 and 0.5%, were found to be significantly different. This indicated that the warming of the stabilized peanut butter samples on 2 d before subjecting to texture analysis brought out the subtle differences between the different stabilizer levels. It was also noted that the amount of energy required by the probe to penetrate through

peanut butter analyzed at 35 °C, was less in comparison to the fresh samples at 26 ˚C. The energy requirement of 0.0% sample at 26 ˚C was 3, 5 and 7-fold higher for 0, 1, and 2 d, respectively, in comparison to that at 35 ˚C. Similarly for 2.0% stabilized samples for 0, 1 and 2 d, the energy values was 1.2, 3 and 2 fold higher for 26 ˚C in comparison to that at 35 ˚C. A greater decrease in the energy requirement was observed for natural peanut butter than for samples containing the additive. This indicated that the crystal network formed by stabilizer enabled the samples to resist its degradation. Also, for samples with 0.5, 1.0 and 1.5% stabilizer levels, a drop in the energy values was noted. This was due to the weakening of weak gel structure from warming to 35 °C. Since the response of these samples was found to be significantly different than the non- stabilized peanut butter, a complete breakdown of structure for these samples did not occur. However in the case of 0.5% stabilized sample, due to presence of a low level of stabilizer, the crystal network formed was not strong enough to resist deterioration at high temperature. Hence was not significantly different in its response from the non-stabilized sample.

Viscosity

Fresh samples at 26 °C

Viscosity values were determined at 8 different rpm values (0.5, 1.0, 2.5, 5.0, 10, 20, 50 and 100) using appropriate spindles. Since the viscosity of peanut butter was determined over a broad range of stabilizer levels, it was not possible to employ a single condition of spindle and rpm, to determine sample viscosity. And therefore, the determination was made using 4 spindles at the shear rates of 0.5 to 100 rpm. The data

was screened by dropping the values that fell outside the range of below 10% and above 90% of the instruments full scale, since in these regions the instrument response is unreliable. The data set was reduced to viscosity measurements obtained at three different shear rates- 10, 20 and 50 rpm. Out of the three shear rates 20 rpm had the maximum value of viscosity within 10 to 90% range. Statistical analysis was conducted on data collected from two replicates for 20 rpm for all the peanut butter samples. Apparent viscosity data of fresh samples of peanut butter at 26 °C for spindles C, D, E and F is presented in figure 4.5. The viscosity of peanut butter was found to be dependent on stabilizer level but independent of day (period of network formation). There was a significant 15-fold increase in peanut butter viscosity from 0.0 to 2.0% using spindle E for 2 d (figure 4.5C). The increase can be attributed to the presence of network in stabilized dispersions and hence provided higher resistance to flow. Citrene and others (2000) also explained the higher yield stress values for stabilized peanut butter in comparison to non-stabilized, on the basis of a strong network of particles formed by stabilizer in the stabilized samples.

Stored samples

Apparent viscosity data for peanut butter samples stored at 35 °C for 3 mo was collected for spindles D, E and F. For Brookfield viscometer the response of the instrument above the 90% and below 10% of the scale is non linear. The spindles D, E and F provided a maximum number of the readings which fell between the acceptable the range of 10-90 % reading of the instrument scale for all stabilizer levels. The apparent viscosities of peanut butter samples evaluated during storage intervals are presented in

figure 4.6. Viscosity of peanut butter samples was significantly affected by the amount of stabilizer level but was found to be independent of day. For the 15 d storage time, as the stabilizer level was increased the peanut butter became more viscous (figure 4.6A). There was no significant difference between the viscosity values with spindle E for 0.5 and 1.0% stabilizer level sample. Peanut butter samples with 0.0%, 1.5 and 2.0% levels of stabilizer had significantly different viscosities for day 15. The increased viscosities of samples with stabilizer levels can be attributed to the presence of crystal network which immobilized the free oil. In 30 d storage time for spindle E, the viscosity of non-stabilized sample increased in spite of the absence of the stabilizer. This indicates the presence of a hard mass at the bottom of the jar formed by the displacement of the separated oil as the top layer, which was decanted before the measurements were taken. There was a significant difference in viscosity of 0.0, 1.5 and 2.0% samples only, for 30 d storage (figure 4.6B). From texture studies conducted on stored samples, one could detect the formation of the compacted layer after 45 d of storage time where as for viscosity it was 30 d. Therefore, the viscosity measurements were found to be more sensitive to changes in peanut butter than texture tests. However, it has to be noted that the hard compact layer was formed at the bottom of the jar, where the Instron probe was not programmed to reach (travels only 9 mm deep through sample); where as Brookfield spindles were allowed to travel very close to the bottom of the sample container. For 45 d storage time an increase was observed for non-stabilized peanut butter, concurrent with its response for texture studies. The increasing trend indicated a further hardening of the mass as it was held an elevated temperature of 35 °C for more than a month. In stabilized samples the increase in the viscosity at 35 °C was due to increased strength of the

structure as it was keep undisturbed in the tempering chamber. There was no significant difference in viscosities of all 5 levels of stabilized peanut butter for 45 d storage time. The decay in the viscosities of the stabilized peanut butter was observed after 60 d storage. There was a significant difference in the viscosities of 0.0, 0.5 and 1.0% and that for 1.5 and 2.0% determined using spindle E for 60 d storage time. A drop of 16.39, 24.87 and 0.80% in viscosity values was observed for samples with 1.0, 1.5 and 2.0% stabilizer levels, respectively, for spindle E. The viscosity for non-stabilized peanut butter increased 4 fold; where as in case of 0.50% stabilizer level samples, the increase was for about 1.6 fold for 60 d for spindle E. For 75 and 90 d interval there were no significance differences in the viscosities of all the five levels of stabilized samples. High viscosities in stabilized samples of peanut butter (1.0, 1.5 and 2.0% levels) were due to the presence of the crystal network. In case of non-stabilized and 0.5% stabilizer level samples, the increase in viscosity over storage at 35 °C for 3 mo, was due to presence of dry compacted layer formed by the breakdown of the dispersion. Therefore, 0.5% stabilizer level was found to be insufficient to prevent oil separation in peanut butter under accelerated storage conditions.

Fresh samples at 35 °C

Apparent viscosity of peanut butter samples determined at 35 °C are presented in figure 4.7. Viscosity was found to be dependent on the stabilizer level but was independent of day. The trend was similar to that observed in fresh samples analyzed at 26 °C. The samples were found to be less viscous at 35 °C as in comparison to 26 °C (fresh samples). This was expected due to weakening of gel network from warming of

peanut butter for one hour prior to evaluation. There was an approximate 2-fold decrease in the viscosity for 0.5 and 1.0% stabilizer levels samples for spindle D at 20 rpm for 0, 1 and 2 d. For 1.5 and 2.0% stabilizer level a decline in viscosity was reported only for 0 and 1 d. In case of the 2 d, there was no decrease in the viscosity. This indicated the strong network present samples in 1.5 and 2.0% stabilized sample on 2 d was able to withstand high temperature and hence showed no decline in its viscosity.

CONCLUSIONS

Texture and viscosity analysis showed stabilizer level to be a significant factor affecting consistency of peanut butter samples. However, these parameters could not trace the subtle changes occurring in the sample during the period of network formation for fresh samples at 26 °C. Pre-warming of the sample at 35 °C resulted in significant differences in texture from 0 to 2 d, which was not observed in samples analyzed at 26 °C. Therefore, an additional step of pre-warming of peanut butter improved the sensitivity of texture analysis to changes taking place in peanut butter under tempering. This was however not found for viscosity analysis at 35 °C. From storage studies it was found that 1.0, 1.5 and 2.0% stabilized samples formed a stable network structure which was capable of withstanding any major changes for three months at 35 °C. And therefore these levels (> 1.0%) were considered adequate quantities of the additive required to stabilize peanut butter.

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Figure legend

Figure 4.1: A modified probe used in texture analysis of peanut butter samples

Figure 4.2: Effect of stabilizer level on texture firmness of fresh samples at 26 °C during the period of network formation

Figure 4.3: Effect of various stabilizer levels on texture of peanut butter stored at 35 °C for three months

Figure 4.4: Effect of stabilizer concentration on texture firmness of fresh samples at 35 °C during the period of network formation

Figure 4.5: Effect of stabilizer level on viscosity of fresh samples at 26 °C during tempering period when measured with various spindles at 20 rpm

Figure 4.6: Effect of stabilizer concentration on viscosity of stored samples at 35 °C for various time periods measured with various spindles at 20 rpm

Figure 4.7: Effect of stabilizer level on viscosity of fresh samples at 35 °C during tempering period when measured with various spindles at 20 rpm

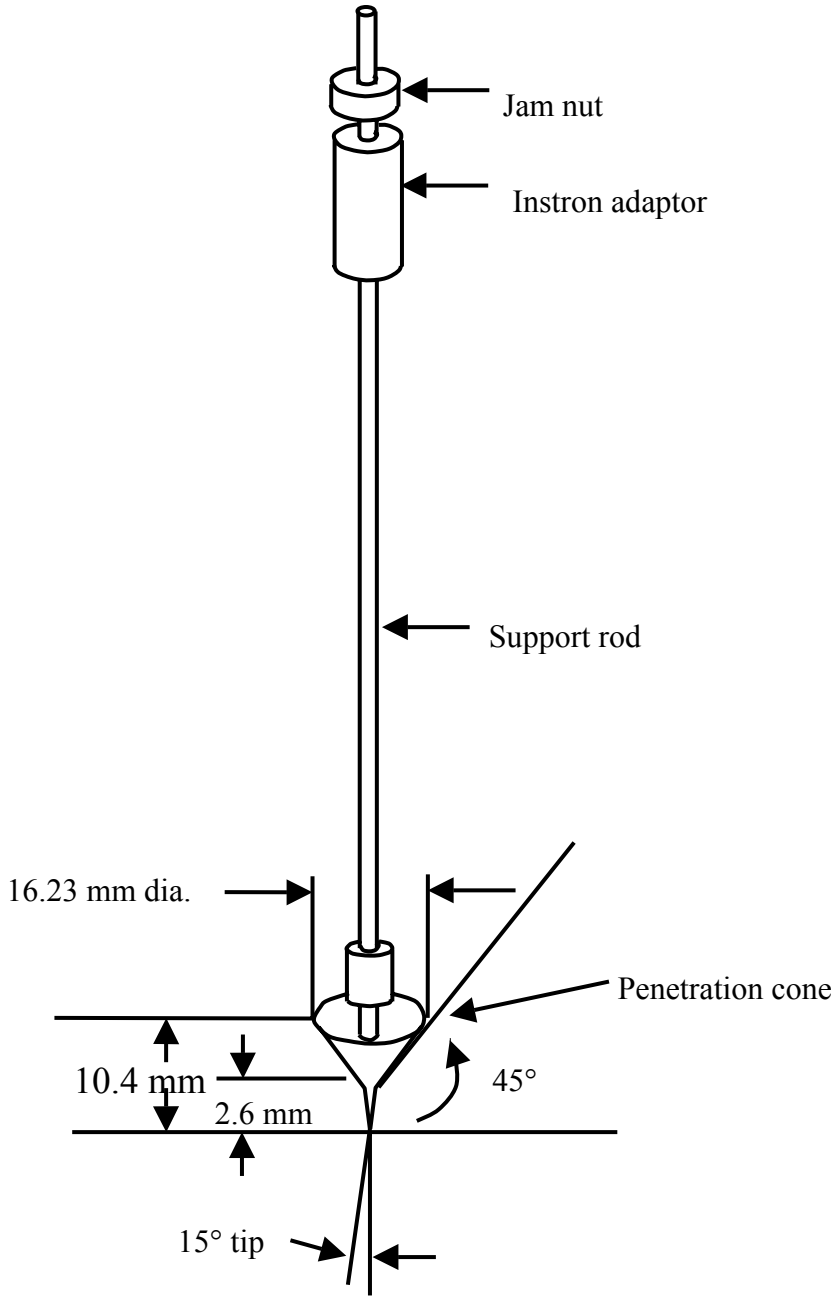
Jam nut
Instron adaptor
Support rod
16.23 mm dia.
Penetration cone
10.4 mm
2.6 mm
45°
15° tip

Figure 4.1

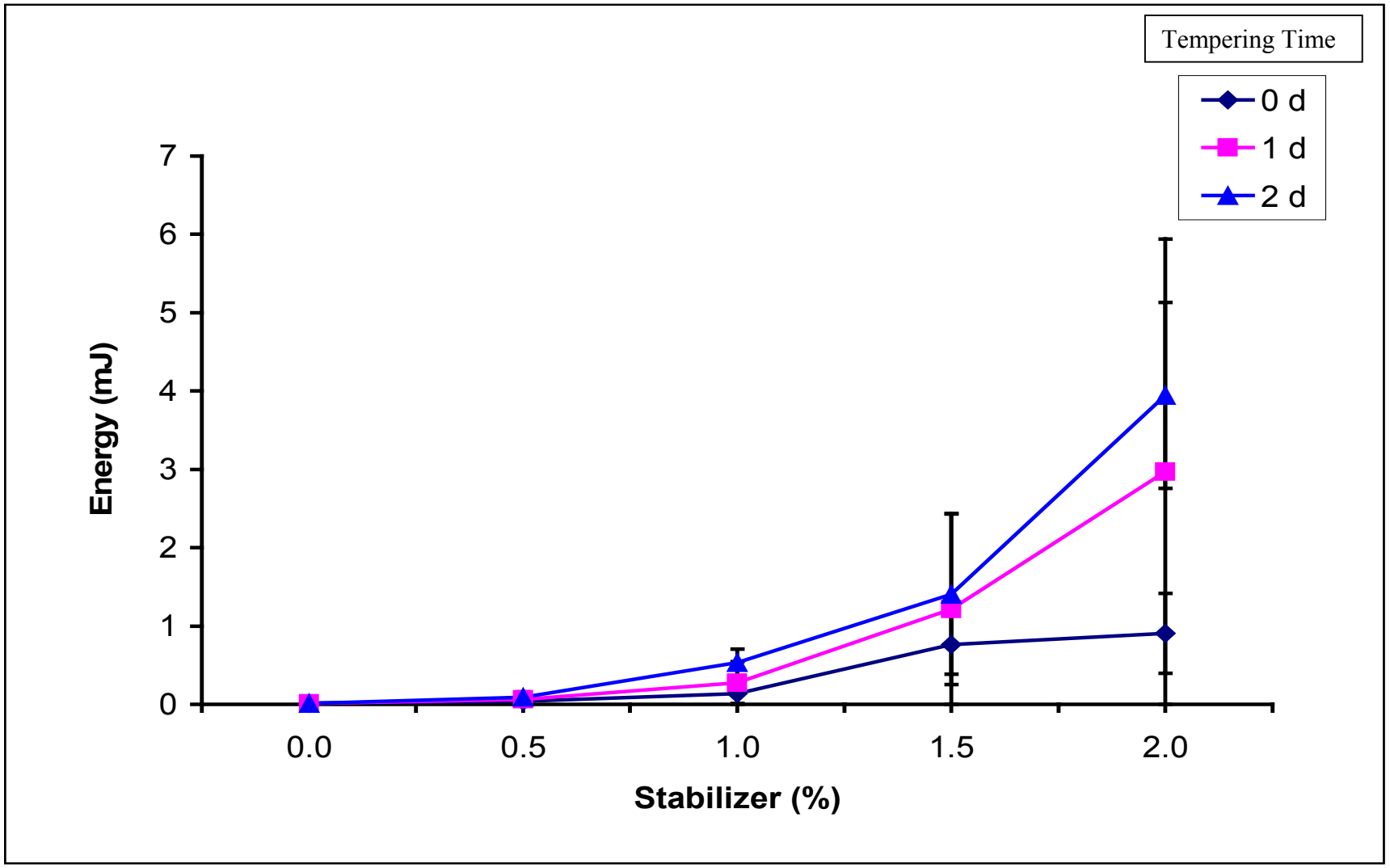
Tempering Time
0 d
1 d
2 d
Energy (mJ)
0
1
2
3
4
5
6
7
0.0
0.5
1.0
1.5
2.0
Stabilizer (%)

Figure 4.2

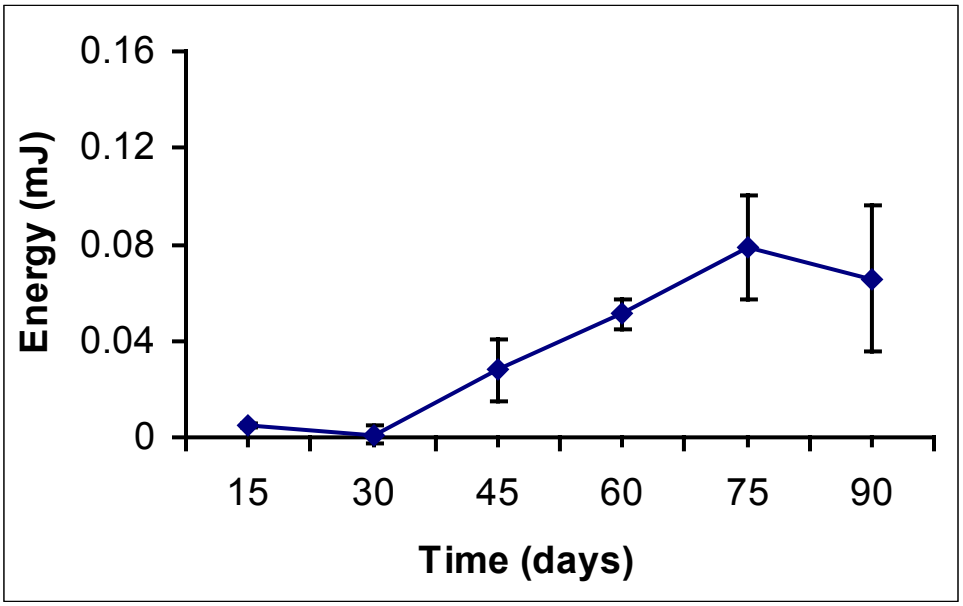

Figure 4.3A: 0.0% stabilizer level

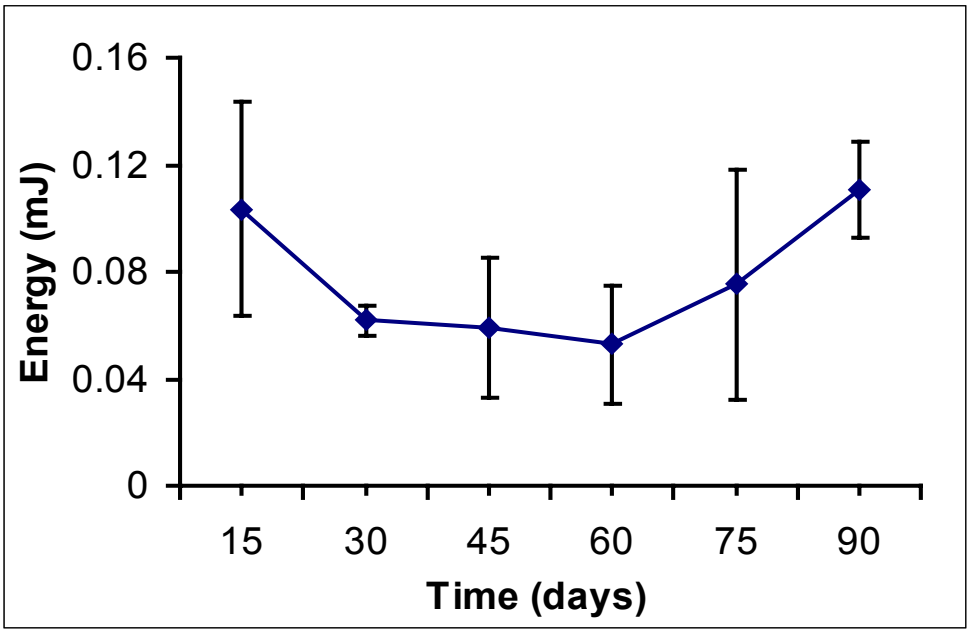

Figure 4.3B: 0.5% stabilizer level

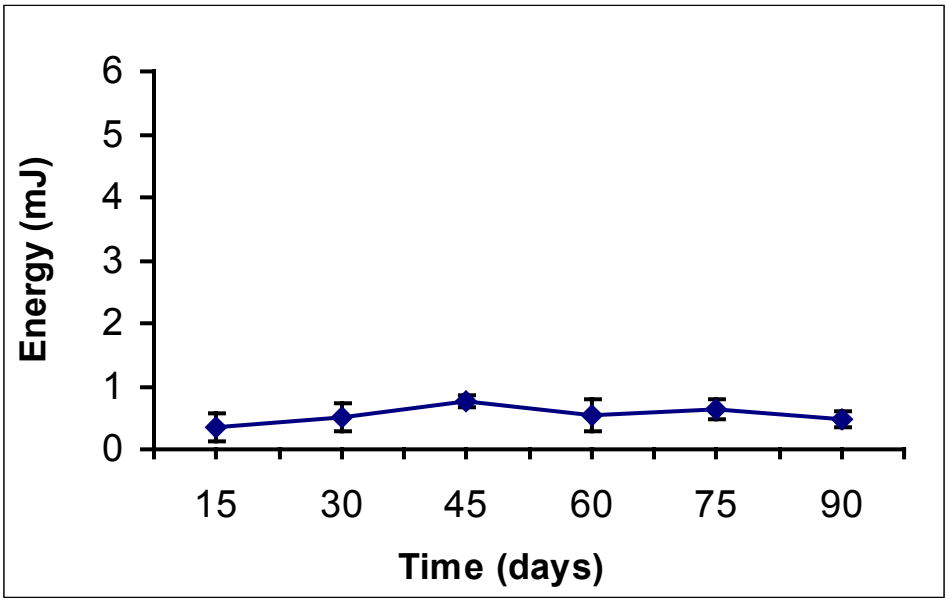

Figure 4.3C: 1.0% stabilizer level

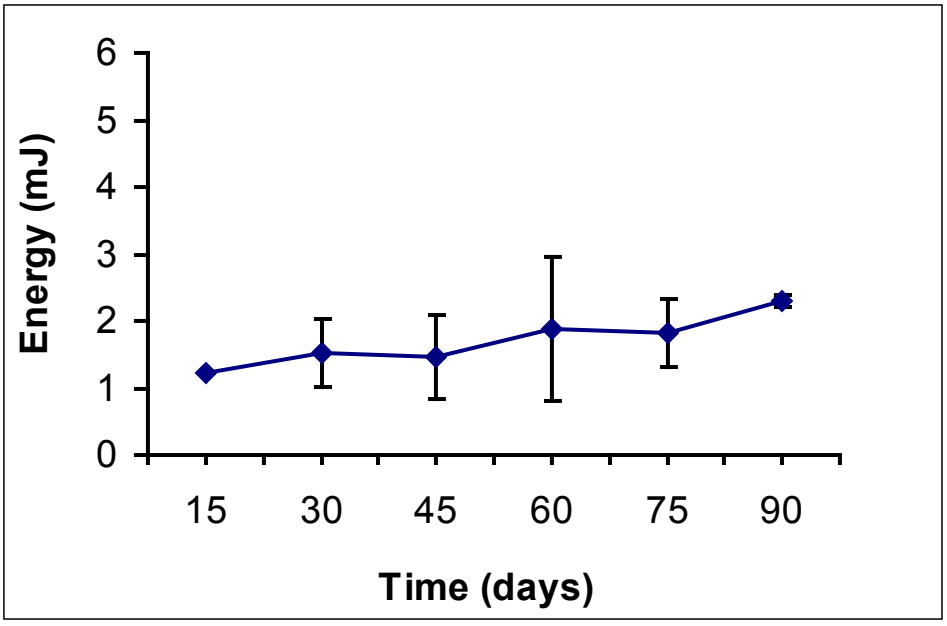

Figure 4.3D 1.5% stabilizer level

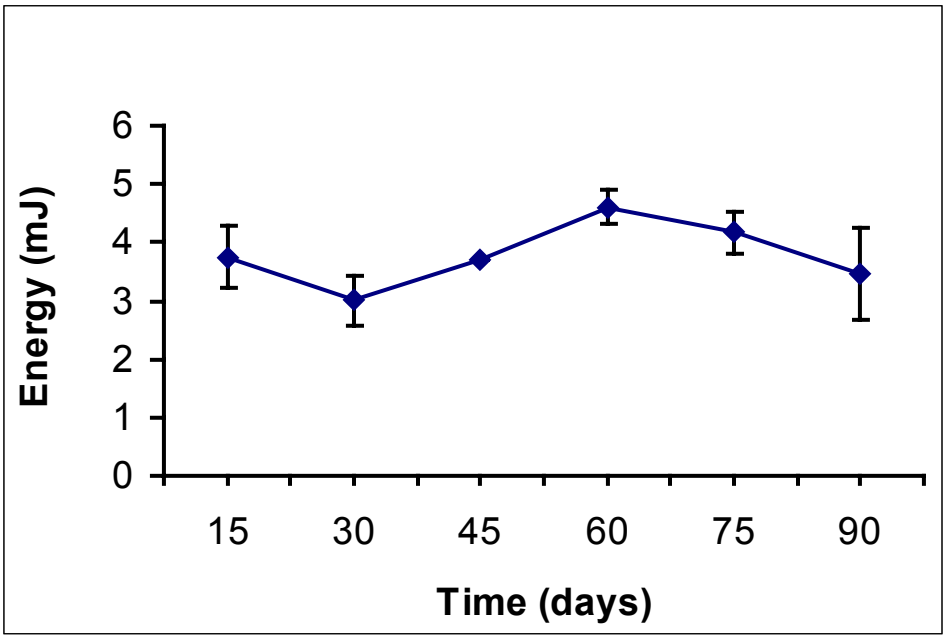

Figure 4.3E: 2.0% stabilizer level

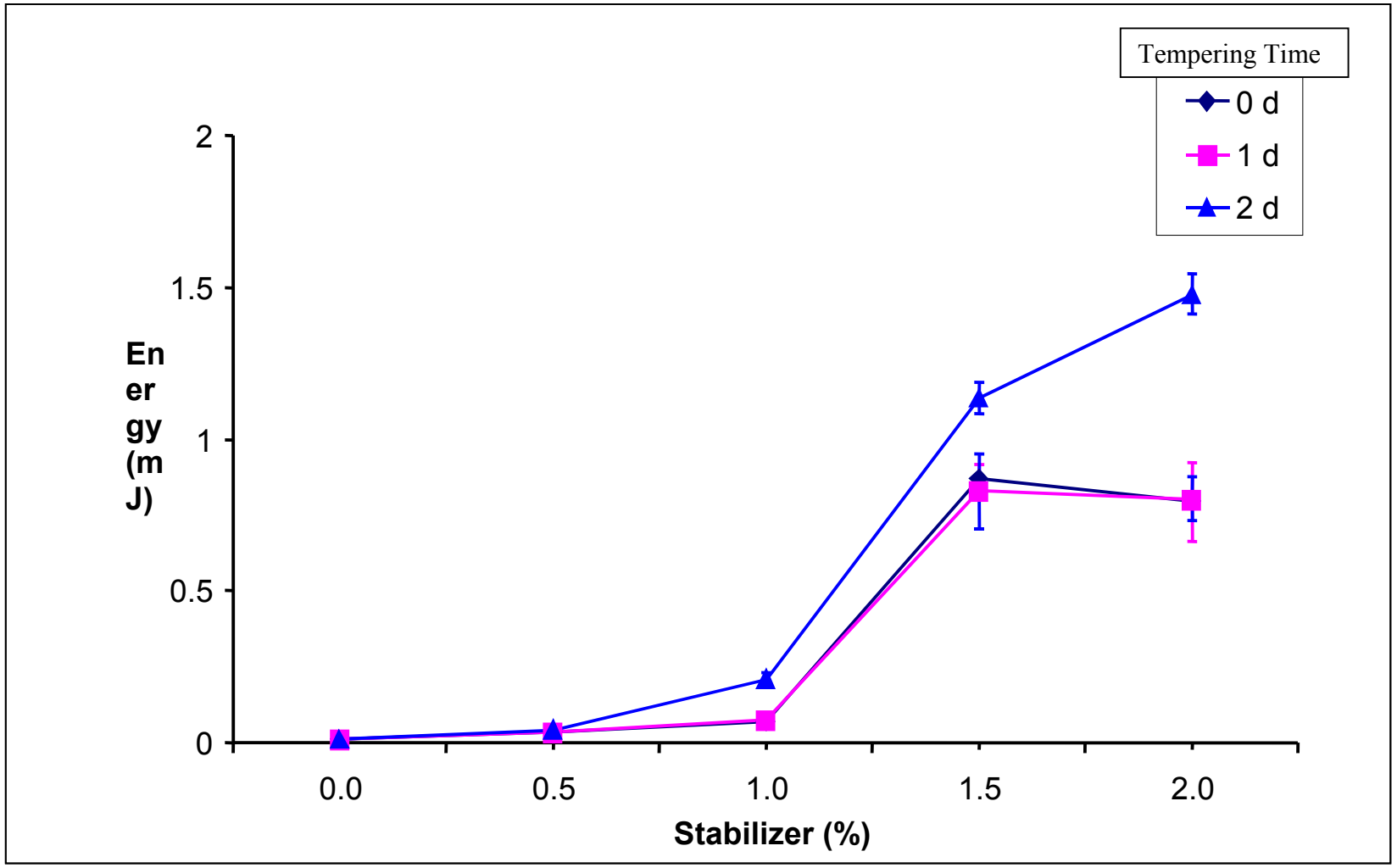
Tempering Time
0 d
1 d
2 d
2
1.5
1
0.5
0
Energy (mJ)
0.0
0.5
1.0
1.5
2.0
Stabilizer (%)

Figure 4.4

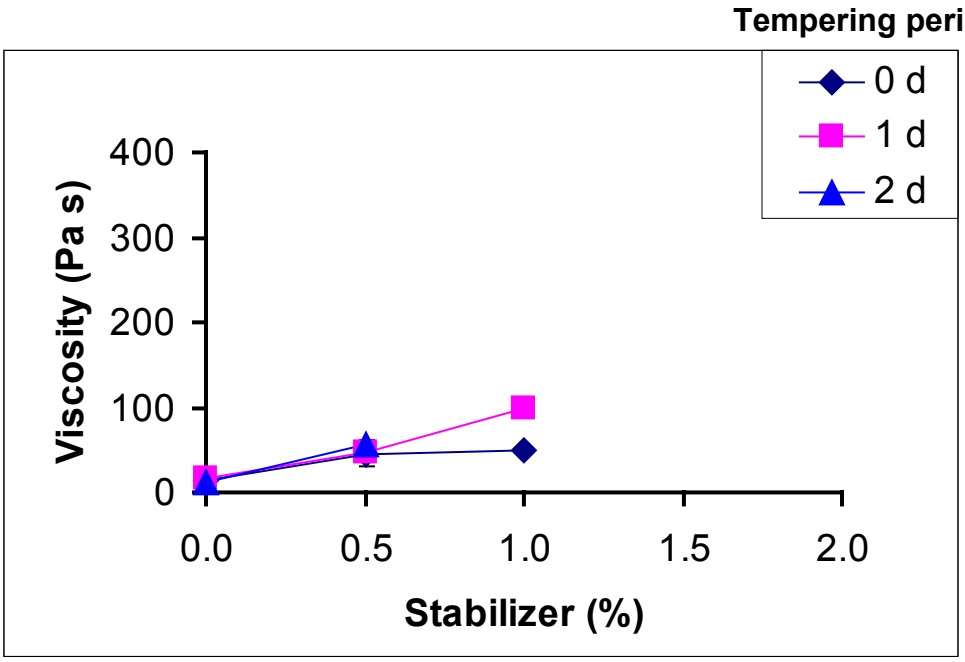

Figure 4.5A: Spindle C

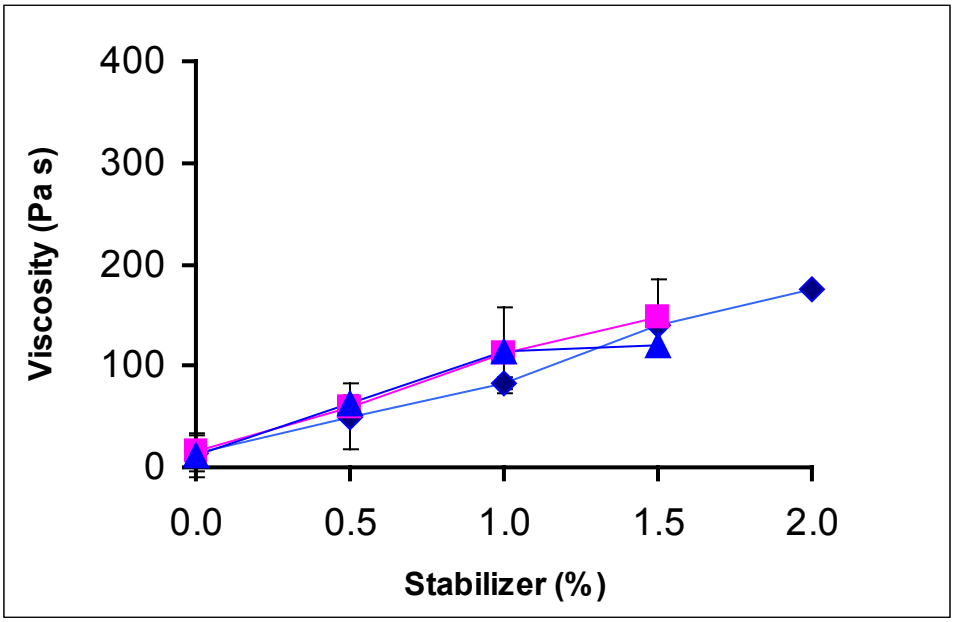

Figure 4.5B: Spindle D

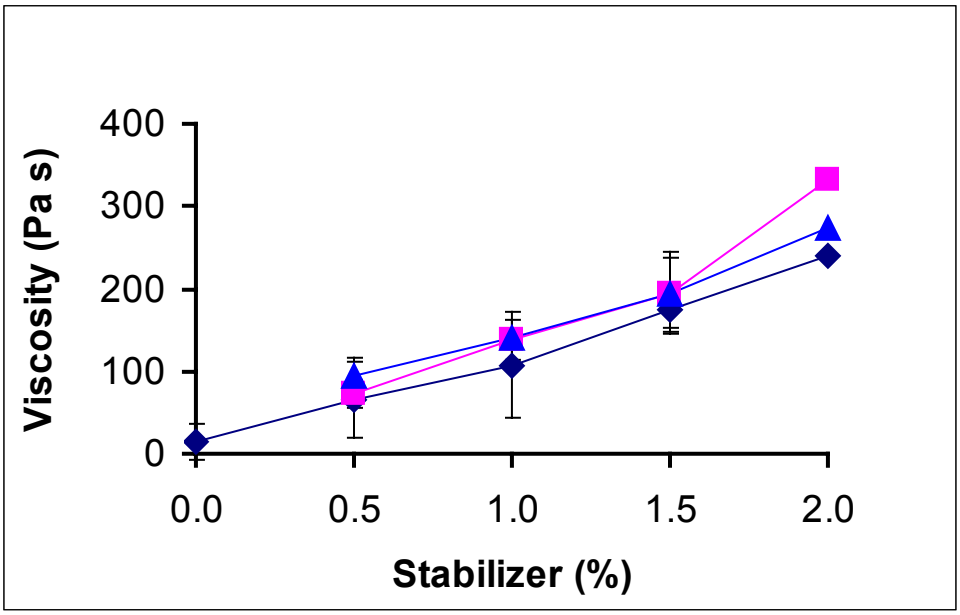

Figure 4.5C: Spindle E

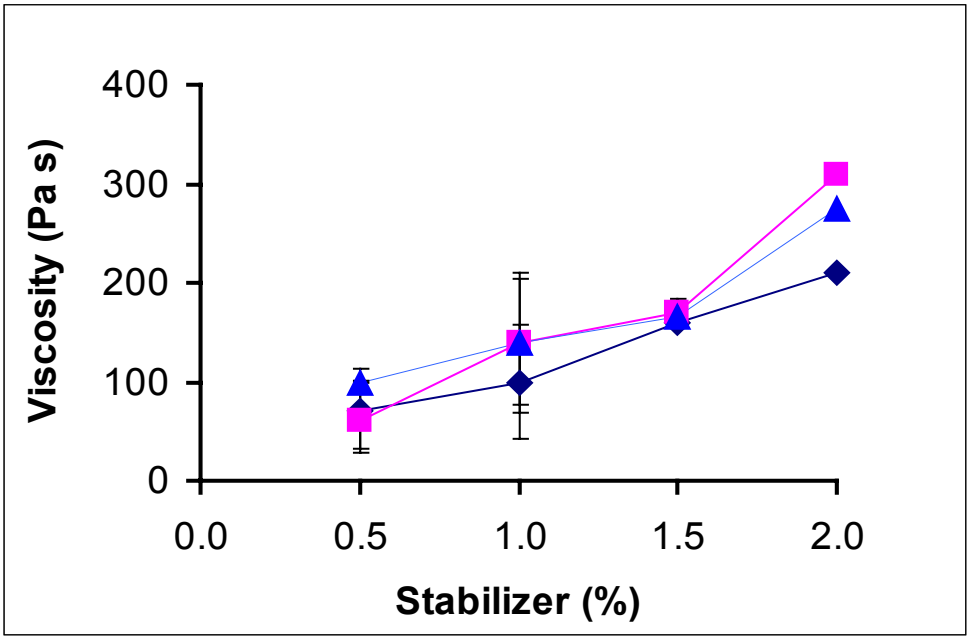

Figure4. 5D: Spindle F

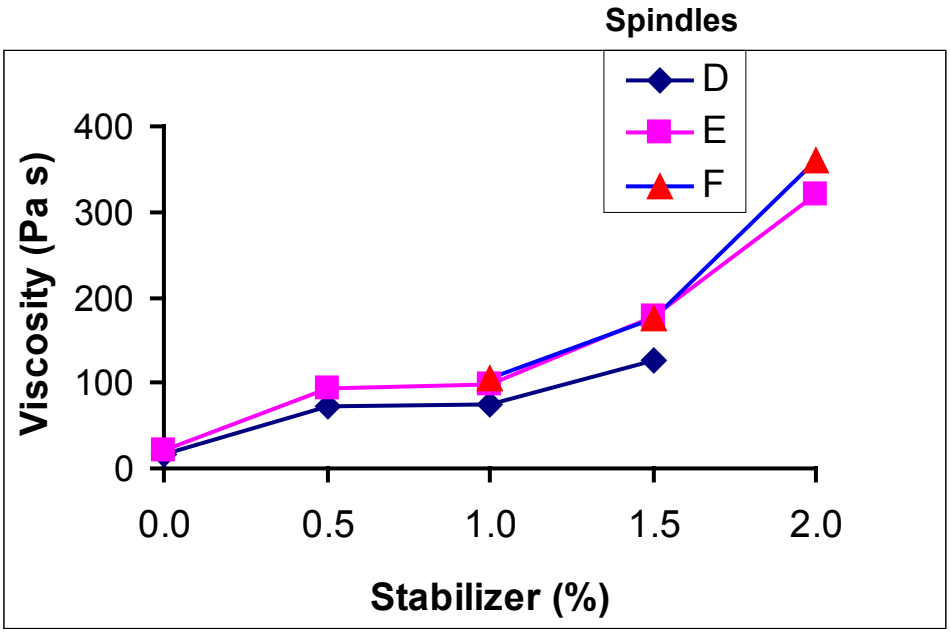

Figure 4.6A: For 15 d sampling time

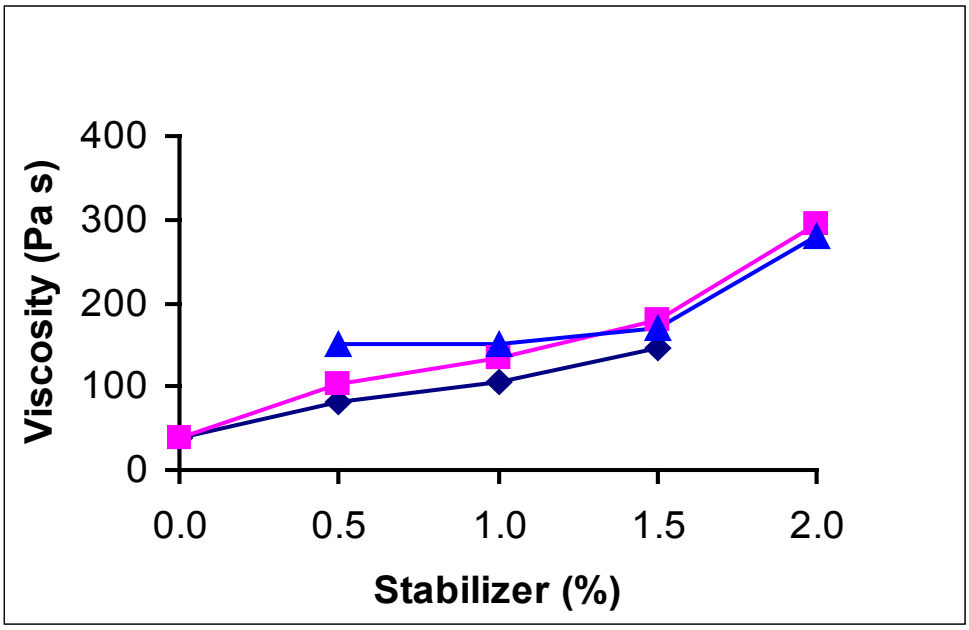

Figure 4.6B: For 30 d sampling time

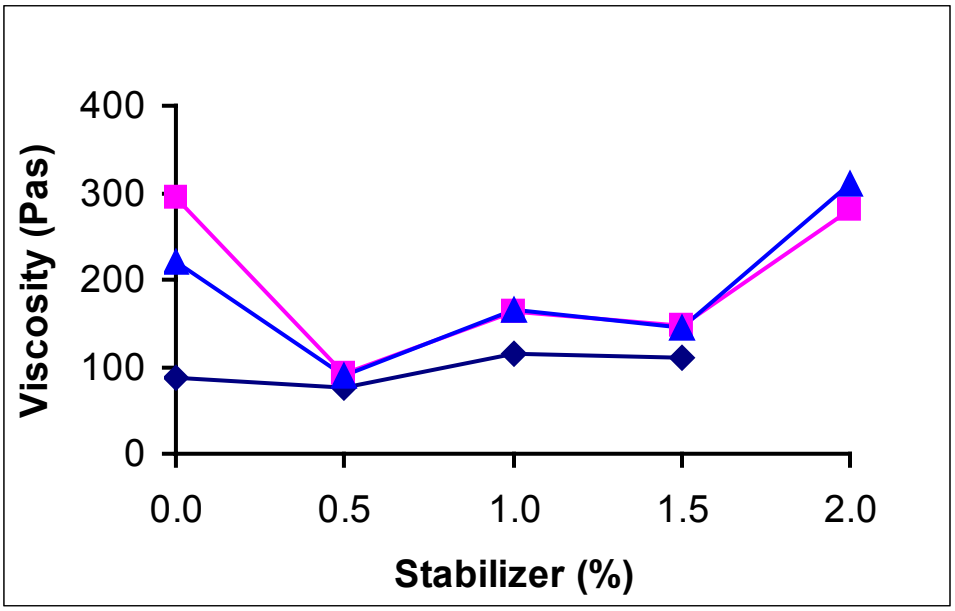

Figure 4.6C: For 45 d sampling time

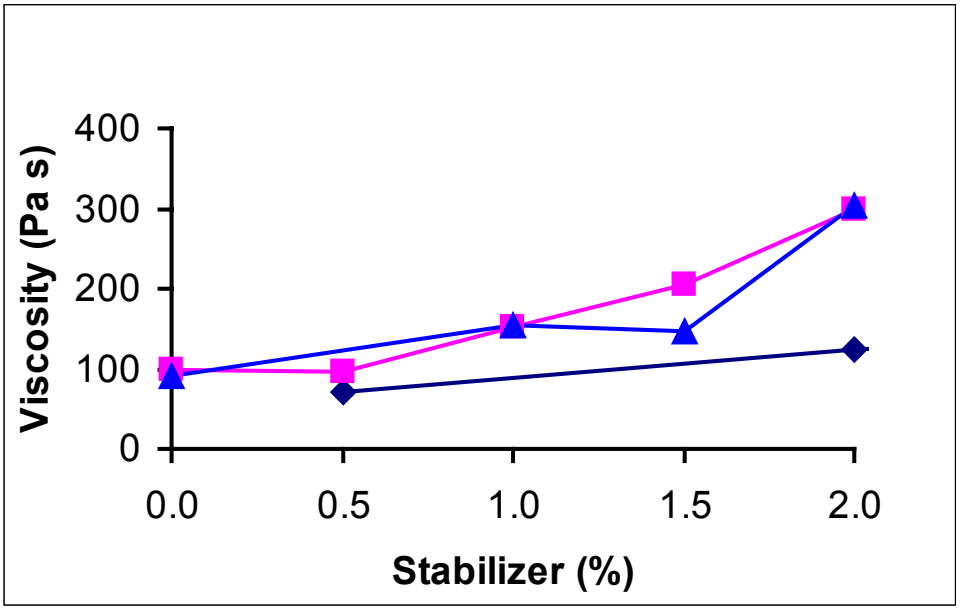

Figure 4.6D: For 60 d sampling time

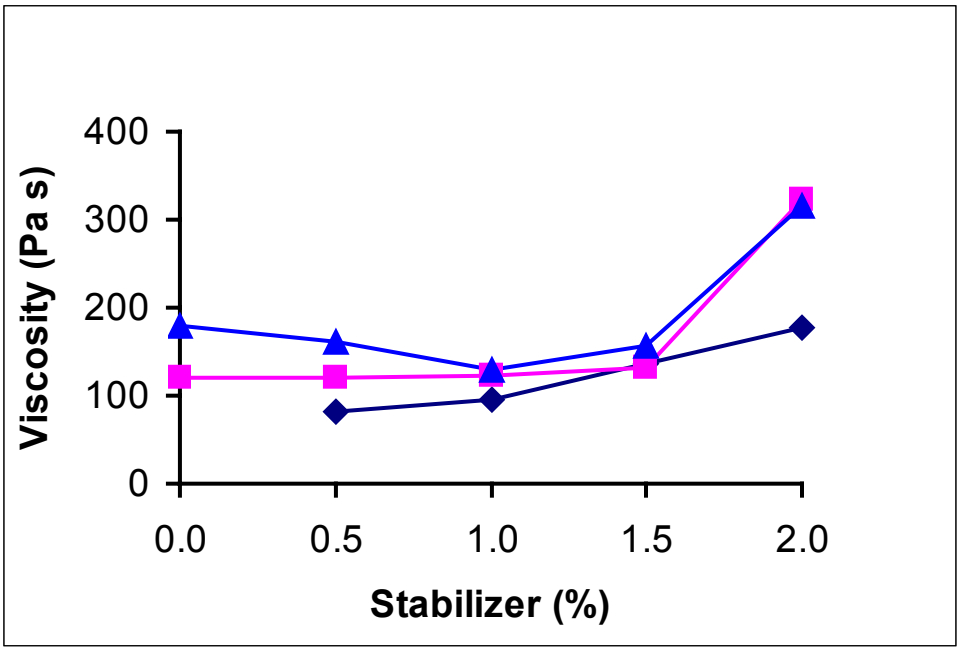

Figure 4.6E: For 75 d sampling time

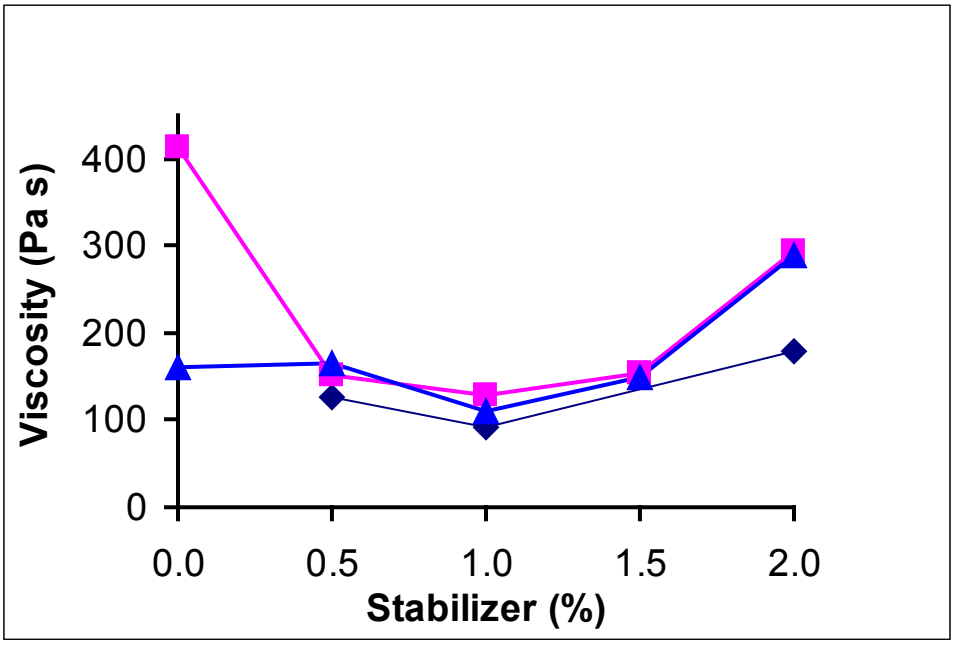

Figure 4.6F: For 90 d sampling time

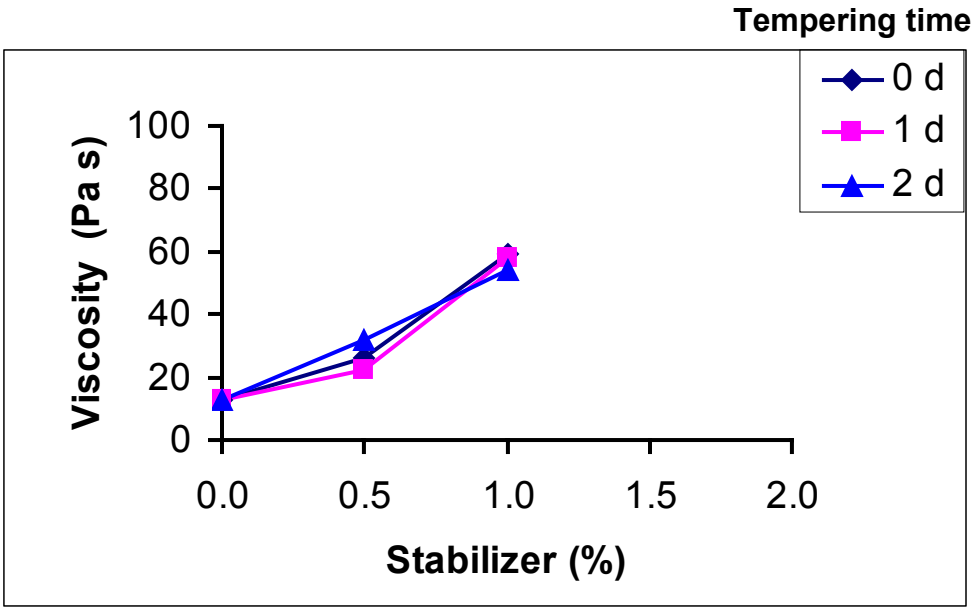

Figure 4.7A: Spindle C

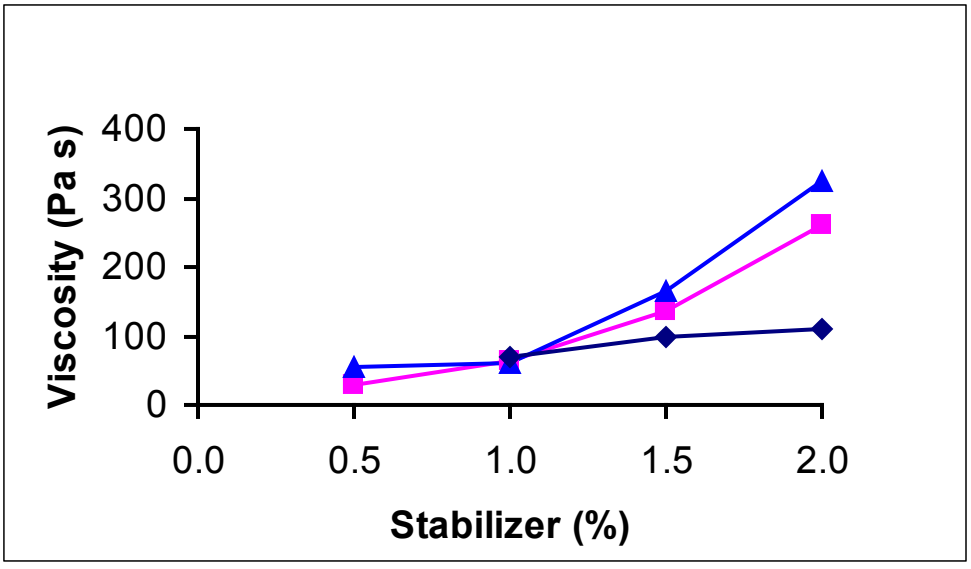

Figure 4.7B: Spindle D

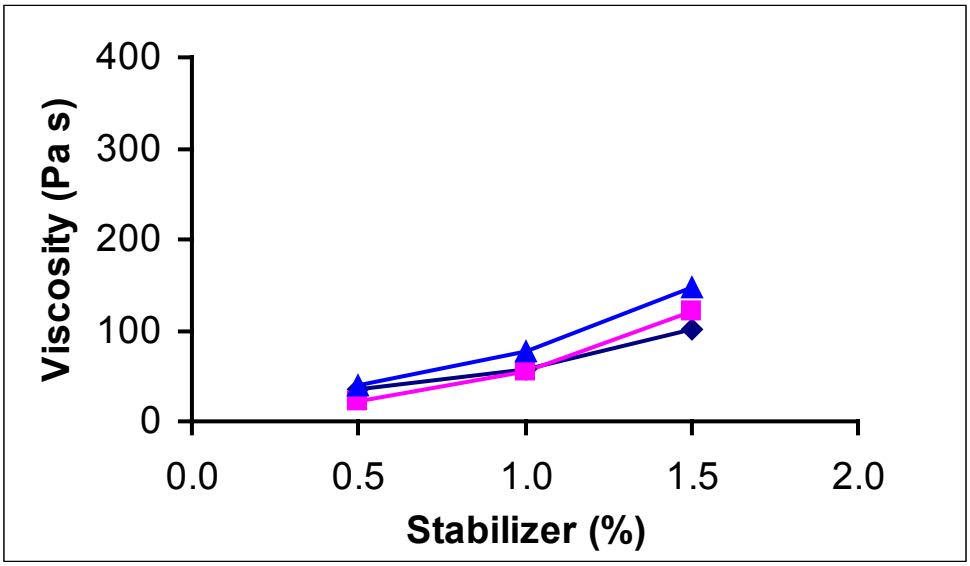

Figure 4.7C: Spindle E

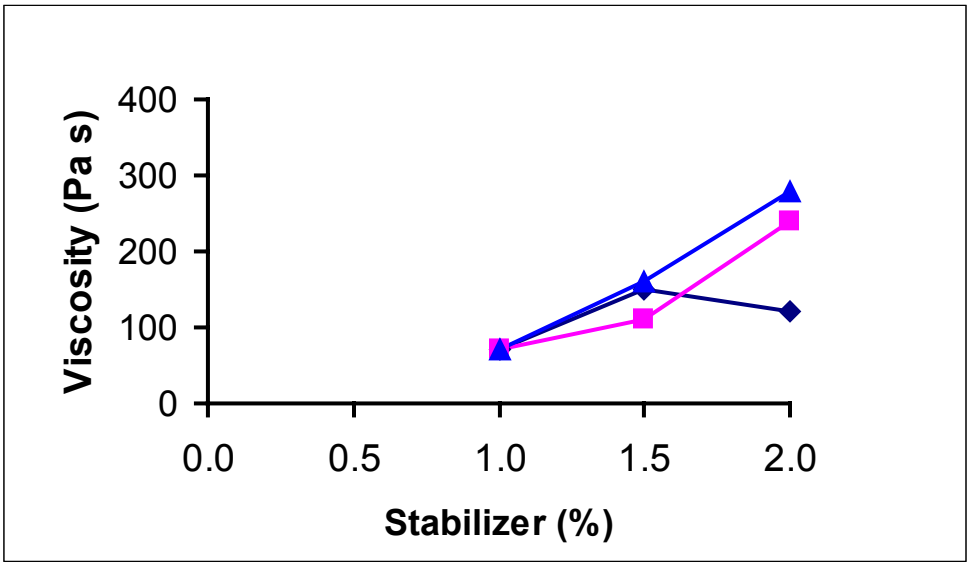

Figure 4.7D: Spindle F

CHAPTER 5

EFFECT OF STABILIZER LEVELS AND STORAGE CONDITIONS ON VISCOELASTIC CHARACTERISTICS OF PEANUT BUTTER[1]

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ABSTRACT

Fresh and stored peanut butter samples with five stabilizer levels (0.0, 0.5, 1.0, 1.5 and 2.0%) were subjected to oscillatory time sweeps, oscillatory stress sweep and creep recovery tests using a controlled stress rheometer. The three tests evaluated the structural strength of network formed by the stabilizer in peanut butter samples which has a direct impact on its viscoelastic properties. From time sweep tests, it was found that as the stabilizer levels were increased, elastic component predominated; the storage modulus increased by 1.2×10^4 for 0.0 to 2.0% stabilizer levels. Oscillatory stress sweeps could detect the LVR of 2.0% stabilized fresh samples. In samples stored at 35 °C for 3 mo, 0.0, 1.5 and 2.0% stabilizer level exhibited the presence of LVR. The viscoelastic behavior of peanut butter samples analyzed by creep recovery tests was explained by the presence of three retardation elastic compliances.

Key words: Controlled stress rheometry, oscillatory time sweeps, oscillatory stress sweeps, creep recovery

INTRODUCTION

Peanut butter has the ability to exhibit viscoelastic nature. Viscoelasticity is not an inherent property of this product but is imparted by the addition of a stabilizer. Stabilizers are hard fatty compounds used to prevent oil separation in peanut butters. The common stabilizers used in the manufacture of peanut butter are partially hydrogenated vegetable oil, mono, di, or tri glycerides, or their combination (Woodroof 1983). These compounds are capable of existing in crystalline form even at room temperature, a characteristic that is exploited in the manufacture of stabilized peanut butter. Freshly prepared peanut butter with the added fat is shock chilled to produce a large number of crystal nuclei. Further tempering of the product, in an undisturbed environment, allows the nuclei to form a network structure, which entraps the free oil preventing its separation and migration to the surface. The network serves a dual purpose of providing stability with respect to oil separation and smooth spreadable texture to the finished product. It also imparts a viscoelastic nature to peanut butter. Since the network prevents oil from separating in peanut butter, understanding its viscoelastic properties may provide valuable information regarding the network formation, and the various factors, which may have an influence on its strength such as stabilizer and storage conditions.

Comprehensive studies on rheological properties of peanut butter have been conducted by Campanella and Peleg (1987) using the technique of squeeze flow viscometry, where they described peanut butter as power law fluid. Citrene and others (2000) undertook one of the recent studies involving advanced techniques of controlled rate and controlled stress for characterizing the rheological properties of stabilized and non-stabilized peanut butter. Citrene and others (2000) reported the presence of a weak

gel like structure in stabilized samples as it displayed higher storage modulus values than non-stabilized ones. In this study, the terms 'crystal network structure' and 'weak gel' have been used interchangeably. The technique of controlled stress has traditionally been applied to understand the deformation and flow properties of polymeric material such as grease structure (Whittingstall 1996). In recent times, food scientists have adopted this unique technique to characterize the viscoelastic properties of food materials (Rosalina and Bhattacharya 2001; Citrene and others 2000; Grosso and Rao 1998; Chronakis 1996; Munoz and Sherman 1990).

The viscoelastic properties are often measured by resolving the viscous and elastic component of the material. The dynamic oscillatory tests are common for two primary reasons. First, the tests are non-destructive. Second, the results can be analyzed in terms of fundamental units, which helps to follow the process of gel formation (network characteristics) in biopolymers (Rao 1999). The structural strength of viscoelastic and gels networks have been studied by creep recovery tests. Katsuta and others (1990) investigated the viscoelastic properties of whey protein gels and the role of protein concentration in gel properties. Gladwell and others (1985) studied the creep recovery response of oil water emulsion and the influence of oil (disperse) phase on the creep behavior.

The rheological investigations that have been conducted on peanut butter were primarily focused on determining the viscoelastic behavior and yield stress (Citrene and others 2000; Campenalla and Peleg 1987). Evaluation of the dynamics of network strength in terms of rheological parameters in peanut butter however has never been undertaken. The current study therefore aimed to: 1) understand the viscoelastic behavior

of peanut butter; 2) examine the influence of stabilizer level on the network strength, and 3) follow the intrinsic process of degradation of network structure under accelerated storage conditions.

MATERIALS AND METHODS

Peanut butter preparation

This study involved measuring the strength of network structure of peanut butter samples at different stabilizer levels. Samples were prepared in the pilot plant by incorporating a commercial stabilizer - Fix-X™ into Kroger Krema® peanut butter. Kroger Krema® served as the base material in preparing all the batches of samples. Stabilizer Fix-X™ (m.p. = 65.5 °C), a blend of fully hydrogenated cottonseed and rapeseed oil, was obtained from Proctor & Gamble, Cincinnati, OH. Peanut butter samples containing five different stabilizer levels (0.0, 0.5, 1.0, 1.5 and 2.0%) were prepared by blending Krema® with pre-melted stabilizer, Fix-X™ in a modified colloidal mill (model M-MS-3, Morehouse industries, Los Angeles, CA). Prior to grinding, the base material was warmed in a steam jacketed kettle to effectively dispense predetermined amounts of stabilizer. The clearance between the mill stones was kept at 5 microns (0.125 mm). The mill temperature was maintained at 70 $\pm$ 2 ˚C. The product temperature exiting the mill was found to be in the range of 88–95 ˚C, which was subsequently lowered to approximately 37-41 °C by passing the material over a specially designed heat exchanger cold plate (42 cm x 50 cm), kept at 5 $\pm$ 1 ˚C as described in the previous chapter. Cooling facilitated the shock chilling of the product, initiating crystallization of the stabilizer.

Peanut butter with 0.0% stabilizer was referred to as "control" sample. However, controls were also subjected to preheating, grinding and chilling like the treatment samples with various stabilizer levels. Upon completing the formulation, the cooled product was distributed into 200 g glass sample jars (5.8 cm i.d). All peanut butter jars with the exception of 0 d samples were first cooled in an ice bath for 4 h and then moved temporarily to a controlled environmental chamber (Environmental Growth Chamber, Chagrin Falls, OH) maintained at 26 ˚C $\pm$ 2 for 'tempering' purposes prior to dividing them up into experimental groups and subgroups. Product tempering at 26 °C for 48 h is a standard practice employed by peanut butter manufacturers to allow the completion of network formation.

Peanut butter samples were grouped into two experimental categories labeled "fresh" and "stored". The samples analyzed on the same day (0 d) and within 24 h (1 d) and 48 h (2 d) of their manufacture were referred to as "fresh" samples. Fresh samples were further split into two subgroups, where one set was analyzed at 26 °C and the other at 35 °C. Following tempering for 48 h at 26 °C, the second category of peanut butter samples referred to as stored were placed in a chamber maintained at 35 $\pm$ 2 ˚C for an extended accelerated storage study for 3 mo. In stored samples, wherever visible oil separation was noticed, the tests were conducted after neatly decanting the oil from the jar.

Controlled stress rheometry

Oscillatory time sweep, oscillatory stress sweep and creep-recovery tests were performed on fresh as well as stored peanut butter samples at 26 ˚C with 40 mm parallel

plate geometry on an advance rheometer (Advanced Rheometer, AR 1000, TA Instruments, New castle, DE). Each peanut butter sample was initially placed in an anti-freeze bath (Endocal, Neslab Instr., Newington, NH) maintained at 26 or 35˚C based on the sample category. Samples (6 ml) were drawn using a straight walled tube (i.d. = 0.525 cm) under the application of 26 inches Hg vacuum. A plunger was used to extrude peanut butter from the tube onto the peltier plate in a uniform layer. Each sample layer was then consistently allowed to relax for 10 min for oscillatory time sweep test and 20 min for oscillatory stress sweep and creep recovery tests. This released the built-up internal stresses developed in the sample due to sampling, loading and gap closure. The gap adjustment of 1000 microns was set for fresh control samples (0, 24 and 48 h) as well as those evaluated at 15 d sampling intervals and for all the rest the gap setting was 2000 microns. Constant frequency of 0.5 Hz was fixed for all gap settings

Oscillatory time sweeps

For time sweep test, following sample relaxation and gap adjustment between the peltier plate and the attachment appropriate to the sample being tested, the excess sample was removed using a stainless steel spatula and subjected to 0.01% strain for 20 min.

Oscillatory stress (torque) sweeps

For oscillatory torque sweep test, each 1.0 to 2.0% stabilized peanut butter sample was subjected to increasing amplitude ranging from 1-50 Pa for 0.0% and 1-200 Pa for 0.5% torque. The measurements were conducted in triplicate.

Creep recovery tests

For creep/recovery testing, the sample was subjected to shear stress of 1 Pa for 5 min (retardation) following which the stress was removed and the sample was allowed to recover for the same amount of time (recovery). Measurements were carried out in triplicate for each individual sample.

Fresh samples at 35 °C were placed in the anti-freeze bath maintained at 35 °C prior to testing. The rheometer test conditions were identical as those used for fresh samples at 26 °C except that the peltier plate temperature was raised to 35˚C. In the case of oscillatory torque sweep, the stress range was set between 1-200 Pa for each sample.

Data Analysis

The data collected from all three tests was analyzed using the Rheology Advantage Data Analysis Software™. The software was supplied by the TA Instruments (New Castle, DE).

Oscillatory time sweeps

The analyses of data for time sweep tests conducted on five levels of freshly prepared peanut butter samples were done by estimating 10 response variables: Oscillatory strain (%), oscillatory stress (Pa), storage modulus (G′, Pa), loss modulus (G″, Pa), complex modulus (G*, Pa), loss viscosity (η′, Pa s), storage viscosity (η″, Pa s), complex viscosity (η*, Pa s), delta (δ, degrees) and tangent delta (tan δ).

Oscillatory stress (torque) sweeps

For oscillatory torque sweeps, the linear viscoelastic region was determined by fitting a straight line across the linear portion of the curve.

Creep recovery tests

The creep compliance J (t) in peanut butter samples was addressed in terms of

$$J(t) = J_o + J_R + J_N$$

$$J_R = \Sigma_i J_i [1 - \exp(-t/\tau_i)]$$

$$J_N = t/\eta_N$$

A graphical representation of creep compliance is given in figure 1.

The creep compliance was therefore expressed as:

$$J(t) = J_o + \Sigma_i J_i [1 - \exp(-t/\tau_i)] + t/\eta_N, \quad \text{where-}$$

1. J_o stands for instantaneous compliance which represents the elastic deformation occurring in the samples under applied stress. In this region (AB), the bonds are stretched elastically and if relaxed, the material is capable of complete recovery (Shama and Sherman 1966).
2. $J_i$is the retardation elastic compliance associated with corresponding retardation time τ_i. In the region (BC), there is an equilibrium between the bonds breaking and reforming and therefore, the material shows a decline in the rate at which the strain is developed (figure 1). Since the rate at which the bonds break and reform is not the same, Shama and Sherman (1966) replaced τ by a series of retardation times- $\tau_1, \tau_2, \tau_3, .. \tau_n$ corresponding to compliances -$J_1, J_2, J_3, \ldots J_n$. The term retardation compliance, J_i represents the viscoelastic behavior of the material.
3. The region of Newtonian flow is represented by the term $J_N = t/\eta_N$ which represents the viscous component of the expression. In this region, the bonds are broken at a higher rate than they are formed. The term $1/\eta_N$ is the slope of Newtonian region in the creep curve (Shama and Sherman 1966).

The viscoelastic nature of peanut butter using creep compliance was expressed in terms of the presence of three retardation elastic compliances along with three retardation times.

$$J(t) = J_o + J_1 [1 - \exp(-t/\tau_1)] + J_2 [1 - \exp(-t/\tau_2)]$$

$$+ J_3 [1 - \exp(-t/\tau_3)] + t/\eta$$

Although creep tests are usually conducted within the linear viscoelastic range (LVR), measurements outside LVR are not unprecedented. Measurement outside the LVR have been reported by Gladwell and others (1985) to observe the structural breakdown of the soybean- oil emulsions by monitoring J_o and η_N in linear as well as the non-linear range. In our study creep tests were conducted outside the LVR for those samples where LVR was either too short or not measurable.

The creep data analysis was done using the discrete retardation spectrum function of the TA Instruments data analysis software™ and was reported in terms of creep compliance J (t) (m^2/N) for the sample. For stabilized peanut butter (0.5 to 2.0% stabilizer level), three retardation compliance terms were used to explain the viscoelastic behavior. For fresh control samples and stored samples for 15 d storage, only one retardation term was used. It may also be noted that the instantaneous elastic compliance ($J_o = 1/G_o$) is reciprocal of the elastic shear modulus. Although some of the authors in literature have used parameter G_o instead of J_o to discuss their results, we have primarily used J_o.

Statistical analysis

To evaluate the significant effects of various factors, analysis of variance (ANOVA) and Duncan's multiple range tests were preformed using General Linear Models (GLM) of Statistical Analysis System (SAS 1990).

RESULTS AND DISCUSSIONS

Oscillatory time sweeps

Fresh samples at 26 °C

All peanut butter samples exhibited marked improvements in their structural characteristics over 48 h period of network formation. In the time sweep study, all the ten response variables were closely monitored: Oscillatory strain, oscillatory stress, storage modulus (G′), loss modulus (G″), complex modulus (G*), loss viscosity (η′), storage viscosity (η″), complex viscosity (η*), delta δ and tangent delta (loss tangent tanδ). The effect of stabilizer levels and the period of network formation (day) are explained as follows:

Oscillatory stress and strain. The typical response of freshly prepared peanut butter samples on 0 d is shown in figure 5. 2. In general, G′ values increased with the stabilizer level. These curves were further analyzed using the TA software. The effects of network formation period on oscillatory stress and strain are presented in figures 5.3A and 5.3B, respectively. The oscillatory stress increased as the stabilizer level was increased. In contrast, the strain developed over the samples decreased as the stabilizer level was increased. Time sweep tests were conducted by controlling the input variable strain (%).

However, it was observed that for stabilizer level 0.0-1.5%, for first 48 h of tempering, stress value was maintained constant at 0.8 Pa by the instrument and percent strain was found to vary. Only at 2.0% stabilizer level the strain could be controlled at the set level of 0.01%. In addition, oscillatory stress at 2.0% stabilizer level was significantly higher than at other stabilizer levels; however, no difference due to tempering period was observed. The strain on the samples decreased with increase in stabilizer percentage (figure 5. 3B). The increase in stress (only for 2.0% level) and the decrease in strain, as clearly depicted, was due to the improvement in the structure of peanut butter over 48 h period. Therefore, both stabilizer level and tempering time of peanut butter samples significantly affected its network structure.

Storage modulus (G′), loss modulus (G″) and complex modulus (G*), storage viscosity (η″), loss viscosity (η′) and complex viscosity (η*). The effects of network formation period on storage modulus (G′), loss modulus (G″) and complex modulus (G*) storage viscosity (η″), loss viscosity (η′) and complex viscosity (η*) are presented in figure 5. 3C, 3D, 3E, 3F, 3G and 3H, respectively. Investigation of network formation in peanut butter in dynamic rheological experiments showed increased values in all three areas relative to increase in the stabilizer level used and tempering time. Peanut butter samples subjected to time sweep analysis clearly demonstrated direct correlation of the structural strength on stabilizer level and tempering time of peanut butter. A sharp increase in both G′(figure 5. 3C) and G″ (figure 5. 3D) was observed for each level of increase in the stabilizer level indicating that the samples became more elastic and viscous at the same time. There was an 11-fold increase in the G′ values for each incremental increase in

stabilizer level (0.0-0.5-1.0%). The G′ value increased 5 and 7-fold for1.0 -1.5 % and 1.5-2.0 % of stabilizer levels, respectively. The increase was found to be higher for 0.0-1.0 % due to the relatively low levels of stabilizer in those samples; therefore, an increase of 0.5% in stabilizer level resulted in a higher G′ value compared to that of higher stabilizer levels (1.5, 2.0%) of. The trend for G′, G″ and G*: $G'_0 < G'_{24} < G'_{48;}$ where G′z is the storage modulus at z = 0, 24 or 48 h sampling intervals. This response clearly illustrates the development of the network structure in peanut butter due to the addition of stabilizer. There was a 5-fold improvement in the storage modulus values of control samples of peanut butter, which might have been due to the settling of peanut solids during 48 h tempering period, since the samples were composed of pure dispersions of peanut solids in oil. The trends for storage viscosity (η″), loss viscosity (η′) and complex viscosity (η*) were found to be similar to G* (figures 5.3F, 5.3G and 5.3H).

Delta (δ) and tan delta (tanδ). The effect of network formation period on delta (δ) and tan delta (tanδ) are presented in figures 5.3I and 5.3J, respectively. The phase lag and loss tangent were not positively affected by the tempering period, but declined with the increase in stabilizer level and tempering period. Oscillatory test using controlled stress rheometer involved manipulating the amount of strain applied on the material and measuring the response in terms of the stress developed over the sample. The phase angle between the applied strain and the oscillatory stress developed as a response is designated as delta δ.

In a typical elastic material, the phase lag (δ) equals 0°, in other words the stress developed over the sample is in phase with the applied strain. In contrast in a typical

viscous material, the lag equals 90°, which means that the stress lags behind the applied strain by an angle of 90°. In viscoelastic materials the phase lag lies between 0 and 90°. The ratio of the applied variable to the response gives the material stiffness, and the phase lag characterizes the viscoelastic nature of the product. The loss tangent represents the ratio of the loss modulus to storage modulus (G″/G′). This function measures the relative contributions of viscous to elastic behavior in a material at the given frequency. In a material where G′ >> G″, elastic component is predominant and exhibits a more solid like behavior –most of energy applied to deform the material is stored. In materials, where G″ >> G′, the material will have more of liquid like a behavior where most of the energy applied is dissipated in the course of material flow deformation (Rao 1999).

Stored samples

***Oscillatory stress and strain*.** The effect of 3 mos storage at 35 °C on the oscillatory stress and strain developed in time sweep tests for stored samples are presented in figures 5.4A and 5.4B, respectively. Control samples at 35 °C underwent a drastic change wherein oil in the peanut butter samples formed a separate layer leaving a hard layer of peanut butter that settled at the bottom. As a result, the control samples registered an abnormally high value of oscillatory stress during the latter part of the tempering period. In control samples, the oscillatory stress was found to be constant at 0.8 Pa for up to 45 d; after 45 d the stress values increased significantly up to 75 d storage and then declined at 90 d samples. Subsequently, the oscillatory strain values registered a steady decline from 1.73 to 0.01% during storage (15 to 75 d).

Peanut butter samples with stabilizer levels 0.5, 1.0 and 1.5% oscillatory stress and strain did not changes significantly due to storage time. Oscillatory strain for 2.0% level also did not change significantly with storage time and was not different from that of samples with stabilizer levels 0.5 to 1.50%; however, at these higher levels of stabilizer, the data showed a steady decline from 14.53 to 4.62 Pa with increase in storage period from 15 to 90 d at 35 °C.

Storage modulus (G′), loss modulus (G″) and complex modulus (G*), storage viscosity (η″), loss viscosity (η′) and complex viscosity (η*). The effects of storage time and temperature (3 mo at 35 °C) on storage modulus (G′), loss modulus (G″), complex modulus (G*), storage viscosity (η″), loss viscosity (η′) and complex viscosity (η*)for stored peanut butter samples are presented in figures 5.4C, 5.4D, 5.4E, 5.4F, 5.4G and 5.4H, respectively.

In general, the trends in these responses were similar to that observed in oscillatory stress tests. This implies that the storage time had very little effect on samples with stabilizer levels of 0.5 to 1.5%. By increasing the stabilizer level up to 2.0%, the magnitude of all modulus and viscosity parameters increased, but this trend reversed with storage time. Control samples did not exhibit any response initially for first 45 d but at subsequent sampling intervals increased very steeply; this increase was attributed to the formation of steadily tougher bottom layers of product in the container.

Delta (δ) and tan delta (tanδ). The effects of storage, time and temperature (3 mo at 35 °C) on delta (δ) and tan delta (tan δ) of peanut butter samples are presented in figures 5.4I and 5.4J, respectively . In control samples, a steady drop in δ and tan δ values was observed for 15 to 75 d; and then it remained constant up to 90 d. The steep decline in the values of δ and tan δ at 75 d and beyond confirmed the presence of solid like behavior in the compacted layer. However, an 83% decrease in the phase lag was reported from 60-75d. Increasing the stabilizer levels from 0.0 to 0.5-2.0%, resulted in reduced values of δ and tan δ; however, these two responses were not significantly affected by time for stabilizer levels in the range of 0.5 to 2.0%.

Fresh samples at 35 °C

The effects of stabilizer level and tempering time on oscillatory stress and strain for fresh samples at 35 °C are presented in figures 5.5A and 5.5B, respectively. There were no significant changes in oscillatory stress and strain responses due to tempering time and stabilizer level, except for 2.0% level where the stress increased and strain decreased with tempering time. Also the strain on the peanut butter samples decreased with increase in the stabilizerlevel. The changes in the storage modulus (G′), loss modulus (G″), complex modulus (G*) for each of the stabilizer levels are presented in figures 5.5C, 5.5D and 5.5E. An increase in the storage, loss and complex modulus was noted with the increase in the stabilizer levels. Similar trend was observed in the case of fresh samples analyzed at 26 °C. However, for samples at 35 °C, the modulus values were lower in comparison to samples tested at 26 °C. The response of loss viscosity (η′), storage viscosity (η″) and complex viscosity (η*) (figure 5.5F, 5.5G, 5.5H) were found to

be similar. The phase lag delta (δ) and loss tangent tan delta are presented in figures 5.5I and 5.5J. Tempering time had no effect on the values of δ and tan δ except for control samples which had higher values of δ and tan δ. This again confirmed the greater elasticity of stabilized samples in comparison to control samples.

Oscillatory stress sweep- determination of linear viscoelastic range (LVR)

Typical plots of oscillatory stress sweep curves are shown in figure 5.6. These plots are from single replication of fresh samples with 2.0% stabilized levels at 26 °C for different tempering periods. The curves show the effect of tempering period on the storage modulus (G′) values (which increased with tempering period). Theses curves also depict LVR, magnitude of stress over which G′ was independent of stress. The LVR values obtained from the types of plot shown in figure 5.9 are presented in Table 5.1. Among the fresh sample tested at 26 and 35 °C, only 2.0% stabilized samples were able exhibit the presence of a linear range. LVR values increased with the tempering period for fresh samples at 26 °C. However for fresh samples at 35 °C, the value of 5.10 Pa was highest for 0 d, and this values was significantly greater than that of fresh samples at 26 °C. Greater values of LVR are generally associated with greater structural strength. However, it is not clear why LVR values were higher for fresh samples at 35 °C.

For control samples, LVR was evident only for storage time at 60 d and beyond; this is attributed to the presence of a compacted solid mass deposited on the bottom of the jar as the oil migrated to the surface of the product. In stabilizer levels of, 1.5 and 2.0%, the LVR was observed for all storage time intervals. The LVR for 1.5 % stabilizer level was lower than 2.0% for all storage intervals. Also for both 1.5 and 2.0% stabilizer

levels, the peak value for LVR was obtained for 30 d storage time, following which a decline was observed. This indicated the degradation of the sample structure of peanut butter over storage. This represents declining network structure over storage for three months. Therefore, oscillatory stress sweep, like time sweeps, was able to trace the changes occurring in the network structure over storage.

Creep recovery test

Fresh samples at 26 °C

The creep compliance of peanut butter containing varying stabilizer levels decreased with increase in stabilizer level and tempering period. The effect on variables J_o, J_1, J_2, J_3, and η_N are presented in figures 5.7A, 5.7B, 5.7C, 5.7D, and 5.7E, respectively. Both the independent variables, stabilizer level and tempering day, showed significant interaction ($p < 0.05$). Creep compliance is the degree of deformation in material under constant application of stress. Therefore, lower creep compliances are a measure of a stronger crystal structure formed by the stabilizer. The amount of strain developed over the sample reduced as the sample became more rigid due to the improved structural strength of the material. Overall, the instantaneous elastic compliance (J_o) decreased with the increase in stabilizer level and tempering period. The value of J_o was found to decrease 216-fold with increase in the stabilizer level from 0.0 to 2.0% for day 0. The decrease in the first, second and third retardation elastic compliance with stabilizer level indicated that a higher level of stabilizer probably yielded a large number of finely divided crystals thereby increasing the rate at which the structure was formed. This increased the strength of undisturbed network leading to reduced structural rearrangement

occurring in the viscoelastic region, thereby reducing the contribution of the retardation elastic compliances (Gladwell and other 1985).

The tempering period did not significantly affect the Newtonian viscosity (η_N). Therefore, only mean values of η_N over 0, 24 and 48 h are presented in fig 7E. The increase in the Newtonian attribute in a sample with increasing additive level reduced the contribution of the viscous component in the expression (t/η_N), which indicates a reduction in the viscous behavior of the sample. Hence, the elastic behavior dominated as the sample became more stable.

Stored samples

The creep tests conducted on the samples stored at accelerated storage conditions of 35 °C for 3 months reflected the structural changes in the samples. The trends for J_o, J_1, J_2, and J_3 for stabilizer levels 0.0, 0.5, 1.0, 1.5 and 2.0%, are presented in figures 5.8, 5.9, 5.10, 5.11 and 5.12, respectively. Stabilizer and storage time and their interaction were found to significantly affect compliances. In the case of the control sample, a single retardation term (J_1) was used to fit the data for fresh samples as well as stored samples analyzed at 15 d storage time. However, due to the increasing compactness of non-stabilized sample necessitated the use of three retardation terms for 30 d storage and beyond. In "control" samples, there was a gradual decrease for instantaneous compliance (J_o) for the first 60 d storage time and then a sharp dip was noted. J_1, and J_2 retardation elastic compliances also decreased with storage time (figures5. 8B, 5.8C). The term J_3 remained constant for 75 d then decreased sharply (figure 5.8D). This behavior in the non-stabilized samples is attributed to the formation of a dry compact layer after

separation of entrapped oil. Due to the absence of stabilizer, the complete breakdown may have occurred after 60 d storage, thereafter a sharp drop in instantaneous compliance was observed.

For 0.5% stabilizer level, there was a decrease in J_o value for 15 to 30 d which signified improvement in the sample structure as a result of tempering (figure5. 9A). An increase of J_o value from 30 to 45 d was due to the breakdown in the network structure as a result of high temperature of storage. Further, from 45 d onwards there was a steady decline in the J_o values similar to that seen in the control sample (figure 5. 9A. Again this is an indication of compactness of the peanut butter due to increasing oil separation. The first retardation compliance was found to decrease from 15 to 30 d time period after which it remained steady for 45 d. The decline in J_1 value was due to an improvement in network structure. The separation of oil, which might have occurred between 30 to 45 d sampling intervals, may not have affected the viscoelastic behavior of the sample. The J_1 value was found to increase further, which is indicative of sample being more viscous at 60 d and beyond (figure 5. 9B). The J_2 value on the other hand, showed an overall decrease for 15 to 90 d with a marginal increase reported for 60 d interval that was not significant (figure 5. 9C). The third retardation compliance also decreased with increase in storage interval.

In samples with 1.0% stabilizer level, a drop in the J_o value was observed from 15 to 30 d that remained low up to 60 d. This was an indication of strengthening crystal network structure in the sample due to higher level of stabilizer as compared to the control and 0.5% level. An increase in the J_o value was observed for storage time from 75 to 90 d (figure 5. 10A), which represented the oil separation occurring in peanut butter

samples due to the reduction in the capacity of the stabilizer to hold peanut oil trapped in the crystal network that formed at higher storage temperature. The prolonged period of storage at higher temperature may have caused a rupture in crystal network bonds formed in the network structure. As the bonds broke, the oil gradually rose to the surface of the container due to lower density and formed a separate layer, leaving below a mass of peanut solids. From the data on $J_{o,}$ we infer that the commercial stabilizer used at 1.0% level was effective for 60 d at storage temperature of 35 °C. No overall change in J_1, J_2 and J_3 values was observed (figure 5. 10B, 5.10C and 5.10D). The viscoelastic component of the system was therefore found to be unaffected during this 90 d storage at 35 °C.

For 1.5% stabilizer level samples, the network strength was found to increase from 15 to 45 d, which is indicative of strengthening network structure during storage (figure 5. 11A). Further, there was a nearly 22-fold increase reported in J_o from 45 to 60 d storage time after which it remained steady for 75 d followed by a gradual increase after 90 d (figure 5. 11A). This trend in the instantaneous compliance (J_o) shows that a slow deterioration occurred in the peanut butter samples. The stability was superior in 1.0% samples apparently due to the presence of a higher level of stabilizer. The first and third retardation compliances did not show any significant change due to storage time indicating that the viscoelastic behavior of the samples remained unaffected over three months period.

A constant decline in instantaneous compliance was observed until 75 d for 2.0% stabilizer level; after which J_o increased from 3.43×10^{-10} to 4.2×10^{-06} for an overall improvement by 10^4 (figure 5. 12A). This implies that the decline in structural strength

occurred only under extended storage when 2.0% sample was stored at 35 °C for longer than 75 d. The 2.0% stabilizer level was also found to lend a better 'keeping' quality than 1.5% stabilizer level. The retardation compliances, J_1 and J_2, remained unaffected by storage time (figure 5. 12B, 12C). The third retardation compliance, J_3, was found to decrease gradually with increase in storage time followed by an increase at 75 d before declining again at 90 d (figure 5. 12D).

The Newtonian viscosity (figure 5. 13) was found to be maximum in controls (0.0%) followed by 2.0, 1.5, 1.0 and 0.5% stabilizer levels. The highest Newtonian viscosity for controls was due to the presence of dried up firm layer that settled at the bottom of the jar. For stabilizer levels 0.5 to 2.0%, the Newtonian viscosity increased with increase in stabilizer level.

Fresh samples at 35 °C

Unlike fresh samples at 26 °C, the response of peanut butter samples analyzed using creep tests at 35 °C, tempering time was not a significant variable affecting their creep compliance behavior. Stabilizer was the only independent variable that affected the response variables (the J_o, J_1, J_2, J_3 and η_N). Values of parameters J_o, J_1, J_2, J_3 and η_N were averaged over tempering periods and are presented in figures 5.14A-5.14E. The instantaneous compliance (J_o) decreased with increase in stabilizer levels. Heating of the samples to 35 °C prior to rheological tests probably adversely affected the sample structure. In the case of 2.0% stabilizer levels, a high concentration of the additive produced a stronger network, which was more temperature resistant than lower stabilizer levels. This behavior was also observed in stored samples. The retardation elastic terms

J_1, J_2, and J_3 were found to decrease with increase in stabilizer level indicating an improvement in undisturbed network strength (figure5. 14B, 5.14C, 5.14D). In the case of Newtonian viscosity (η_N) values, a sharp 496- and 71-fold increase occurred for 0.0 to 0.5% and for 1.5 to 2.0% stabilizer levels, respectively (Fig 14E). An increased Newtonian viscosity decreases the contribution of the viscous component and hence the viscous contribution in the network structure.

CONCLUSIONS

The three tests, oscillatory time and stress sweeps and creep recovery, performed on peanut butter samples successfully traced the improvement in terms of strengthening of the sample structure during the 48 h period of network formation. The trend in the storage modulus (G′) values with increase in the stabilizer levels was: $G'_{0.0} < G'_{0.5} < G'_{1.0} < G'_{1.5} < G'_{2.0}$ for fresh; and $G'_{0.0} > G'_{2.0} > G'_{1.5} > G'_{1.0} > G'_{0.5}$ in the case of stored peanut butter samples; where G'_z represents the storage modulus for peanut butter sample for stabilizer level z. The three tests were also able to trace its degradation under accelerated storage condition at 35 °C. The 2.0% stabilized samples showed the least deterioration in sample structure. Therefore, the higher the stabilizer level, the more resistant was the network structure to temperature changes. For oscillatory stress sweep conditions stabilizer levels of only 2.0% were able to exhibit LVR range for fresh samples. For stored samples, 0.0, 1.5 and 2.0% stabilizer levels exhibited the LVR. In creep tests, the viscoelastic behavior of stabilized peanut butter was expressed by the presence of three retardation elastic compliances for samples containing 0.5 to 2.0% stabilizer levels. The elastic shear modulus G_o (= $1/J_o$) was found to rise with increase in stabilizer levels

which confirmed the formation of stronger undisturbed network structure due to the high concentration of crystals.

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Table5. 1: LVR (Pa) for peanut butter samples determined by oscillatory stress sweeps

Tempering or storage time (d)	Stabilizer level (%)				
	0.0	**0.5**	**1.0**	**1.5**	**2.0**
Fresh samples at 26 °C					
0	*	*	*	*	1.08
1	*	*	*	*	1.86
2	*	*	*	*	2.87
Fresh samples at 35 °C					
0	*	*	*	*	5.10
1	*	*	*	*	2.95
2	*	*	*	*	3.98
Stored samples					
15	*	*	*	1.99	7.74
30	*	*	*	2.03	8.41
45	*	*	*	1.02	6.39
60	12.06	*	*	1.0	5.90
75	21.31	*	*	1.02	5.54
90	13.90	*	*	0.42	2.72

* could not be estimated

Figure legend

Figure 5. 1: Schematic representation of creep curve for a viscoelastic material

Figure 5. 2: Response of peanut butter samples to different stabilizer levels in time sweep tests, at 26 °C

Figure 5. 3: Effect of stabilizer levels and tempering time on oscillatory stress and oscillatory strain, storage modulus (G′), loss modulus (G"), complex modulus (G*), storage viscosity (η"), loss viscosity (η'), complex viscosity (η*), phase lag delta (δ), and loss tangent (tanδ) in fresh samples, at 26 °C

Figure 5. 4: Effect of stabilizer levels and three months storage at 35 °C on oscillatory stress and oscillatory strain, storage modulus (G′), loss modulus (G"), complex modulus (G*), storage viscosity (η"), loss viscosity (η'), complex viscosity (η*), phase lag delta (δ), and loss tangent (tanδ) in stored samples

Figure 5. 5: Effect of stabilizer levels and tempering time on oscillatory stress and oscillatory strain, storage modulus (G′), loss modulus (G"), complex modulus (G*), storage viscosity (η"), loss viscosity (η'), complex viscosity (η*), phase lag delta (δ), and loss tangent (tanδ) in fresh samples, at 35 °C

Figure 5. 6: LVR (Pa) for fresh peanut butter sample with 2.0% stabilizer level, at 26 °C in oscillatory stress and sweep tests

Figure 5. 7: Effect of stabilizer levels and tempering time on instantaneous compliance (J_o), first retardation compliance (J_1), second retardation compliance (J_2), third retardation compliance (J_3), and Newtonian viscosity (η_N) in fresh samples, at 26 °C

Figure 5. 8: Effect of 0.0% stabilizer level and three months storage at 35 °C on instantaneous compliance (J_o), first retardation compliance (J_1), second retardation compliance (J_2), and third retardation compliance (J_3) in stored samples

Figure 5. 9: Effect of 0.5% stabilizer level and three months storage at 35 °C on instantaneous compliance (J_o), first retardation compliance (J_1), second retardation compliance (J_2), third retardation compliance (J_3) in stored samples

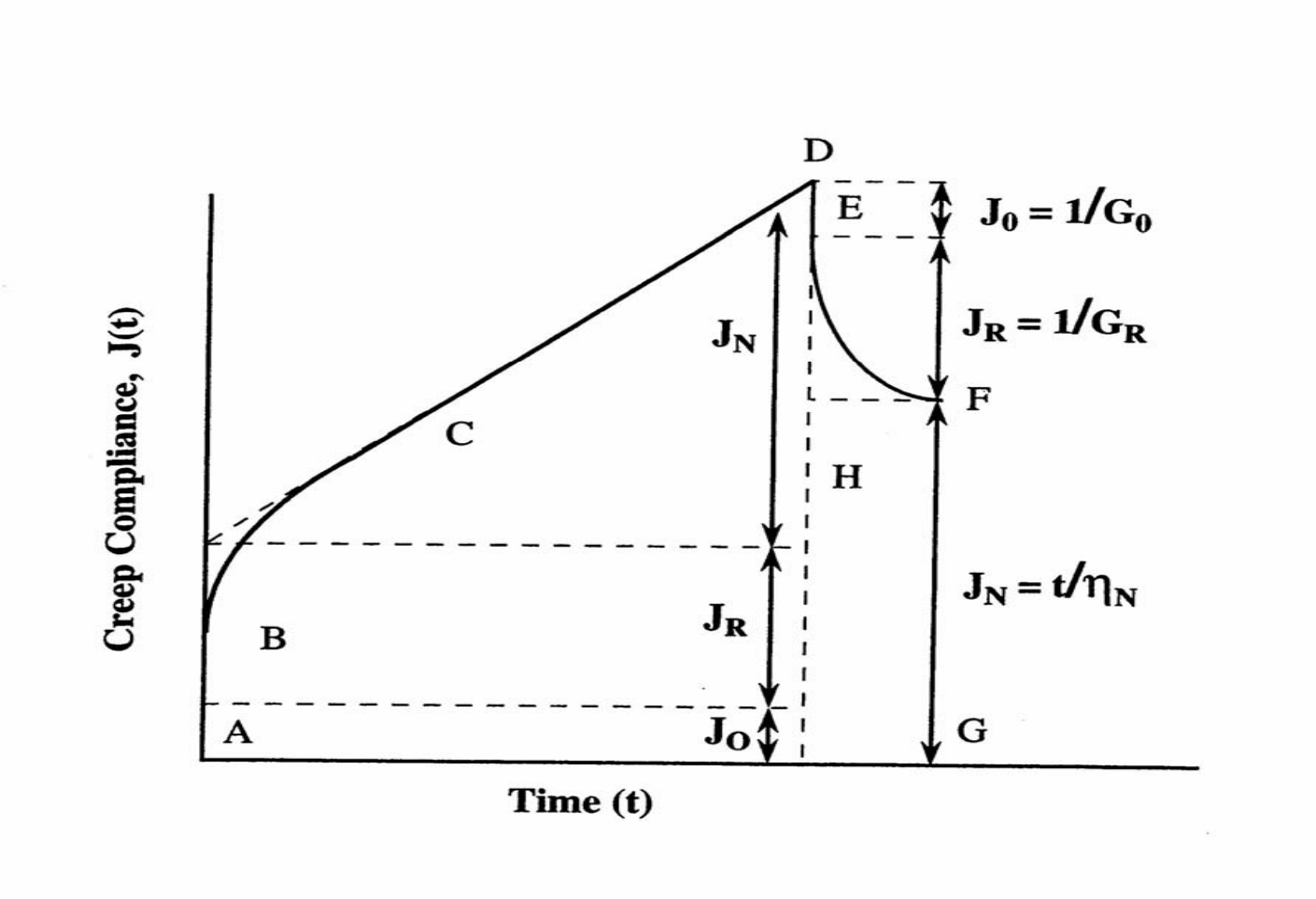

Figure 5. 1 (Rao 1999)

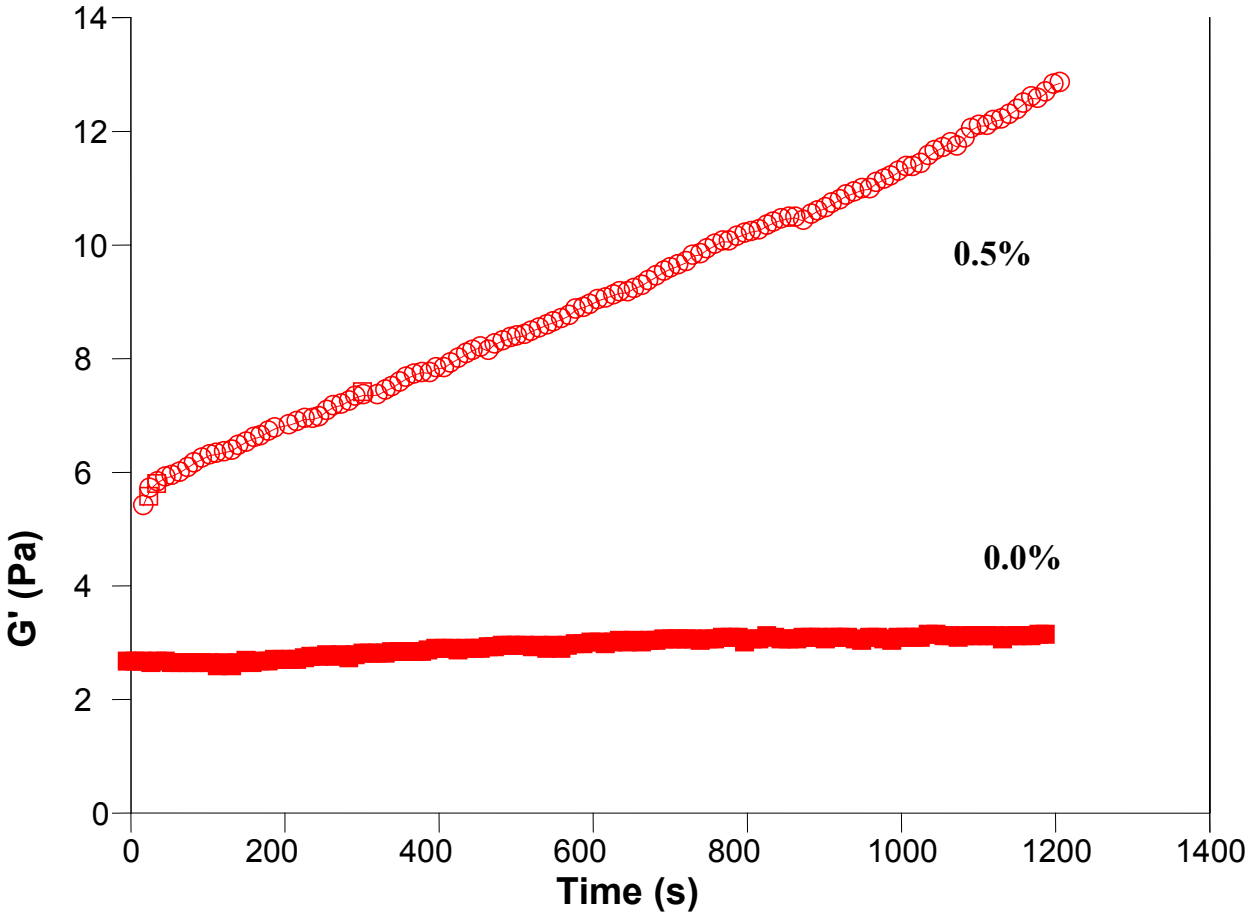

Figure 5. 2A: 0.0 and 0.5% stabilizer levels

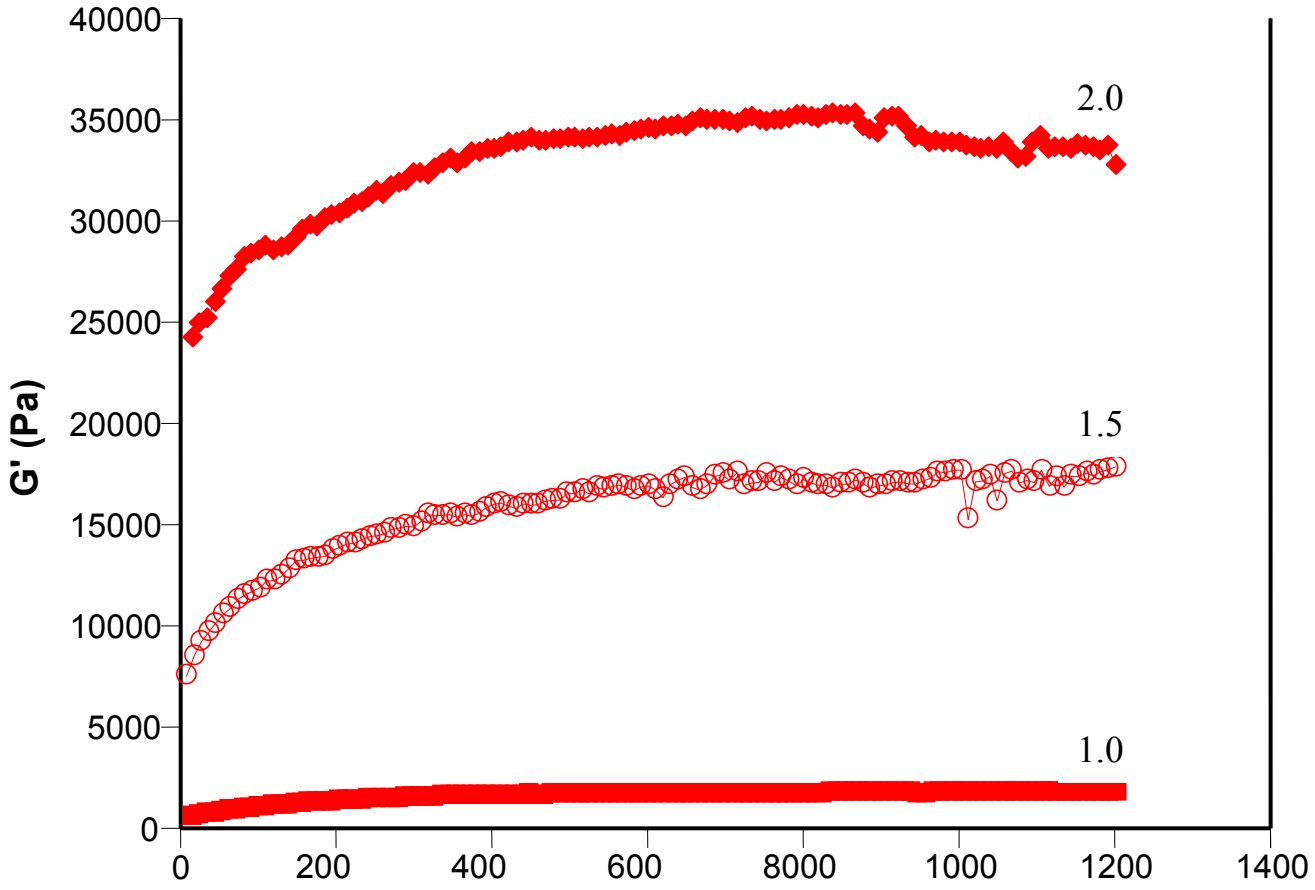

Figure 5. 2B: 1.0, 1.5 and 2.0% stabilizer levels

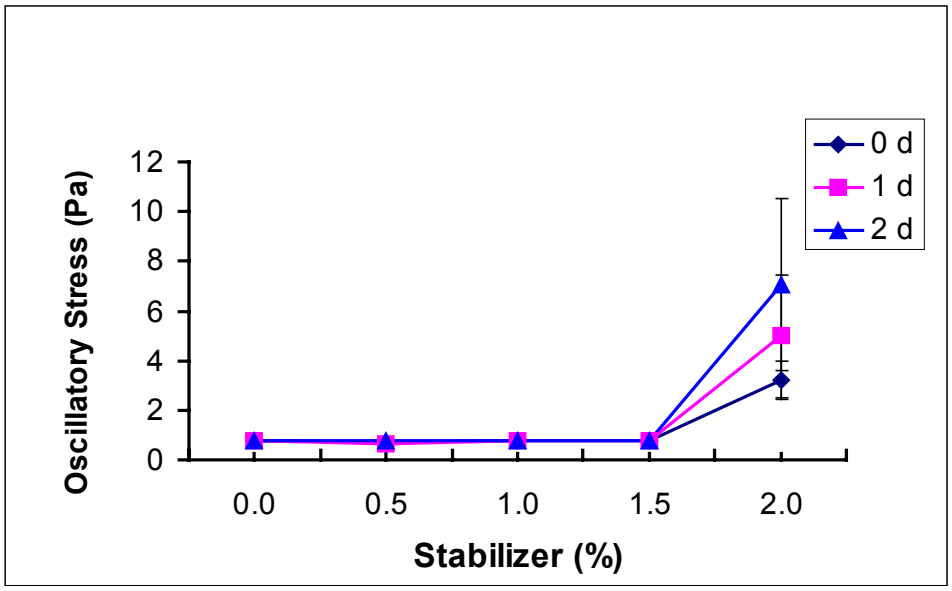

Figure 5.3A: Oscillatory stress (Pa)

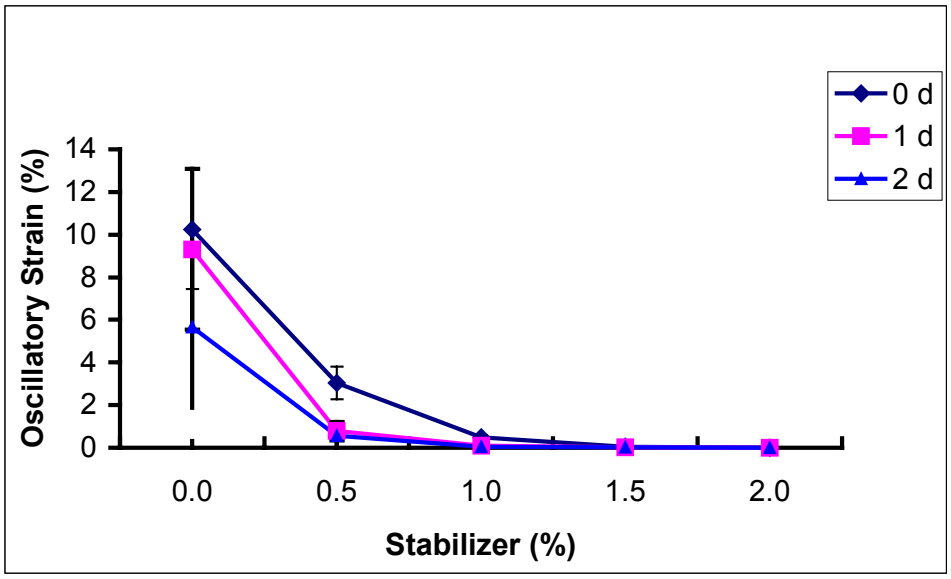

Figure 5.3B: Oscillatory strain (%)

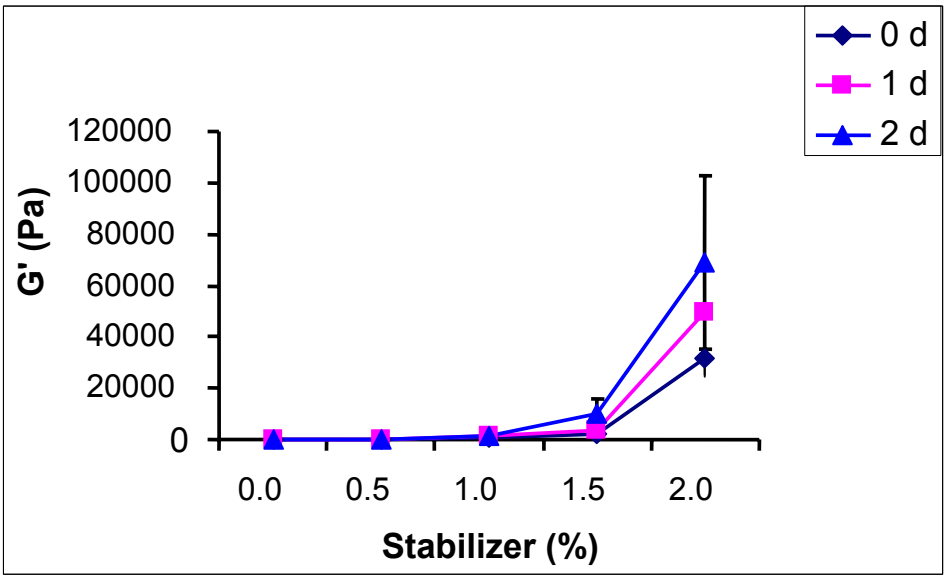

Figure 5.3C: Storage modulus (G', Pa)

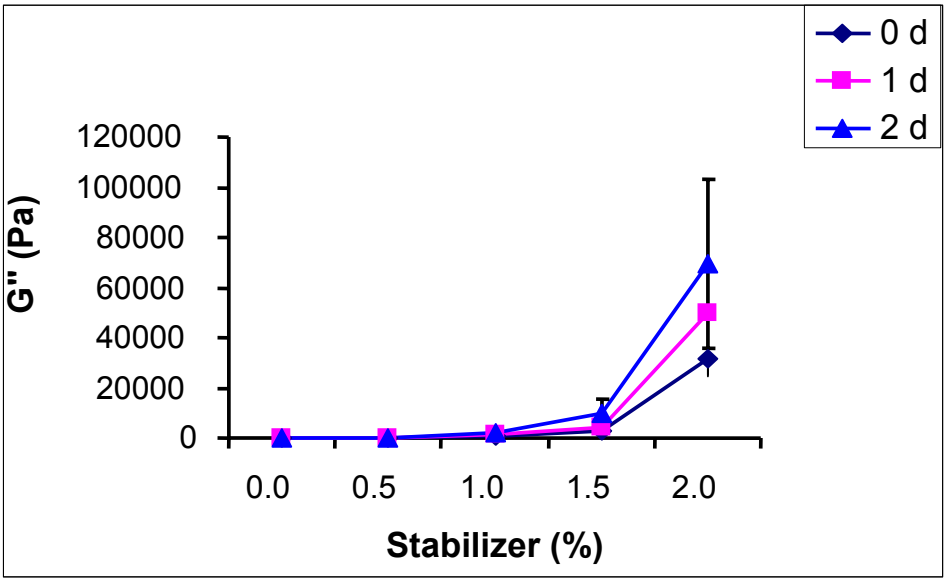

Figure 5.3D: Loss modulus (G'', Pa)

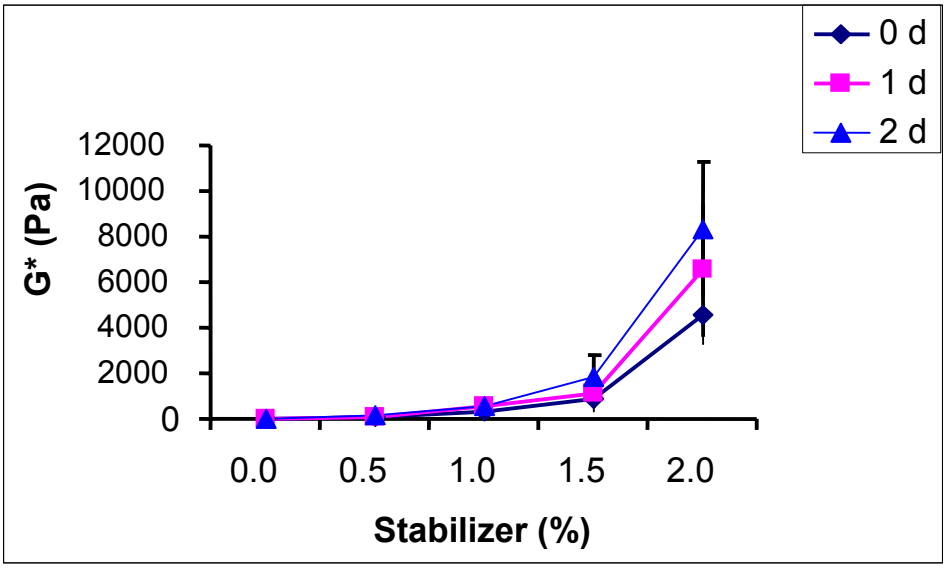

Figure 5.3E: Complex modulus (G*, Pa)

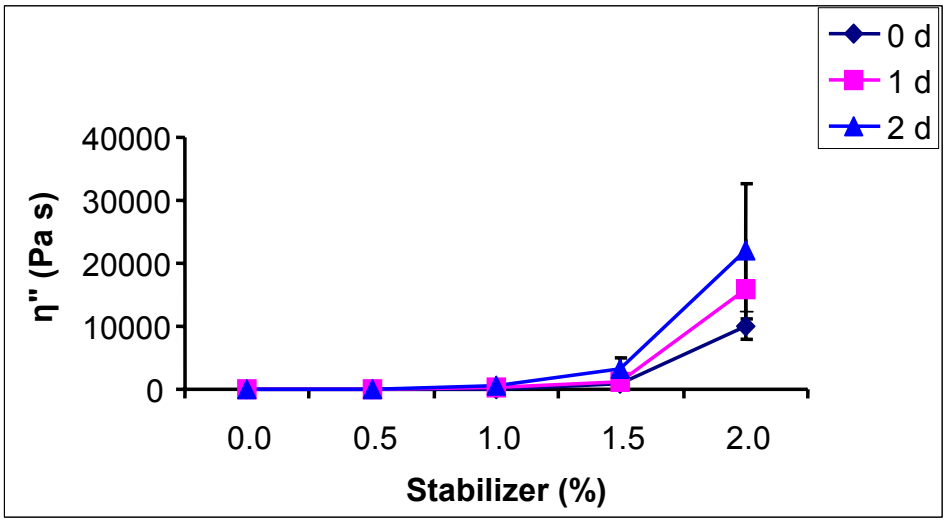

Figure 5.3F: Storage viscosity (η′′, Pa)

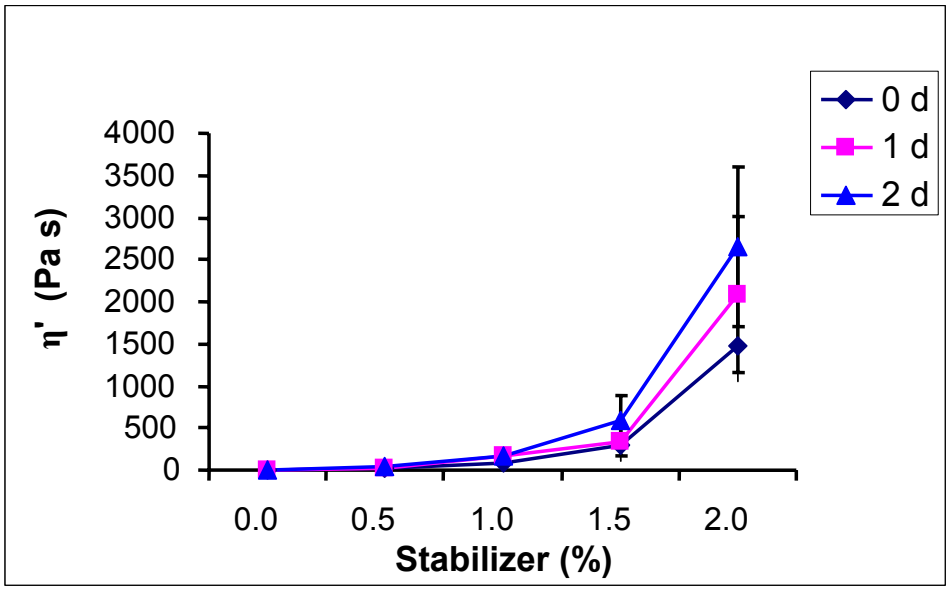

Figure 5. 3G: Loss viscosity (η', Pa s)

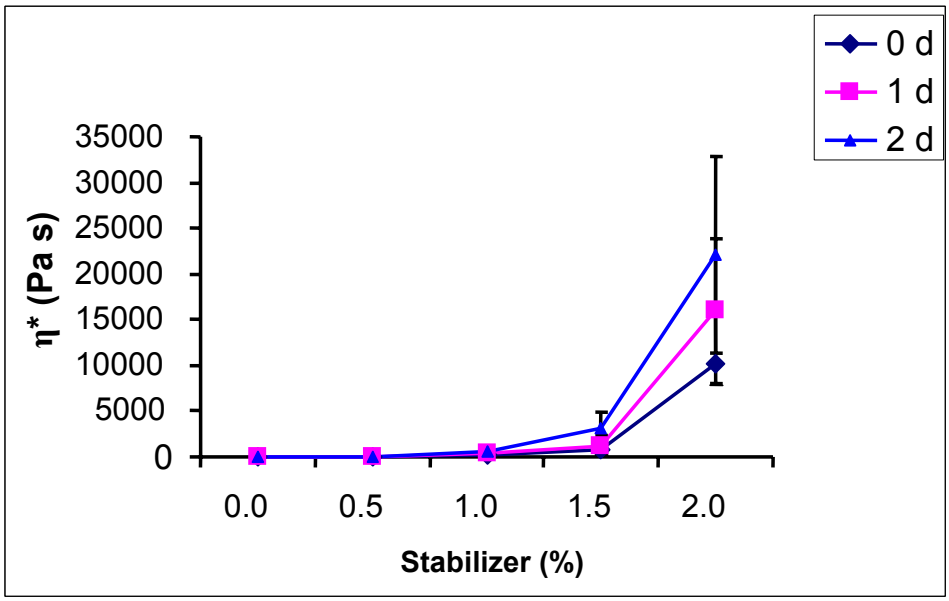

Figure 5.3H: Complex viscosity (η*, Pa s)

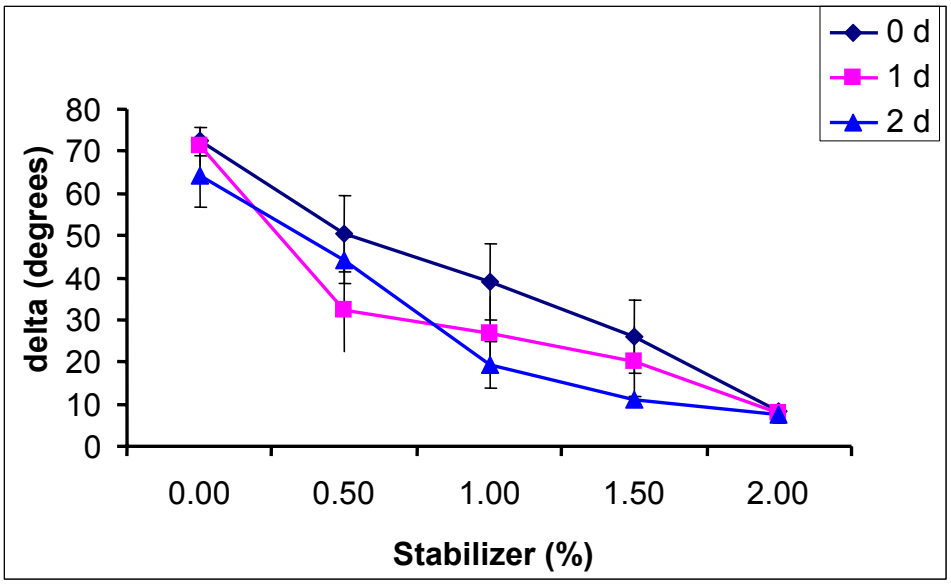

Figure 5.3I: Delta (δ, degrees)

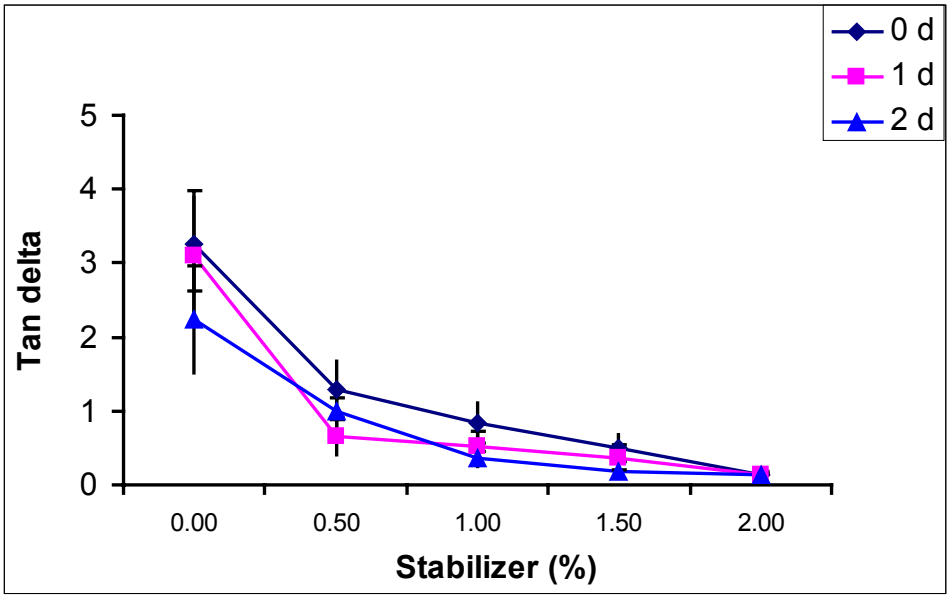

Figure 5. 3J: Tan delta (tan δ)

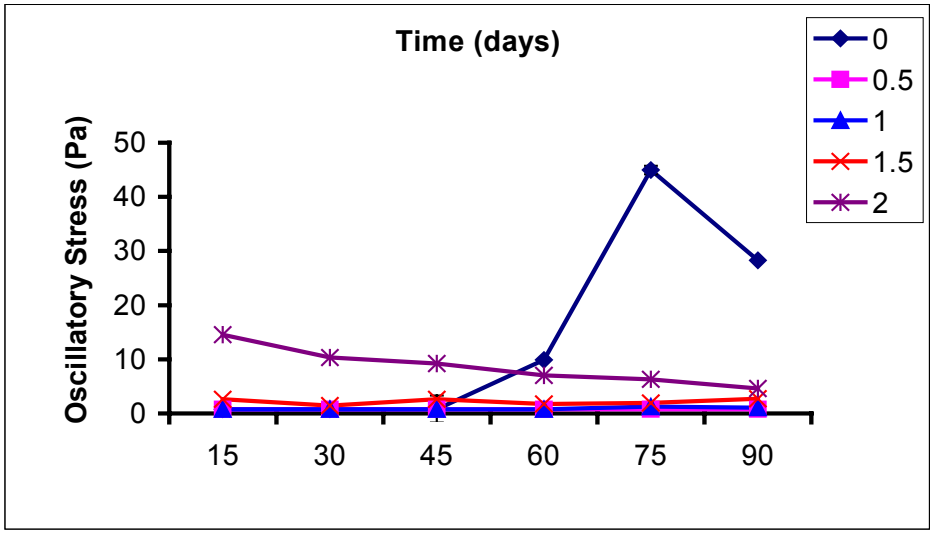

Figure 5. 4A: Oscillatory stress (Pa)

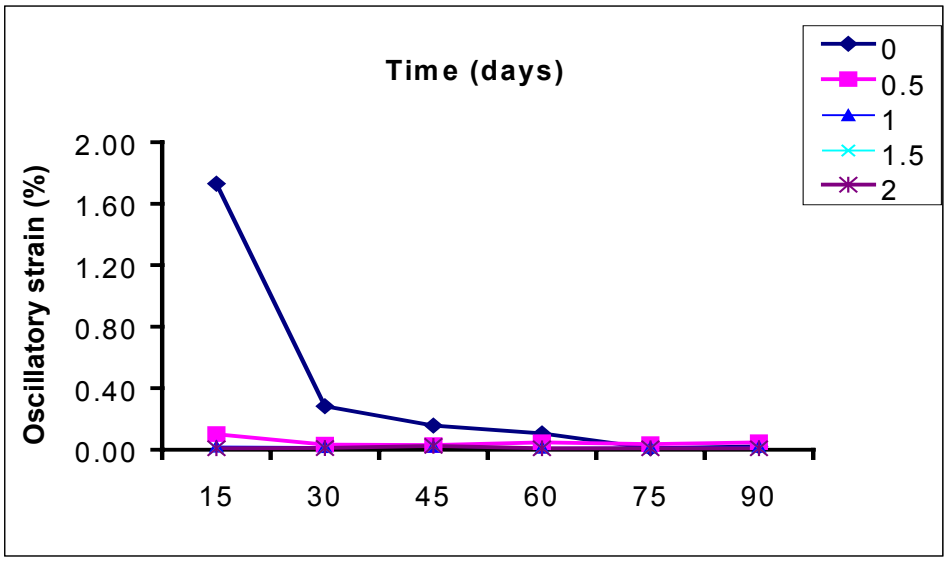

Figure 5.4B: Oscillatory strain (%)

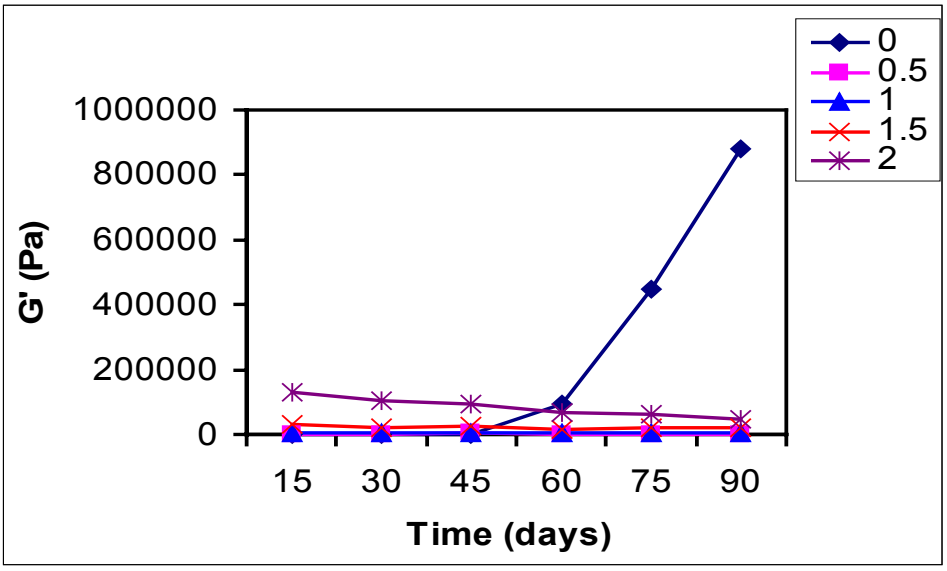

Figure 5.4C: Storage modulus (G', Pa)

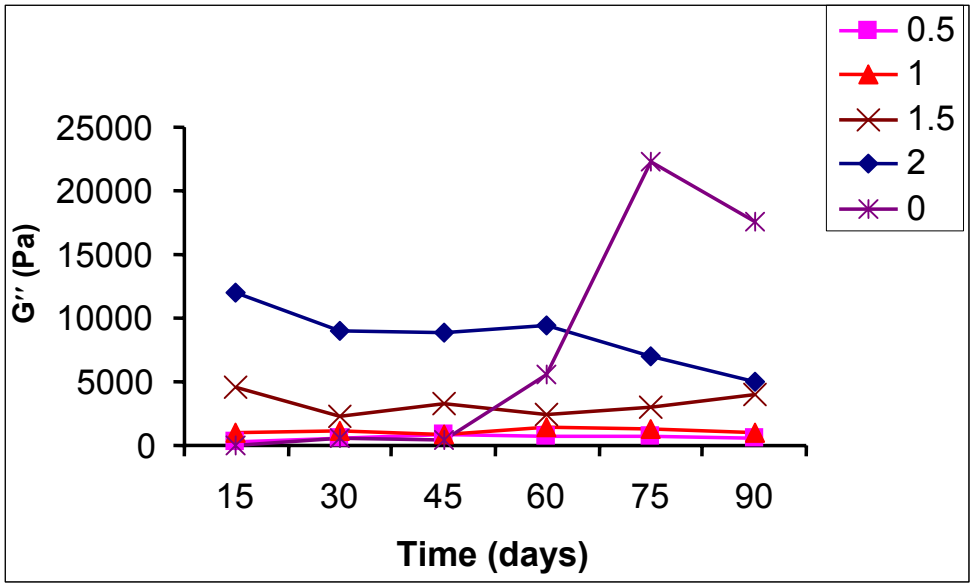

Figure 5.4D: Loss modulus (G'', Pa)

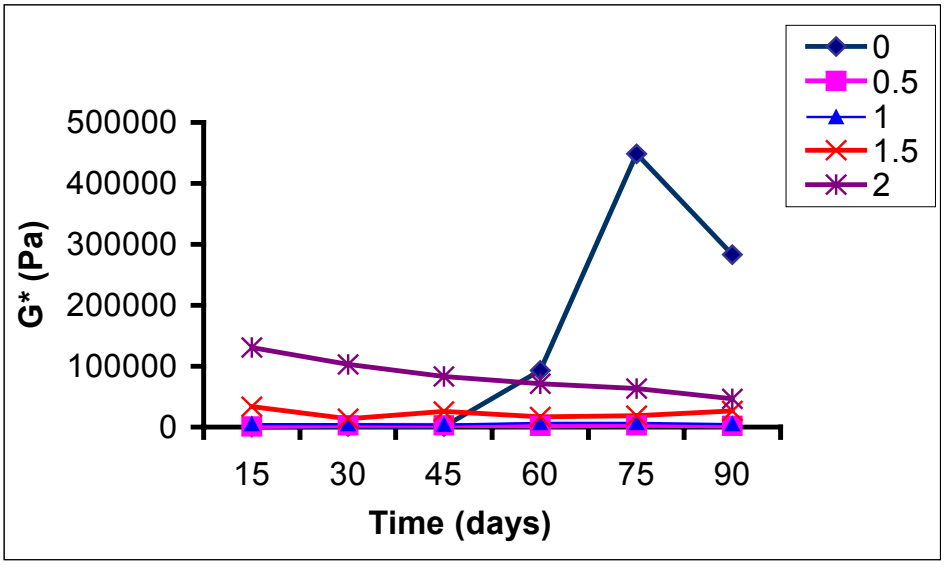

Figure 5.4E: Complex modulus (G*, Pa)

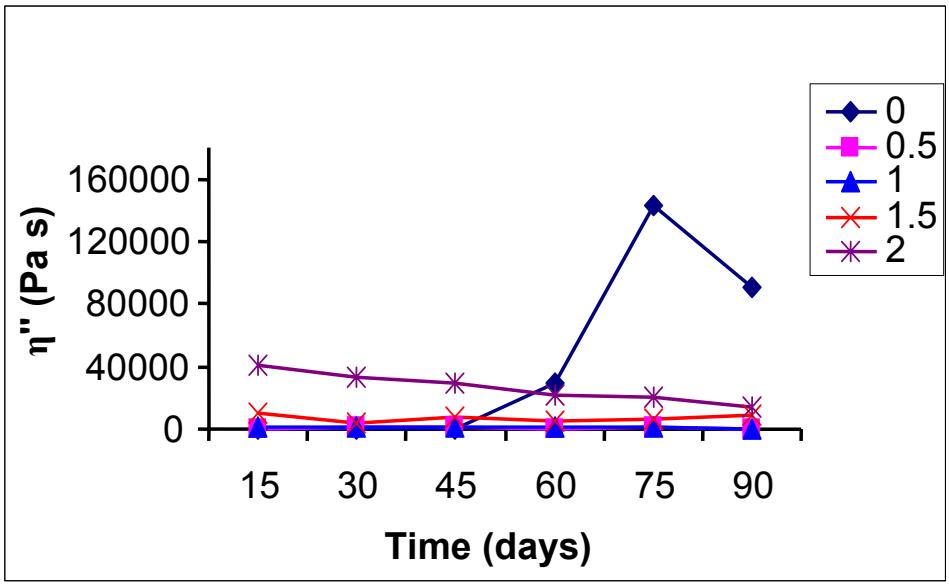

Figure 5.4F: Storage viscosity (η'', Pa s)

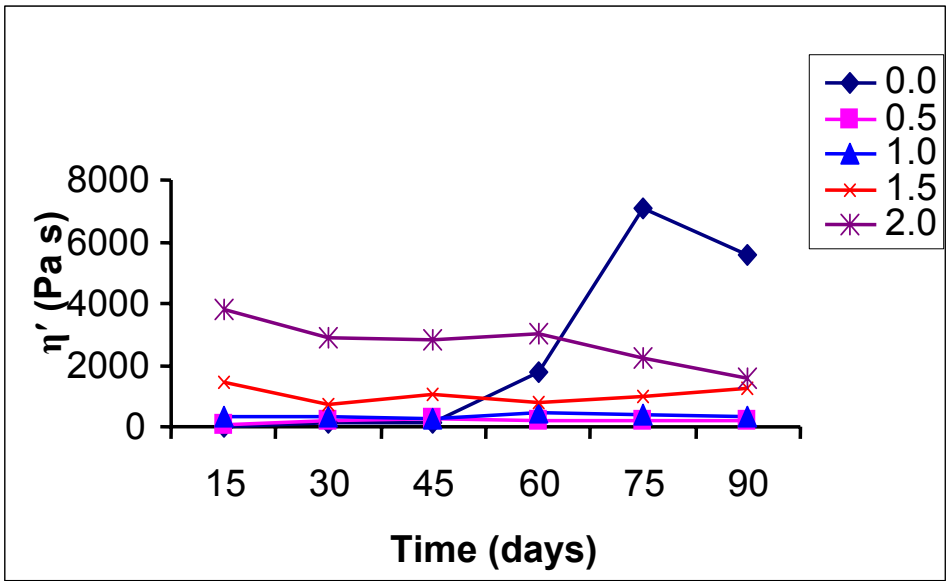

Figure 5.4G: Loss viscosity (η', Pa s)

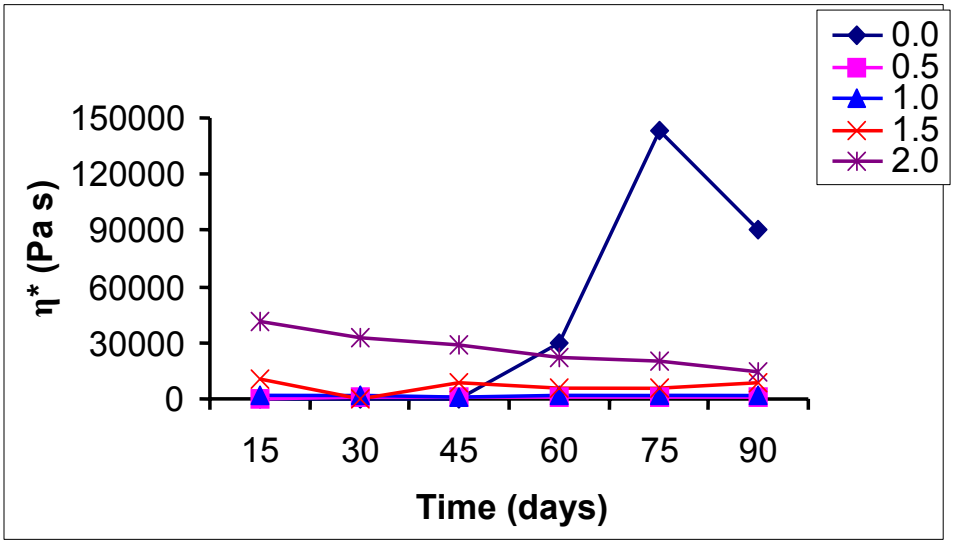

Figure 5. 4H: Complex viscosity (η*, Pa s)

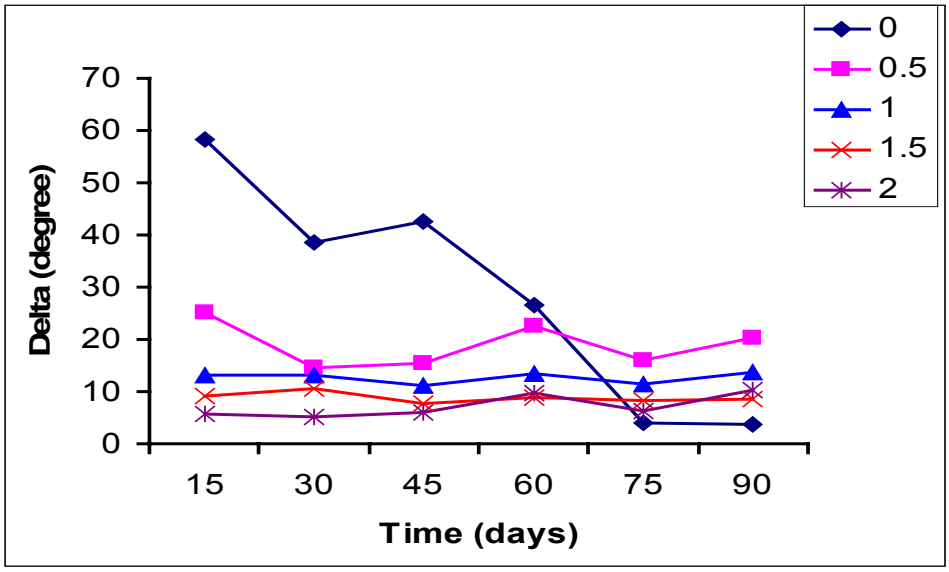

Figure 5.4I: Delta (δ)

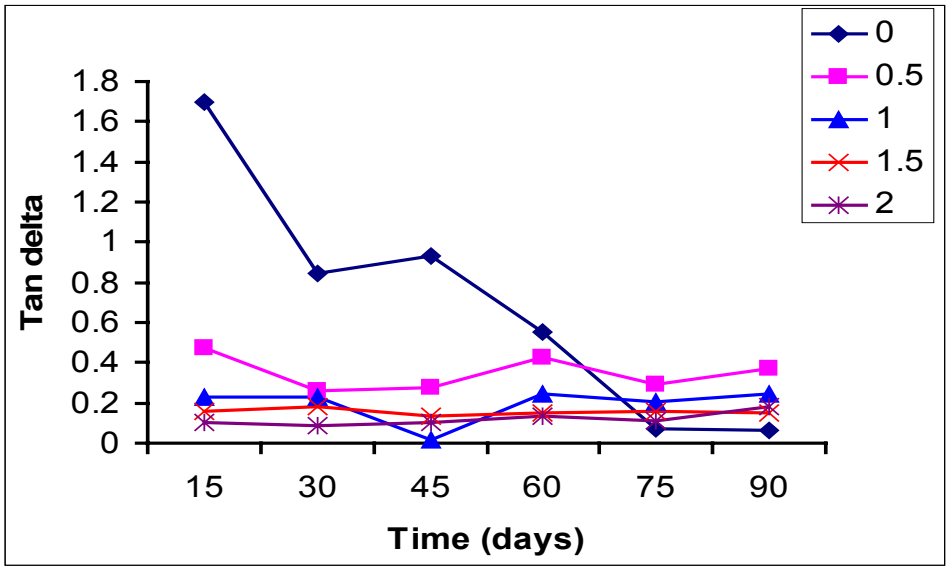

Figure 5.4J: Tan delta (tan δ)

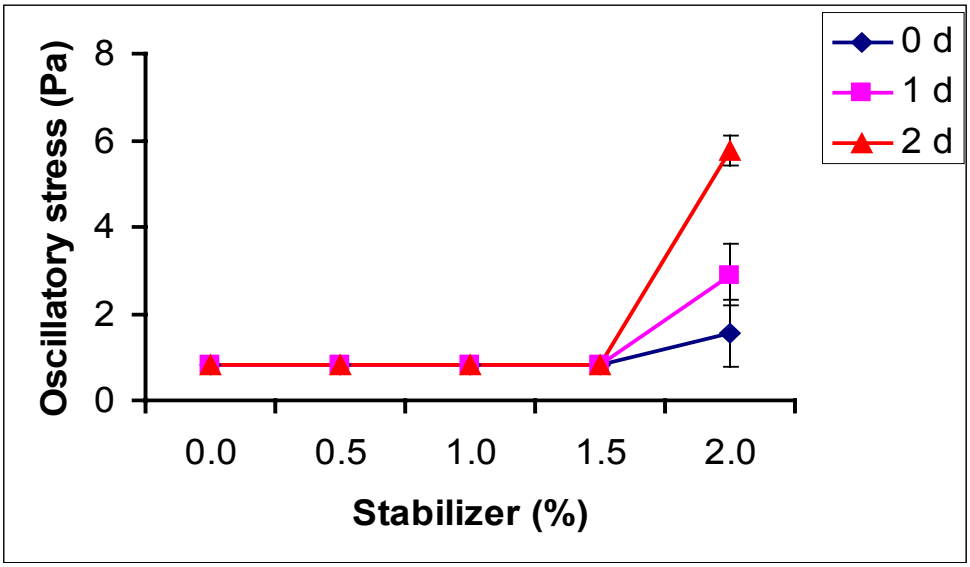

Figure 5.5A: Oscillatory stress (Pa)

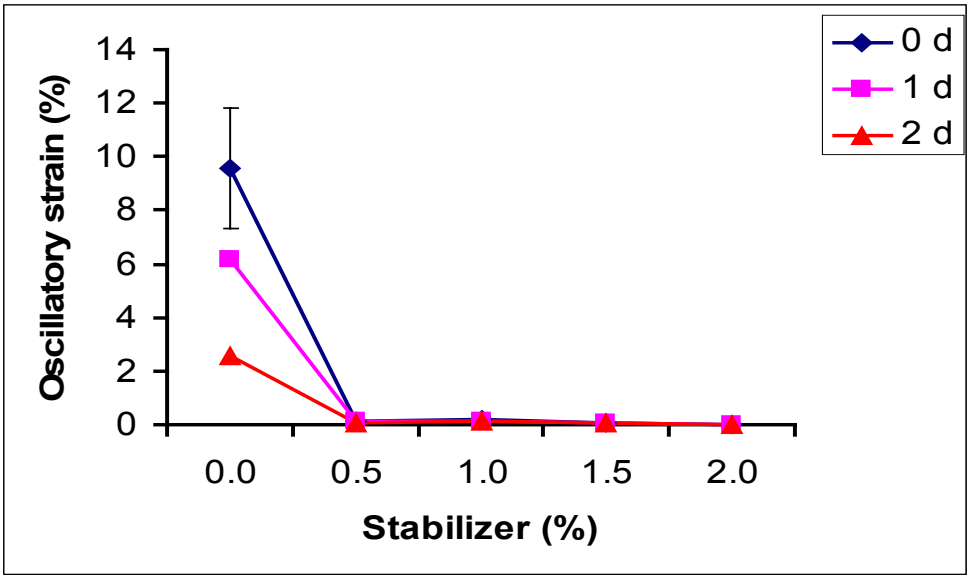

Figure 5.5B: Oscillatory strain (%)

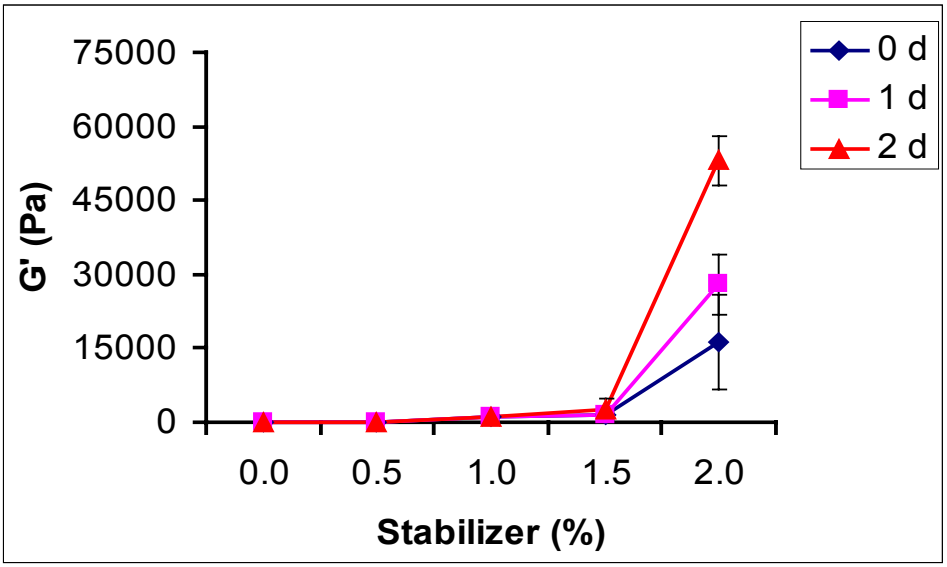

Figure 5.5C: Storage modulus (G′, Pa)

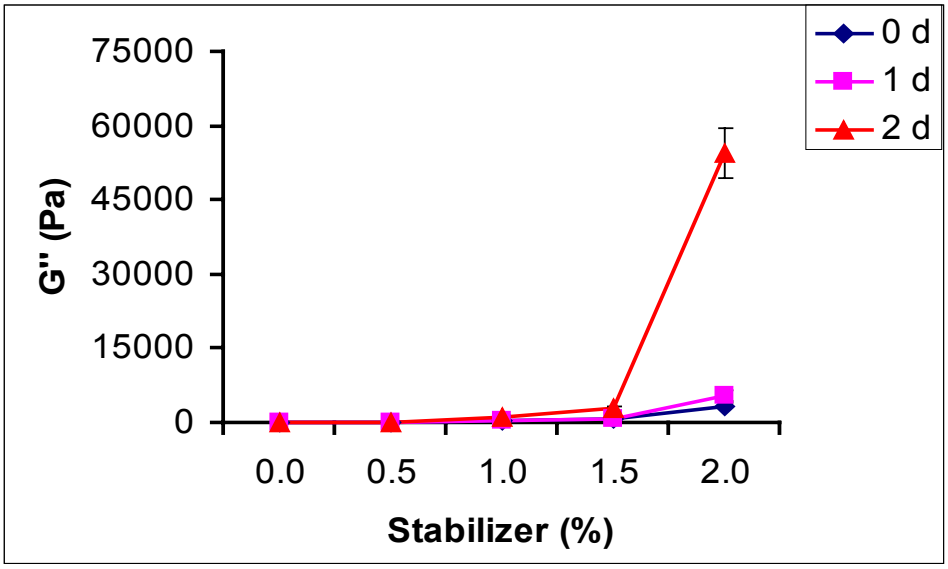

Figure 5.5D: Loss modulus (G″, Pa)

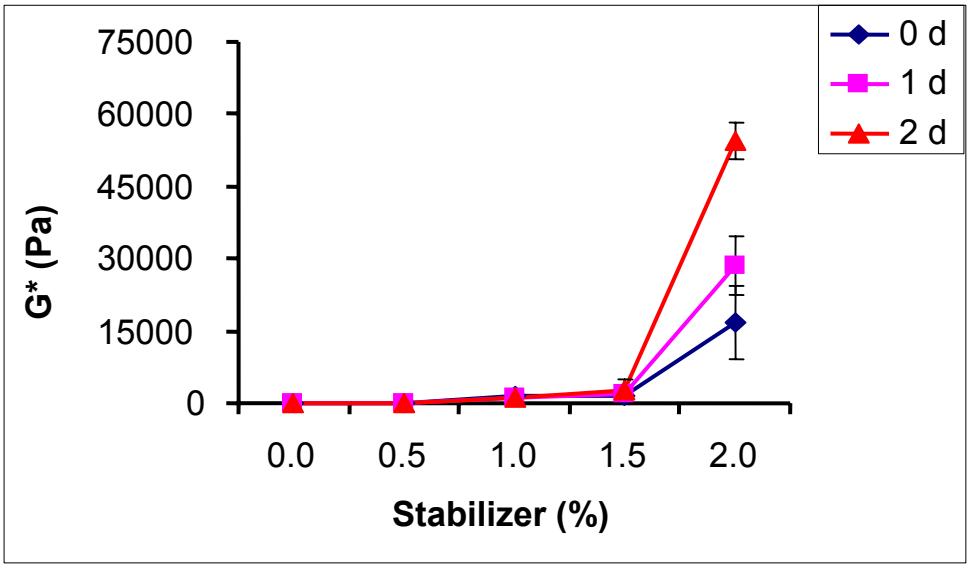

Figure 5.5E: Complex modulus (G*, Pa)

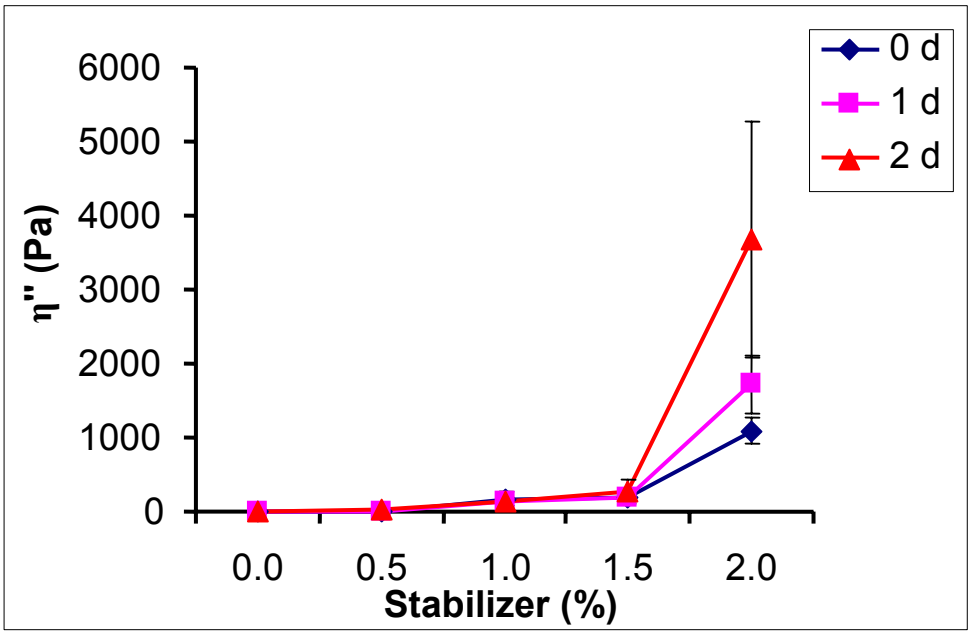

Figure 5. 5F: Storage viscosity (η′′, Pa)

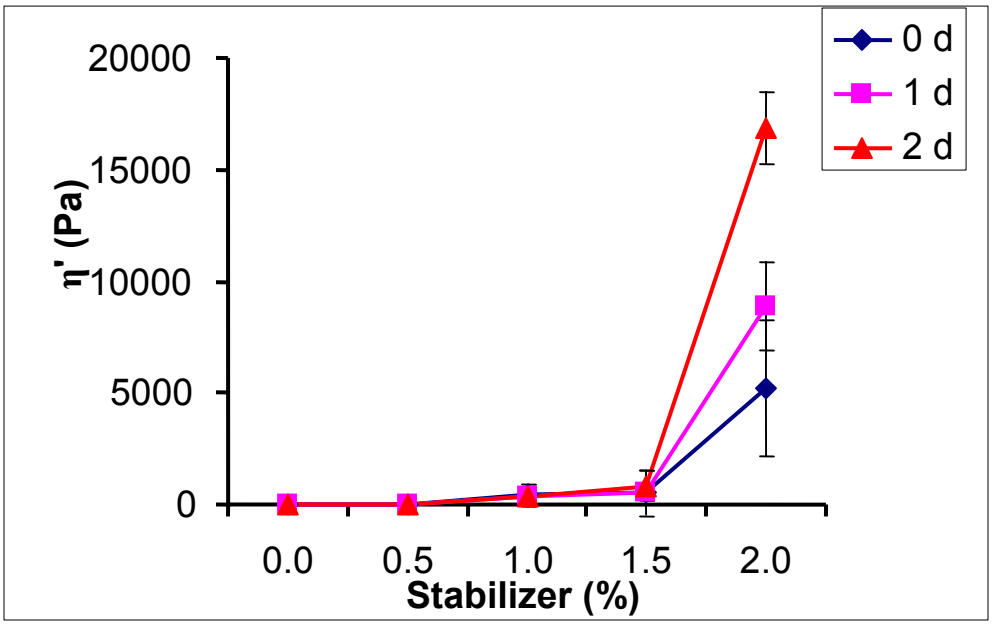

Figure 5.5G: Loss viscosity (η′, Pa)

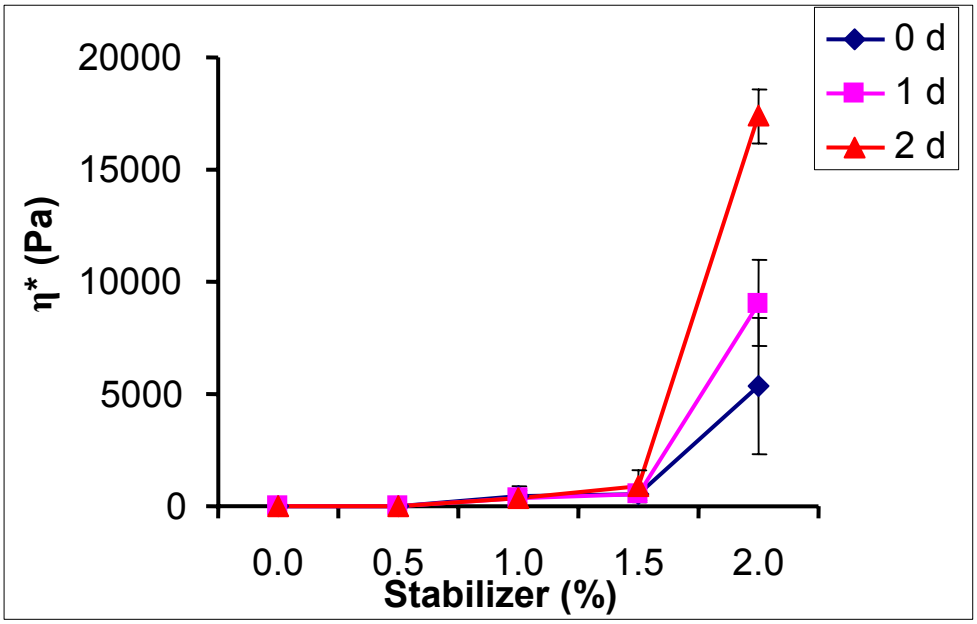

Figure 5.5H: Complex viscosity (η*, Pa)

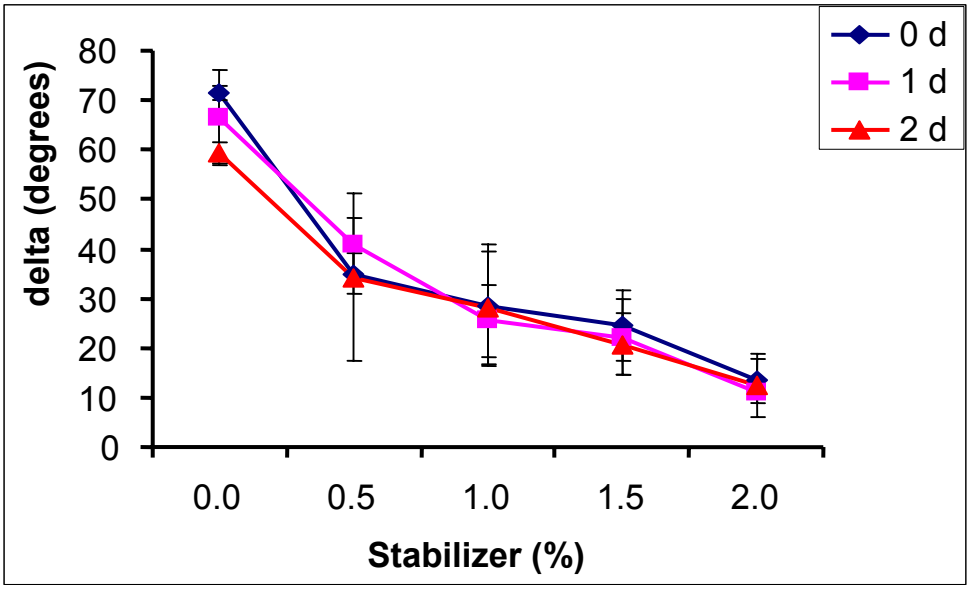

Figure 5.5I: Delta (δ, degrees)

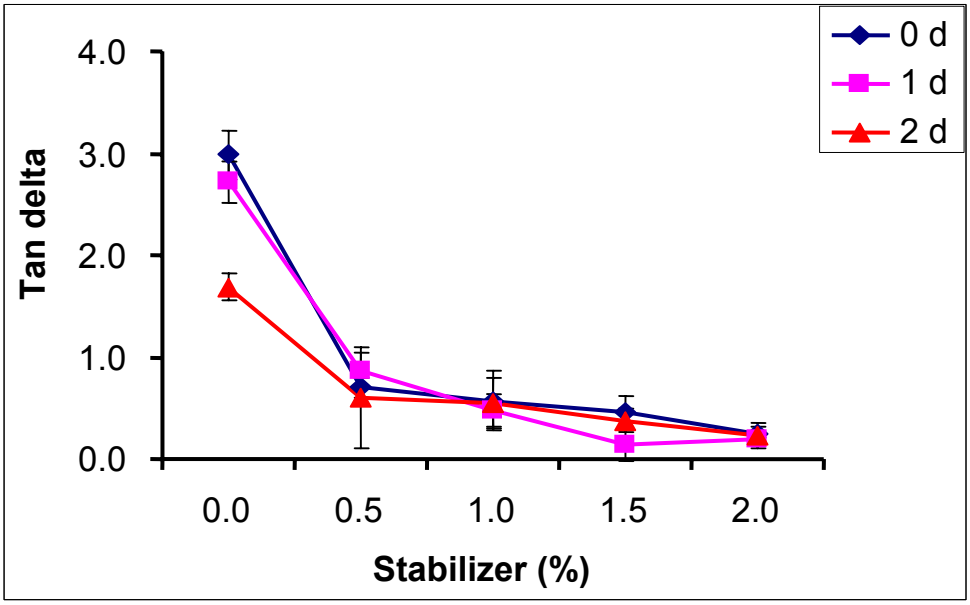

Figure 5. 5J: Tan delta (tan δ)

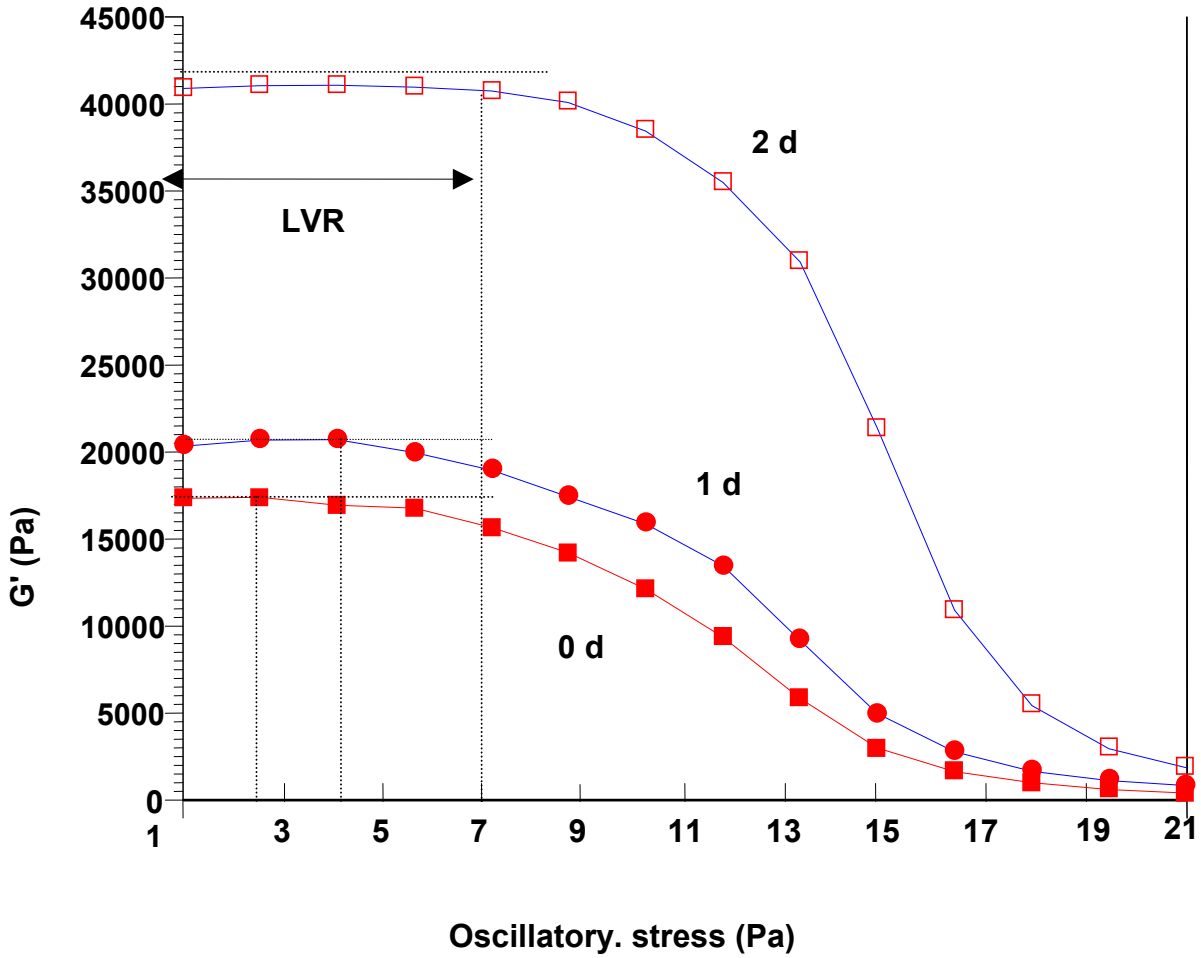
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
G' (Pa)
LVR
2 d
1 d
0 d
1
3
5
7
9
11
13
15
17
19
21
Oscillatory. stress (Pa)

Figure 5.6

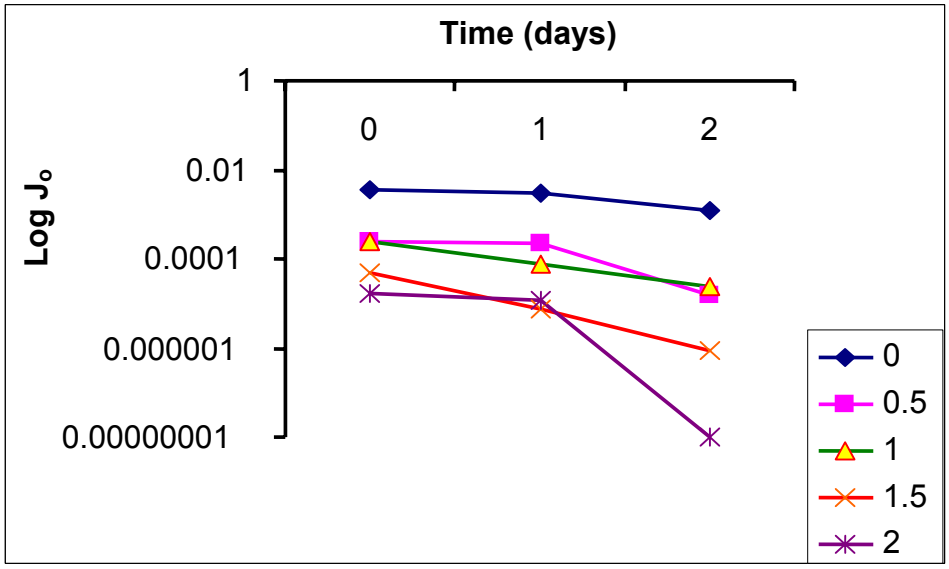

Figure 5.7A: Instantaneous compliances (J_o, m^2/N)

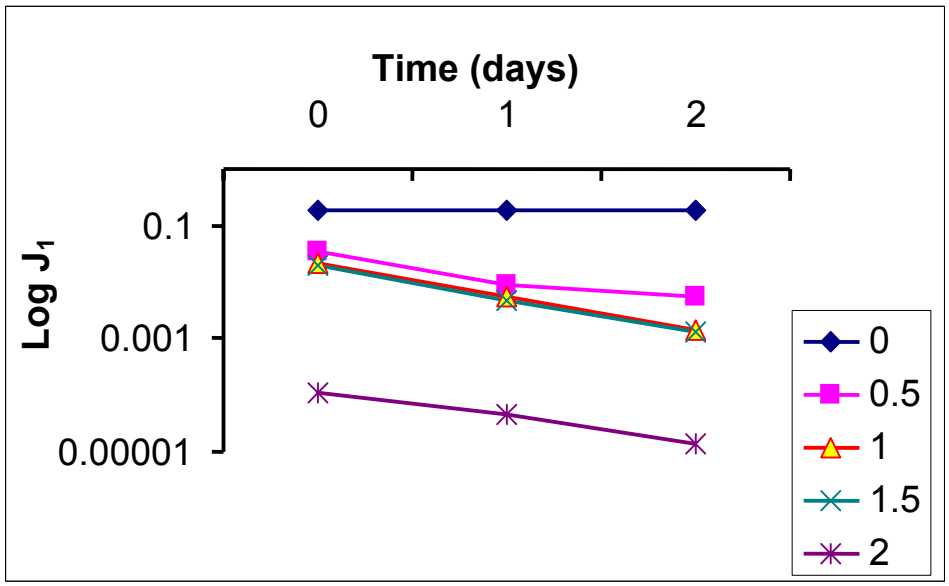

Figure 5.7B: First retardation compliance (J_1, m^2/N)

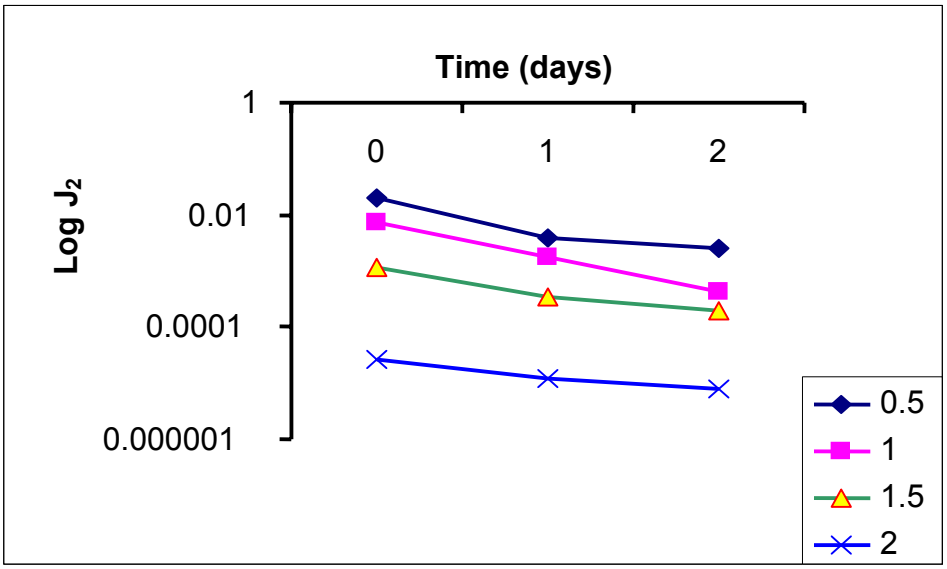

Figure 5.7C: Second retardation compliance (J_2, m^2/N)

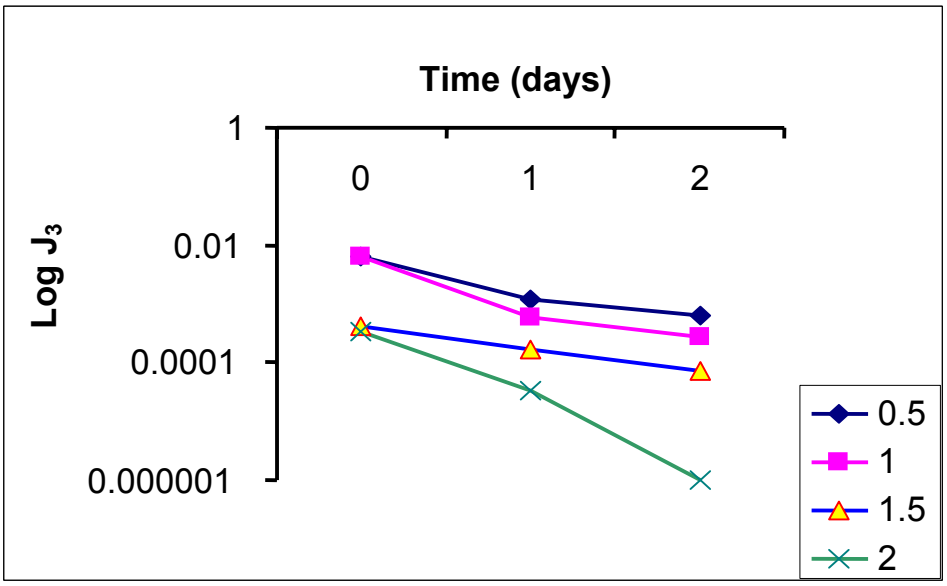

Figure 5.7D: Third retardation compliance (J_2, m^2/N)

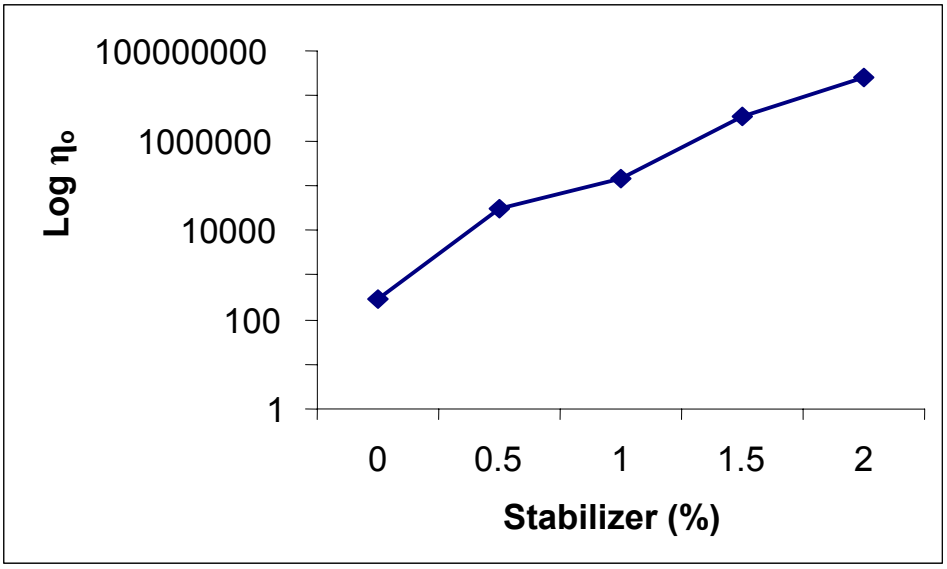

Figure 5.7E: Newtonian viscosity (η_N, Pa s)

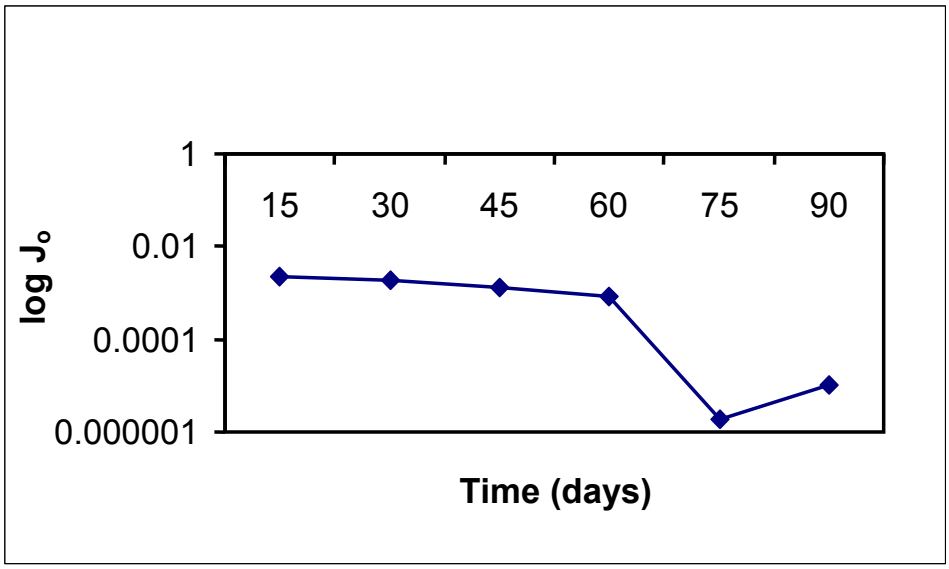

Figure 5.8A: Instantaneous compliance (J_o, m2/N)

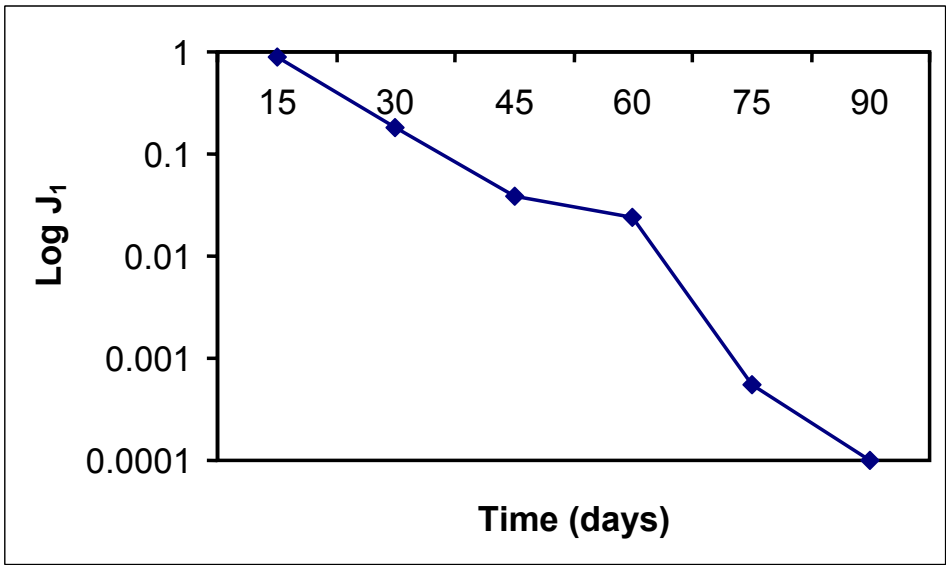

Figure 5.8B: First retardation compliance (J_1, m^2/N)

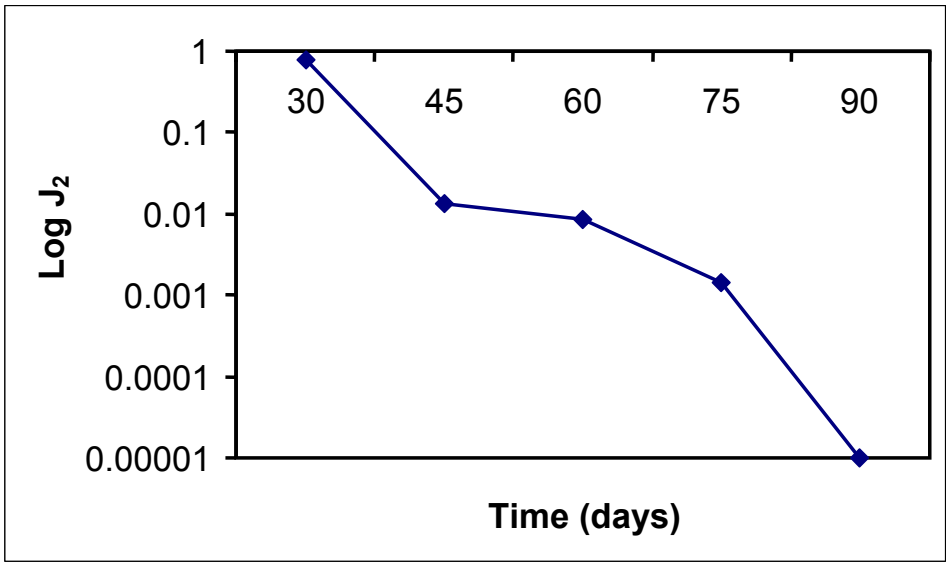

Figure 5.8C: Second retardation compliance (J_2, m^2/N)

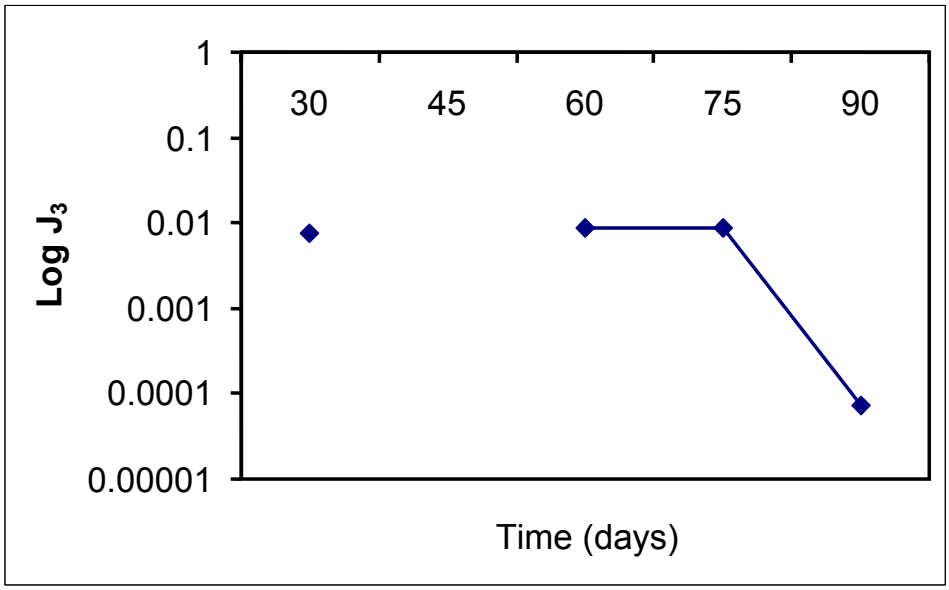

Figure 5.8D: Third retardation compliance (J_3, m^2/N)

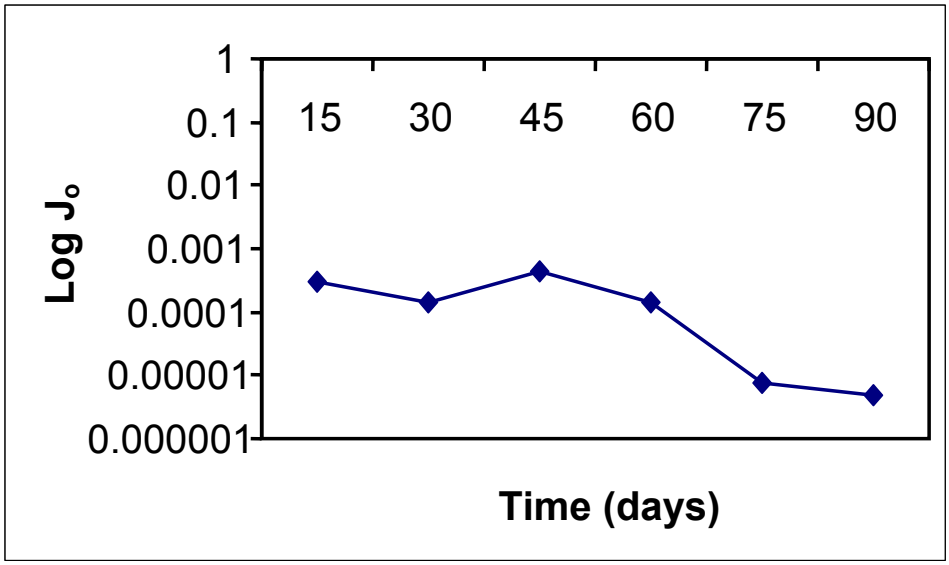

Figure 5.9A: Instantaneous compliance (J_o, m^2/N)

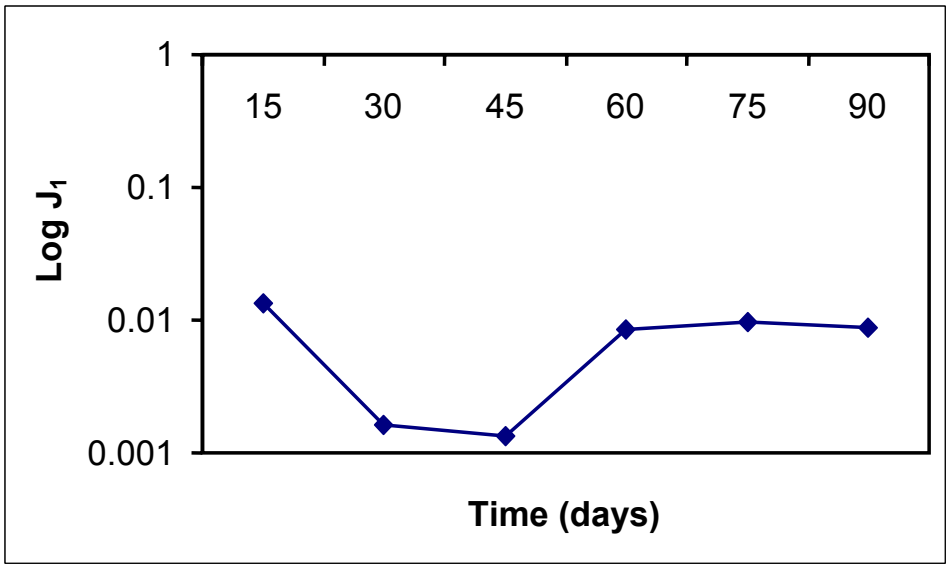

Figure 5.9B: First retardation compliance (J_1, m^2/N)

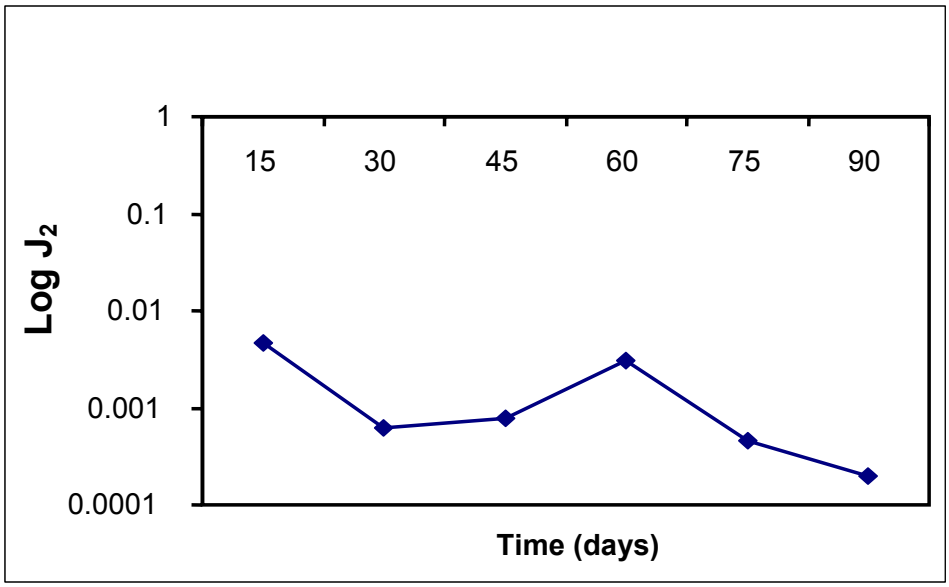

Figure 5.9C: Effect Second retardation compliance (J_2, m^2/N)

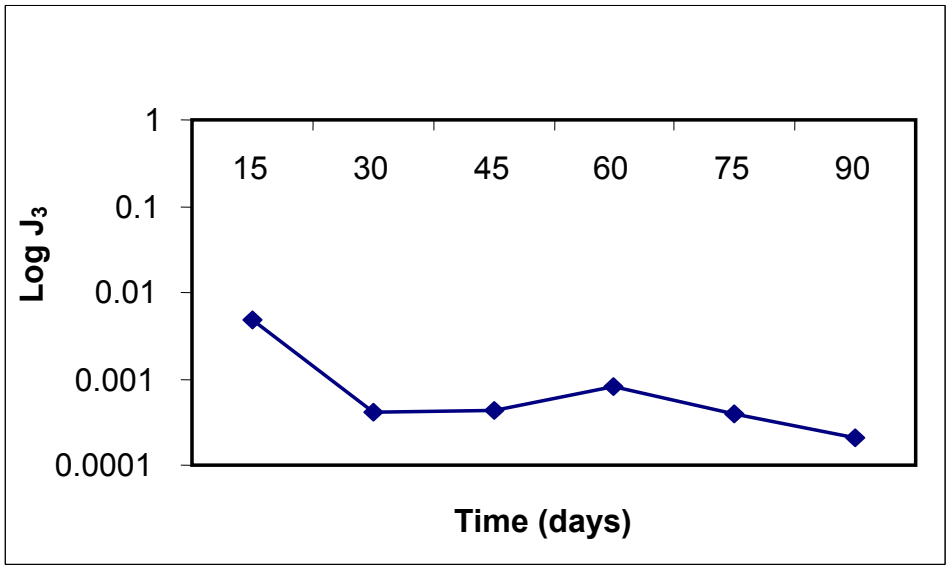

Figure 5.9D: Third retardation compliance (J_3, m^2/N)

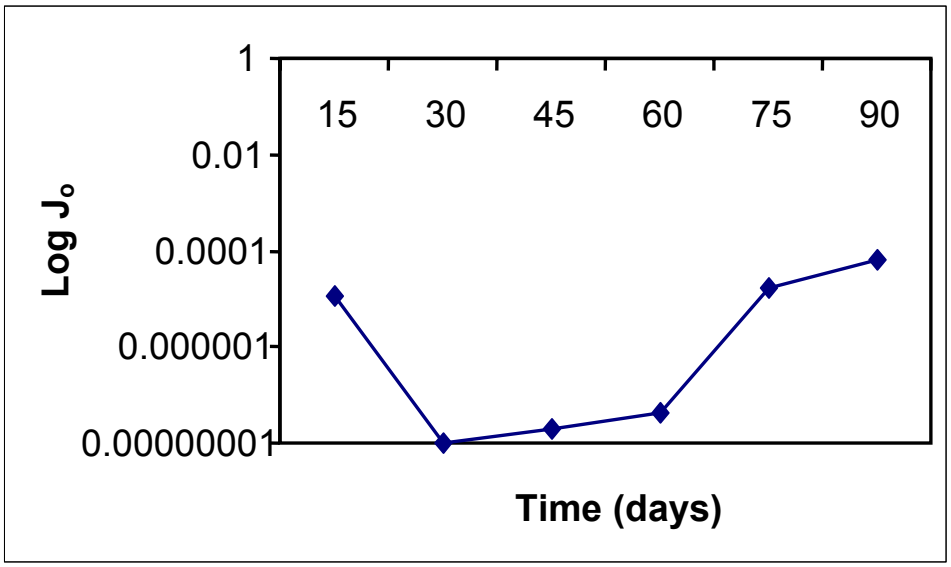

Figure 5.10A: Instantaneous compliance (J_o, m^2/N)

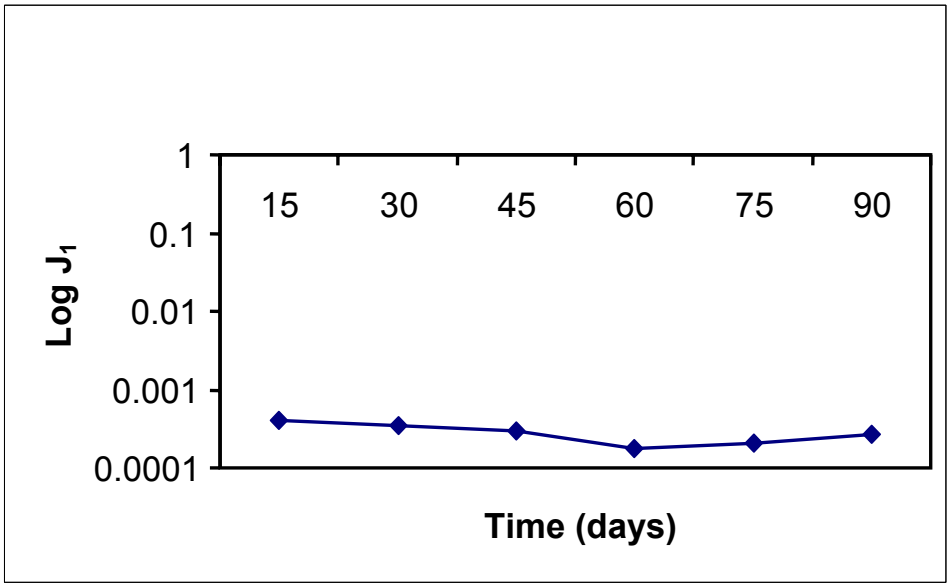

Figure 5.10B: First retardation compliance (J_1, m^2/N)

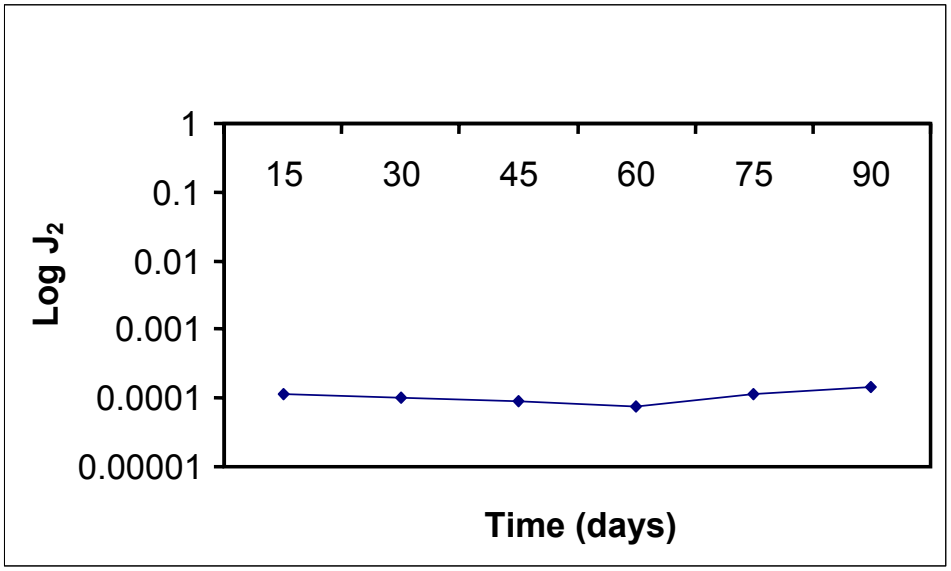

Figure 5.10C: Second retardation compliance (J_2, m^2/N)

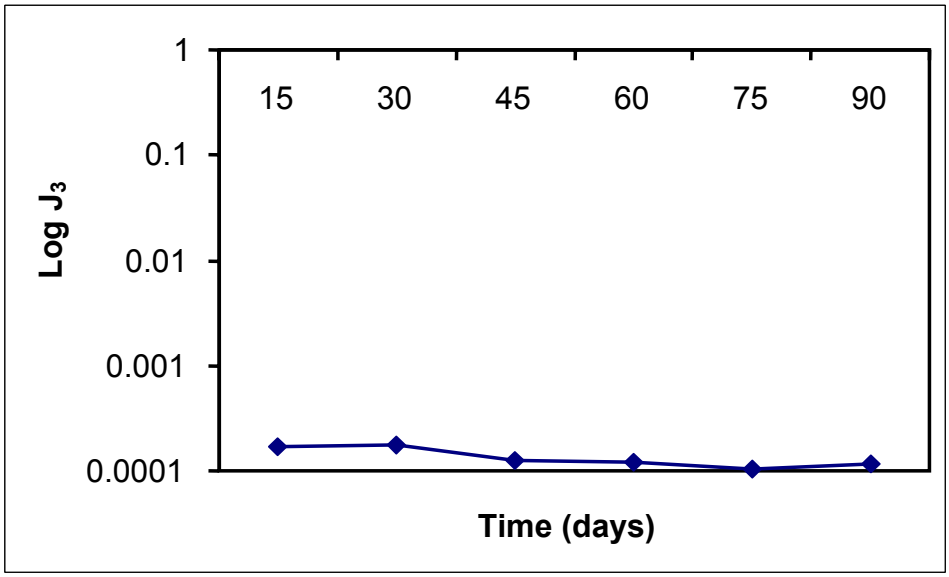

Figure 5.10D: Third retardation compliance (J_3, m^2/N)

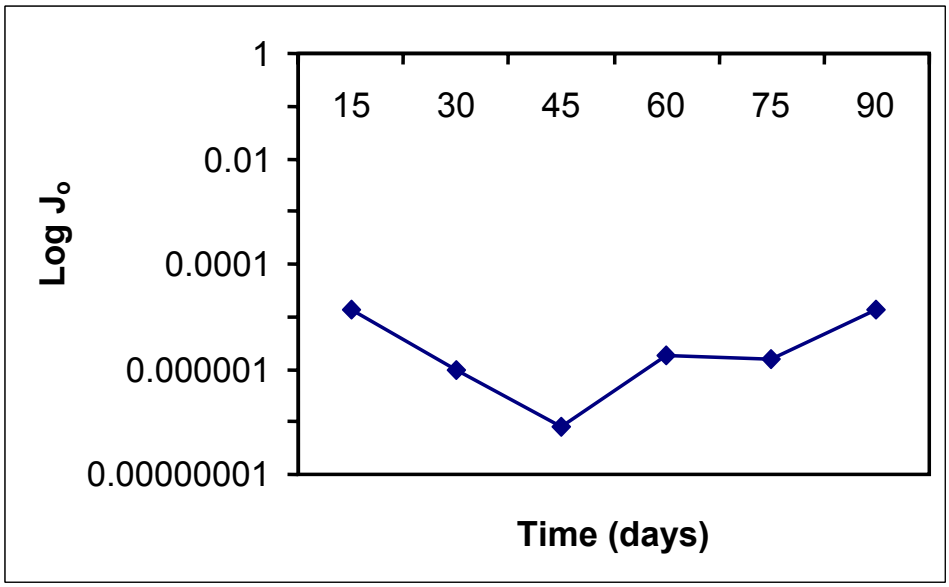

Figure 5.11A: Instantaneous compliance (J_o, m^2/N)

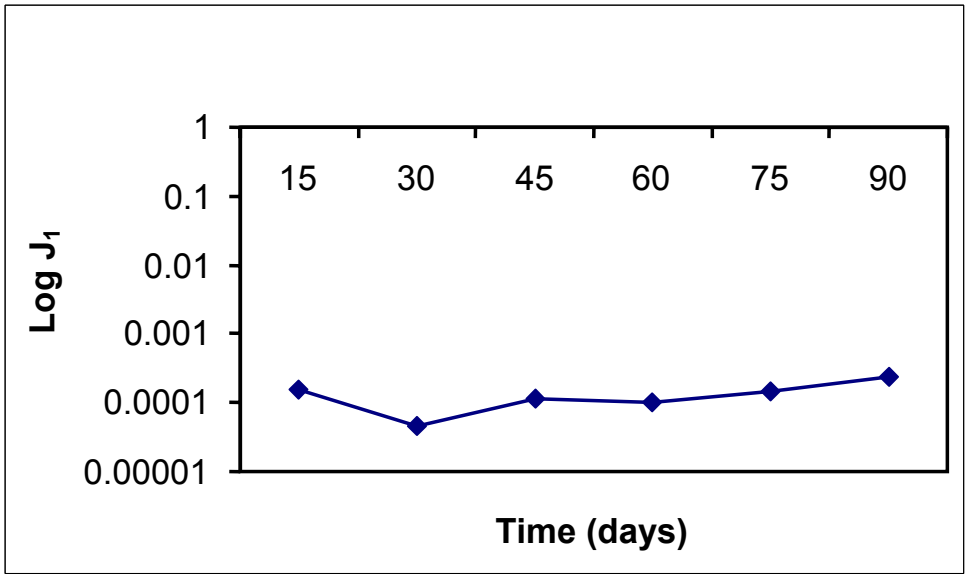

Figure 5.11B: Second retardation compliance (J_1, m^2/N)

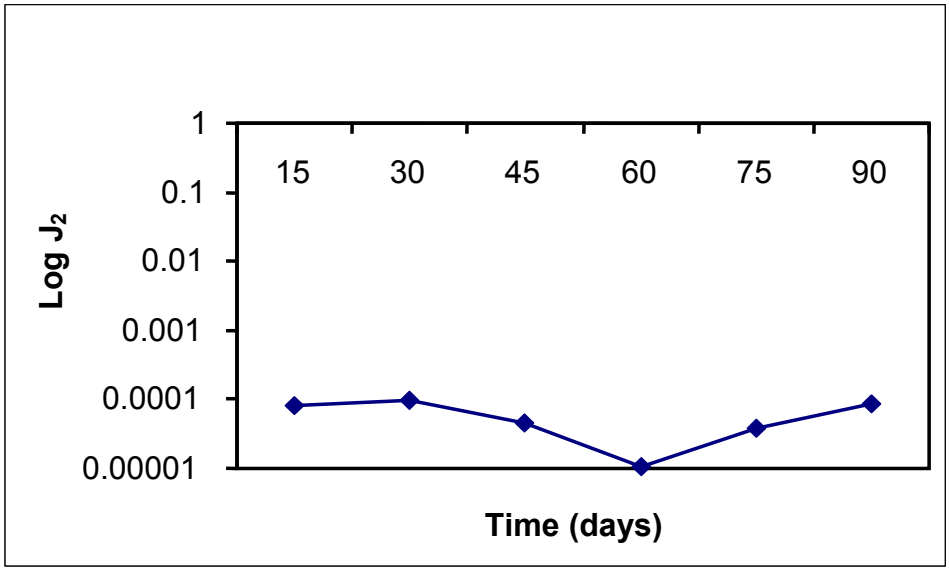

Figure 5.11C: Second retardation compliance (J_2, m^2/N)

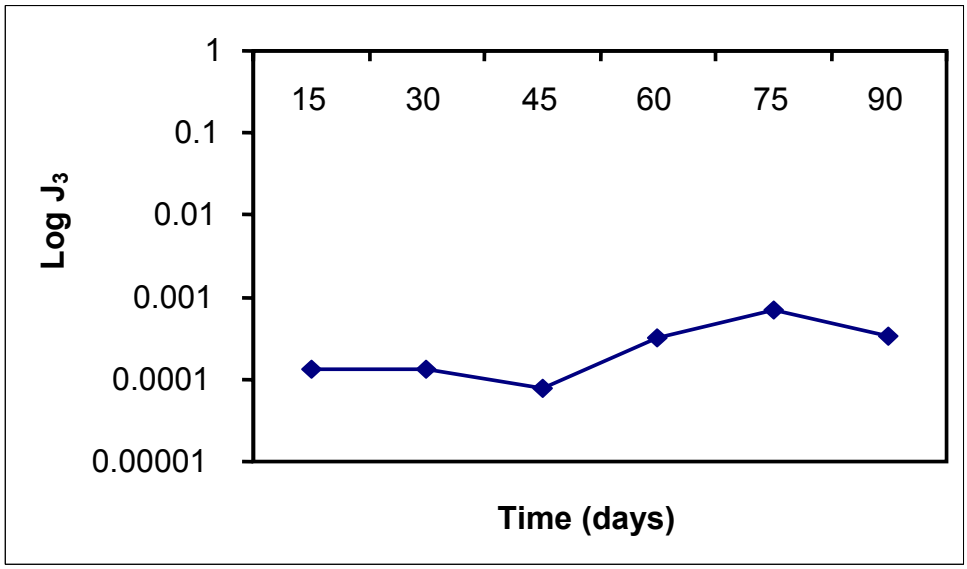

Figure 5.11D: Third retardation compliance (J_3, m^2/N)

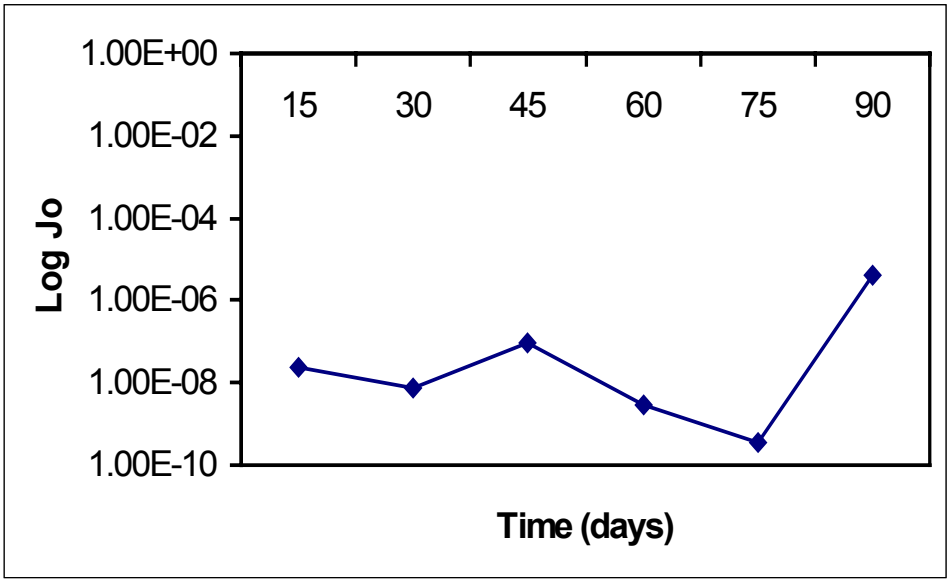

Figure 5.12A: Instantaneous elastic compliance (J_o, m^2/N)

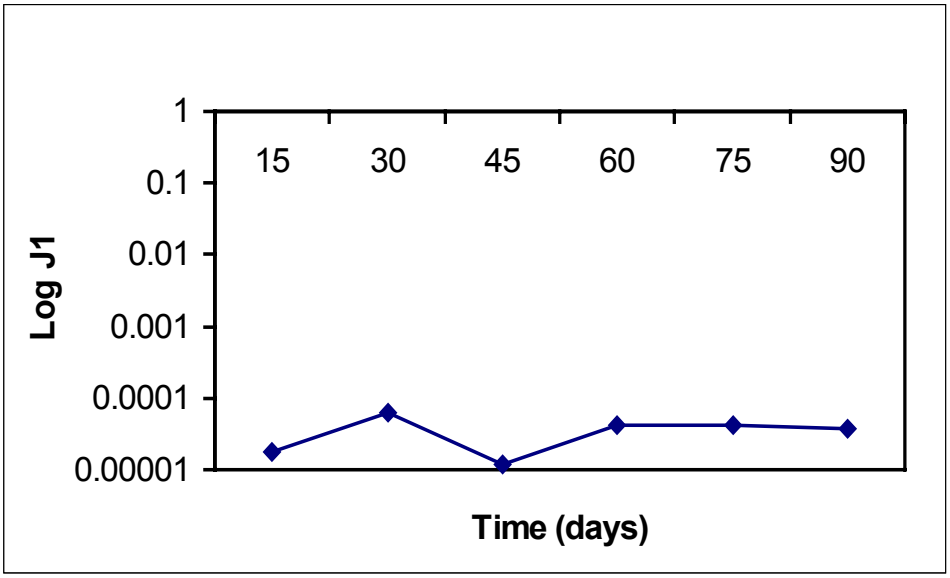

Figure 5.12B: First retardation compliance (J_1, m^2/N)

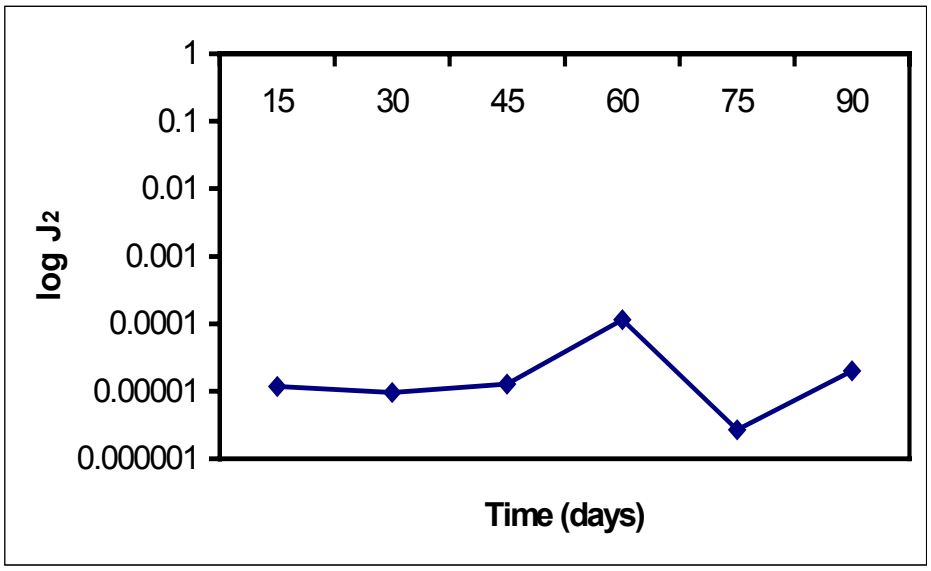

Figure 5.12C: Second retardation compliance (J_2, m^2/N)

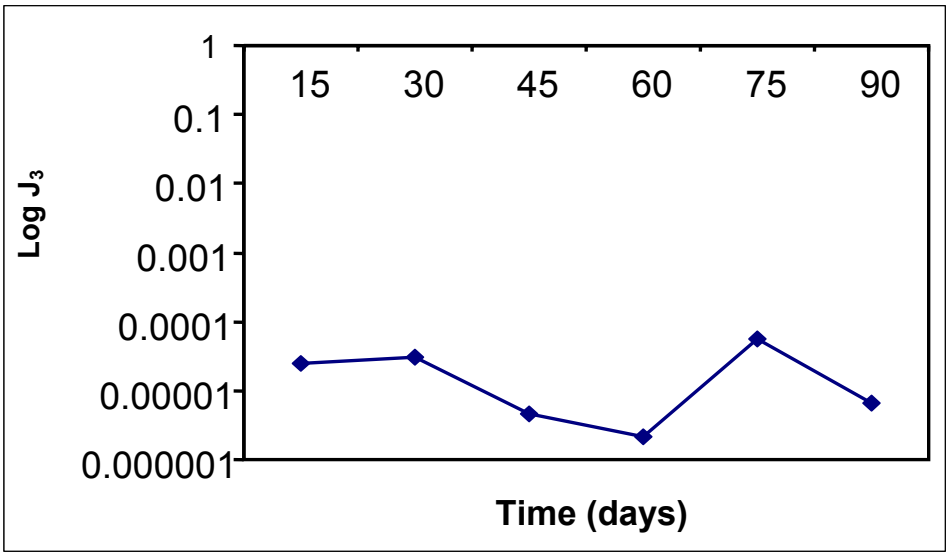

Figure 5.12 D: Third retardation compliance (J_3, m^2/N)

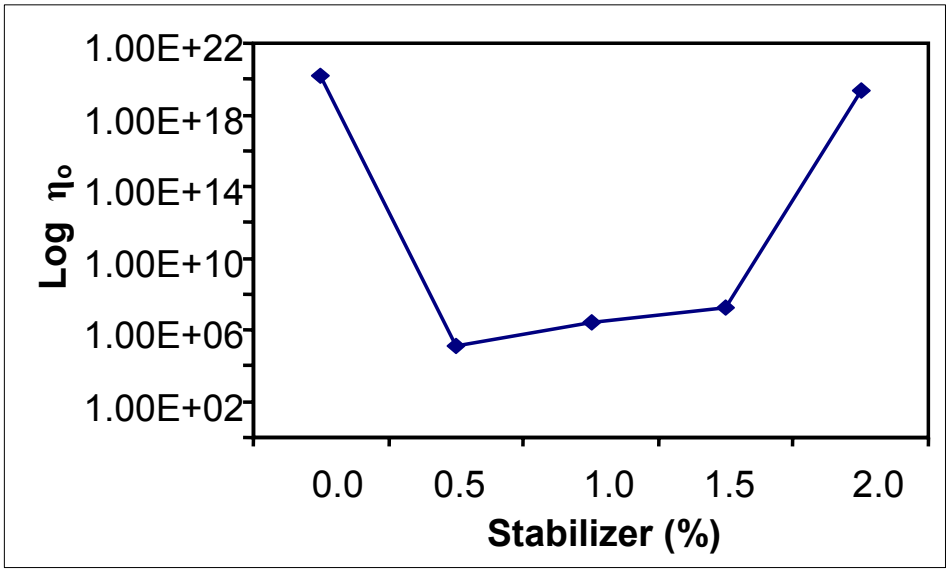

Figure 5.13: Newtonian viscosity (η_N, Pa s)

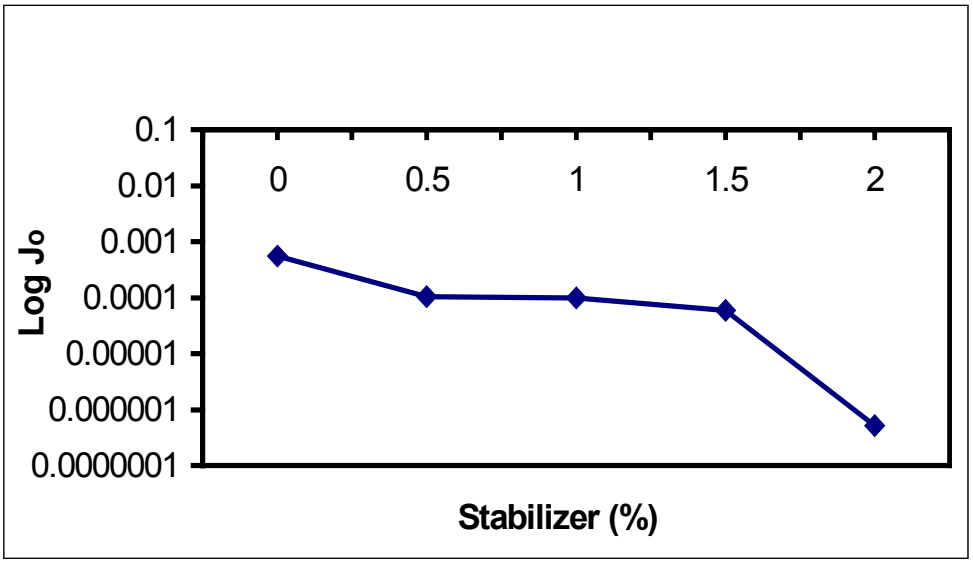

Figure 5.14A: Instantaneous elastic compliance (J_o, m^2/N)

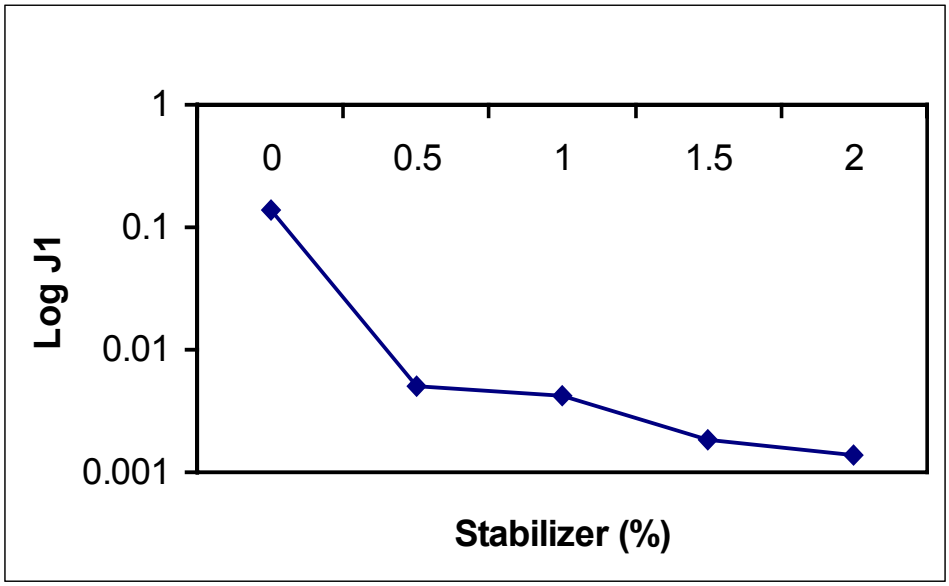

Figure 5.14B: First retardation compliance (J_1, m^2/N)

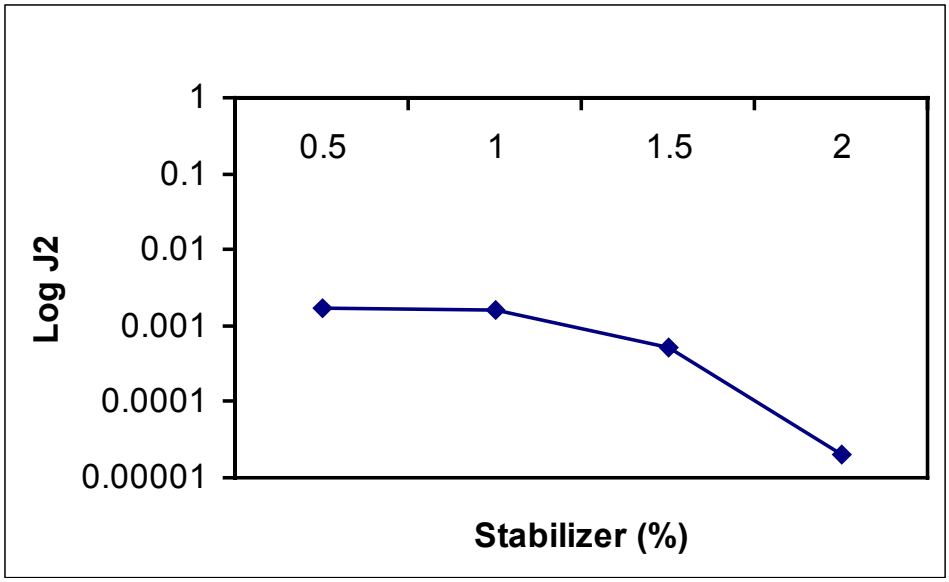

Figure 5.14C: Second retardation compliance (J_2, m^2/N)

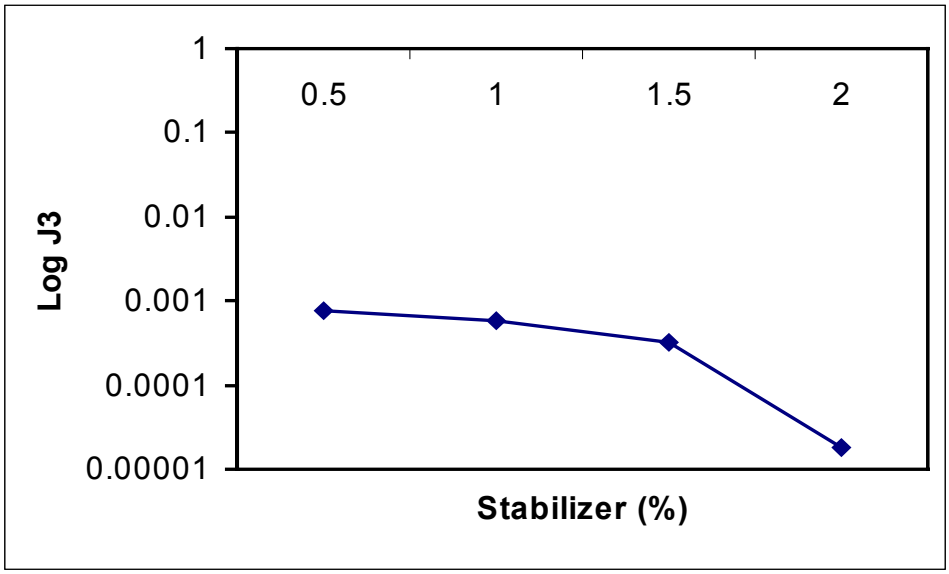

Figure 5.14D: Third retardation compliance (J_3, m^2/N)

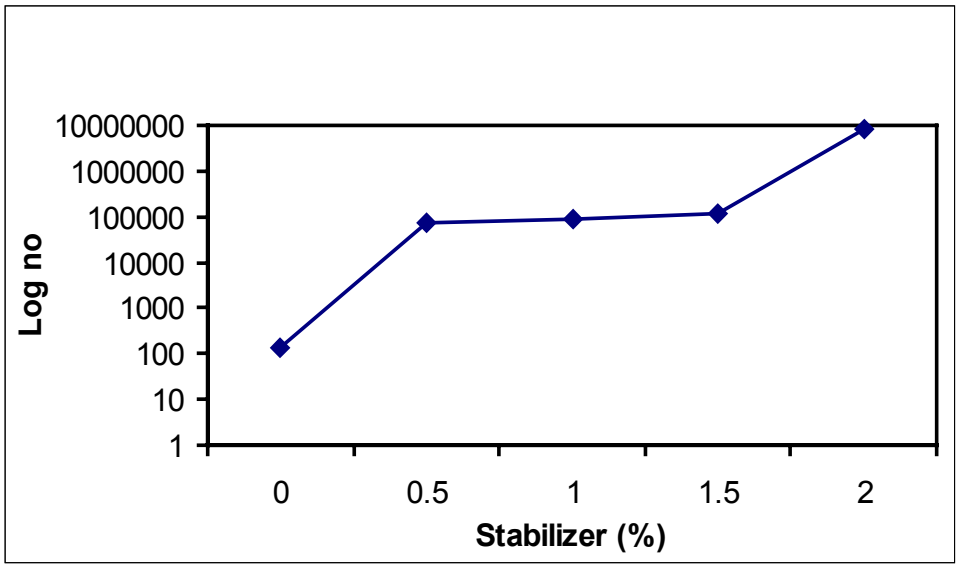

Figure 5.14E: Newtonian viscosity (η_N)

CHAPTER 6

SUMMARY AND CONCLUSIONS

The role of stabilizer in the structure formation was investigated using the techniques of centrifugation, controlled stress rheometry, texture, and viscosity analysis. The various techniques applied to study oil separation in peanut butter were aimed at devising a reliable testing method that would rapidly determine the shelf life of peanut butter. The optimum combination, 10035m/s^2 centrifugal force and 10 min was selected after conducting extensive analysis on laboratory formulated peanut butter samples with five different stabilizer concentrations. Peanut butter when combined with the optimum amount of stabilizer forms the crystal lattice in the matrix that traps oil and keeps the matrix stable. The variable day(s) of formulation was not found to be significant in influencing oil separation in peanut butter samples. The response measured in terms of oil separation simulated in fresh peanut butter samples was then correlated with that of samples at accelerated storage condition of 35 °C. Based on the criterion of maximum oil separation (0.5%) at 35 °C in stabilized samples, the shelf life of peanut butter at 21-24 °C was predicted to be 1-2 yr. Texture firmness and apparent viscosity determinations conducted confirmed the significant influence of optimum stabilizer concentration (>1.0 %).

The rheological characterization of peanut butter was accomplished using the technique of controlled stress rheometry with oscillatory tests such as, time and torque sweeps as well as, creep recovery. The network structure formation in peanut butter was confirmed to be dependent on both, the stabilizer concentration and tempering time of samples. Time sweep and creep-recovery tests were able to trace the structure formation in fresh samples and monitored the degradation of the same in samples placed in accelerated storage conditions for three months. Storage modulus was the most sensitive

indicator of the viscoelasticity of peanut butter. With increase in the level of additive, from 0.0 to 2.0%, the storage modulus showed 1.2 *10^4 for 0d. The loss tangent, which is the ratio of G″/ G′, was found to drop from 3.25 for 0.0% to 0.14 for 2.0% stabilized samples. Therefore, at 0.0% level, peanut butter samples having a predominantly viscous component, exhibited elastic nature with the addition of stabilizer in the sample due to the formation of viscoelastic structure. Oscillatory time sweep tests were able to differentiate amongst peanut butter samples depending upon the concentration of stabilizer present in the sample. Linear viscoelastic range determined by the oscillatory stress sweeps could identify LVR for only 2.0% level in fresh peanut butter samples; in stored samples 0.0% at 60, 75 and 90 d intervals and 1.5% and 2.0% at all sampling intervals in 35 °C conditions. Creep recovery tests conducted within the linear and non linear viscoelastic range for fresh samples showed a decrease in J_o, J_1, J_2, and J_3 with increase in the stabilizer concentration and tempering time in which the samples were placed in an undisturbed environment. This confirmed the strengthening of the network structure in peanut butter samples. Also stored samples with 0.5, 1.0, and 1.5% stabilizer concentration showed improvement in the network structure in 30, 60 and 45 d of storage at 35 °C, after which a decline in network strength set in due to the high temperature of storage. Non-stabilized peanut butter samples when stored under at 35 °C conditions, showed a sharp increase in storage modulus and a drop in instantaneous compliance. This was due to the hard mass left at the bottom of the jar by the migration of natural oil to the top of the container. Peanut butter known for its “soft, semi-solid mass with a weak gel-like behavior” (Citrene and other 2000), can be best monitored by the changes that occur in the viscoelastic properties during the 48 h tempering period. Controlled

stress techniques such as, creep-recovery and time sweep can successfully trace the minute changes occurring in the peanut butter structure, which could not be tracked by employing centrifugation, firmness and viscosity tests.