# RHEOLOGY OF STIRRED YOGURT

By

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#### ABSTRACT

Rheological behavior of two commercial brands of stirred yogurt were investigated using a Haake RV 20 rotational viscometer. Shear stress was measured under a programmed 3-cycle up and down shear rate at  $100 \text{ s}^{-1}/\text{min}$  from 0 to 500 s<sup>-1</sup> (5 min), as well as under steady shear at selected rates (100-500 s-1). Tests were carried out at several temperatures.

For samples from both brands, the upward shear-rate flow behavior generally followed the Herschel-Bulkley model and the downward flow curves were intear. They demonstrated progressive structural degradation with repeated shearing. In the steady shear runs, all samples exhibited apparent thixotropic behavior and did not attain the equilibrium condition even after 60 min of continuous shearing. The time dependent stress decay behavior of all samples were accurately described by Weltman's logarithmic time model. The rheological properties of both yogurt brands were qualitatively similar. Both Arrhenius and Turian models were found suitable to assess the temperature influence in the range 10-25°C.

The influence of pectin (0.0 to 0.5%) and fruit concentrates (raspberry and strawberry) [64<sup>0</sup>B, 0 to 10%] on the rheology of stirred yogurt were evaluated. A steady increase in some parameters (consistency coefficient and apparent viscosity) were noted with the addition of both pectin and fruit concentrates. The study indicated that several rheological parameters could be used to model the flavor yogurt rheology.

The influence of storage time at  $2^{\circ}$ C up to a period of four weeks on the rheological properties of the two brands were evaluated. The study indicated that the effect of storage on chemical composition (acidity, fat, moisture, protein, lactose) was small but significant (p<0.05). However, the resulting effect on various rheological parameters was generally non-significant.

### RÉSUMÉ

Les caractéristiques rhéologiques de deux marques de yaourt brassé commercial ont été étudiées en utilisant un viscosimètre rotatif Haake RV20. Les forces de cisaillement ont été mesurées au cours de trois cycles croissant /décroissant de taux de cisaillement préalablement programmés de 0 à 500 s<sup>-1</sup> à raison de 100 s<sup>-1</sup>/min (5 min) ainsi que pour des taux constants (100 - 500 s<sup>-1</sup>), à différentes températures.

Pour les deux marques, les courbes obtenues avec des taux de cisaillement croissants suivent globalement le modèle Herschel-Bulkley, alors que pour les taux décroissants elles sont linéaires. Une dégradation progressive de la structure est apparue au fur et à mesure des tests. A taux de cisaillement constant, tous les échantillons ont montré un comportement thixotrope et n'ont pas atteint l'équilibre même après 60 min de cisaillement continu. La consistance de tous les échantillons suivait avec précision le modèle logarithmique de Weltman. Les propriétés rhéologiques des deux marques étaient qualitativement similaires. Les modèles d'Arrhenius et de Turian conviennent pour estimer l'influence de la température (10 à 25  $^{\circ}$ C).

L'influence de pectine (0.0 à 0.5%) et de concentrés de fruits (framboise et fraise - 64<sup>0</sup>B, 0 à 10%) sur la rhéologie du yaourt brassé a été evaluée. Une augmentation constante de certains paramètres (coefficient de consistance et viscosité apparente) a été constatée lors de l'ajout de pectine et de concentrés de fruits. L'étude a montré que plusieurs paramètres rhéologiques pouvaient être utilisés pour modéliser la rhéologie du yaourt aromatisé.

L'influence du temps de conservation à  $2^{\circ}$ C, jusqu'à une durée de 4 semaines, sur les propriétés rhéologiques des deux marques a été evaluée. L'étude a montré que l'effet de l'entreposage sur la composition chimique (acidité, matière grasse, humidité, protéines, lactose) est faible mais significatif (p<0.05). Par contre, l'effet sur divers paramètres rhéologiques n'est généralement pas significatif.

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#### CHAPTER 1

#### INTRODUCTION

In recent years, fermented dairy products have gained a special importance in the North American diet. Among the various fermented milk products, yogurt, a thermophilic semi-solid coagulum, has attracted a widespread attention on the international scene. The exact origin of yogurt is not well known, but literature reveals that fermentation of milk with lactic acid bacteria is one of the oldest known method of food processing and preservation used by mankind. The nature and form of yogurt is determined by geographical location, ecology, diet and social structure of the place.

Yogurt was originally considered to be a highly ethnic and local food item and rated as "insipid and unenjoyable" because of its tart taste and characteristic nutly flavor. Now, it is generally accepted as a nourishing diet and has gradually become a mainstream food. With the advent of vastly improved processing technology, it has been possible to carefully control the fermentation process to produce yogurt with superior. nutritional, functional and sensory qualities. As a result, its consumption has increased tremendously in North America; in Canada, for example, the consumption has tripled in last 10 years (Hoppner and Lampi, 1990). Hershorn and Lemay (1989) predicted that by 1995 the total market value of yogurt based products may reach as high as 1 billion dollars in Canada i.e., four times the present value. The major reason behind this huge popularity is the introduction of fruit/flavored yogurt products (Valenzky, 1978; Dairy Field, 1984). Although, the blending of yogurt with fruit has been known for a long time (Kosikowski, 1977), it is only in recent years that the product has undergone the tremendous improvement in terms of quality and variety, and the product is enjoying an ever increasing popularity (Eden, 1988). Nutritional qualities of yogurt has been well documented (Ayebo, 1980; Gurr, 1984 and Kaup et al., 1987). Yogurt has been credited

to be a (i) source of essential minerals such as calcium and phosphorous (Deeth and Tamime, 1981), (ii) source of more easily digestible protein than skim milk, (iii) more acceptable dairy base for people who are intolerant to lactose (Holsinger, 1978; Bahrs, 1971), and (iv) reduced calorie diet. Some controversies exist regarding the therapeutic effects of yogurt, yet its overall nutritional value has never been questioned (Tamime and Robinson, 1985).

Broadly, yogurt can be of classified in to three main categories: (I) Plain/Natural yogurt, (II) Fruit yogurt and (III) Flavored yogurt. Each of them may again either be set or stirred type which are distinguished from one another by their gel characteristics and manufacturing process. Recent developments had led to marketing of yogurt in several different forms, namely pasteurized/UHT yogurt, concentrated yogurt, frozen yogurt, dried yogurt, yogurt beverage, yogurt tablets and yogurt confectionery. Their chemical constituents, physical characteristics and organoleptic qualities may vary widely depending on the method employed for their processing.

The organoleptic quality of the yogurt product is dependent on physical parameters such as texture and/or consistency (rheology) both of which depend on the chemical composition and the fermentation process. Rheological properties therefore are key parameters in the development, and quality control of all yogurt based products. The rheological properties will also provide engineering data necessary for product handling during the processing and for the usage of proper process equipment. Rheological properties such as apparent viscosity of most food products are influenced by the rate of shear. Continuous shearing even at a constant rate has a detrimental effect on the yogurt structure. Temperature is another important factor influencing the rheological properties of yogurt. Additives such as starch and pectin added to flavored yogurt have a profound influence on the product's rheology. Further, storage time and temperature may affect the rheological and organoleptic properties of the product. Published information on rheology of yogurt, especially the stirred type, is generally scarce (Martens, 1972; Hellinga et al., 1986; Inagaki, 1986; Nishijima and Inagaki, 1987) and most of these works deal with the influence of different manufacturing steps on rheology. No published information is available on the timedependency of the stirred yogurt rheology. Information on flavored yogurt rheology is even more scarce. There is a complete lack of rheological investigation on the addition of fruit concentrates to yogurt.

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**Objectives:** The overall goal of thesis research was to relate the rheological properties of stirred yogurt to its sensory characteristics. The following were the specific objectives:

- (1). To study the rheological behavior of plain stirred yogurts under dynamic as well as steady shear state conditions in order to evaluate (a) the shear stress shear rate relationship, (b) temperature effects on rheological parameters and (c) the stress decay behavior as a function of steady shear rate, time and temperature.
- (2) To investigate the effects of pectin and fruit concentrates such as raspberry and strawberry on the rheological behavior of stirred yogurts.
- (3) To examine the influence of storage time up to a period of four weeks at 2°C on the physico chemical and rheological behavior of natural stirred yogurt under the conditions as mentioned in (1) above.

The thesis is prepared in nine chapters with the first three covering introduction and literature review on concepts in rheology and pertinent information on yogurt. The next five chapters (IV-VIII) address specific aspects of yogurt rheology: time-independent and time-dependent flow behavior of yogurts, rheology of flavored yogurts (raspberry and strawberry), and finally rheological changes during storage. This particular format was used because these five chapters have been prepared as manuscripts for publication in scientific journals (in process). All references are listed in the final Chapter IX.

#### **CHAPTER II**

#### **CONCEPTS IN RHEOLOGY**

The majority of foods range from simple dilute solutions to complex multiphase systems consisting of water, oil, soft fats, high polymers like fibrous material, proteins and carbohydrates. Because of the diverse nature of the constituents, foodstuffs generally vary in textural characteristics as well as physical states. They are characterized by various textural properties such as fluidity of liquid and semisolid foods, hardness of candy, crispness of vegetables, juiciness of fresh fruits, viscosity of thick puree, tenderness of meats and other similar terms (Tung, 1978; Bourne, 1982).

The term texture, meaning "interweave" in Latin, has been used in the past to describe the closeness or roughness of pictures or paintings (Sone, 1969). Rheology involves the study of the deformation (texture) and flow of matter under the influence of external force/stress. Drinking, biting, swallowing, chewing etc. provide the force/stress to the food while eating and in processing of food products they are a consequence of pumping, mixing, homogenization, etc. Rheological behavior of food products play an important role in their acceptability, quality control, product development, processing and handling.

The rheological behavior of substances that flow is characterized by the measurement of viscosity which is defined as the internal friction or resistance experienced by the fluid, as it moves over another layer of the fluid. An ideal viscous fluid is incompressible, non-elastic and possesses isotropic structure. It is important to note that a fluid under the influence of applied stress like in mixing or pouring, will not return to its original state even on removal of the applied force. However it will continue to flow during the application of the stress.

Isaac Newton formulated the basic law of viscometry which states that shear

stress ( $\sigma$ ) is directly proportional to shear rate of ( $\gamma$ ) an ideal liquid (Scott-Blair, 1969):

$$\sigma = \eta. \gamma \tag{1}$$

The proportionality constant  $(\eta)$  is called viscosity coefficient, absolute viscosity, dynamic viscosity or apparent viscosity.

#### **TYPES OF VISCOUS BEHAVIOR**

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Depending on the flow behavior under imposed shearing forces, fluids can be classified into two main categories namely, Newtonian and non-Newtonian. For Newtonian type of rheological behavior, the fluid maintains a constant consistency irrespective of the rate of shear. The flow behavior can thus be expressed by Eq.(1). The flow curve (rheogram) shows a linear relationship between shear stress and shear rate (Figure 1), and the slope determines the fluid viscosity. Water, milk, dilute sugar syrups, honey, edible oils, filtered juice, carbonated beverages and watery beverages e.g. tea, coffee and beer are examples of fluids exhibiting Newtonian flow. In practice, however, a majority of liquid and semisolid foods encountered in the food system do not exhibit Newtonian character. So they do not bear a linear relationship between shear stress and shear rate. For these fluids, the viscosity which changes with shear rate, is termed apparent viscosity  $(\eta_a)$ . The term apparent is used to imply a Newtonian type of measurement to a non-Newtonian system. Recent studies have revealed that non-Newtonian flow behavior occurs only when macromolecular chains are sufficiently long to entangle. In order to allow this to happen, the molecular weight of the polymer must be of a critical value which is not dependent upon shear rate (Sabia, 1964). Examples of non-Newtonian systems are concentrated solution of macromolecules like starch, pectin, gums and other hydrocolloids, colloidal systems such as emulsions, pastes and suspensions.

The non-Newtonian flow behavior is broadly classified into three main groups: (1) Time-independent flow in which the shear stress depends only on the shear rate (dilute purees and colloidal systems), (2) Time-dependent flow in which the shear stress can be a function of magnitude and duration of the shear rate as well as the time lapse between two consecutive applications of shearing treatment (egg albumin and gelatinized foodstuffs), and (3) Viscoelastic flow in which the fluid exhibits the property of partial elastic recovery upon the removal of the shearing stress (gel, dough and some egg products).

### Time-Independent Flow

The time-independent flow behavior is further characterized as a) plastic, b) pseudo-plastic and c) dilatant flow depending on the influence of shear rate on the shear stress.



Figure 1. Idealized flow curves for various rheological systems

**Plastic or Bingham Flow:** This type of flow is displayed by fluids which behave like a solid until a minimum shear stress known as the "yield stress" is overcome before the flow can begins. Bingham and Green (1919) observed this type of properties in oil paints, hence such materials are termed "*Bingham plastic*". Elastic deformation is exhibited at stresses below yield value, while the plastic flow is observed at high shear stresses (*Figure 1*). This system is characterized by an offset straight-line relationship between shear stress and shear rate, and shows a decreasing viscosity with an increasing rate of shear after yield value is exceeded.

The physical behavior of matericity with a yield stress is usually explained in terms of a three-dimensional intermolecular bonding structure that is capable of preventing fluid motion for small shear stress. When the applied shear stress exceeds the value of yield stress, the internal structure collapses and allowing the fluid to flow. In actual practice, it is difficult to find a pure Bingham body. In most cases, a "mixed type" (Ellis fluid) flow behavior is commonly observed in which the shear stress-s' car rate plot is non-linear above the yield stress (Figure 1). Plastic flow is not always as simple as shown in Figure 1. Accurate estimation of yield value is difficult, because the flow curve of shear stress vs shear rate actually shows three yield values at low shear rates for a non-Bingham body (Houwink, 1958) as represented in Figure 2. The extrapolation of the experimental straight-line to zero shear rate shows the plastic or Bingham nature of the flow. The shear stress at which curvature begins in the shear stress-shear rate plot is defined as "Upper yield value or Upper Houwink value"; the intercept in the vertical axis from the extrapolation of the straight line of the curve is known as the "extrapolated yield value or Bingham value" and the actual intersection of the shear stress-shear rate plot on the vertical axis is known as the "Lower yield value or Lower Houwink value".

The concept of yield stress in Bingham plastic was questioned by Barnes and Walters (1985) who proposed that given a sufficient time, such fluids will not exhibit a

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yield stress. However, such a time allowance is not possible in practice especially in food processing operations. Therefore, the yield stress parameter can not be avoided. The magnitude of yield stress in some semisolic foods such as sauces, spreads, baby foods, cultured and fermented dairy products etc., is an extremely important criterion in determining its quality.



Figure 2. Types of yield values found with some plastic fluids.

**Pseudoplastic** Flow: Pseudoplastic flow behavior is the most commonly observed among the non-Newtonian fluids. This is characterized by shear-thinning over a large range of shear rate; thus the apparent viscosity decreases with the increase in shear rate (Figure 1). Shear stress-shear rate curve shows a concavity and follow a near linear relationship at very high and low shear rates. The slopes of the linear portion of the curve at low and high shear rates are referred to as "zero shear viscosity" ( $\eta_0$ ) and "infinite shear viscosity" ( $\eta_{oo}$ ) respectively. The region of constant viscosity at low shear rate may not be observed under common testing conditions because of lack of sensitivity at low shear rates of most commonly used rheometers. The intermediate concave region represents the shear-thinning property. On logarithmic coordinates, these three regions are more noticeable as represented by the apparent viscosity vs shear rate plot in Figure 3. The pseudoplastic flow behavior is generally characterized by a power law model.

Pseudoplastic behavior is possibly explained by the existence of an interaction between particles and polymer chains. Such interaction may involve Van der Waal, electrostatic and other similar types of interactions or they may be due to the alignment of rigid and very asymmetrical macromolecules or particles in the direction of flow. At a given shear stress, a quasi-instantaneous equilibrium between the breakdown of orientation and build-up is reached; an increase in a shear rate results in the shifting of the equilibrium towards less orientation. Such a phenomenon is instantaneously and completely reversible, and the orientation of particle is random (Doublier and Lefebvre, 1989; Tung, 1978). Some common examples of pseudoplastic flow are colloidal suspensions, dispersions, soups, purees etc.

**Dilatant Flow:** Dilatant flow is opposite of pseudoplastic flow and therefore the apparent viscosity of the fluid increases (shear-thickening) with an increase in shear rate (*Figure 1*). Two types of dilatancy are observed namely, volumetric dilatancy and rheological dilatancy. The term volumetric dilatancy is used when "swelling" of the fluid

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takes place during shearing. Rheological dilatancy refers to an increase in the apparent viscosity to increasing shear rate.

Dilatant behavior is shown in densely packed particles in which there is only sufficient liquid to fill the voids. As the shear rate is increased, this dense packing must be broken down to permit the particles to flow past one another. The resulting expansion leaves insufficient liquid to fill the voids and is opposed by surface tension forces. Because of its inability to saturate the system to the space, the viscosity increases. This type of behavior is exhibited by liquids containing a high percentage of insoluble rigid particles in suspensions. Some examples of this type are solid, raw starch suspension, some chocolate syrup etc.





### Time-Dependent Flow

The fluids in this category exhibit shear rate as a function of both the magnitude and the duration of shear, and time lapse between successive shearing action. The apparent viscosity for such a system depends on its previous shearing history.

Thixotropic Flow: Thixotropic flow is characterized by a reversible decrease in shear stress with time at constant shear and temperature (Figure 4). This phenomenon is explained by the break down of forces that exist between the particles of a system which later reform on standing. Hahn et al. (1959) assumed thixotropic system as consisting of two types of molecules, a non-Newtonian type that is extended entangled and Newtonian type that is coiled and disentangled. In actual practice, only a part of the long molecule may remain as entangled while the other part is untangled. The disentangled molecules are contained in entangled molecules forming a threedimensional network. The equilibrium constant determines the relative amounts of entangled and disentangled components. The position of the equilibrium is shifted by high shear stress, which destroy the network, changing a solid to liquid like substance.



Figure 4. Time dependent flow behavior.

When a sample is subjected to a continuously increasing shear rate followed immediately by the continuously decreasing shear rate, the resulting flow curve encompasses a hysteresis loop. The area enclosed by the hysteresis loop is taken as a measure of the thixotropic effect or the magnitude of structure breakdown. Sheth (1976) demonstrated that the structure breakdown may be completely reversible, partially reversible or irreversible, as determined by the extent of recovery of the original structural viscosity. Other researchers (Hahn et al., 1959; Van Wazer et al., 1963; Cheng and Evans, 1965) have also defined thixotropy as a completely reversible process; however, the majority of food products exhibit only partially reversible or non reversible character. A fluid may exhibit thixotropic behavior in addition to other viscous properties. Yield stress is often associated with thixotropic shear thinning behavior termed as *viscoplastic* flow. Cheng and Evans (1965) and Harris (1972) characterized a *thixo-viscoelastic* behavior of a fluid which undergees structure breakdown. *Thixo-viscoelasticity* is considered to be present in varying degrees in real material.

**Rheodestructive and Rheopectic flow**: The time dependent loss of structure in many fluids is not recoverable and fluids that permanently lose structure are called *rheodestructive* (Mozes and Vamos, 1966). This shear thinning behavior is also termed as *rheomalaxis* as proposed by Reiner and Scott-Blair (1967). Examples of this behavior are egg albumen, some gum and starch pastes. Ideal *thixotropic* and *rheodestructive* fluids are compared in *Figure 5*. *Rheopectic* behavior is the reverse of *thixotropy* (*Figure* 4) and that is why it is also known as *antithixotropy*. The apparent viscosity increases with an increase in shear rate and the structure solidifies with the progress of flow. After resting, the system returns back to its original state of viscosity if no phase or chemical changes has taken place. Rheopectic behavior is observed in egg white foam and whipped cream.



# Figure 5. Ideal flow curves for thizotropic and rheodestructive dispersions.

### Viscoelastic Flow

A viscoelastic fluid possesses both the properties of an *elastic* (solid like) and viscous a fluid (liquid like) simultaneously. For this type of material, a partial elastic recovery is obtained once the stress is removed. The flow behavior of this fluid is also time dependent but differs from *thixotropic* fluid as non-instantaneous. In particular, the initial deformation rate of a viscoelastic material is controlled by the inertia of the fluid, whereas the initial deformation rate of a thixotropic material depends primarily on its initial viscosity. This dual nature is evident for some fluids and semisolids such as flour dough, cake batters, melted cheese, honey and aged condensed milk.

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#### **RHEOLOGICAL MODELS**

#### TIME-INDEPENDENT MODELS

Several mathematical models have been proposed to characterize the flow behavior of fluids. Most models are based on relating shear stress to shear rate under a given set of conditions. Such models are useful in quantifying the rheological behavior for various applications. The original Newtonian model (Eq. 1) in which shear stress and shear rate are linearly related is too simplistic to explain the rheological behavior of most foods. The more popular and extensively used model relating shear stress and shear rate is the power-law model represented by Eqs. 2 & 3.

$$\sigma = m \dot{\gamma}^{n} \tag{2}$$

or 
$$\eta = \sigma/\dot{\gamma} = m\dot{\gamma}^{n-1}$$
 (3)

where: n (flow behavior index) and m (consistency coefficient) are constants relating the shear stress ( $\sigma$ ) or apparent viscosity ( $\eta$ ) and shear rate ( $\dot{\gamma}$ ). The flow behavior index gives a convenient measure of shear thinning (n<1) and shear thickening (n>1) nature of the pseudoplastic flow. In the special case where n = 1, the behavior becomes Newtonian. The power-law model results in a linear plot on logarithmic coordinates. This model is applicable to several fluid foods over a range of intermediate shear rates (Holdsworth, 1971; Rao, 1977).

One of the early models which characterizes the shear stress/shear rate behavior for a fluid exhibiting a yield stress is the classical Bingham Plastic [Eq. 7],

$$\sigma - \sigma_0 = \eta_B \cdot \dot{\gamma} \text{ for } \sigma > \sigma_0 \tag{4}$$

The rheogram of Bingham plastic flow would be linear on arithmetic coordinates of shear stress versus shear rate having yield stress as the constant and  $\eta_B$ , the plastic viscosity as slope. Although most foods do not follow a true Bingham plastic flow, this model has been used to describe the flow behavior of apricot puree, minced fish paste

and cooked cassava paste (Schaller and Knorr, 1973; Nakayama et al., 1980 and Odigboh and Mohsenin, 1975).

One limitation of above equation is that it does not account for the yield stress which is the minimum stress necessary to cause the fluid to flow. A modified power law equation accommodating the yield stress ( $\sigma_0$ ) is the Herschel-Bulkley model represented below:

$$\boldsymbol{\sigma} - \boldsymbol{\sigma}_{\mathbf{0}} = \mathbf{m} \cdot \boldsymbol{\dot{\gamma}}^{\mathbf{n}} \tag{5}$$

The yield stress is generally determined by extrapolation of the flow curve to zero shear rate (Halmos and Tiu, 1981). The Herschel-Bulkley model has been applied to several food systems at intermediate ranges of shear (Rao, 1977; Rao et al., 1981; Duran and Costell, 1982; Barbosa Canovas and Peleg, 1983; and Dervisoglu and Kokini, 1986).

Casson model (Casson, 1959) relating the square root of shear stress to the square root of shear rate has been applied successfully for the characterization of molten chocolate. This model as shown below is particularly applicable for non-thixotropic suspension of attracting particles:

$$\sigma^{1/2} - K_{00} = K_{01} \dot{\gamma}^{1/2} \tag{6}$$

The casson yield stress  $K_{0C}^2$  has been used by many researchers (Charm, 1963; Tung et al., 1970; Hermansson, 1975 and Rao et al., 1981) as parameter in the Herschel-Bulkley model.

Mizrahi and Berk (1972) (Eq. 6) model is a modified Casson model used to describe the flow behavior of suspended particles in an aqueous medium containing dissolved sugars, salts, acid and pectins.

$$\sigma^{1/2} - K_{\rm oM} = K_{\rm M} \dot{\gamma}^{\rm n}_{\rm M} \tag{7}$$

In this equation,  $K^2_{OM}$  denotes the magnitude of the yield stress which is influenced by the concentration of suspended particles, dissolved pectins and other factors. The constants,  $K_M$  and  $n_M$  determine the rheological properties of the solvent, hence,  $n_M$  is 0.5 for Newtonian fluids and less than 0.5 for pseudoplastic fluids. Mizrahi and Berk (1972) noted that this generalized method is in better agreement with a experimental data over a wide range of shearing rates. Mizrahi and Firstenberg (1975) reported that Mizrahi-Berk model fitted more closely than the Herschel-Bulkley model for the rheological behavior of low pulp concentrated orange juice.

The models discussed above, are best applicable for intermediate shear rate range. Since, shear thinning fluids display a Newtonian viscosity at very low and high shear rates, their rheological properties can not be fully described in terms of the above models. The Powell-Eyring model (Eq. 8) was developed to describe the flow behavior of a shear thinning fluids based on a zero shear and an infinite shear viscosity represented by  $\eta_0$  and  $\eta_{\infty}$ , respectively. This model (Eq. 8; b as a constant) has been found suitable to describe the rheology of food systems (Rozema and Beverloo, 1974).

$$\sigma = \eta_{\infty} \dot{\gamma} + \left[ (\eta_{\Omega} - \eta_{\infty}) / \beta \right] \sinh^{-1} (\beta \dot{\gamma})$$
(8)

Doublier and Launay (1974) applied the model developed by Cross (1965) to characterize the flow behavior of guar gum solutions over a wide range of shear rate  $(0.16 - 17,6005^{-1})$ .

$$\eta = \eta_{\infty} + (\eta_{0} - \eta_{\infty}) / [1 + \alpha \dot{\gamma}^{2/3}]$$
(9)

Ellis model (Eq. 10) has been found useful to describe pseudoplastic flow at low through intermediate shear rate because the model includes zero shear apparent viscosity.

$$1/\eta = 1/\eta_{O} \left[1 + (\sigma/\sigma_{0,5})^{\alpha-1}\right]$$
(10)

where:  $\sigma_{0.5}$  corresponds to the shear stress for non-Newtonian viscosity of 0.5  $\eta_0$ . The parameter  $\alpha$  indicates the shear thinning region of the pseudoplastic rheogram.

Michaels and Bolger (1962) postulated that the stress required to produce deformation or flow at a constant rate consists of three parts as shown below:

$$\sigma = \sigma_n + \sigma_{cr} + \sigma_{vi} \tag{11}$$

where:  $\sigma_n$  and  $\sigma_{cr}$  are stresses required to break the network structure and structural bonds formed by shear induced collision of particles and  $\sigma_{vi}$  is the stress needed to overcome the viscous resistance to produce flow. This model explains the flow of mechanism of suspension of fruit puree. At zero shear rate, the network zero yield stress,  $\sigma_n$ , is equivalent to  $\sigma_0$ , and  $\sigma_{cr}$  is equivalent to  $\sigma_b$  (Bingham yield stress) at high shear rate. The  $\sigma_{vi}$  equivalent to  $\eta_{\infty}$ , the viscous flow at infinite shear rate. The principle contribution of this model is the introduction of the three parameters  $\sigma_0$ ,  $\sigma_b$  and  $\eta_{\infty}$ , and the roles played by the particle concentration and particle properties. This model has been successfully applied by Duran and Costell (1982) and Qiu and Rao (1988) to evaluate the flow behavior of apple sauce, apricot puree etc.

Recently, Ofoli et al. (1987) proposed a versatile rheological model consisting of four parameters for viscometric flow as stated below:

$$\eta = [(\sigma_0/\dot{\gamma})^n] + \eta_\infty \dot{\gamma}^n 2^{-n} 1]^{1/n}$$
(12)

where:  $n_1$  and  $n_2$  are functions of shear stress, yield stress and shear thinning as well as related to fluid flow behavior. This model is believed to represent accurately the shear stress vs. shear rate or apparent viscosity vs. shear rate relationship for several nonelastic food materials. All the conventional rheological models can be obtained from the above model by appropriate specification of the four parameters.

#### TIME-DEPENDENT RHEOLOGICAL MODELS

1.1

The common approach employed to characterize the time dependent flow behavior is either (i) to evaluate the stress decay under a steady shear over a specified time, or (ii) to measure the hysteresis loop, the area between up and down curves with the shear rate programmed to vary as a function of time. The first approach gives a more complete information on the time dependent rheological behavior and can easily be evaluated by the single point viscosity measuring devices used commonly in food research.

The following model was proposed by Weltman (1943) to describe the change in

apparent viscosity with time,

$$\eta = \mathbf{A}_1 - \mathbf{B}_1 \log (\mathbf{t}) \tag{13}$$

where:  $A_1$  is the shear stress at unit time (t) and  $B_1$  is the time coefficient of thixotropic breakdown. This model describes the continual decay of stress, without reaching the state of equilibrium even on prolonged shearing.

A second model developed by Hahn et al. (1959) to include an equilibrium shear stress that followed the first order type relationship was used by Duran and Costell (1985) and Paredes et al. (1988):

$$\log (\sigma - \sigma_e) = A_1 - B_1 t \tag{14}$$

Longrée et al. (1966) studied viscosity of custard systems containing sugar using a similar equation:

$$\ln \left(\eta - \eta_{e}\right) = Ct \tag{15}$$

where: C is the rate of structural breakdown and  $\eta_e$  is the apparent viscosity at equilibrium at a given shear rate. A modified Hahn et al. model, in the form of Eq. 16, was reported to better describe the time dependency of some foods (Tung et al., 1971):

$$\log (\eta - \eta_e) = A_1 - B_1 \log (t)$$
 (16)

Cheng and Evans (1965) proposed a model based on theoretical considerations related to state and rate:

State Equation: 
$$\sigma = \eta (\lambda, \dot{\gamma}) \dot{\gamma}$$
 (17a)

Rate Equation : 
$$d\lambda/dt = g(\lambda, \dot{\gamma})$$
 (17b)

where:  $\lambda$  is a structural parameter ranging from zero to one, and g is another structural parameter which is a function of both  $\dot{\gamma}$  and  $\lambda$ . The viscosity and rate of breakdown are treated as a function of shear rate and structural parameter in the above equations. Cheng and Evans (1965) reported that these equations are applicable to any single process of structural change.

Woodmann and Marsden (1966) introduced the following empirical relationship to describe the stress decay of a thixotropic pharmaceutical lotion:

$$\log (\sigma_1/\sigma_2) = k \log (t_2/t_1)$$
(18)

where:  $\sigma_1$  and  $\sigma_2$  represent shear stresses at times  $t_1$  and  $t_2$  respectively. The rate constant, k, was reported to remain approximately constant at shear rates below 200 s<sup>-1</sup>. This equation reveals a continuous destruction of structure for a long shearing time.

Higgs and Norrington (1971) determined the rate of structural breakdown of sweetened condensed milk, by measuring the coefficient of thixotropic breakdown with time, "B" and the coefficient of thixotropic breakdown due to increasing shear rate, "M" (Green, 1949; Wilkinson, 1960) as given by the following equations:

$$\mathbf{B} = (\eta_1 - \eta_2) / \ln (t_2 / t_1)$$
(19)

$$\mathbf{M} = (\eta_1 - \eta_2) / \ln (N_2 / N_1)$$
(20)

where:  $\eta_1$  and  $\eta_2$  were viscosities at times  $t_1$  and  $t_2$  (Eq. 19), and at the angular speeds N<sub>1</sub> and N<sub>2</sub> (Eq. 20), respectively.

Tiu and Bolger (1974) proposed a rheo-kinetic model to describe the rheological behavior of mayonnaise which exhibits a yield stress, pseudoplastic behavior and time dependent characteristics. This model was based on Herschel-Bulkley model (Eq. 3) modified to include a structural parameter  $\lambda$ , ranging from an initial value of unity for zero shear time, to an equilibrium value,  $\lambda_e$ , being <1.

$$\boldsymbol{\sigma} = \boldsymbol{\lambda} \left( \boldsymbol{\sigma}_{0} + \mathbf{K} \, \boldsymbol{\dot{\gamma}}^{\mathbf{n}} \right) \tag{21}$$

According to Petrellis and Flumerfelt (1973), the rate of decay of structural parameters followed a second order rate equation:

$$d\lambda/dt = -k_1 (\lambda - \lambda_p)^2 \quad \text{for } \lambda > \lambda_p \tag{22}$$

Since apparent viscosity is defined as  $\eta = \sigma/\gamma$ ,  $\lambda$  will be related to viscosity as,

$$\lambda = \eta \dot{\gamma} / \sigma_0 + K \dot{\gamma}^n \tag{23}$$

Under equilibrium conditions,  $\lambda$  and  $\eta$  are replaced by  $\lambda_e$  and  $\eta_e$ . Another form of equation was obtained from Eqs. 22 and 23 relating apparent viscosity and time:

$$1/(\eta - \eta_e) = 1/(\eta_o - \eta_e) + a_1 t$$
(24)

This model was shown to be in agreement with the behavior exhil ited by time dependent emulsions like fruit purees (Ford and Steffe, 1986), soft cheese (Massaguer-Roig et al., 1984; Martinez-Padilla and Hardy, 1989). It was also pointed that only a limited part of the curve namely at the initial period when it behaves in a linear fashion, should be used to evaluate the rate constant (Martinez-Padilla and Hardy, 1989).

Xu et al. (1984) proposed a more sophisticated model, which employs a series of two first order rate functions (denoted by subscripts 1 and 2) yielding a sum of two exponential functions:

$$\sigma - \sigma_{e} = (\sigma_{o,1} - \sigma_{e,1}) \exp(-K_{1}t) + (\sigma_{o,2} - \sigma_{e,2}) \exp(-K_{2}t)$$
(25)

Recently, Martinez-Padilla et al. (1989) introduced an empirical relation correlating the thixotropic behavior with three variables namely, shear stress, shear rate and time via multiple regression. Like the power law (log s vs log g), the time effect is also included in the logarithmic form of this model. Another significant aspect of this model is the inclusion of yield stress. This proposed relationship is based on the Herschel-Bulkley model which includes the time effect:

$$\sigma - \sigma_0 = K \dot{\gamma}^n t^p$$
(26)

where p represents a thixotropic stress parameter.

Mottar et al. (1989) estimated the resistance to structural (R%) breakdown by the comparison of up  $(\eta_1)$  and down  $(\eta_2)$  viscosity at specific shear rates:

$$R(\%) = 100 (\eta_2/\eta_1)$$
(27)

#### FACTORS INFLUENCING VISCOSITY

#### Temperature

Temperature has an inverse effect on the viscosity of liquids. This effect is explained by the reaction rate theory of viscosity (Eyring, 1936; Ewell, 1938) which postulates that the energy of activation for a flow process results from the formation of a number of "holes" or extra spaces. The total volume occupied by the holes, termed as "free volume", allows the molecules to flow into. Any factor like temperature, which changes the free volume will affect the viscosity. At lower temperatures, the fluid becomes thick, so a larger hole or higher activation energy is necessary for flow and, as a result, the viscosity increases. On the other hand, at higher temperatures, the fluid becomes thinner, needs a smaller hole to flow and thus the viscosity decreases.

Since the viscosity of a fluid is highly temperature dependent, the knowledge concerning the effect of temperature on the viscosity has a special significance in determining the conditions of precessing to be adopted during evaporation, pasteurization, sterilization, concentration and handling. Recent work by Anantheswaran and Rao (1985), Rao et al. (1985) and Teixeira and Manson, (1983) revealed that heat transfer to and from non-Newtonian fluids can be best analyzed if the pertinent rheological parameters are fully established.

For Newtonian behavior, the Arrhenius equation has been employed to describe the effect of temperature on viscosity (Saravacos, 1970; Rao and Anantheswaran, 1982; and Rao et al., 1984):

$$\eta = F \exp \left( E_a / RT \right)$$
(28)

where:  $\eta$  = viscosity,  $E_a$  = activation energy for viscous flow, R = gas constant, T = absolute temperature and F = frequency factor. The activation energy of flow is defined as the minimum energy necessary to be overcome before the flow begins.

Rao et al. (1986) found Fultcher (Eq. 29) model to be more suitable for the temperature dependence of high sugar food products such as syrups and concentrated fruit juices at low temperature:

$$\ln \eta = A + B/(T - T_0)$$
<sup>(29)</sup>

Arrhenius equation is also employed for non-Newtonian fluids with some modifications. Thus,  $\eta$  should be replaced by  $\eta_a$  to represent the apparent viscosity at a specific shear rate.

Corey (1972) found that the activation energy and concentrations (C) of suspensions were related by the general equation (A, B and a were constants):

$$\mathbf{E} = \mathbf{A} \exp \left(-\mathbf{B} \mathbf{C}^{\mathbf{a}}\right) \tag{30}$$

The value of constant "a" was reported to be 1/2, 1, 3/2 and 2 for a mineral oil, propylene glycol, silicone oil and  $61^{0}$ Brix sucrose solution respectively.

Turian (1964) related the flow parameters, such as m and n, to temperature in an attempt to evaluate their temperature dependence:

$$\log m = \log m_0 - AT \tag{31}$$

$$n = n_0 + BT \tag{32}$$

During the heat sterilization, a fluid is subjected to both high temperatures and shear gradients. Power law model and Arrhenius equation have been combined as follows (Christiansen and Craig, 1962; Harper and El-Sahrigi, 1965):

$$\sigma = K_{TC} \left( C \exp E_{aC} / RT \right)^n$$
(33)

$$\sigma = K_{TH} \exp \left( E_{aH} / RT \right) C^{n}$$
(34)

where, n is an average value for data of all the temperatures. Though not identical (Vitali and Rao, 1984), the two activation energies are interrelated as follows:

$$\mathbf{E}_{aH} = \mathbf{n} \, \mathbf{E}_{aC} \tag{35}$$

Harper and EL-Sahrigi (1965) proposed the following model to combine the effects of temperature and concentration of tomato juice concentrate:

$$\eta_a = \alpha \exp\left(\frac{E_a}{RT}\right)C^{\beta}$$
(36)

where:  $\alpha$  and  $\beta$  are constants and C is concentration in <sup>O</sup>Brix. In most practice, this equation is valid only over a limited range of variables (Vitali and Rao, 1984).

Rao et al. (1981) combined the Arrhenius model and the exponential form of the effect of concentration to obtain apparent viscosity,

$$\eta_a = \mathbf{A} \exp \left( \mathbf{E}_a / \mathbf{RT} \right) \exp \left( \mathbf{B} \mathbf{C} \right)$$
(37)

The coefficients A and B are obtained experimentally by multiple regression. In the above equation, consistency index may replace apparent viscosity (Rao et al., 1984).

### Concentration

Extensive studies have been carried out on the effect of solids concentration on viscosity at a given temperature. The flow character of many food systems may be greatly modified by the changes in the concentration of one or more soluble solids. In general, viscosity increases with increasing concentrations. Higher concentration of soluble solids can lead to non-Newtonian or plastic dilatant flow behavior. This is explained by increased particle-particle or particle-medium interaction and by the competition among the various solutes present for the available water.

The early theoretical work relating viscosity to volume concentration may be attributed to Einstein (1906, 1911) who proposed that,

$$\eta = \eta_{\rm s} \left( 1 + {\rm a}\phi \right) \tag{38}$$

 $\phi$  is the volume concentration of the particles, and a is a constant having value 2.5. This equation is valid only for dilute suspension where  $\phi$  is less than 0.05 and no particle-particle interaction occurred, and particles are uncharged.

The flow behavior of suspensions at higher concentration deviates from the Einstein equation due to hydrodynamic interactions between particles and the viscosity increases exponentially. Two general equations have been proposed to relate viscosity and concentration (Harper and El-Sharigi, 1965; Rao et al., 1981).

$$\mathbf{K} = \mathbf{K}_1 \ \mathbf{C}^{\mathbf{A}_1} \tag{39}$$

$$\mathbf{K} = \mathbf{K}_2 \exp \mathbf{A}_2 \mathbf{C} \tag{40}$$

where: C is the concentration and  $A_1$  and  $A_2$  are constants. The power law equation *(Eq.39)* has been applied to pureed fruit and vegetable products while the exponential form fitted data for apple juice (Vitali and Rao, 1982; Harper and El-Sahrigi, 1965 and Rao et al., 1984). A modified exponential equation was proposed by Ibarz et al. (1989) for the rheology of clarified pear juice as influenced by concentration and temperature :

$$\eta = K_1 \exp(E_a/RT + AC + BC^2)$$
(41)

#### CHAPTER III

#### YOGURT: CLASSIFICATION, MANUFACTURE AND RHEOLOGY

Yogurt is one of the oldest processed food products, yet until recently the product has been very poorly defined and understood in the literature (Kroger, 1989). A single common definition for yogurt is difficult in view of the large variety of products presently available in market place, all differing in chemical composition, microbiological status (active or inactivated starter culture), biochemical characteristics and organoleptic properties. In the general sense, yogurt may be referred to as a semifluid fermented milk product with a smooth texture and a mildly sour taste and flavor. The bacterial culture for the fermentation usually consists of selected strains *Streptococcus thermophilus* and *Lactobacillus bulgaricus*. The characteristic flavor of yogurt is due to the aroma compounds acetaldehyde, acetone, ethanol, butane-2-one, diacetyl and ethyl acetate, with lactic acid contributing to the acid taste.

The organoleptic characteristics of yogurt is dependent on the physical characteristics of end product such as consistency/viscosity, texture, firmness, body, taste and flavor. These characteristics are in turn influenced by the chemical constituents of milk such as fat, protein, lactose and minerals (ash). Of these constituents, fat produces a rich and creamy texture with an excellent mouthfeel to the yogurt. Protein is mostly responsible for the viscosity or consistency of the product. Lactose provides the source of energy for starter organisms. The sensory properties of the yogurt depends therefore on the type and composition of milk.

### **TYPES OF YOGURT**

Several types of yogurts are available commercially which can be classified in

different ways based on (i) chemical constituents (ii) method of production (iii) nature of the flavor present and finally (iv) on the nature of post incubation process. Yogurt may also be categorized based on their physical form.

In terms of chemical constituents (mainly fat) yogurts are classified into three groups: full or high fat, partially skimmed or medium fat and skimmed or low fat yogurt.

Based on the method of production, yogurts may either be set or stirred type. For set type yogurt, the gel structure is formed directly in the container during the fermentation/incubation step, leading to the formation of a continuous semi-solid mass. For the stirred type, on the other hand, the initially formed gel structure is broken by agitation during the cooling process, yielding a smooth and semi-viscous product (Tamime and Robinson, 1985). A third type of yogurt, *fluid yogurt*, is a stirred yogurt of low viscosity and low solid content obtained by mixing yogurt and water.

Yogurts may be differentiated on the basis of fruit or flavor added. Thus, they can be of three types, namely plain or natural, fruit and flavored. Plain yogurts are natural form of yogurt without any additives except sugar or sweetening agent in some cases. They posses a distinct nutty aroma and sharp acidic taste. Fruit yogurts are made by the addition of fruits in the form of preserves, purees, jams or concentrates and sugar or sweeteners. These yogurts may either be sundey or swiss style. The former is made from set type of yogurt with the fruit at the bottom of the container whereas for latter, the additives are incorporated uniformly in the stirred yogurt. Flavored yogurts are those which are enriched with fruit juices/concentrates, synthetic/natural flavorings, colorings, sweetening agents and stabilizers.

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Yogurt is marketed in several forms following the fermentation/incubation process to extend their shelf-life: pasteurized, frozen, or dried product. Such modifications would result in changes of chemical compositions, physical characteristics and organoleptic properties of the end product. UHT/pasteurized yogurt is a heat treated product to reduce the microbial level and may result in the level of volatile compounds that are associated with flavor of yogurt. Frozen yogurt, either as a hard or soft pack, is sold like ice cream or a frozen stick, and is popular due to the delightful taste and health reputation. High quantity sweeteners and emulsifiers/ stabilizers are needed to maintain the structure during the freezing process.

*Concentrated/condensed/strained yogurt* are prepared by the partial elimination of whey from yogurt. Their rheological properties and characteristics differ from those of original yogurt because of the changes in their physical form. These concentrated forms of yogurt are consumed directly or as ingredients in the preparation of many types of dairy products in some parts of the world (mainly Middle East and Europe).

Dried yogurt is another form of yogurt obtained by the post incubation dehydration by sun, spray or freeze drying. "Kashak" a typical example of sun dried yogurt, containing herbs as extra ingredients, available in the Middle East. The nature and quality of the dried yogurt depends on the number of viable cells in the product which in turn determine their applications as starter culture or as an ingredient. Two forms of dried yogurts are commercially available. One of them (reconstituted yogurt) requires incubation to facilitate gel formation whereas the second one known as "Instant Yogurt" needs only a short period of time for coagulation due to its increased hydrophillic nature.

A recent addition to the list is the *drinking yogurt*, prepared by mixing low-fat yogurt with fruit juice, sugar or sweeteners and stabilizers such as pectin. Pasteurized drinking yogurt can be stored at room temperature up to 6 months. These yogurts are light (reduced calorie) and refreshing but not thirst quenching unless carbonated.

Low calorie yogurt is prepared by fermenting low fat milk (1% or less fat) and blended with additives such as carrageenan, gelatin, etc., for building the texture. Another variation is the *low lactose yogurt* achieved by the use of an enzyme,  $\beta$ -Dgalactosidase, which hydrolyzes the lactose leading to a sweeter product. This product is particularly suitable for lactose intolerant (hypolactasia) people.

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#### **MANUFACTURE OF YOGURT**

The art of making yogurt has been known to mankind since ancient times but scientific details of the manufacture, until recently, were not clearly understood. Since the milk necessary for the manufacture of yogurt may be procured from several mammalian sources, their chemical constituents and consequently the physical properties of the end product will differ widely. This causes the necessity of standardization and fortification of yogurt milk.

Clarification is the first step in the processing yogurt milk to remove the visible dirt and somatic cells by either filtration or in a specially designed separator in the yogurt industry. Following this, the fat content of milk is standardized (1 to 4%) according to legal compositional standard that may vary in different parts of world.

# Fortification of yogurt milk

The major aim of fortification of milk is to increase the level of protein content thereby enhancing the consistency/viscosity and firmness of the end product. The fortification can be carried out either by addition of protein rich powder (solids-not-fat, SNF) or by concentration of milk.

SNF in the yogurt industry is mainly of dairy origin eg. milk powder (skimmed), caseinate, co-precipitate and whey protein concentrates/powders. Some limited application of plant protein to enrich total solid content is also reported in the literature (Schmidt et al, 1980).

Supplementation with skim milk powder (3-4%) is a common practice to increase the SNF of the yogurt milk. Excessive use of skim milk powder induces a powdery flavor to the yogurt and leads to the production of an increased level of acid during storage. Yogurt may also be fortified with butter milk but its use is not very common because of its limited availability. Caseinates directly increase the level of protein. However higher level (>2%) of caseinates in the basic mix results in an undesirable and uncontrolled thickness of the product. The level of whey powder generally recommended is around 1-2%. Higher level is avoided to prevent undesirable whey flavor and build of lactose content. Evaporation and concentration by reverse osmosis have also been resorted to increase the solids level in the yogurt milk.

# Addition of stabilizers

Stabilizers or hydrocolloids are often mixed during yogurt manufacture. Such additions bear a greater significance particularly during the mechanical treatment such as pumping, mixing etc. of yogurt gel after incubation. Stabilizers may be natural, modified or synthetic gums but their use must have prior sanction from appropriate authorities and is subject to legislation and regulation. Stabilizers function as thickeners or gelling agents due to their hydration property and stabilizing action on the protein leading to restricted movement of water molecule. The chemical nature of the stabilizers determines the exact step at which they are to be added. Thus, stabilizers may be incorporated to either cold milk before pasteurization, or to the hot milk immediately after pasteurization or to gel/coagulum after incubation. Appropriate selection of stabilizers and its level of concentration play a major role to achieve the desired characteristics. Flavored yogurt, UHT/pasteurized yogurt, frozen yogurt and other yogurt based products require stabilizers to improve their quality.

### Sweeteners

Sweeteners are routinely added during the manufacture of fruit or flavored yogurt and plain sweetened yogurt in order to mask the acidity and to enhance the added flavoring material (i.e. fruit or berry). The amount of added sugar varies from 3-4% for plain yogurt to 8-12% for fruit-based yogurt (McGregor and White, 1987). The addition of sugar is desirable before the heat treatment as the damage to milk coagulum

is minimized. The level of added sugar should be carefully controlled to prevent an extensive proteolysis leading to bitter flavor (Slocum et al, 1988). Alternate sweeteners such as high fructose corn syrup, sorbitol, cyclamate, saccharin, fructose have also been used (Hyvönen and Slotte, 1983; McGregor and White, 1986).

# Homogenization

Commercially, homogenization is generally carried out at  $60-70^{\circ}$ C under 100-200 kg/cm<sup>2</sup> pressure prior to heat treatment. Homogenization reduces sizes of fat globules (<1.0µm) which gets adsorbed onto the casein micelles (Tamime and Robinson, 1985). This increases the effective total volume of suspended matter which in turn improves viscosity/consistency of the product.

# **Pasteurizatio**:

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Milk may be pasteurized by several techniques: vat pasteurization (85° C for 10-40 minutes), high-temperature short time or HTST treatment (98°C for 0.5-1.87 min) and ultra high temperature or UHT treatment (140°C for 2-8 sec). UHT processing of milk offers certain advantages in terms of better process control, sanitation, potential energy, time saving over the conventional batch type heating. The role of above heat treatment is to destroy any pathogenic microorganisms present in the yogurt milk. It produces certain factors that can stimulate the activity of starter culture and also redistribute calcium, phosphorus and magnesium containing minerals between the soluble and colloidal particles which affect the formation of curd particles and help to decrease the rate of coagulation. Besides the above functions, heat treatment of yogurt milk also changes the physico-chemical structure of milk proteins, an important aspect related to yogurt texture.

Milk protein is composed of casein which exists as colloidal aggregates and globular whey or serum protein in solution. The interaction between denatured whey

proteins and caseins determines the stability of the yogurt gel.

Scanning electron microscopic studies reveal that the size of the casein micelles increases gradually on heating and form a chain matrix (Kalab and Harwaiker, 1973). As a result, particles are uniformly distributed throughout the yogurt entrapping aqueous phase within the network. The resulting coagulum becomes firm and less susceptible to syneresis. On the contrary, unheated milk yields weak coagulum of coarse network by forming aggregates with unevenly distributed proteins which impairs immobilization of water (Kalab et al., 1983).

The degree of denaturation of whey protein is an important factor affecting the texture of end products. The desired level of denaturation depends on the type of the product manufactured. Plain yogurt with the minimum content of total solid (9.5-12%) needs extensive denaturation of whey protein while yogurt containing higher level of total solids (above 14%) or fruit/flavored yogurt require less denaturation (Puhan, 1988).

# Cooling & Inoculation

The treated hilk is cooled to the optimum incubation temperature of starter culture:  $40-45^{\circ}$ C (short incubation method) or  $30^{\circ}$ C (long incubation method). The next step is inoculation which is carried out with a freshly made bulk starter or deep frozen dried form of concentrated starter and mixed at a rate of 2-3% under the desired conditions of temperature with milk. Commonly mixed starter culture consists of a mixture of *S.thermophillus* and *L. bulgaricus* in a 1:1 ratio. The choice of starter culture is not solely restricted to the above two.

# Incubation

Immediately after inoculation, the warm mix is pumped into fermention vessels, the nature of which depend on the type of yogurt desired: set or stirred. For production of set type yogurt, the fermentation/incubation is carried out in the retail container. The containers are incubated at the appropriate temperature in a cabinet or a tunnel. In case of stirred yogurt, the inoculated milk is delivered into a fermentation tank for bulk incubation at the optimum temperature for 3-6 hr. This fermentation process can be either of batch-type or of continuous type, the former being more common. The continuous fermentation procedure is carried out in two stages. In the first stage, known as pre-fermentation of milk, bacterial multiplication takes place, the pH being kept constant with the addition of fresh milk. In the subsequent stage, formation of texture occurs with further acidification. In a completely continuous process, the formation of a good structure in the final product is difficult to obtain.

During incubation, lactose is converted to lactic acid by the lactose dehydrogenase present in the *S. thermophillus* and *L. bulgaricus*. The lactic acid destabilizes the casein micelles by converting the colloidal calcium phosphate complex in the micelles to the soluble form. The resulting gradual loss of calcium from the micelles leads to coagulation of casein at pH 4.6-4.7 and formation of the yogurt gel/coagulum.

The incubation temperature and time both affect the texture of the coagulum formation (ropiness or roughness), the organoleptic properties (aroma production) and also the degree of proteolysis. Excessive proteolysis may result in synerasis and undesirable flavors (Slocum et al., 1988).

## Cooling and Storage

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As soon, as the desired acidity is achieved, the yogurt coagulum is cooled to  $<10^{\circ}$ C. The main purpose of cooling is to reduce the activity of microorganisms and is achieved either by one phase or two phase methods. In the one phase method, the yogurt is cooled directly from incubation temperature to below  $10^{\circ}$ C. In two phase cooling, the temperature is lowered first to  $15-20^{\circ}$ C and finally to below  $10^{\circ}$ C, the latter

being performed in the retail container to avoid any damage to the viscosity. Bulk cooling can take place either in incubation vessels (in-tank cooling) or in tubular or plate heat exchanger, the latter being faster. The rate of cooling determines the continued activity of the microorganisms and is therefore important with reference to the acidity of the end product. For cooling of set yogurt, a cold air tunnel or cabinets is employed. On the other hand, for stirred yogurt, different processes are adopted to attain desired viscosity (Anon, 1977) through the following steps: (i) breaking .he coagulum in incubation tank till homogeneous, (ii) pre-cool to  $24^{\circ}$ C and packaged (iii) final cooling at 5-6°C in the cold store. The manufacture of stirred yogurt needs careful consideration because of the potential danger of serum separation in the final product (Webb and Whitter, 1970).

## Addition of fruit and flavor

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A variety of different ingredients (fruit preserves, canned/frozen fruit, syrup, puree, concentrate, natural or synthetic flavors, colorings etc.) can be incorporated into the yogurt to impart the desired characteristic.

For flavored yogurt, flavoring agents (solids or essence) are added to the yogurt basic mix before incubation. This is not possible in case of fruit or honey yogurt as lactic acid fermentation is affected by the large amount of sugar. In sundae style set yogurt, 15-18% by weight of fruit puree, fruit preserve or syrup is poured on to the bottom of the container followed by the inoculated milk. The containers are sealed and incubated.

For mixing of yogurt with fruit two main types of methods are followed. In batch system, yogurt and fruit are blended together in the tank either manually or mechanically. In continuous systems, this is done by using pumps and in-line static mixers.

## Storage

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The temperature at which the yogurt product is finally stored determines its shelf life. The common storage temperature is around  $5^{\circ}$ C. At this temperature, the quality can be preserved for a period of 3-4 weeks. A common consequence of storage is the over acidity resulting from the metabolic activity of the starter culture. The high acidity will lead to increase in proteolysis and a higher level of free amino acid which may be of precursors for undesirable flavors such as bitterness (Groux, 1976; Viani and Horman, 1976). Production of excess lactic acid during storage also results in a strong undesirable acid taste. Over acidity can also modify the physical characteristics of yogurt and alter the product consistency/viscosity (Driessen, 1988). Another important aspect of storage is the increased lipolytic activity of the starter organisms resulting in hydrolysis of fat and production of more free fatty acids.

## **RHEOLOGY OF YOGURT**

Of the two types, set yogurt may be considered as a visco-elastic solid where elasticity is prominent; whereas, stirred yogurt is essentially a visco-elastic liquid meaning viscosity is predominant. Thus, both contain an elastic component as well as viscous component, but their relative proportion varies considerably from one another.

Majority of the published literature on yogurt relates to set type yogurt (Galesloot, 1958; Webb and Whittier, 1970; Nielson, 1972; Prentice, 1972; Dannenberg and Kessler, 1988a,b; Rohm, 1989). A few studies have also been carried out on stirred yogurt (Martens, 1972; Inagaki, 1986; Nishijima and Inagaki, 1987; Hellinga et al. 1986.), especially on the studies relating to stress decay behavior. Yogurt has been generally recognized as having a non-Newtonian, thixotropic, time-dependent, shear thinning flow behavior with an associated yield stress. It is commonly observed that shear stress increases rapidly at the beginning showing a yield point. This phenomena indicates a strong binding force giving it the character of an elastic solid. In less firm and soft yogurts, the gel structure undergoes only elastic deformation; but at high shear rates exceeding the yield value, gel structure undergoes a breakdown resulting in viscous flow behavior (Dannenberg and Kessler, 1988b).

To evaluate the flow behavior of stirred yogurt, Casson and Herschel-Bulkley model has been more widely employed (Inagaki, 1986). Hellinga et al. (1986) characterized rheological properties in terms of a modified power-law equation of Ostwald-de Waele. They calculated the initial values of viscosity by extrapolating the curves to zero time.

Yogurt has also been characterized as undergoing a stress decay behavior with time of shear showing highly irreversible decrease of viscosity (Nishijima and Inagaki, 1987: Hellinga et al., 1986; Driessen, 1988). The observed diminishing stress corresponds to the decreasing average hydrodynamic diameter of protein particles, which is a function of shearing time and rate of shear for a given sample. Korolczuk and Mahaut (1989) characterized the stress decay behavior of acid type cheese which have a similar structure to stirred yogurt, by using Weltman logarithmic time-logarithmic viscosity model. The magnitude of structural breakdown was quantified by comparison of the viscosity of upward and downward curves and expressed as per cent of shear resistance (Mottar et al., 1989). The area of under the hysteresis loop was used to evaluates the time dependent thinning of gel structure (Dannenberg and Kessler, 1988b). The structural regeneration of yogurt gel is not complete (Ramanauskas and Urbene, 1973; Fokeev, 1973) and is likely to be dependent on the process shear history and other process variables (Steventon et al. 1990; Rohm, 1989). However, according to Bottazzi (1976) such a recovery is complete. Steventon and co-workers (1990) studied the effect of processing and shear on the viscosity of yogurt under the conditions which simulate the manufacturing system.

# Effects of processing variables on rheology

The textural characteristics of the yogurt gel depend on each step in the manufacturing technology discussed earlier, namely standardization, heat treatment, choice of culture, incubation temperature and time, etc.

Higher total solid content in the yogurt has been associated with higher viscosity/firmness of the gel (Puhan, 1988; Wolfschoon-pombo et al., 1983; Becker and Puhan, 1989; Rohm, 1989; Tamime, 1977; Tamime and Deeth, 1980). A small difference (~1%) in the solids could result in significant differences in viscosity of yogurts (Dannenberg and Kessler, 1988b; Becker and Puhan, 1989). Caseinate acts as a stabilizer and increases the viscosity and consistency of the product (Tamime and Robinson, 1985). In the Na-caseinate fortified yogurt, the gel strength is enhanced as compared with skim milk powder and whey protein (Modler et al. 1983; Robinson and Tamime, 1986). Beyond a certain level, whey protein gives softer coagulum in comparison to other dairy protein mixes (Modler and Kalab, 1983; Tratnik and Krsev, 1988). Gassem and Frank (1990) found that milk treated with microbial protinase had significantly higher firmness and viscosity compared to untreated yogurt or yogurt treated with plasmin. Non conventional proteins (peanut, soy and sunflower protein) have been shown to influence the viscosity of yogurt (Schmidt et al., 1980; Bilani et al., 1989).

The viscosity of stirred yogurt increases with increase in homogenization pressure (Puhan, 1988) due to a decrease in the size of fat globules.

The heat treatment appears to have a significant influence on the rheological properties of yogurt gel caused by the denaturation of milk proteins. The yogurt prepared from the vat processed milk has a greater apparent viscosity and firmness because the level of whey protein denaturation is greater compared to the UHT treatment (Puhan, 1988; Schmidt et al., 1985; Parnell-Clunies et al., 1986; Salji et al., 1984). Several additional studies have also demonstrated the influence of heat

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denaturation of whey protein and casein micelles on the viscosity and firmness of yogurt gel (Kalab et al., 1983; Ernstrom, 1974; Mottar et al., 1988; Parnell-Clunies et al., 1986, 1988; Labropoulas et al., 1981, 1984). Recently, Dannenberg and Kessler (1988a,b) and Rohm (1989) correlated denaturation of  $\beta$ -lactoglobulin(LG) and physical properties of gel. Mottar et al., (1989) pointed out that at the initial stage of the heating process, a considerable proportion of both  $\beta$ -LG and  $\alpha$ -lacatalbumin(LA) associate with  $\kappa$ -cassien. But at the later stage, denatured  $\beta$ -LG forms a filament on the surface of the micelle, thereby partially preventing the micelle fusion to take place during the fermentation of the milk; this results in a texture of inferior quality. However at a high heat intensity,  $\alpha$ -LA precipitates on to the micelle thereby filling the gaps between the two consecutive filaments. This produces a smoother texture of yogurt.

Other processing variables which influence the rheological properties is the nature and proportion of the two starter cultures, the incubation temperature, pH during cooling and the cooling rate (Martens, 1972). Some strains of the starter culture produce polysaccharides of high thickening ability (ropiness). This gives rise to the yogurt product of high viscosity and smooth appearance (Dellaglio, 1988; Teggatz and Morris, 1990; Vlahopoulou and Bell, 1990; Robinson, 1988). The gels produced by ropy strains give weaker viscoelastic structure compared to non-ropy strains (Vlahopoulu and Bell, 1990). It has also been noted (Yuguchi et al., 1989) that the rate of fermentation procedure may also affect the viscosity among many other physical properties. This is because the size of the particles of the vogurt curd depends on the rate at which yogurt is fermented. Frozen culture produces a smoother texture because of its slower initial growth. Whereas fast-set cultures produce a grainy structure for the coagulation of protein in large particles (Duame, 1979). It is also reported that any large variations from the optimum ratio of 1:1 of the two microorganisms may produce poor rated yogurt in terms of consistency or flavor (Kroger and Weaver, 1973; Kroger, 1975; Nielsen, 1975).

Several handling operations during the yogurt manufacture also may influence the gel structure of the product. During the commercial preparation, stirred yogurt is subjected to several mechanical treatments between the incubation tank to the packaging machine. Several types of equipments such as agitators, pumps, coolers, pipes, extractors and packaging units are used. In addition, fruit metering/mixing machines are included for fruit/flavored yogurt. During the course of the above treatments, the three dimensional net work of the coagulum is damaged, resulting in smaller casein particles. The stirring step in the preparation of stirred yogurt plays a key role. Excessive stirring will cause a significant reduction in viscosity contrary to the formation of rough structure in case of insufficient stirring (Driessen, 1988). Pumping of stirred yogurt through pipes has a decreasing effect on viscosity (Steenbergen, 1971a). To control the structural damage, the use of either large stroke volume or positive displacement pumps is recommended. The dimensions of pipeline also affect viscosity adversely (Steenbergen, 1971b). Thus the viscosity decreases with increasing pipe length if the velocity and the diameter of the pipe are kept constant. On the other hand, keeping the length of the pipe constant causes minimum structural damage in wider pipe. Nodules, commonly termed as lumpy or granular is considered as one of the texture defects in yogurt. Guirguis et al. (1987) found that nodulation is reduced with increasing speed of stirring leading to the decrease in viscosity.

Use of stabilizers or viscosity modifiers such as starch, pectins and other hydrocolloids to improve viscosity of fruit/flavored or other types of yogurts (UHT/pasteurized, drink etc.) has long been a common practice Of various products used, pectin finds widespread application largely owing to its thickening and gelforming ability. Use of modifiers brings about stabilization of acid milk products (Iversen, 1984). With yogurt drink, addition of pectin helps to keep the casein micelles in suspension (Pilnik, 1990). According to Hooydonk et al. (1982), the best stabilizing action with least sedimentation can be achieved with approximately 0.4% pectin level

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which bring about 70% of fortification. It seems most probable that pectin stabilizes the protein by increasing the viscosity of the serum phase and volume fraction of the dispersed material. Low methoxy pectins are potentially of more useful because of their higher gelling ability with calcium ions and at low soluble solid contents (Kratz et al., 1989). The use of carrageenan to rebuild viscosity, firmness, as well as consistency is also a common practice (Petersen, 1989). Various types of natural starch are also employed as yogurt modifiers and all of them improve the viscosity (Hansen and Armagost, 1990; Chawla and Balachandran, 1986; Vanderpoorten and Martens, 1976). Application of synthetic modifiers such as propylene glycol alginate, carboxymethyl cellulose are also cited in the literature but their use is much limited because their adverse effect on the quality (Foley and Mulcahy, 1989; Shukla et al., 1988). Depending on the time of coagulation and the ratio of starter culture, the addition of 0.2% sodium alginate induces a satisfactory texture at room temperature (Rao et al., 1982).

### Rheological measurements

Since yogurt represents a very delicate gel, its rheological measurements present many difficulties. Such a measurement must be very precise, as it ultimately determines the organoleptic properties. Several fundamental types of viscometers and other related instruments are currently employed for the measurement of consistency, firmness and other rheological parameters.

To measure the firmness of set yogurt, penetrometers are widely used (Tamime and Robinson, 1985). For set type of yogurt, measurement of elastic property in terms of firmness and spreadability are a common practice. These are expressed as force necessary to penetrate the sample to a given depth. Alternatively, it can be assayed in terms of penetration depth achieved in a specified time. Penetrometers measure the force-penetration curves from which such parameters as breaking force and flow coefficient are evaluated. Bostwick and Adams consistometers are employed to evaluate the spreadibility and fluidity of set yogurt.

Measurement of viscosity/consistency of both set and stirred type yogurt is routinly carried out by using viscometers based on coaxial cylinder and cone and plate system under controlled shear rate or shear stress. For stirred yogurt, the rheological properties are almost solely expressed in terms of viscosity since it possesses higher viscous properties than elastic properties. Rotational viscometers (Vlahopoulu and Bell, 1990, Kynast, 1972; Rasic and Kurmann, 1978) and Posthumus funnel (Posthumus, 1954) have been largely used in recent years for the measurement of viscosity of yogurt. Several parameters including apparent viscosity, yield stress, time dependency and shear thinning can be assessed with rotational instrument. A major limitation of Posthumus funnel is that a range of shear stress is applied to the sample. During the measurement, shear rates vary with time and location. Hellinga et al. (1986) used a mathematical model to quantify them.

To obtain the dynamic measure of the gel structure, an oscillatory viscometer (cone and plate system) is used (Steventon et al. 1990; Vlahopoulou and Bell, 1990; Hellinga et al., 1986; Noel, 1988). Such an instrument provides more information about structure of yogurt gel as well as viscous and elastic properties.

All the methods described above are either fully or partly destructive in nature. Recently, some methods have been reported for measuring rheological properties of yogurt gel in a non-destructive manner (Jearcocke et al. 1988; Yuguchi et al. 1989). One of these methods (Jearcocke et al. 1988) is based on the measurement of apparent moment of inertia and angular velocity under the influence of a standard torque. It has been shown that the viscosity and amount of inertia bears a linear relationship to one another.

#### **CHAPTER IV**

### TIME-INDEPENDENT RHEOLOGY OF STIRRED YOGURT

## ABSTRACT

Rheological characteristics of two commercial brands of stirred yogurt were evaluated using a Haake Rotovisco Model RV 20 with an M5-Osc measuring head and MV-1 rotor assembly from measured shear stress values under a programmed 3-cycle upand down-shear rate at 100 s<sup>-1</sup>/min from 0 to 500 s<sup>-1</sup> (5 min). The upward shear-rate flow behavior of the yogurt samples could be described by a Herschel-Bulkley model while the downward shear-rate curves were essentially linear. Both upward and downward shear rate curves demonstrated progressive structural degradation with repeated shearing. The dependency of rheological parameters on temperature in the range 10-25<sup>o</sup>C followed both Arrhenius and Turian models.

# INTRODUCTION

Yogurt, a fermented dairy product, has achieved special prominence and economic importance in recent years due to its positive nutritional attributes. A variety of new flavored yogurt-based products are appearing on the market. Yogurt is mainly available in two forms: set-type and stirred-type, both in plain or flavored format. The characteristic gel-structure of the set-type of yogurts is allowed to form in containers during the fermentation/incubation phase while in the stirred-type the gel structure formed during bulk incubation is normally destroyed by agitation during cooling to give the product a smooth and semi-viscous flow behavior (Tamime and Robinson, 1985). Several studies have evaluated the textural characteristics of set-type yogurts (Dannenberg and Kessler, 1988; Galesloot, 1958; Martens, 1972, Nielson, 1972; Prentice, 1972; Webb and Whittier, 1970), but there has been no detailed published study on stirred yogurt rheology (Hellinga et al., 1986; Inagaki, 1986; Nishijima and Inagaki, 1987). Majority of studies on stirred yogurt are limited to evaluation of the consistency, apparent viscosity or firmness as influenced by its chemical composition: especially fat, protein and carbohydrate (lactose) content (Bianchi-Salvadori and Zambrini, 1988; Driessen, 1988; Galesloot, 1958; Martens, 1972; Nielsen, 1972; Prentice, 1968). Becker and Puhan (1989) reported that small differences (~1%) in protein and nonfat solids could result in significant differences in viscosity of yogurts. Yogurts exhibit a complex, shear-thinning, time-dependent flow behavior, and therefore yogurt rheology is of importance with reference to their processing, handling, process design, product development and quality control aspects.

The objectives of this research were (i) to study the time-independent dynamic flow behavior of stirred yogurts, i.e., to evaluate the nature of relationship between shear stress and shear rate, and (ii) to study the effect of temperature on the evaluated rheological parameters.

#### MATERIALS AND METHODS

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Several samples of commercially available plain stirred yogurts produced by two different manufacturers (Agropur Co-operative Agro-Alimentaire, Granby, PQ, and Delisle Food Ltd., Boucherville, PQ) were obtained from a local supermarket. In Quebec, the retail containers arrive at supermarkets with a shelf-life of about 4-5 weeks (identified by their expiration dates on the containers). All samples were obtained 3-4 week before their expiration dates and were stored at  $2^{\circ}$ C until use (maximum one week). Prior to testing they were gently mixed by hand using a spatula to get a uniform sample and handled carefully to minimize any structural breakdown. They were held in the sample cup for temperature equilibration (about 20 min) before measurements were made. Samples from the two commercial brands were compared at  $10^{\circ}$ C, while additional tests were performed with only one brand to evaluate the influence of temperature.

Rheological measurements were made using a Haake RV20 rotational viscometer (Haake Mess-Technik GmbH u. Co., Karlsruhe, Federal Rep. Germany) equipped with an M5 OSC measuring head and MV1 rotor (20.04 mm OD; 60 mm height) in a concentric cylindrical cup (21.00 mm ID) assembly interfaced to a microcomputer for control and data acquisition. The rotor and cup assembly was jacketed to maintain sample temperatures and a controlled temperature water bath/circulator was used to pass water through the jacket. All samples were maintained at the desired temperature before testing and all experiments were triplicated each time using samples from different containers.

Test samples of yogurts were subjected to a simple harmonic (dynamic) shear at a programmed rate of 100 s<sup>-1</sup>/min linearly increasing from 0 to 500 s<sup>-1</sup> in 5 min and subsequently decreasing from 500 to 0 s<sup>-1</sup> in another 5 min. This cycle of upward and downward shear rates was repeated two more times with the same test sample to study the structural breakdown resulting from successive up and down shear-cycles. Temperature effects on flow curves were evaluated for one of the Brands by subjecting the samples to dynamic shear as described above while maintaining the samples at the various temperatures ( $10^{\circ}$ C,  $15^{\circ}$ C,  $20^{\circ}$ C and  $25^{\circ}$ C). With the other Brand, experiments were carried out only at  $10^{\circ}$ C. All experiments were replicated three times.

The flow curves were evaluated by one of the following models (previously detailed in Chapter II):

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1. Power law model:

$$\sigma = m \dot{\gamma}^n \tag{4-1}$$

2. Casson model:

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$$\sigma_{\rm c}^{1/2} = \sigma_{\rm oc}^{1/2} + \eta_{\rm c} \dot{\gamma}^{1/2} \qquad (4-2)$$

3. Herschel-Bulkley model:

$$\sigma = \sigma_0 + m \dot{\gamma}^n \qquad (4-3)$$

4. Linear model (only downward curves):

σ

$$= \sigma_0 + \eta_a \dot{\gamma} \qquad (4-4)$$

The Arrhenius equation was used to study the effect of temperature on rheological properties:

$$\eta_a = F \cdot \exp(E_a/RT) \tag{4-5}$$

The activation energy of flow ( $E_a$  at constant shear-rate) was evaluated at each of the selected shear-rates for both up- and down-curves from the regression of natural logarithm of apparent viscosity vs. reciprocal of the absolute temperature.

The flow-behavior index and consistency coefficients of the up-curves were also related to temperature by Turian (1964) approach:

$$\log (m) = A - B (T)$$
 (4-6)

$$n = a + b(T)$$
 (4-7)

For the linear down-curves, the resulting yield stress and viscosity were related to temperature by a similar approach employing Turian model:

$$\sigma_0 = A - B(T) \tag{4-8}$$

$$\eta = a + b (T) \tag{4-9}$$

Chemical composition (fat, protein and lactose) of yogurt samples from each container was evaluated in triplicate by the rapid IR spectrophotometric method of van de Voort (1980) after adjusting the pH to 6.5 using 1N NaOH. Moisture content of each replicate was determined by drying in a vacuum oven at  $70^{\circ}$ C for 24 hr.

## **RESULTS AND DISCUSSION**

The chemical composition of yogurt samples from the two commercial brands employed in the study indicated only marginal differences between them (Table 1) with Brand II containing slightly higher fat and protein than Brand I. The compositional information printed on containers confirmed these findings and also indicated that the samples contained only milk solids and bacterial culture without any added stabilizer.

Table 1. Composition of the two commercial yogurts employed in the study.

Yogurt	Moisture (%)	Fat (%)	Protein (%)	Lactose (%)
Brand I	81.8 <u>+</u> 0.4	1.9 <u>+</u> 0.01	6.6 <u>±</u> 0.01	6.3 <u>+</u> 0.02
Brand II	81.6 <u>+</u> 1.5	2.1 <u>+</u> 0.01	6.7 <u>+</u> 0.02	6.4 <u>+</u> 0.03

# Characterization of flow curves

Typical flow curves for the two commercial brands of stirred yogurts under a dynamic 3-cycle shearing sequence are shown in Figure 6. The flow patterns are qualitatively similar but have some quantitative differences. The overall shear stress encompassing the test range of shear rates was about 30% higher for the Brand II samples than for Brand I indicating a stronger structural rigidity with the former. The



Figure 6. Shear stress - shear rate relationships (flow curves) for two commercial yogurts during a programmed 3-cycle (10 min each) up and down shearing between shear rates of 0 and 500 s<sup>-1</sup>.

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shape of the flow curves indicate the presence of a yield stress, shear thinning (thixotropic) nature of the test samples in consistent with findings by Inagaki (1986). The figure also demonstrates that a major change in the rheological behavior appears after the first shearing cycle. This is consistent with the characteristic flow behavior of a previously unsheared virgin sample for curve 1 while the other curves represent the flow behavior of shear degraded samples. Similar results were reported by Halmos and Tiu (1981) for several meat and yeast extracts and by Paredes et al. (1988) for salad dressings.

The area enclosed between the up- and down-curves (hysteresis loop) is a measure of the extent of structural breakdown during the shearing cycle. The hysteresis loop associated with the first cycle is relatively larger than that associated with the second or third cycle indicating that the 1st shearing cycle caused the major degradation of sample structure. Hysteresis loop-areas associated with the 2nd and 3rd shearing cycles were also small and comparable, indicating similar structural changes within these cycles. However, the three successive up-curves were clearly separated with one lying below the other (Figure 6) indicating a continual breakdown of structure with each shearing cycle. However, there is some evidence that the structural loss in the upward shearing process may be partially recovering during the downward shearing as indicated by the overlapping of 2nd and 3rd up-curves with their preceding down-curves (Figure 6).

Additional tests were carried out to test the recovery of the thixotropic structural breakdown. The sample after the 3-cycle upward and downward continuous shearing was allowed to rest in the cup for an hour and then the test was repeated. Figure 7 compares rheograms of the virgin sample with that of the sheared sample following relaxation. The results indicate that the apparent thixotropic structural breakdown is almost irreversible. The first up-ward curve of the shear-relaxed sample is nowhere near the first up-curve of the previously unsheared sample. In fact, the set of 3 upward curves following relaxation were below the three upward curves of the first run sample. Each shearing cycle resulted in a some nonrecoverable structure loss. Similar results were observed with the down-ward flow curves (Figure 7). The progressive thixotropic breakdown could be characterized by the steady lowering of viscosity (slope of the nearly linear downward curves) through the six shearing cycles (viscosity values given in Pa.s): 0.10 (down-1), 0.085 (down-2), 0.078 (down-3, first run), 0.073 (down-1), 0.069 (down-2), 0.066 (down-3, second run after relaxation).

## Modelling of the flow curves

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The Casson model gives a relatively poor fit for the experimental data, especially for first up-curves with  $\mathbb{R}^2$  values ranging from 0.73 to 0.85. The Herschel-Bulkley model required data on yield stress which sometimes is obtained from the Casson model (Tung, 1978). This procedure however resulted in a poor fit for Herschel-Bulkley model. When yield stress values were from linear regression of shear-stress vs. shearrate data at low shear rates, the Herschel-Bulkley model resulted in a better fit of data with  $\mathbb{R}^2$  values generally above 0.95 (Table 2). Typical Herschel-Bulkley plots for the three upward curves are shown in Figure 8 using linear co-ordinates (the fitted line follows the log-log format of Herschel-Bulkley model). For the 2nd and 3rd up-curves, the results from Casson and Herschel-Bulkley models were generally comparable. The latter model was chosen in the present studies so that a single model could be used for all three up-curves thereby providing parameters for comparing different test samples.

The downward flow curves could be described by a simple linear model showing Newtonian flow-characteristics (Table 3); typical linear plots for the three successive down curves are also shown in Figure 8. Small deviations from linearity were observed at the lower and higher ends of the shear rate span ( $<50 \text{ s}^{-1}$  and  $>450 \text{ s}^{-1}$ ); however, these end effects were not considered significant since the associated R<sup>2</sup> values were generally very high (>0.99; Table 2).



Figure 7. Flow curves for Brand I stirred yogurt during a first run 3-cycle up and down shearing and a similar rerun after one hour of relaxation.

	B	rand I				Brand	l II	
	σο	m	n	R <sup>2</sup>	σο	m	n	R <sup>2</sup>
	(Pa)				(Pa)			
#1	11.2	13.7	0.212	0.97	24.7	28.8	0.129	0.93
#2	9.4	1.46	0.540	0.99	17.1	5.19	0.373	1.00
#3	7.6	1.36	0.538	0.99	13.7	3.62	0.418	1.00

Table 2. Rheological constants for the three successive up-curves for two brands of yogurt using Herschel-Bulkley model.

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Table 3. Rheological constants from three successive down-curves for two commercial brand yogurts using a linear model.

		Brand I			Brand II	
	σ <sub>0</sub> (Pa)	η <sub>a</sub> (Pa.s)	R <sup>2</sup>	σ <sub>o</sub> (Pa)	η <sub>a</sub> (Pa.s)	R <sup>2</sup>
#1	15.3	0.0887	0.99	21.3	0.109	0.99
#2	13.8	0.0747	1.00	26.0	0.0867	0.99
#3	12.3	0.0687	1.00	22.8	0.0797	0.99



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Figure 8. Typical Herschel-Bulkley (for upward curves) and linear (for downward)

plots for Brand I stirred yogurt during a 3-cycle up and down shearing.

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The flow behavior index and consistency coefficient were used to compare the rheological characteristics of the two commercial samples under repeated shearing (Tables 2 & 3). Compared to Brand II, Brand I samples had a higher flow behavior index (n), a lower yield stress and a lower consistency coefficient (m), all indicative of a comparatively thicker structural rigidity with the former. It is also clear from Table 2 that m decreases and n increases with repeated shearing. Changes in both m and n were more pronounced between the 1st and 2nd cycle than between 2nd and 3rd, indicating that most structural breakdown occurs in the 1st shearing cycle. Every sample possessed yield stress (Tables 2 & 3) even during the third successive shearcycle although the values decreased gradually. Similar results were observed with downward curves (Table 3). During the downward shearing, the yield stress decreased almost linearly from an average value of 15.3 Pa to 12.3 Pa for the Brand I samples and 31.4 Pa to 22.8 Pa for Brand II. Yield stress appears to be an inherent property of this product even though the test samples have shear-thinning characteristics. The downward viscosity changes through successive shearing cycles were almost linear. The viscosity of the Brand II yogurt was higher than that of the Brand I consistent with the previous discussion.

### Effect of temperature on flow behavior

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Table 4 shows the Herschel-Bulkley rheological constants of the upward curves for Brand I samples at four temperatures and Table 5 shows the linear model constants (downward flow) of the same brand yogurt for the same four temperatures. Both the Turian and Arrhenius approaches were found to be satisfactory to describe the temperature influence on rheological parameters. Yield stress, consistency coefficient and apparent viscosity decreased with an increase in temperature while the flow behavior index showed an increasing trend with temperature. Table 4.Rheological constants of Brand I yogurt (three up curves) at differenttemperatures using the Herschel-Bulkley model.

No.

UP CURVE 1					UP CUI	CURVE 2			UP CURVE 3			
 Tem	ρ σ <sub>0</sub>	m	n	R <sup>2</sup>	σο	m	n	R <sup>2</sup>		σο	m n	R <sup>2</sup>
( <sup>0</sup> C)	(Pa)				(F	Pa)			(	Pa)		
10	11.9	14.6	0.207	0.98	8.04	1.82	0.506	0.98	6.94	1.43	0.531	0.99
15	7.65	9.63	0.265	0.98	8.44	1.49	0.513	0.9 <del>9</del>	7.16	1.21	0.532	0.99
20	4.92	5.56	0.335	0.98	7.47	0.98	0.562	0.99	6.34	0.86	0.568	0.99
25	3.53	3.01	0.400	0.96	5.96	0.74	0.577	0.98	5.45	0.61	0.596	0.99

Table 5. Rheological constants of Brand I yogurt (three downcurves)

at different temperatu	ires using	a linea	r model.
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	DOV	WN CUR	Æ 1	DOWN	CURVE	2 DO	WN CUR	VE 3	<u> </u>
Tem ( <sup>o</sup> C)	pσ <sub>o</sub> (Pa)	η <sub>a</sub> (Pa.s)	R <sup>2</sup>	σ <sub>0</sub> (Pa)	η <sub>a</sub> (Pa.s)	R <sup>2</sup> σ <sub>0</sub>	η <sub>a</sub> (Pa)	R <sup>2</sup> (Pa.s)	
10	14.8	0.090	0.99	13.4	0.074	1.00	11.9	0.068	1.00
15	14.5	0.078	0.99	12.9	0.065	1.00	11.4	0.060	1.00
20	12.1	0.0 <b>69</b>	1.00	10.5	0.058	1.00	9.87	0.053	1.00
25	9.67	0. <b>057</b>	1.00	8.83	0.049	1.00	8.27	0.045	1.00

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Using the Turian approach (equations 6 and 7) for characterizing the temperature dependence of Herschel-Bulkley parameters, it was possible to incorporate the influence of temperature on the shear-stress vs. shear-rate relationship in to a single model (combining equations 3, 6 and 7). Typical relationship for the first up-curve is:

$$\log (\sigma - \sigma_0) = [1.64 - 0.0459 (T)] + [0.141 + 0.0130 (T)] \log (\dot{\gamma})$$
(4-10)

A similar relationship for the downward curve by combining equations 4, 8 and 9 is given below:

$$\sigma = [19.0 - 0.356 (T)] + [0.112 + 0.0022 (T)] (\dot{\gamma})$$
(4-11)

In order to use the Arrhenius approach to describe the effect of temperature on the flow behavior of stirred yogurt, apparent viscosities were evaluated at selected shear rates of 100, 200, 300 and 400 s<sup>-1</sup> and regressed against the reciprocal absolute temperature. The associated activation energies ( $E_a$ ) of flow are summarized in Table 6 which showed that the  $E_a$  values gradually decreased as the shear-rate increased in the first up-curve (virgin curve). The  $E_a$  values at various shear rates the second and third up-curves and the three down-curves varied only slightly. The range of calculated values for  $E_a$  was 4.2 to 5.2 (5.8 to 8.95 kcal/mole with the first up-curve).

## CONCLUSIONS

Stirred yogurt rheology can be described by Herschel-Bulkley and linear models during successive up-ward and down-ward shearing sequence. Temperature dependence of rheological parameters follow Arrhenius and Turian models. Stirred yogurt characteristically exhibits partially reversible thixotropic flow behavior with a recurring yield stress. Characterization of stirred yogurt rheology is the first step in our overall objective of developing scientific procedures for fabricating the desired consistency in flavored yogurt-based beverages by blending the stirred yogurt with hydrocolloids and flavor concentrates.

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	UP C	URVE 1	UP C	URVE 2	UP C	URVE 3	
Shear rate (s <sup>-1</sup> )	Ea	R <sup>2</sup>	Ea	R <sup>2</sup>	Ea	R <sup>2</sup>	
100	9.0	0.99	5.1	0.98	5.1	0.98	
200	7.7	0.99	5.2	0.97	5.0	0.98	
300	6.5	0.99	5.0	0.97	4.9	0.99	
400	5.8	0.98	4.8	0.98	4.7	0.99	
••••••••••••••••••••••••••••••••••••••	DOWN CURVE 1		DOW	DOWN CURVE 2		DOWN CURVE 3	
Shear rate (s <sup>-1</sup> )	Ea	R <sup>2</sup>	Ea	R <sup>2</sup>	Ea	R <sup>2</sup>	
100	5.2	0.95	4.6	0.93	4.3	0.95	
200	5.0	0.96	4.6	0.96	4.3	0.98	
300	4.9	0.96	4.6	0.98	4.3	0.98	
400	4.9	0.97	4.5	0.98	4.4	0.99	

Table 6. Activation energy (kcal/mole) of flow from dynamic shear experiments.

### **CHAPTER V**

### TIME DEPENDENT RHEOLOGY OF STIRRED YOGURT

## ABSTRACT

Stress decay behavior of two stirred yogurt samples was evaluated at various shear rates (100-500 s<sup>-1</sup>) and selected temperatures (10-25<sup>o</sup>C) using a Haake Rotational viscometer. Results showed that time-dependent shear thinning was evident under all testing conditions and an equilibrium shear stress was not reached even after 60 min of continuous shearing. Weltman's logarithmic time model accurately described the stress decay behavior at each shearing condition and the temperature influence on Weltman parameters showed a linear trend. The temperature influence could also be evaluated using the Arrhenius model and resulting activation energies ranged from 4.9 to 14.6 kcal/mole.

#### INTRODUCTION

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As pointed out in the previous chapter, there has been very little published study on stirred yogurt rheology despite the fact that these products have attained significant commercial importance in recent years. Most published information deal with the evaluation of the consistency, apparent viscosity or firmness as influenced by its chemical composition. The shear thinning behavior of rheology of stirred yogurt was detailed earlier. Yogurt has also been known to exibit time dependent flow behavior (Tamime and Robinson, 1985; Hellinga et al., 1986) which is an important factor to characterize the rheological properties of the final product.

The objectives of this research was to evaluate a possible methodical approach for the study of stress decay behavior of stirred yogurt as a function of steady shear rate, time and temperature. Such an approach will be useful in assessing the structural damage due to product handling as well as structural stability of formulated yogurt based products.

## MATERIALS AND METHODS

Time dependency of the rheological characteristics were evaluated using an Haake RV 20 rotational viscometer (detailed in Chapter IV) by subjecting test samples to a 10 min (or 60 min in some runs) shear at each of the following fixed shear rates: 10, 100, 200, 300, 400 and 500 s<sup>-1</sup>. A fresh sample was used for each measurement. Temperature effects on the time dependent behavior were evaluated by subjecting test samples to steady shear at four temperatures: 10, 15, 20 and 25°C. All samples were maintained at the desired temperature before testing and all experiments were triplicated each time using samples from different containers.

The stress decay behavior of test samples was evaluated using a modified logarithmic-time model suggested by Weltman (1943):

$$\sigma = A - B \left[ \log \left( t/t_m \right) \right]; \ t \ge t_m \tag{5-1}$$

where:

 $\sigma = \text{Shear stress (Pa)}$  t = Time (s)  $t_{m} = \text{Time at maximum observed shear stress (12 s in the present study)}$   $A = \text{Intercept when log (t/t_{m}) = 0 or t = t_{m} (Pa)}$  B = Slope (time coefficient of thixotropic breakdown, Pa)

The constants A and B were obtained from regression of  $\sigma$  vs log (t). The nature of relationship of these constants, A and B, with shear rate were explored by regression techniques (both linear and logarithmic).

The Arrhenius equation (detailed elsewhere) was also used to study the effect of temperature on rheological constants and to evaluate the activation energy of viscosity decay:

$$\eta = F e^{(Ea/RT)}$$
(5-2)

The viscosity value ( $\eta$ ) for the Arrhenius equation was obtained as a ratio of A value to the rate of shear ( $\gamma$ ):  $\eta = A/\dot{\gamma}$ , thus  $\eta$  represented the apparent viscosity of the sample following shearing for t = t<sub>m</sub> (12 s, in these studies). In a second set of analysis, the time coefficient, B, which indicates the magnitude of stress decay over a ten fold change in the shearing time was also used in the viscosity computation:  $\eta = B/\dot{\gamma}$ , thus  $\eta$  in this situation represented a change in apparent viscosity (due to structural damage) through one log-cycle of shear time (between 12 and 120 s, for example). The activation energies (E<sub>a</sub>) were evaluated from the regression of natural logarithm of  $\eta$  vs. reciprocal of the absolute temperature.

Weltman parameters, A and B, obtained at each shear rate were also related to temperature by the Turian (1964) approach:

$$A = A_1 + A_2$$
 (T) (5-3)

$$B = B_1 + B_2 (T)$$
(5-4)

where  $A_1, A_2, B_1$  and  $B_2$  were parameters obtained from linear regression of A and B vs temperature.

# Stress decay comparison of the two commercial yogurts

Typical stress decay curves for the two commercial brand stirred yogurts during a 10 min steady shear at selected shear rates are compared in Figure 9 which generally indicate that the two samples exhibit somewhat similar flow patterns. There were small differences in their magnitudes: the shear stress associated with Brand II was slightly higher than that of Brand I at the high shear rates (400 and 500 s<sup>-1</sup>) while these differences were small at the lower shear rates. The 10 min shearing period employed in these studies was insufficient to achieve an equilibrium stress condition in any test run. Stress decay behaviors at different shear rates were similar, and the differences in the stress values initially observed with reference to various shear rates persisted throughout the 10 min shear rate of 10 s<sup>-1</sup>, shown with Brand I, the magnitude of stress decay was relatively small. In the hand mixing of samples used to get a uniform sample prior to testing in our studies, the shearing could be expected to be much smaller. Hence, the extent of structure breakdown of samples due the brief hand mixing was considered negligible.

## Modelling of the flow curves

The stress decay curves were next analyzed using established mathematical models: Weltman (1943), Hahn et al. (1959) and Tiu and Boger (1974). The two latter models required data on the equilibrium shear stress ( $\sigma_e$ ) following long time shearing. Most reported literature data indicate that equilibrium conditions are generally achieved within the first 30 min of shearing (Weltman, 1943; Tiu and Boger, 1974; Massaguer-



Figure 9. Stress decay curves of two commercial stirred yogurts over a 10 min.

shear at selected shear rates.

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Roig et al., 1984; Ford and Steffe, 1986, Rao, 1977; Tung et al., 1970). However, our results demonstrated that even after 60 min shearing at various shear rates between 100 and 500 s<sup>-1</sup>, test samples of stirred yogurt continued to show structural decay (Figure 10). Hence, in our studies, we chose to use the logarithmic-time model (Weltman, 1943) to describe the time dependency of shear stress under constant shear. Figure 10 illustrates the goodness of fit ( $R^2 = 0.97$ -1.0) of this model to experimental data (shown as points) up to 60 min under each of the three shear rates (lines show the fitted log-time regression models).

Weitman model regression parameters, A and B (Table 7), were used to compare the stress decay behavior of the two commercial samples. For both samples, the Weitman model accurately described the stress decay behavior ( $\mathbb{R}^2 > 0.98$ ), indicating similarity in their flow behavior. Up to a shear rate of 300 s<sup>-1</sup>, the A values for both brands were comparable, while at the two higher shear rates (400 and 500 s<sup>-1</sup>), Brand II had a higher intercept coefficient (A value) than the Brand I. These results suggest a slightly higher start up viscosity with Brand II, especially at the higher shear rates. Since a zero-time stress or viscosity is non-existent in the logarithmic time model (s reaches infinity as time tends to zero), the intercept coefficient representing the stress at the time, t = i<sub>m</sub>, when it reached a maximum value was used in the comparison (12 s in our measurements). This time, t<sub>m</sub>, is usually a function of the instrument's data acquisition/measuring system and as well as scan time.

The manufacturer (Haake) supplied data acquisition software permitted gathering 50 data pairs in any given shear/time scan, hence  $t_m$  actually represented the second data point in our 10 min test runs. The first data point with shear stress about half of this maximum was not included in the analysis. Zero-time shear stress  $(\sigma_0)$  for each condition was separately obtained by a linear graphical procedure as outlined by Massaguer-Roig et al. (1984) to compare the results of this study with dynamic shear experiments described previously in Chapter IV. Weltman A values



Figure 10. Stress decay curves of Brand I stirred yogurt over a 60-min shear at selected shear rates.

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Shear rate	Initial stress	A value	B value	R <sup>2</sup>
(s <sup>-1</sup> )	(Pa)	(Pa)	(Pa)	
Brand I				
100	55 ± 6.5	53 ± 5.6	$11.6 \pm 1.6$	0.98
200	$70 \pm 2.0$	$65 \pm 2.0$	$15.6 \pm 0.5$	0.99
300	<b>77</b> $\pm 4.1$	$70 \pm 1.9$	$17.6 \pm 1.3$	0.99
400	$89 \pm 3.6$	80 ± 3.4	$21.8 \pm 1.2$	0.99
500	$100 \pm 6.1$	$90 \pm 5.9$	$24.4 \pm 1.5$	0.99
Brand II				
100	47 ± 4.7	46 ± 3.7	8.3 ±0.5	0.98
200	$72 \pm 4.1$	67 ± 3.9	$15.7 \pm 2.1$	1.00
300	$80 \pm 7.6$	74 ± 9.3	$18.4 \pm 2.9$	1.00
400	99 ± 9.6	90 ± 9.9	$23.0 \pm 2.6$	1.00
500	$125 \pm 9.2$	115 <u>+</u> 8.4	$32.7 \pm 4.2$	1.00

Table 7: Weltman model regression parameters for commercial stirred yogurts at 10°C.

showed a highly correlated linear relationship with these zero-time shear stress values (hereafter referred to as initial stress):

Brand I: $A = 0.87 \sigma_0 + 7.6$ ,  $R^2 = 0.99$ Brand II: $A = 0.89 \sigma_0 + 3.2$ ,  $R^2 = 0.99$ 

This should be expected since both Weltman A (stress at t = 12 s) and  $\sigma_0$  (at t = 0 s) were measures of stress at specific times. The time coefficient of stress decay (Weltman B value) was generally comparable between the two brands up to a shear rate of 400 s<sup>-1</sup>, while at 500 s<sup>-1</sup> Brand II had a higher B value than Brand I. These differences in A and B values were statistically non-significant (p>0.05) except at the highest shear rate
$(500^{-1})$ . The small compositional differences between these two brand yogurts support these observations. The differences in Weltman parameters between the two brands from two different manufacturers were therefore considered to be characteristic of sample to sample variation and for the purpose of evaluating the stress decay, the two brands were assumed to be behaving similarly and representing similar product types.

All the above parameters, the initial stress ( $\sigma_0$ ) as well as A and B values were found to be linearly related to the shear rate,  $\dot{\gamma}$  (Figure 11). Our earlier studies under dynamic shear testing conditions indicated that the flow behavior of stirred yogurt was well described by a Herschel-Bulkley model (Chapter IV) which relates the logarithm of shear stress to logarithm of shear rate  $[\log(\sigma_0 - \sigma) = \log m + n \log (\dot{\gamma})]$ . Characteristically, since Weltman parameters represent different measures of shear stress, one would expect such a logarithmic relationship behavior between them and the shear rate In the present studies, with only five shear rates employed for testing in the range of 100 to 500 s<sup>-1</sup>, the logarithmic model offered no significant advantage over the linear model, all yielding high R<sup>2</sup> values. For simplicity, the linear models were chosen to characterize variations in A and B as function of  $\dot{\gamma}$ .

Brand I:

Α	2	44.5 + 0.090 γ <mark>΄</mark> ,	$R^2 = 0.99$
в	=	8.68 + 0.032 γ <mark>΄</mark> ,	$R^2 = 0.99$
σο	=	45.1 + 0.110 γ <mark>΄</mark> ,	$R^2 = 0.99$

Brand II:

A =  $29.4 + 0.16 \dot{\gamma}$ ,  $R^2 = 0.97$ B =  $2.80 + 0.056 \dot{\gamma}$ ,  $R^2 = 0.96$  $\sigma_0$  =  $29.3 + 0.18 \dot{\gamma}$ ,  $R^2 = 0.94$ 



Figure 11. Stress decay parameters as a function of shear rate for two commercial stirred yogurts.

# Effect of temperature on flow behavior

Temperature sensitivity of the rheological parameters (Table 8) of yogurt samples from Brand I were analyzed by the Turian model and the Arrhenius approach; both were found to be satisfactory. An increase in temperature decreased both A and B values, and similar results were observed when these A and B values were converted to their viscosity counterparts ( $A/\dot{\gamma}$  and  $B/\dot{\gamma}$ ) indicating that the apparent viscosity of test samples decreased as the temperature increased.

High  $R^2$  values (>0.97) were obtained for the Turian approach linearly relating A and B values to temperature at various shear rates. Since both these parameters were also linearly related to shear rate as discussed earlier, the combined influence of shear rate and temperature on A as well as B was evaluated using a multiple regression technique. The resulting equations showed significantly high correlations for both A and B as functions of shear rate and temperature (T, expressed in <sup>o</sup>C):

A = 
$$64.2 + 0.089 \dot{\gamma} - 1.98$$
 T R<sup>2</sup> = 0.98  
B =  $16.2 + 0.030 \dot{\gamma} - 0.67$  T R<sup>2</sup> = 0.98

The three-dimensional plots of A and B values as functions of temperature and shear rate are shown in Figures 12 and 13. With this approach, it will be possible to incorporate the influence of temperature on the stress-time relationship in to a single model. Abbreviating the coefficients obtained above in a general manner as  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_1$ ,  $B_2$ , and  $B_3$ , the combined equation can be written as shown below:

$$\sigma = A_1 + A_2 (g) - A_3 (T) - (B_1 + B_2(\dot{\gamma}) - B_3(T)) \log (t/t_m); \quad t \ge t_m$$
(5-5)

Temp	Parameter					
( <sup>0</sup> C)		100	200	300	400	500
10	A (Pa) Mean	48.9	63.6 1 <b>7</b>	69.8 1 1	82.4 2 5	87.2 0.7
	B (Pa) Mean	10.6	15.7 0.6	17.5 1.6	22.6 0.9	24.3 0.4
	R <sup>2</sup>	0.98	0.99	0.99	0.99	0.99
15	A (Pa) Mean s.d	44.4 0.4	54.2 1.5	63.7 1.3	74.5 3.7	78.6 1.7
	B (Pa) Mean s.d	8.55 0.3	11. <b>7</b> 0.6	15.1 0.3	18.9 1.3	20.7 0.8
	R <sup>2</sup>	0.97	0.99	1.00	1.00	1.00
20	A (Pa) Mean s.d	31.0 0.8	43.0 2.4	54.7 0.9	61.3 0.5	63.6 1.8
	B (Pa) Mean s.d	4.90 0.3	8.32 0.6	12.2 0.6	14.5 0.6	15.7 0.2
	R <sup>2</sup>	0.95	0.99	1.00	1.00	1.00
25	A (Pa) Mean s.d	22.2 0.6	33.3 2.1	42.4 3.0	52.3 5.5	57.6 2.3
	B (Pa) Mean s.d	2.96 0.2	5.20 0.3	7.58 0.3	11.1 1.6	12.8 0.4
	R <sup>2</sup>	0.92	1.00	1.00	1.00	1.00

 Table 8. Stress Decay constants for stirred yogurt (Brand I) at different shear rates and

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Figure 12. Weltman A values as a function of temperature and shear rate for

Brand I stirred yogurt.



Figure 13. Weltman B values as a function of temperature and shear rate for Brand I stirred yogurt.

In order to use the Arrhenius approach to describe the effect of temperature on the flow behavior of stirred yogurt, apparent viscosities were evaluated as  $A/\gamma$  ratios at the different shear rates of 100, 200, 300, 400 and 500 s<sup>-1</sup>, and regressed against the reciprocal absolute temperature. A typical Arrhenius plot is illustrated in Figure 14 which shows the effect of temperature and shear rate on the apparent viscosity. The associated activation energies (Ea) of stress/viscosity decay are summarized in Table 8 which showed that the E<sub>a</sub> values gradually decreased as the shear-rate increased. The range of calculated values for  $E_a$  using the A/ $\dot{\gamma}$  approach was 4.9 to 9.1 kcal/mole. These values were similar to the activation energies reported elsewhere (Chapter IV) for the same yogurt brand while obtaining shear stress-shear rate data under a 3-cycle programmed upward and downward ramp shearing sequence (5.8 to 9.0 kcal/mole with the first up-curve). Activation energies calculated using the initial viscosity values  $(\sigma_0/\dot{\gamma})$ showed results similar to those calculated using  $A/\dot{\gamma}$  (5.5 - 9.3 kcal/mole). Since both A and  $\sigma_0$  values are estimates of shear stress prior to structure decay, the activation energy from A/ $\dot{\gamma}$  and  $\sigma_0/\dot{\gamma}$  can be expected to match activation energies of flow found in the earlier studies. These  $E_a$  values thus show the temperature sensitivity of the inherent sample viscosity.

Activation energies were also calculated using the time coefficient of apparent viscosity (B/ $\dot{\gamma}$  values) which showed a trend similar to that observed while using the A/ $\dot{\gamma}$  values (Table 9); the magnitudes were, however, much larger (7.4 to 14.6 kcal/mole). B/ $\gamma$  values, unlike A/ $\dot{\gamma}$ , are a measure of viscosity decay over a given time and therefore represent a stability parameter. The activation energies found from the B/ $\dot{\gamma}$  values, therefore, represent temperature sensitivity of sample viscosity when subjected to a constant shear. Increasing temperature can therefore be considered to have a dual effect on viscosity of a sample subjected to a steady shear: a decreased start-up viscosity and a less pronounced viscosity decay.

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Temperature (1/K)



		Viscosity parameter							
Shear rate		Α/γ̈́ να	alue	σ <sub>0</sub> /γ̀	value	B/γ̈́ va	B/y value		
		E <sub>a</sub> R <sup>2</sup>		I E <sub>a</sub>	R <sup>2</sup>	Ea	R <sup>2</sup>		
(s <sup>-1</sup> )	(s <sup>-1</sup> ) (kcal/mole)			(kcal/mole)		(kcal/mole)			
100		9.1	0.95	9.3	0.94	14.6	0.97		
200		7.3	0.99	7.9	0.99	12.3	0.98		
300		5.5	0.94	5.5	0.97	9.1	0.92		
400		5.2	0.99	6.2	0.99	8.0	0.99		
500		4.9	0.98	5.8	0.98	7.4	0.99		

Table 9. Activation energy of viscosity decay for stirred yogurt (Brand I).

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A = Weltman A value; B = Weltman B value;  $\sigma_0$  = Initial stress;  $\dot{\gamma}$  = shear rate

## CONCLUSIONS

The stress decay behavior of stirred yogurt under a constant shear  $(100-500 \text{ s}^{-1})$  can be adequately described by the Weltman logarithmic-time model for up to 60 min. Weltman parameters show linear trends with shear rate and temperature, and hence can be incorporated in to a composite model. Temperature effects can also be described by the Arrhenius approach which gives activation energies in the same range obtainable under dynamic shear testing conditions. The initial stress or start-up viscosity decreases with increasing temperature and is partly compensated by a lower viscosity decay rate.

Characterization of the stress decay behavior constitutes an important step in our overall objective of developing procedures for fabricating the desired consistency and stability in flavored yogurt-based products by blending stirred yogurt with hydrocolloids and flavor concentrates.

### **CHAPTER VI**

## **RHEOLOGY OF RASPBERRY FLAVORED YOGURT**

### ABSTRACT

The influence of pectin (0.0-0.5%) and raspberry concentrate (64°B; 0-10%) on the rheological characteristics of commercial stirred yogurt was evaluated using a computer controlled Haake RV20 equipped with a M5 OSC measuring head and MV1 rotor. The study indicated a steady increase in the consistency coefficient (upward flow) and apparent viscosity (downward flow) with the addition of pectin and concentrate. The study also indicated that the of the raspberry flavored yogurt could be fabricated with desired rheological properties by post-fermentation mixing of stured yogurt with pectin and raspberry concentrate.

### INTRODUCTION

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Data presented by Valenzky (1978), Ryan et al. (1984), McGregor and White (1987) and Eden (1988) flavored yogurt drinks would be accepted by a major segment of the North American consumer market and that the most popular flavor is raspberry. Due to its positive nutritional attribute, a variety of new flavored-yogurt products are filling commercial vending machines. Flavored yogurts are made by prior addition of flavoring substances like fruit concentrates or syrups along with such additives as pectin etc. to improve the viscosity before/after the fermentation process. Added flavor ingredients decrease the consistency of the product and therefore these products are often stabilized with viscosity modifiers such as starches or pect'n (Tamime and Robinson, 1985).

The objective of the present investigation was to study the effect of pectin and raspberry concentrate on the rheological behavior of stirred yogurt in order that the desired product viscosity could be achieved by mixing pectin and concentrate to the stirred yogurt.

### MATERIALS AND METHODS

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Citrus pectin (methoxy content, 9.5%; Sigma Chemical Co.) and raspberry concentrate ( $64^{0}B$ ) were used as additives for test samples of stirred yogurt obtained from the local market. A stock solution of pectin (5% by weight) was prepared by dispersing it in warm distilled water to facilitate addition. A full factorial design of experiments with six levels of pectin (0, 0.1, 0.2, 0.3, 0.4 and 0.5%) and three levels of concentrate (0, 5 and 10%) was employed with three replicates. Each test sample was prepared by adding appropriate amounts of pectin stock solution (0, 2, 4, 6, 8 or 10 g) and concentrate (0, 5 or 10 g) to 80 g of yogurt and made up to 100 g using distilled water. Prior to testing they were mixed gently to get a uniform sample and handled carefully to minimize any structural breakdown. They were held at  $10^{\circ}$ C in the sample cup for 20 min before measurements were made.

The methodology for obtaining rheological data during a programmed 3-cycle continuous upward and downward shearing sequence using the Haake RV20 rotational viscometer and the models used for their treatment (Herschel-Bulkley for the upward curves and linear model for the downward curves) are detailed in Chapter IV. The rheological parameters m, n,  $\sigma_0$  and  $\eta$  were used to assess the influence of added pectin and concentrate on the flow behavior of test samples. The breakdown of rheological structure due to repeated shear was evaluated by comparing the apparent viscosity (downward shearing) of test samples obtained from the third shear-cycle to those from the first cycle.

## **RESULTS AND DISCUSSION**

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Figure 15 shows the first upward and downward flow curves for test samples of stirred yogurt containing different concentrations of pectin without added raspberry concentrate. Figures 16 & 17 show similar curves for samples containing 5% and 10% raspberry concentrates. All test samples exhibited typical thixotropic flow behavior with yield stress. In confirmation with our earlier findings (Chapter IV), the first upward curves of all samples could be adequately described by the Herschel-Bulkley model ( $R^2$ ~0.99, Table 10). It is evident from Figures 15-17 that pectin and concentrate had a considerable effect on the flow behavior of stirred yogurt. Addition of pectin resulted in an upward shifting of the flow curves (building up of structure leading to increased sample viscosity). This behavior was enhanced by the addition of raspberry concentrate.

Similar results were observed with the downward curves which were essentially linear over the broad range of shear rates employed in the study (Table 10). Since the slopes of these curves indicate their apparent viscosity ( $\sigma/\dot{\gamma} = \eta$ ), the relative effects of added pectin and concentrate on the viscosity of test samples could be easily visualized from these curves; the trend was essentially the same.

An analysis of variance of the fully randomizeu factorial design (Table 11) indicated both pectin and concentrate to be significant parameters (p<0.01) influencing all rheological parameters (m, n,  $\sigma_0$  and  $\eta$ ). As expected the three replicates were not significantly (p>0.05) different in any analysis. In addition, all two-way interactions were also found to be non-significant (p>0.05) except the pectin-concentrate interaction with the apparent viscosity. The effect of added pectin was non-linear and was somewhat similar with reference to the consistency coefficient (m) from upward curves and the yield stress ( $\sigma_0$ ) from downward curves as shown in Figures 18 and 19.



Figure 15. Typical upward and downward flow curves of stirred yogurt at various levels of pectin and no raspberry concentrate.

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Figure 16. Typical upward and downward flow curves of stirred yogurt at various levels of pectin and 5% raspberry concentrate.

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Figure 17. Typical upward and downward flow curves of stirred yogurt at various levels of pectin and 10% raspberry concentrate.

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Pectin	Rasp		m	n	R <sup>2</sup>	σο	η	R <sup>2</sup>
(%)	(%)		(Pa)			(Pa)	(Pa.s)	
0.0	0	Mean	1.31	0.46	0.97	3.97	0.043	0.99
		s.d.	0.04	0.01		0.17	0.001	
0.1	0	Mean	1.18	0.53	0.99	3.80	0.056	1.00
		s.d.	0.11	0.03		0.48	0.003	
0.2	0	Mean	1.37	0.53	0.99	4.30	0.071	1.00
		s.d.	0.05	0.01		0.30	0.003	
0.3	0	Mean	1.60	0.53	1.00	5.30	0.087	1.00
		s.d.	0.04	0.01		0.48	0.002	
0.4	0	Mean	1.81	0.53	0.99	6.08	0.102	1.00
		s.d.	0.02	0.00		0.37	0.001	
0.5	0	Mean	<b>2</b> .57	0.51	1.00	7.91	0.121	1.00
		s.d.	0.04	0.02		0.11	0.003	
0.0	5	Mean	1.67	0.45	0.98	4.39	0.049	0.99
		s.d.	0.23	0.02	-	0.44	0.001	
0.1	5	Mean	1.58	0.50	0.99	4.40	0.064	1.00
	-	s.d.	0.16	0.01		0.14	0.002	••••
0.2	5	Mean	1.78	0.52	1.00	5.49	0.085	1.00
	-	s.d.	0.04	0.01		0.61	0.005	
0.3	5	Mean	2.06	0.52	1.00	6.07	0.099	1.00
		s.d.	0.25	0.02		0.22	0.002	
0.4	5	Mean	2.47	0.53	0.99	7.60	0.121	1.00
		s.d.	0.42	0.03		0.14	0.001	
0.5	5	Mean	3.49	0.49	0.99	9.37	0.141	1.00
		s.d.	0.37	0.02		0.16	0 005	
0.0	10	Maam	0.07	0.44	0.00	4.75	0.059	0.00
0.0	10	Mean	2.07	0.44	0.99	4.75	0.058	0.99
~ 1	10	S.a.	0.14	0.00	0.00	0.04	0.003	1.00
0.1	10	Mean	2.30	0.40	0.99	5.12	0.075	1.00
<u>_</u>	10	s.a.	0.17	0.01	0.00	0.28	0.002	1.00
0.2	10	Mean	2.24	0.50	0.99	0.10	0.093	1.00
<u>^ 2</u>	10	S.Q.	0.27	0.02	0.00	0.31	0.002	1.00
0.3	10	mean	2.59	0.50	0.99	0.03	0.110	1.00
0.4	10	S.U. Maam	0.31	0.02	0.00	0.21	0.003	1.00
U.4	10	ivican	0.40	0.49	0.99	0.32	0.100	1.00
0 E	10	S.a.	0.09	0.01	0.00	0.47	0.002	1.00
0.0	10	Mean	J.60	0.50	0.90	11,00	0.100	1.00
		s.a.	0.17	0.01		0.01	0.002	

Table 10. Mean and standard deviations in rheological parameters of stirred yogurts as influenced by the addition of pectin and concentrate.

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Source of var	ce lation	d.f.	m	n	σ <sub>o</sub>	η	η <sub>3</sub> /η <sub>1</sub>
Main	Effects						
	Pectin	5	••	**	**	**	**
	Concentrate	2	**	**	**	**	**
	Replicate	2	ns	ns	ns	ns	ns
Two-F Intera	factor actions						
	Pectin-Conc.	10	ns	ns	ns	**	ns
	RepConc.	4	ns	ns	ns	ns	ns
	PecRep.	10	ns	ns	ns	ns	ns
Total		53					
ns **	not significant, p significant, p < 0.	> 0.05 01					

Table 11. Significance of effect of pectin and concentrate on the

rheological parameters of stirred yogurt (analyses of variance).

The flow behavior index (n) increased up to a pectin concentration of 0.3% and decreased thereafter (Figure 18). The apparent viscosity (n) from the downward curves varied linearly with pectin concentration (Figure 19). The effect of addition of raspberry concentrate on all these parameters could be described by a linear function within the range (0-10%) employed in the study. This was somewhat expected because raspberry fruit juice concentrates have been described to exhibit Newtonian flow characteristics in the low (<30°B) concentration range (Sarvacos, 1970; Rao, 1977; Ibarz and Pagan, 1987).

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Figure 18. Upward flow consistency coefficient and flow behavior index of stirred yogurt as influenced by added pectin.



Figure 19. Downward flow shear stress and apparent viscosity of stirred yogurt as influenced by added pectin.

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Repeated shear cycles progressively degraded the rheological structure of stirred yogurt as shown typically in Figure 20 for representative upward and downward curves of samples containing 0.5% pectin and 10% raspberry concentrate. The shear destruction patterns were similar at other conditions confirming our earlier findings (Chapter IV) of continual and irreversible structural decay with repeated shear. In order quantitate the influence of added pectin and concentrate on shear to degradability/stability of yogurt structure, the rheological parameters from the third cycle were compared with those from the first cycle. A shear stability indicator was defined as a ratio  $(\eta_3/\eta_1)$  of the apparent viscosities of third cycle and first cycle downward flow curves. The downward-flow parameter  $(\eta)$  was chosen because of the linear relationship between shear stress and shear rate. The ratio of apparent viscosities  $(\eta_3/\eta_1)$  as a function of pectin and concentration are shown in Figure 21.



Figure 20. Typical flow curves showing structure breakdown of stirred yogurt in a

3-cycle upward and downward shearing sequence.





 $\eta_{3}/\eta_{1}$ )

of stirred yogurt as influenced by added pectin and raspberry concentrate.

Analysis variance results indicated both pectin and concentrate to be highly significant (p<0.01) factors influencing the shear degradability/stability. Their influence however were opposite. While pectin improved the structural stability (higher  $\eta_3/\eta_1$  values at higher pectin content), the concentrate increased the sensitivity of the samples to shear degradability (Figure 21). However, it should also be noted that earlier results (Table 10; Figures 19) indicate that addition of both pectin and concentrate increase apparent viscosity level of test samples. These results show that while addition of pectin favors both viscosity increase and shear stability, addition of concentrates will only result in an apparent increase in sample viscosity which may be more easily degraded by repeated shear.

# A Model for Fabricating Flavored Yogurt Rheology

In order to develop a model to fabricate the rheology of raspberry flavored yogurt, the relative influence of the addition of pectin and concentrate on a rheological parameter need to be quantified. Ideally, if m, n,  $\sigma_0$  and  $\eta$  could be predicted accurately as functions of added pectin and concentrate, the upward flow curve could be described by the Herschel-Bulkley model and likewise the downward curve could be described by the Herschel-Bulkley model and likewise the downward curve could be described by the Herschel-Bulkley model and likewise the downward curve could be described by a linear model. A multiple regression technique with a second order polynomial suitable for generating a response surface plot (Statgraphics<sup>TM</sup> Statistical Graphics System, STSC, Rockville, MD) was employed to relate the rheological parameters to pectin and concentrate levels. The multiple regression coefficients for the dependent variables and the associated R<sup>2</sup> values are summarized in Table 12. The regression fitting was good (R<sup>2</sup>>0.89) except for the flow behavior index (R<sup>2</sup> = 0.70). Because of the high R<sup>2</sup> value and the relative ease at which it can be determined by various instruments, the apparent viscosity ( $\eta$ ) was chosen as the parameter for determining levels of pectin and raspberry concentration in the flavored yogurt formulation.

					Coefficient						
Parameter	R <sup>2</sup>	c <sub>1</sub>	с <sub>2</sub>	c <sub>3</sub>	C <sub>4</sub>	с <sub>5</sub>	с <sub>6</sub>				
n	0.70	0.474	0.430	-0.71	-0.004	0.00	0.005				
m	0.89	1.340	-2.00	8.956	0.066	0.124	0.001				
σο	0.94	4.10	-4.77	25.3	0.142	-0.009	0.417				
η	0.99	0.044	30.1 <b>09</b>	0.093	0.001	0.00	0.005				

Table 12. Multiple regression coefficients for rheological parameters.

Regression Equation [P = Pectin (%); R = Raspberry concentrate (%)]:

Parameter =  $C_1$  + P. $C_2$  + P<sup>2</sup>. $C_3$  + R. $C_4$  + R<sup>2</sup>. $C_5$  + P.R. $C_6$ 

Figure 22 shows the three dimensional response plot of apparent viscosity as a function of pectin and raspberry concentration levels. Also superimposed on the figure (shaded) is the range of apparent viscosity observed with commercial raspberry flavored yogurts. Pectin concentrate required to increase the sample viscosity to commercial levels with no concentrate added is 0.25-0.4% while the range is 0.1 to 0.25% when the sample contained 10% raspberry concentrate. The exact level of concentrate would depend on organoleptic properties of the formulation.



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Figure 22. Apparent viscosity of stirred yogurt as a function of added pectin and raspberry concentrate.

# CONCLUSIONS

The rheological properties of stirred yogurt were influenced by the addition of pectin and raspberry concentrate. Upward shear flow curves demonstrated Herschel-Bulkley flow pattern with yield stress, while the downward shear flow curves were essentially linear. The apparent viscosity from downward curves could be used to assess the shear degradability of yogurt samples. Pectin resulted in increased sample viscosity that was more shear stable while the increased viscosity resulted from the addition of concentrate was less shear stable. The rheology of flavored yogurt could be fabricated by mixing stirred yogurt with the right proportion of pectin and fruit concentrates.

In this study, the pectin and concentrate have been added to yogurt after the fermentation process. Further, the prepared yogurt had been diluted to some extent to facilitate proper incorporation of pectin and raspberry concentrate. Building of the desired viscosity has still been possible. In some formulations, pectin or other stabilizers are added to the milk prior to fermentation while the concentrate is added following the fermentation process. In these situations, the amount of pectin and concentrate necessary for achieving the desired consistency may be somewhat different, the concept would still be applicable.

#### CHAPTER VII

### **RHEOLOGY OF STRAWBERRY FLAVORED YOGURT**

### ABSTRACT

The influence of pectin (0.0-0.5%) and strawberry concentrate ( $64^{0}B$ ; 0-10%) on the rheological characteristics of commercial stirred yogurt was evaluated using a Haake RV20 with an M5 OSC measuring head and MV1 rotor. All rheograms included an upward flow curve through a linear ramp shear (0 to 300 s<sup>-1</sup> in 3 min), a stress decay curve at a steady shear rate (10 min at 300 s<sup>-1</sup>), followed by a second flow curve through a downward ramp shear (300 to 0 s<sup>-1</sup> in 3 min). In consistence with previous findings, all upward flow curves followed the Herschel-Bulkley model, downward curves were linear and the stress decay behavior followed the Weltman logarithmic time model. The study indicated that the rheology of flavored yogurt was influenced by both pectin and concentrate levels and that the desired product viscosity could be obtained by post-fermentation mixing of stirred yogurt with pectin and strawberry concentrate.

# **INTRODUCTION**

Among the flavored yougurts, the second most popular flavor appears to be strawberry following raspberry. Flavoring ingredients as well as added modifiers can have profound effect on the rheology of yogurt based products. The objective of the current investigation was to study the effect of pectin and strawberry concentrate on the rheological behavior of stirred yogurt. Once again the ultimate aim was to simulate the rheology of strawberry flavored yogurt through the addition of pectin and strawberry concentrate to the post-fermented stirred yogurt.

### MATERIALS AND METHODS

A full factorial design of experiment with six levels of pectin (0, 0.1, 0.2, 0.3, 0.4) and 0.5%) and three levels of concentrate (0, 5 and 10%) was employed with three replicates. Each test sample was prepared by adding appropriate amounts of pectin stock solution (0, 2, 4, 6, 8 or 10 g) and concentrate (0, 5 or 10 g) to 80 g of yogurt and made up to 100 g using distilled water.

Rheological studies were carried out using an Haake RV20 rotational viscometer described earlier. Test samples were subjected to a ramp shear rate of  $100 \text{ s}^{-1}/\text{min}$  changing linearly from 0 to  $300 \text{ s}^{-1}$  in 3 min, were held at the maximum shear rate of  $300 \text{ s}^{-1}$  for 10 min and then subjected to a linear ramp down shear to  $0 \text{ s}^{-1}$  in the next 3 min. The models employed to characterise the two types of flow curves (upward and downward) were essentially the same as described in previous Chapter. The stress decay behavior was characterised by using Weltman model which is slightly different from that used in the previous study.

Weltman Model:

$$\sigma = A - B \log (t); t > 1s$$
 (7-1)

Since the stress decay was initiated in a sample that previously was brought to the test shear rate (300 s<sup>-1</sup>), use of a time factor  $t_m$  as employed in Chapter V was not necessary. Even so, since a zero time viscosity is non-existent in the logarithmic-time model, the results would be valid only beyond a certain time (dependent on the system). Based on experimetal results, a time of 1 s was chosen as the lower limit and since on a logarithmic scale this represents a zero value [log (1) = 0], the shear stress corresponding to this time is actually represented by the intercept coefficient (A value) of the Weltman model.

The rheological parameters m, n,  $\sigma_0$ ,  $\eta$ , A and B were used to assess the influence of added pectin and concentrate on the flow behavior of test samples.

# **RESULTS AND DISCUSSION**

Figure 23 shows the complete rheogram for test samples of stirred yogurt containing different concentrations of pectin without added strawberry concentrate. Figures 24 & 25 show similar curves for samples containing 5% and 10% strawberry concentrates. All test samples exhibited typical thixotropic flow behavior with yield stress. Further, the curves were generally similar except for the progressive upward shifting as a result of the addition of pectin and/or concentrate. It is therefore evident that pectin and concentrate had a considerable effect on the flow behavior of stirred yogurt especially contributing to building up of structure (increased sample viscosity). In confirmation with previous findings (Chapter IV), the upward curves of all samples could be adequately described by the Herschel-Bulkley model ( $\mathbb{R}^2$ -0.95, Table 13).

Similar results were observed with the downward curves which were essentially linear (R<sup>2</sup>>0.97, Table 13) over the range of shear rates employed in the study. Since the slopes of these downward curves indicate their apparent viscosity ( $\sigma/\dot{\gamma} = \eta$ ), the relative effects of added pectin and concentrate on the viscosity of test samples could be easily visualized from these curves; the trend was same as discussed earlier.

The stress decay behavior at the constant shear rate of 300 s<sup>-1</sup> was obtained from the middle part of the rheogram (Figures 23-25). The logarithmic time model chosen (Weltman, 1943) well described the stress decay behavior ( $R^2$ -0.97, Table 13) for all conditions tested. Logarithmic stress decay models based on an equilibrium stress (Hahn et al., 1959 and Tiu and Boger, 1974) were not suitable for stirred yogurt because of their continual stress decay with time as described in Chapter V.



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Figure 23. Typical rheograms of stirred yogurt at various levels of pectin and no

strawberry concentrate.



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Figure 24. Typical rheograms of stirred yogurt at various levels of pectin and 5%

strawberry concentrate.

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Figure 25. Typical rheograms of stirred yogurt at various levels of pectin and 10%

strawberry concentrate.

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<b>.</b>			Up-curve			Dowr	Down-curve			Weltman		
Pectin	Straw	bery	m	n	R <sup>2</sup>	σ0	η	R <sup>2</sup>	A	В	R <sup>2</sup>	
(%)	(%)		(Pa)			(Pa)	(Pa.s)		(Pa.s)	(s <sup>-1</sup> )		
0.0	0	Mean	2.04	0.38	0.95	4.42	0.04	0.99	19.8	3.41	0.97	
		s.d.	0.10	0.00		0.22	0.00		1.1	0.32		
0.1	0	Mean	1.86	0.44	0.97	4.32	0.05	1.00	24.9	4.22	0.97	
		s.d.	0.48	0.02	• • • •	0.45	0.01		2.6	0.39		
0.2	0	Mean	2.22	0.44	0.98	4.44	0.07	1.00	30.6	5.35	0.97	
	~	s.d.	0.28	0.02	• • •	0.23	0.00		0.2	0.03	0.00	
0.3	0	Mean	2.92	0.42	0.97	4.98	0.08	1.00	36.1	6.20	0.96	
~ •	•	s.d.	0.35	0.01	0.00	0.40	0.01	0.00	2.4	0.32	0.07	
0.4	0	Mean	2.52	0.48	0.99	5.97	0.11	0.99	45.2	7.69	0.97	
۰. <del>۲</del>	•	s.a.	0.38	0.03	0.00	0.21	0.00	0.00	0.6	0.33	0.07	
J.5	0	Mean	2.81	0.49	0.99	0.81	0.13	0.99	52.7	8.21	0.97	
		s.a.	0.59	0.03		0.29	0.00		0.4	0.34		
0.0	5	Mean	2.89	0.35	0.94	4.92	0.04	0.99	22.8	4.70	0.97	
		s.d.	0.33	0.01		0.54	0.00		1.2	0.29		
0.1	5	Mean	2.97	0.37	0.96	4.66	0.05	1.00	27.1	5.63	0.98	
		s.d.	0.28	0.01		0.28	0.00		0.6	0.09		
). <b>2</b>	5	Mean	2.66	0.43	0.98	5.14	0.07	1.00	34.9	7.19	0.97	
		s.d.	0.06	0.01		0.19	0.00		0.8	0.41		
0.3	5	Mean	3.28	0.44	0.98	5.38	0.09	1.00	41.8	8.17	0.98	
		s.d.	0.56	0.03		0.48	0.00		1.2	0.28		
).4	5	Mean	3.45	0.46	0.99	6,69	0.12	0.99	52.0	9.46	0.97	
		s.d.	0.12	0.02		0.20	0.01		2.8	0.57		
).5	5	Mean	3.58	0.48	0.99	7.19	0.14	0.99	58.4	9.85	0.97	
		s.d.	0.95	0.03		0 75	0.01		4.8	1.51		
0.0	10	Mean	3.82	0.33	0.93	5.73	0.05	0.99	25.8	5.97	0.98	
		s.d.	0.26	0.02		0.25	0.00		0.5	0.13		
). 1	10	Mean	4.61	0.32	0.96	5.27	0.06	0.97	31.4	7.40	0.98	
		s.d.	0.38	0.01		0.15	0.00		1.7	0.55		
).2	10	Mean	4.76	0.36	0.98	5.69	0.08	1.00	40.4	8.91	0.98	
		s.d.	0.23	0.01		0.09	0.00		0.7	0.21		
).3	10	Mean	4.12	0.42	0.98	5.93	0.10	1.00	46.9	9.75	0.98	
		s.d.	0.62	0.02	. –	0.52	0.01		2.3	0.41		
).4	10	Mean	4.96	0.42	0.99	7.32	0.13	1.00	58.0	11.5	0.98	
		s.d.	0.38	0.02		0.22	0.00		2.4	0.86		
.5	10	Mean	5.67	0.44	0.99	9.99	0.16	0.99	71.0	12.7	0.98	
		s.d.	1.12	0.03		1.02	0.00		0.4	0.48		

 Table 13.
 Mean and standard deviations in rheological parameters of stirred

yogurts as influenced by the addition of pectin and concentrate.

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An analysis of variance of the fully randomized factorial design (Table 14) indicated that both pectin and concentrate were significant parameters (p<0.01) influencing all rheological parameters (m, n,  $\sigma_0$ ,  $\eta$ , A and B). The differences between the replicates were small and generally non-significant (Table 14). In addition, all two-way interactions were also non-significant except pectin-concentrate interactions with the flow behavior index, apparent viscosity and Weltman A value.

Table 14. Significance<sup>1</sup> of effect of pectin and concentrate on the rheological parameters of stirred yogurt (analyses of variance).

Source of variation	d.f.	m	n	σ <sub>o</sub>	η	Weltman A	Weltman B
Main Effects	··						
Pectin	5	**	**	**	**	**	••
Concentrate	2	**	**	**	**	**	**
Replicate	2	ns	**	ns	ns	ns	ns
Two-Factor							
Interactions							
Pectin-Conc.	10	ns	•	ns	**	**	ns
RepConc.	4	ns	ns	ns	ns	ns	ns
PecRep.	10	ns	ns	ns	ns	ns	ns
Total	53						

1 Significance at 1% level

\*\* significant

ns not significant

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The overall effects of added pectin and concentrate on the various rheological parameters are shown in Figures 26-28. The effects were generally non-linear except with reference to the apparent viscosity, and Weltman parameters. The strawberry concentrate was a more dominant factor than pectin content in influencing the consistency coefficient (Figure 26). With reference to the flow behavior index (n), the effects of pectin and concentrate were opposite. While added pectin increased the flow behavior index, the addition of concentrate caused it to decrease (Figure 26).

The stress constant calculated as the intercept of the downward curves ( $\sigma_0$ , Eq. 7-2) varied somewhat exponentially with pectin and concentrate while the apparent viscosity ( $\eta$ ) varied linearly with both pectin and strawberry concentration (Figure 27). Juice concentrates at low concentration levels '<30<sup>o</sup>B) have been generally described to exhibit Newtonian flow characteristics (Sarvacos, 1970; Rao, 1977; Ibarz and Pagan, 1987). The non-linear effect of addition of strawberry concentrate on some rheological parameters are somewhat in contrast with the above studies.

Both stress decay parameters, Weltman A and B values, showed a linear trend with added pectin and concentrate (Figure 28). Weltman A value increased almost by three folds with addition of 0.5% pectin while addition of 10% strawberry concentrate increased it, on an average, by about 50%. Somewhat similar results were observed with Weltman B values.

Weltman A value which is the shear stress at a time equal to 1 s (in this study), is a structural parameter that generally has a close correlation with the yield stress (Chapter V). Higher values indicate a stronger resistance to start up shear. The Weltman B value, usually referred to as the time coefficient of stress decay, is a measure of the rate of structure breakdown. Higher B values indicate that the sample is more susceptible to structure loss. In this study, both A and B values increased with the addition of pectin as well as concentrate. This implies that the addition of pectin and concentrate helped building up of the start-up viscosity and also



Figure 26. Upward flow consistency coefficient and flow behavior index of stirred yogurt as influenced by added pectin and strawberry concentrate.

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Figure 27. Downward flow shear stress and apparent viscosity of stirred yogurt as influenced by added pectin and strawberry concentrate.



Figure 28. Weltman parameters of stirred yogurt as influenced by added pectin and strawberry concentrate.

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increased their sensitivity to stress decay. The viscosity of pectin and concentrate enriched samples remained higher through out because of the more dominant effect on structure build-up. For example, the average start up shear stress in samples containing 0.5% pectin was ~60 Pa as compared win ~22 Pa for samples without pectin. The corresponding average B values were approximately 10 and 4.5 s<sup>-1</sup> respectively. The calculated viscosity of the former would thus be higher (0.07 Pa.s as compared to 0.007 Pa.s) even after continuous shearing for four logarithmic time cycles (10000 s or about 2.8 hr) at 300 s<sup>-1</sup>.

## A Model for Fabricating Flavored Yogurt Rheology

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In order to develop a model to fabricate the rheology of strawberry flavored yogurt, the relative influence of the addition of pectin and concentrate on a rheological parameter need to be quantified. Ideally, if m, n,  $\sigma_0$  and  $\eta$  could be predicted accurately as functions of added pectin and concentrate, the upward flow curve could be described by the Herschel-Bulkley model and likewise the downward curve could be described by a linear model. A multiple regression technique with a second order polynomial suitable for generating a response surface plot (Statgraphics<sup>TM</sup> Statistical Graphics System, STSC, Rockville, MD) was employed to relate the rheological parameters to pectin and concentrate levels. The multiple regression coefficients for the dependent variables and the associated  $R^2$  values are summarized in Table 15. The multiple regression fitting was especially good ( $\mathbb{R}^2$ >0.9) with the apparent viscosity and Weltman parameters. Because of the high  $R^2$  value and the relative ease at which it can be determined by various instruments, the apparent viscosity  $(\eta)$  was chosen as the parameter for determining levels of pectin and strawberry concentration in the flavored yogurt formulation. Figure 29 shows the three-dimensional response plot of apparent viscosity as a function of pectin and strawberry concentration levels. Also superimposed on the



Pectin (%)

Figure 29. Three-dimensional multiple regression model of apparent viscosity of stirred yogurt as a function of added pectir, and strawberry concentrate.

			Coefficient						
Parameter	R <sup>2</sup>	<b>c</b> <sub>1</sub>	с <sub>2</sub>	C <sub>3</sub>	C4	С <sub>5</sub>	с <sub>6</sub>		
m	0.74	2.06	0.483	2.27	0.0489	0.0155	0.0896		
n	0.75	0.384	0.279	-0.147	-0.00327	-0.000413	0.0063		
σ <sub>o</sub>	0.84	4.72	-5.83	20.7	-0.0205	0.00974	0.293		
η	0.98	0.0406	0.105	0.136	-0.000156	0.000054	0.00604		
Weltman A	0.97	20.5	37.5	54.3	0.178	0.0303	2.35		
Weltman B	0.94	3.31	11.0	-2.40	0.228	0.00431	0.325		

Table 15. Multiple regression coefficients for rheological parameters.

figure (shaded) is the range of apparent viscosity observed with commercial strawberry flavored yogurts. Pectin concentrate required to increase the sample viscosity to commercial levels with no concentrate added is 0.3-0.4% while the pectin range required is 0.2 to 0.3% when the sample contained 10% strawberry concentrate. The exact level of concentrate would depend on organoleptic properties of the formulation.

## CONCLUSIONS

The rheological properties of stirred yogurt were influenced by the addition of pectin and strawberry concentrate. Both pectin and strawberry concentrate increased the sample viscosity. Although the shear stability of the pectin and concentrate treated samples were lower, the beneficial effect could be realized under practical conditions due to the higher start-up viscosity. The rheology of flavored yogurt could be fabricated by mixing stirred yogurt with the right proportion of pectin and fruit concentrates.

#### CHAPTER VIII

# RHEOLOGICAL BEHAVIOR OF STIRRED YOGURT DURING STORAGE AT 2<sup>O</sup>C

#### ABSTRACT

The influence of storage at  $2^{\circ}C$  up to 4 weeks on the rheological characteristics of commercial stirred yogurt was evaluated using the Haake RV20 rotational viscometer. The flow behavior was evaluated under dynamic shearing with a 3-cycle programmed upward and downward shear rates (0 to 500 s<sup>-1</sup>; 5 min) as well as at a selected steady shear rate of 300 s<sup>-1</sup>. In consistence with previous findings, all upward flow curves followed Herschel-Bulkley model while the downward curves were linear, and stress decay behavior followed the Weltman logarithmic model. The study indicated only marginal changes (generally not significant, p>0.05) in the flow behavior parameters of yogurt under dynamic as well as steady shear during the storage. The chemical composition also changed only slightly during the storage, although the results were statistically significant (p<0.01).

## **INTRODUCTION**

Due to its increasing popularity as a nutritious food, yogurt and yogurt based products such as fruit yogurt (Swiss style), set and stirred fruit flavored yogurts, yogurt drinks, yogurt ice-cream etc., are becoming more available in the market. According to Agriculture Canada (1988), the per capita consumption of yogurt has increased by two folds in the last five years. Yogurt is a perishable food and has a shelf-life of about four weeks under refrigerated conditions. Deterioration of quality and functionality of the product poses a major problem for the widespread use of yogurt and related products. Continued microbiological activity in yogurt based products during storage has been associated with some chemical changes: souring (Sinha et al. 1989; Jordano et al., 1988), proteolysis of milk proteins (Tamime and Robinson, 1985; Lacroix and Lachance, 1990) and hydrolysis of fat (Dellaglio, 1988). These chemical reactions may adversely affect the sensory, rheological as well as functional properties of yogurt. Low temperature storage obviously is the choice for controlling these changes.

Latic et al. (1987) have demonstrated that the duration of storage of yogurt at a constant temperature ( $8^{\circ}$ C) affects the rheological characteristics which in turn changes the organoleptic properties. O'Neil et al. (1979) reported that the acidity and consistency increased slightly during a 2-week storage at 4°C. At the same time they reported that fat and total solid contents varied depending on the nature of the commercial yogurt used.

The current study was undertaken to investigate the influence of storage time of up to four weeks at 2°C on the physico-chemical and rheological behavior of stirred yogurt under dynamic and steady shear testing conditions.

## MATERIALS AND METHODS

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The same two commercial brands of yogurts (Brand I and Brand II) reported earlier were used in the current study. They all had a residual shelf-life of four weeks based on the expiration date on the containers and were stored at 2°C for various periods prior to analyses.

Rheological evaluations were made during a programmed 3-cycle continuous upward and downward shearing sequence (described in Chapter IV) as well as at a fixed shear rate of  $300 \text{ s}^{-1}$  (detailed in Chapter V) using the Haake RV20 rotational viscometer. The models employed to evaluate the upward and downward flow curves

and the time dependency were essentially the same as discussed in the earlier chapters. Rheological parameters m, n,  $\sigma_0$ ,  $\eta$ ,  $\eta_3/\eta_1$ , Weltman A and Weltman B values were used to assess the influence of storage time on the flow behavior of test samples.

Moisture content was estimated from the oven drying method of AOAC method (1980), with a slight modification: drying was done in a vacuum oven at 70°C for 24 hr instead of usual 4 hr at 100°C. The loss in weight of the sample expressed as a percentage of the initial weight was taken as the wet basis moisture content. The pH of the samples was determined using a Digital pH meter (Chemcadet model 5984-50). Titrable acidity was evaluated by titration with 0.1N NaOH according to the AOAC method (1980). Acidity was expressed as percentage lactic acid. Fat, protein and lactose contents were analyzed using the rapid IR spectrophotometric method (van de Voort, 1980) using a Multispec MK1 infrared milk analyzer from measured absorbance values at respective wavelengths [for fat (5.73  $\mu$ m), protein (6.46 $\mu$ m) and lactose (9.61 $\mu$ m)]. The samples were adjusted to pH 6.5 using 1N NaOH prior to the IR measurements.

Rheological evaluations and chemical analyses were performed on samples from both Brands at three day intervals during storage for four weeks at 2°C.

### **RESULTS AND DISCUSSION**

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### Effect of storage on rheological parameters

Figure 30 illustrates typical upward and downward flow curves of test samples from Brand I and Brand II following storage at 2°C for selected periods. All curves confirmed a thixotropic, shear thinning behavior with an yield stress; however, they showed no specific trend with respect to storage time. The overall pattern of the flow curves for the two brands remained qualitatively similar but some quantitative differences were noticeable. In agreement to our previous findings (Ramaswamy and Basak, 1991a), test samples of Brand II exhibited a slightly higher viscosity compared to that of Brand I as indicated by the associated larger shear stress at a given shear rate. All upward curves for both brands could be well described by a Herschel-Bulkley Model ( $R^2$ ~0.99; Table 16). With Brand I, the magnitudes of rheological parameters, s<sub>0</sub> and m both increased up to midway through the storage, beyond which they gradually decreased and nearly returned back to their original values by the end of the storage. The reason for this is not clear. In contrast for Brand II, there were no specific trends for the rheological parameters during the entire period of storage. The value of n showed a similar pattern but in the opposite direction, i.e., they decreased first and then increased. The downward flow curves of test samples from both brands were linear (Figure 30, Table 16,  $R^2$ ~0.99; Brand I showing slightly lower viscosity than Brand II).

As previously noted all the test samples showed progressive degradation of rheological structure on repeated shear. In order to make a quantitative measurement of the shear degradation of yogurt structure and to assess how it is influenced by storage, the values of the apparent viscosity from the third cycle were compared with those from the first cycle. The ratio of these two viscosities,  $h_3/h_1$ , was defined as a shear stability index, higher values indicating larger stability. During the storage, the stability index ranged from 0.79 to 0.81 for Brand I and from 0.76 to 0.78 for Brand II indicating only marginal differences between them and small changes to be associated with storage.

Stress decay curves for the two commercial brands during a 10 min steady shear at the selected shear rate of 300 s<sup>-1</sup> are shown in Figure 31. Weltman regression parameters A and B values were used to compare the stress decay behavior of the two test samples. Weltman A value which is the shear stress at time =  $t_m$  (12 s in this study), is a structural parameter that generally has a close correlation with the yield stress (Ramaswamy and Basak, 1991b). Higher values indicate a stronger resistance to start up shear. Weltman B values is usually referred to as the time coefficient of stress decay, and is a measure of the rate of structure of breakdown. Higher B values indicate that sample is more susceptible to structure loss. For both Brands, the stress decay behavior was accurately described by Weltman model ( $\mathbb{R}^2 = 1.0$ ) As observed previously (Ramaswamy and Basak, 1991b), the stress curves for the two samples were nearly similar but their magnitudes differed slightly. The effect of storage time on the Weltman parameters A and B are given in Table 16. Weltman A values showed a trend similar to the yield stress. It must be stressed that these changes during storage were quite small (<5% on the average) to have any real impact on the overall rheological property of the sample. Similar trends were also observed for the other Weltman parameter B.

Results of the analysis of variance for the changes in rheological parameters during storage of the two commercial yogurts are shown in Table 17. For Brand I, the rheological parameters  $\sigma_0$  and m showed no significant change during storage whereas the changes with reference to the flow behavior index, n, were significant (p<0.05). With Brand II, all these rheological parameters were non-significant. With reference to the downward curves, for Brand I, values of both stress constant and apparent viscosity were significant (p<0.01). For Brand II, on the other hand, stress constant was significant (p<0.05) but not the apparent viscosity. The storage time was not a significant factor influencing shear degradibity/stability  $(\eta_3/\eta_1)$  in both cases. The analysis of variance also revealed that the storage time did not have any significant effect on the values of Weltman A or B. In spite of the statistical significance, the magnitudinal changes in major rheological parameters were considered small, especially as related to the influence other major factors. Overall, the parameter values changed by less than 7% (except for yield stress which varied by up to 18%) during the entire storage period. Relatively, this represented a change of smaller magnitude than contributed by, for example, a 5°C change in sample temperatures (Chapters IV & V).

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Figure 30. Typical upward and downward flow curves of two commercial stirred yogurts following storage at 2°C for various periods.

	Upcurve			Down o	Down curve			Weltman	
Time	σ	m	n	σ <sub>c</sub>	η	η <sub>3</sub> /η <sub>1</sub>	A	В	
0	6.92	11.8	0.24	14.9	0.09	0.80	65.4	18.1	
	(a)	(a,b)	(a,b)	(a)	(a,b)	(a)	(a)	(a)	
3	10.2	11.5	0.25	16.3	0.09	0.81	64.6	17.4	
	(a,b)	(a,b)	(a,b)	(a,b,c)	(a,b,c)	(a)	(a)	(a)	
6	11.3	11.9	0.24	16.6	0.09	0.80	62.3	15.9	
	(a,b)	(a,b)	(a,b)	(a,b,c,d	) (a,b)	(a)	(a)	(a)	
9	11.4	15.5	0.21	18.8	0.09	0.80	72.6	20.1	
	(a,b)	(a,b)	(a)	(d)	(c,d)	(a)	(a)	(a)	
.2	12.8	14.2	0.21	18.7	0.09	0.79	71.7	19.5	
	(a,b)	(a.b)	(a,b)	(c,d)	(c.d)	(a)	(a)	(a)	
5	13.6	11.6	0.25	18.2	0.09	0.80	65.6	18.0	
	<b>(b</b> )	(a.b)	(a.b)	(c.d)	(d)	(a)	(a)	(a)	
8	10.9	12.4	0.24	18.0	0.09	0.80	72.7	19.2	
-	(a.h)	(a h)	(a.b.)	(b.a)	(a.h.c.)	(a)	(a)	(a)	
21	9.86	12.9	0.23	17.8	0.09	0.81	64.8	16.8	
	(a h)	(a h)	(a b)	(h c d)	(2)	(2)	(a)	(1)	
4	7.09	16.1	0.20	177	0.00	0.80	65 0	176	
-	(2)	(b)	(2)	(h c d)	(a h c)	(a)	(a)	(a)	
7	0.35	107	(a) 0.25	15 4	(a,0,c)	0.70	(a) 68 6	(a) 19.9	
• •	(ab)	(a, b)	(h)	(a h)	(a)	(n)	(a)	(a)	
					······				
D	14.9	16.3	0.21	23.4	0.10	0.78	73.8	19.2	
_	(a)	(a)	(a,b)	(a,b,c)	(a,b)	(a)	(a)	(a)	
3	15.7	17.2	0.21	23.3	0.10	0.78	75.2	20.5	
	(a)	(a)	(a,b)	(a,b)	(a,b)	(a)	(a)	(a)	
5	14.5	16.9	0.21	23.5	0.10	0.78	74.0	19.7	
	(a)	(a)	(a,b)	(a,b,c)	(a,b)	(a)	(a)	<b>(</b> a)	
•	18.3	19.9	0.18	26.7	0.10	0.77	81.1	21.3	
	(a)	(a)	(a)	(b,c)	(a,b)	(a)	(a)	(a)	
2	17.2	19.1	0.19	25.6	0.11	0.77	80.5	21.4	
	(a)	(a)	(a,b)	(a,b,c)	(a,b)	(a)	(a)	(a)	
5	14.0	14.9	0.23	23.5	0.10	0.78	74.1	19.4	
	(a)	(a)	(b)	(a,b,c)	(a,b)	(a)	(a)	(a)	
	15.5	16.8	0.21	24.7	0.10	0.77	<b>79.7</b>	21.8	
8	(a)	(a)	(a,b)	(a,b,c)	(a,b)	(a)	(a)	(a)	
8	· · · · ·			223	0.10	0.77	73.0	19.1	
8	14.9	14.5	0.21		-				
8	14.9 (a)	14.5 (a)	0.21 (a.b)	(a)	(a)	(a)	(a)	(a)	
8 1 4	14.9 (a) 16.4	14.5 (a) 15.7	0.21 (a,b) 0.22	(a) 24.8	(a) 0.10	(a) 0.78	(a) 73.0	(a) 19.5	
8 1 4	(a) (a) 16.4 (a)	14.5 (a) 15.7 (a)	0.21 (a,b) 0.22 (a,b)	(a) 24.8 (a.h.c.)	(a) 0.10 (a.b)	(a) 0.78 (a)	(a) 73.0 (a)	(a) 19.5 (a)	
8 1 4 7	(2) 14.9 (a) 16.4 (a) 174	14.5 (a) 15.7 (a) 19 1	0.21 (a,b) 0.22 (a,b) 0.20	(a) 24.8 (a,b,c) 27.4	(a) 0.10 (a,b) 0.11	(a) 0.78 (a) 0.76	(a) 73.0 (a) 72.2	(a) 19.5 (a) 19 2	

Table 16. Changes<sup>\*</sup> in rhealogical parameters during storage at  $2^{0}$ C

\*For each brand, column values not sharing a common letter are significantly different (p<0.01)



Figure 31. Typical stress decay curves of two commercial stirred yogurts following storage at 2<sup>o</sup>C for various periods.

parameters of Brand I and II yogurts.

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Particulars	Parameter	Bran I	d Brand II
Up-curve parameters	σο	ns	ns
	m	ns	ns
	n	*	ns
Down-curve parameters	σο	**	٠
	ຖັ	**	ns
	$\eta_{3}/\eta_{1}$	ns	ns
Weltman parameters	A value	ns	ns
	B value	ns	ns

Table 17. Significance of effect of storage on rheological

significant, p < 0.05

\*\* significant, p <0.01

ns not significant, p>0.05

# Effect of storage on chemical composition

The 4-week storage influenced the relative amounts of principal constituents of the two yogurt brands tested to a small extent (Table 18). Such effects though small was not negligible. Among all the major constituents, the levels of titrable acidity increased with storage time (1.58-1.62%, for Brands I & II) and in consistence with a gradual loss in the lactose content which upon hydrolysis is expected to yield lactic acid (6.30-6.21%, Brand I; 6.37-6.23%, Brand II). The increase in acidity showed a corresponding decrease in the pH of the product (4.19-4.09, Brand I; 4.21-4.10, Brand II).

Brand	Time (days)	Fat (%)	Protein (%)	Lactos (%)	e Lactic acid (9	рН 6)	Moist <b>ure</b> (%)
Brand I	0	1.85	6.54	6.30	1.58	4.19	82.1
	•	(g)	(e)	(d)	(a)		(a)
	3	1.84	6.51	6.31	1.59	4.18	82.0
		(I.g)	(e)	(D)	(D)	4.17	(a)
	0	1.82	0.42	0.20	1.60	4.17	82.5
	•	(1,9)	(D)	(C)	(C)		(a)
	9	1.83	6.42	6.25	1.60	4.17	82.2
		(t,g)	(D)	(b,c)	(c)		(a)
	12	1.81	6.38	6.24	1.60	4.16	82.5
		(d,e)	(b,c)	(a,b,c)	(c,d)		(a)
	15	1.81	6.39	6.23	1.61	4.14	82.4
		(c,d,e)	(c,d)	(a,b,c)	(d,e)		(a)
	18	1.80	6.36	6.22	1.61	4.13	82.1
		(b,c,d)	<b>(a,b,c)</b>	(a,b,c)	(e)		(a)
	21	1.80	6.35	6.21	1.61	4.11	82.4
		(b,c)	<b>(a,b</b> )	<b>(a)</b>	(f)		(a)
	24	1.79	6.35	6.21	1.61	4.10	82.5
		(a,b)	<b>(a,b)</b>	(a,b)	(f)		(a)
	27	1.78	6.33	6.21	1.62	4.09	82.3
		(a)	(a,b)	<b>(a)</b>	(g)		(a)
Brand II	0	2.07	6.68	6.37	1.58	4.21	80.3
	-	(d)	(d)	(e)	(a)		(a)
	3	2.04	6.62	631	1.58	4 19	82.8
	0	(c d)	(c)	(d)	(a b)	7.17	(b c d)
	6	2 03	6 57	6 29	1 50	4 18	877
	v	(h c)	(h)	(c d)	(a h c)	4,10	$(\mathbf{b}_{c})$
	9	2 02	6 57	6.28	1 50	4 17	83.0
	,	(a h c)	(h)	0.20 (h c d)	(h c)	7.17	(1)
	12	2 02	6 57	6 27	1 50	4 16	(U) 83.8
	12	(a h c)	(b)	(h, c, d)	(o.d)	4.10	02.0 (h c d)
	15	(a, 0, c)	(U) 6 <b>5</b> 7	(U,C,U)	(U,U) 1.60	4 1 4	(U,C,U)
	15	2.02	0.37 (b)	(0.27)	1.00	4.14	62.9 (a.d)
	19		(U) 6 8 6	(a,0,c)	(0)	4.1.4	(0,0)
	10	2.01 (- h)	0.30	0.27	1.00	4.14	82.1
	21	(a,0)	(a,D)	(a,D,C)	(e)	4.12	(b) 02.0
	21	2.01	0.54	0.25	1.61	4.13	83.0
	•	(a,d)	(a,b)	(a,b,c)	(e)		(d)
	24	2.01	6.53	6.25	1.61	4.11	82.6
	•5	(a,b)	(a)	(a,b)	(f)		(b,c,d)
	27	2.00	6.53	6.23	1.62	4.10	82.7
		(a)	(c)	(a)	(g)		(b.c.d)

Table 18. Changes<sup>\*</sup> in the chemical composition of yogurt during storage at 2<sup>o</sup>C.

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\* For each brand, column values not sharing a common letter are significantly different (p<0.01)

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The other principal components eg. protein and fat also decreased slightly during storage (protein: 6.54-6.33% and 6.68-6.53% and fat: 1.85-1.78% and 2.07-2.00%, for Brands I & II, respectively). Moisture content of test samples generally ranged from 82.1-82.3% for Brand I and 82.1-83.0% for Brand II during the period of investigation. Most of the changes that took place during the storage occurred in the first twelve days of storage. Similar observation was reported previously by Jordono et al. (1988) and Salji and Ismail (1983), at higher storage temperatures.

Analysis of variance of all the above constituents except moisture showed that they were very significantly influenced during the storage for both brands (p<0.01). The values for moisture was significant for Brand II, due to the lower value observed on day 0; the changes in moisture with reference Brand I were non-significant.

## CONCLUSIONS

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The data presented in this paper indicates small, but significant changes :: chemical composition during the relatively low temperature storage of 2°C. The influence of these changes on the rheological behavior was generally small and mostly non-significant. The 2°C storage temperature therefore appears to be a good choice to maintain the structural qualities of yogurt samples during marketing.

### CHAPTER IX

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