CHAPTER 2 THERORY AND LITERATURES REVIEW

2.1 Papaya and its Composition

Papaya (*Carica papaya* Linn.) is the member of the small family Caracaceae having four genera and 31 species. It is cultivated throughout the tropic for its fruit. The fleshy papaya is a berry, 5 to 40 cm long and can weight to over 5 kilogram. The shape of fruit may be spherical or oblong depend on pistil late or hermaphrodite flowers. The skin is smooth and thin, shading from deep orange or yellow when ripe. The fruit is normally composed of five longitudinal carpel untied laterally with the flesh surrounding a five angle large center cavity where the numerous seed are attached to placentas in parietal position. The flesh varies from 2.5 to 5.0 cm in thickness and color is red-orange. Papaya fruits consist mostly of water and carbohydrate, low in calories and rich in natural vitamins and minerals, particularly in vitamins A and C, ascorbic acid and potassium. It also contains the enzyme papain, a natural meat tenderizer. Papaya is the best eat after meal to aid digestion as the papain enhances the assimilation of valuable nutrients derives from the food. A table of nutrient content of ripe papaya which is composed mostly of 89% water is shown in Table 2.1

Table 2.1 Nutrient content of ripe papaya

Constituent	Appropriate value
Water	89 %
Calories	39 kcal
Protein	0.61 g
Fat	0.14 g
Carbohydrate	9.8 g
Calcium	24 mg
Iron	0.1 mg
Phosphorous	5 mg
Potassium	257 mg
Magnesium	10 g
Sodium	3 mg
Niacin	0.34 mg
Pantothenic acid	0.22 mg
Vitamin A	1094 IU
Vitamin E	0.73 mg

Source: USDA Nutrient Database for Standard Reference, Release 18 (2005).

2.1.1 Papaya Puree

Puree is one kind of food product that made from fruit or vegetable. It is a fine mash of smooth and thick consistency. The processing of papaya puree starts with cleaning of full ripe papaya to get rid of pesticides and contaminate substances. Other step are halving, deseeding, peeling, cutting and blending to produce the final papaya puree product that is important intermediate papaya product for concentrated papaya puree, papaya juice and cocktail. Thermal processing is needed for preparation of concentrated papaya puree.

2.2 Microwave Heating and Dielectric Properties

2.2.1 Microwave Heating

Microwave heating depends on the ability of specific material to absorb microwave energy and convert into heat. Microwaves are electromagnetic wave which are electric and magnetic field. The electric field causes heating by two mechanical are dipole rotation and ionic polarization. The first mechanism is dipole rotation, heat is generated when microwaves irradiated. It must possess dipole moment, the dipole of the sample align in the applied electric field. As the applied field oscillates, the dipole field realigns itself with the alternating electric field and energy is lost in forms of heat through molecular friction (Kappe, 2004). The second mechanism is ionic polarization. As the dissolved charged particles in a sample oscillate under the microwave field so they collide with neighboring molecules or atom and this causes agitation or motion. These collisions cause agitation or motion, create heat (Savjani et al., 2010).

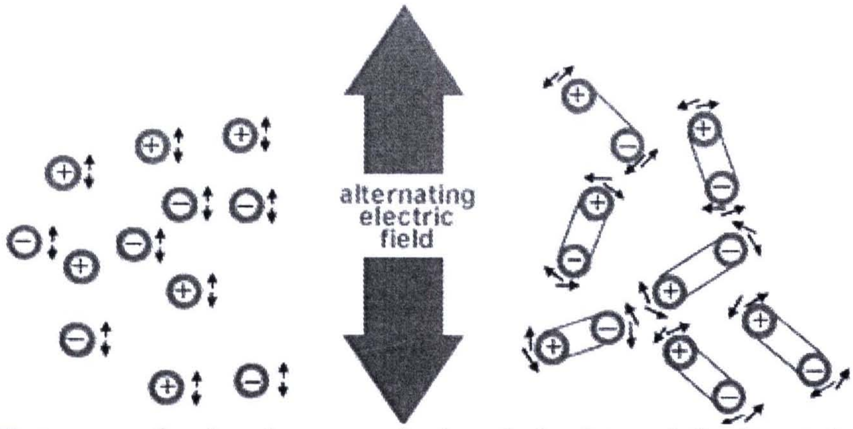

Figure 2.1 Heat generation in microwave: Ionic polarization and dipole rotation

2.2.2 Dielectric Properties

Dielectric material is electrical insulator material. Most foods are dielectric material. Therefore, it is necessary to investigate the dielectric properties for process improvement such as microwave oven. Microwave heating is widely used in food cooking because it can achieve rapid and simple heating. In order to achieve optimum microwave heating, it is necessary to know the dielectric properties of material. Dielectric properties of materials are important, because these properties affect the interaction of electromagnetic energy with the material. Reflection, transmission and absorption of microwave energy are controlled by the material dielectric properties. (Tanaka et al., 2005)

Food materials are, in general, electric insulators. They have the ability to store and dissipate electric energy when subject to an electromagnetic field. The dielectric properties of a material are given by:

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (2.1)$$

The real part ε′ is referred to as the dielectric constant that is related to the material's ability to store electric energy in the electric field in the material when compare with ability to store electric energy of air or vacuum (for vacuum ε′ = 1), while the loss factor ε″ that is the imaginary part and indicates dissipation of electric energy in the material by conversion of electric energy into heat. Dielectric loss factor is composed of two components: dipole loss and ionic loss. Dipole loss results from the rotation of water dipoles, while ionic loss results from migration of ions. Generally dipole loss decreases with temperature, while the ionic loss component increases with temperature at the microwave frequencies (915 and 2450MHz) (Sipahioglu et al., 2003; Tang et al., 2002 and Wang et al., 2003 cited by Al-Holy et al., 2005). Dielectric properties of food materials are affected by many factors, including frequency of the microwaves, food temperature, moisture content, salt content, and other constituents.

2.2.2.1 Effect of Frequency

The frequency-dependent trend of dielectric properties can provide important information of the material characteristics. In theory, electric conduction and various polarization mechanisms (including dipole, electronic, ionic, and Maxwell–Wagner) contribute to the dielectric loss factor. For moist dielectric materials ionic polarization is a major at lower frequencies (< 200 MHz) but at microwave frequencies both ionic polarization and dipole rotation are a combined role. For original soy sauce at frequencies between 0.3 and 3GHz 20 °C. The dielectric constant decreases with increasing frequency. The loss factor decreases inversely proportional to frequency (Tanaka et al., 2005). For low-moisture media, bound water is a major role in dielectric heating in the frequency range between 20 and 30 GHz at room temperature (20 °C).

For a pure liquid, the Debye describes the frequency-dependent dielectric properties as shown in Equation (2.2)

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} - j\frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \tag{2.2}$$

Where; ε_∞ is the infinite or high frequency relative permittivity, ε_s is the static or zero-frequency relative permittivity and τ is the relaxation time in seconds of the material and the larger the molecules, the longer the relaxation time. For a pure liquid, such as water, the dielectric loss factor reaches the maximum at a critical frequency relates to the relaxation time ($f_c = 1/2\pi\tau$). Water molecules are polarity and the most important constituent that contributes to the dielectric properties of high-moisture dielectric. Water molecules bind to the surface of polar materials in monolayer or multilayer has much longer relaxation times than free water molecules (Komarov et al., 2005).

2.2.2.2 Effect of Temperature

The typical frequency dependence of both important effects on the loss factor can be seen schematically in Figure 2.3 together with their temperature dependency. Figure 2.3 shows that the relaxation peaks as well as the contribution of the ionic conductivity in ε″ are shifted to higher frequency due to the smaller viscosity of the solution and the corresponding higher mobility of ion (Mudgett, 1985).

Generally, the loss factor increases with increasing temperature at low frequencies due to ionic conductivity and decreases with increasing temperature at high frequencies due to free-water dispersion. In multi-dispersion materials, for example, the transition is gradual because of the combined effects of relaxation and the ionic conduction and there is a U-shape frequency response in ε″.

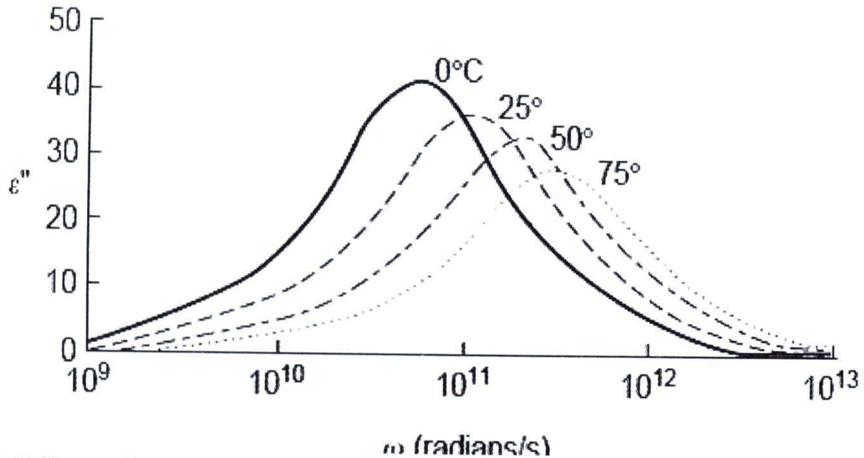

Figure 2.2 Effect of temperature on dielectric constant ε′ and loss factor ε″ of free water (ω = 2πf, where f is frequency in Hz) (From Mudgett, 1985)

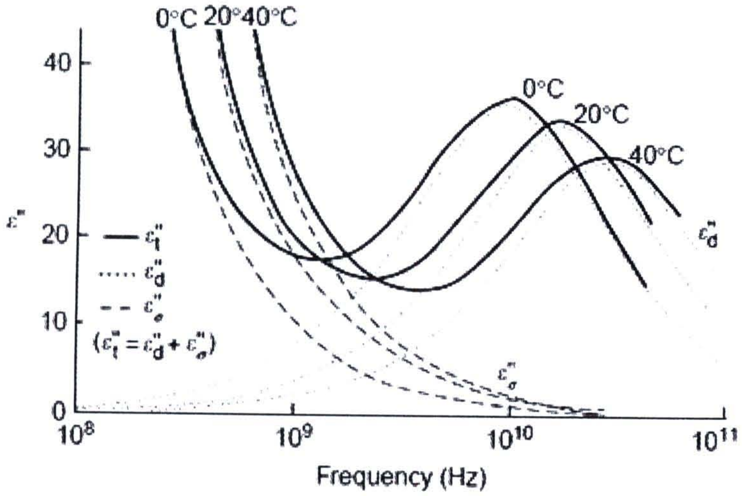

Figure 2.3 Effect of temperature on dielectric loss factor ε″ of 0.5N aqueous sodium chloride at three temperatures (From Roebuck and Goldblith, 1972)

In theory, ionic conductivity and dipole rotation are the dominant loss mechanisms (Metaxas and Meredith, 1993; Kuang and Nelson, 1998) that is:

$$\varepsilon'' = \varepsilon''_d + \varepsilon''_\sigma = \varepsilon''_d + \frac{\sigma}{\varepsilon_0 \omega} \tag{2.3}$$

$$\omega = 2\pi f_c = \frac{1}{\tau} \tag{2.4}$$

Where subscribes "d" and "σ" stand for contribution due to dipole rotation and ionic conductivity, respectively; ω represents angular frequency of the microwaves, ε_o is the permittivity of free space (8.85×10^{-12} F/m), f_c is relaxation frequency and τ is relaxation time.

An important concept in understanding how frequency and temperature affect dielectric properties due to dipole loss, ε_d in Equation (2.3), is the relaxation time (τ). It is defined as the time required for preferentially oriented dipolar molecules such as water, under a static external electric field, to relax back to the original condition on sudden removal of the external field. The dipole loss ε_d reaches the maximum at the relaxation frequency ($f_c = 1/2\pi\tau$). As temperature rises, relaxation time for water decreases. The shifting of the relaxation time toward a smaller value as temperature increases (thus the frequency at the maximum dipole loss, ε_d shifts toward a larger value as temperature increases) that reduces the value of dipole loss, ε_d for water after relaxation frequency as shown in Figure 2.3.

2.2.2.3 Effect of Moisture Content

Moisture content is one of the major components of food composition. It lies on within cells and a part of water occurs in the extra cellular space. In addition, water is a major absorber of microwave energy in the foods. Consequently, the higher moisture contents, the higher dielectric constants of the foods (Venkatesh, 2004). Dielectric properties decrease rapidly with decrease moisture content to a critical moisture level. The dielectric constant and loss factor of flour samples increased steadily with increasing moisture content at 915 MHz and 2450 MHz. (Al-Muhtaseb et al ., 2010)

2.2.2.4 Other Factors

Salt can bind free water in the system so when increase in the salt concentration dielectric loss factor increase (Coronel et al., 2008). Sugar molcules are relatively large and non-polar. An increase in sugar content reduces the dielectric constant. Dielectric constant and dielectric loss factor increase with sugar concentration and temperature. This may be attribute to the lack of polarization generated by sucrose molecules and binding of water to sucrose molecules (Coronel et al., 2008).

2.2.3 Dielectric Measuring System

Many measurement techniques for measuring permittivity are available. There are three popular techniques for dielectric determination; Open-Ended Coaxial Probe System, Transmission Line Method and Resonance Cavity Method. Measurements of the dielectric properties are performed by numerous methods employing various sizes and shapes of materials (Westphal et al., 1972). Their advantages and limitations are the reasons for measuring system selection. Table 2.2 shows the comparison of dielectric properties measurement techniques.

Table2.2 The comparison of dielectric properties measurement techniques

Open-ended coaxial probe system	**Transmission line method**	**Resonance cavity method**
Suitable for liquids or soft solid food materials.	Not suitable for oil, paper, plastics, glass or wood	Suitable for oil, paper, plastics, glass or wood
Large range of frequencies (from 0.2 to up to 20 GHz)	Narrow bands of frequencies	Fixed frequency
The sample thickness needs (>1 cm)	The precise sample shape is required	The precise sample shape is required
The accuracy (± 5%)	The accuracy (± 4%)	The accuracy (± 2%)
A few minute for measurement	Time consuming	Time consuming

According to the advantages and limitations as showing in Table 2.2, the proper method for dielectric properties of papaya puree measurement is Open-Ended Coaxial Probe System.

The coaxial probe is a convenient and broadband technique for lossy (low dielectric loss factor) liquids and solids (Venkatesh, 1998). It is non-destructive and little or no sample preparation is required for liquids or semi-solids. Air gap can be a significant source of error. It operates at frequencies between 0.2 to up to 20 GHz. The technique assumes the material under test to be non-magnetic and uniform throughout. It should be noted that the accuracy in the coaxial probe measurements is about ± 5%. Moreover, this technique requires only a few minute for measurement.

For open-ended coaxial probe system, the microwave signal launch by a vector network analyzer is reflected by the sample. The analyzer receives the reflected waves (S_{11}), and the dielectric constant and loss factor are then calculated that shown in Figure 2.4.

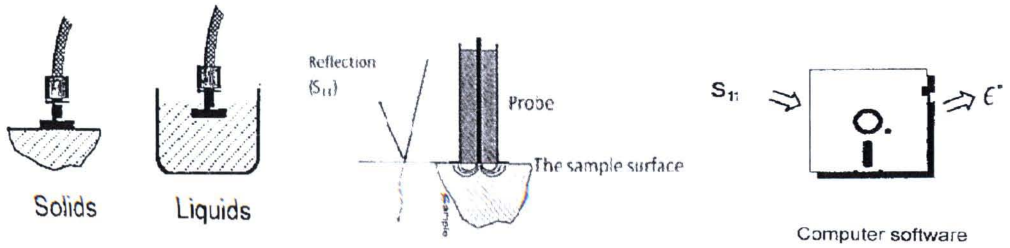

Figure 2.4 Open-ended coaxial probe and dielectric property measurement system (Tang et al., 2002)

The measured admittance of the probe can be calculated from Equation (2.5) (Zajicek et al, 2008).

$$Y = Y_0\left(\frac{1-S_{11}}{1+S_{11}}\right) \tag{2.5}$$

Where S_{11} is the measured reflection coefficient, Y is the measured admittance of the probe, $Y_0 = 1/(50\Omega)$ is characteristic admittance of the probe.

And then dielectric properties ε_c are calculated from Equation (2.6)

$$Y = j\omega\varepsilon_c C_0 + \sqrt{\varepsilon_c^5}\, G_0 \tag{2.6}$$

Where C_0 and G_0 are constants given by the equivalent circuit of the probe in free space The solving steps of the complex equation (Equation 2.6) were splitting it into real and imaginary parts to obtain a set of two real nonlinear equations for the two real unknowns, which are C_0 and G_0 that used to calculate permittivity ε_c of the papaya puree sample (Zajicek et al., 2008).

2.2.4 Literatures Review for Dielectric Properties

Wang et al., (2011) studied dielectric properties of potato puree with different salt contents (1-7% NaCl) and sucrose contents (3-15%) as a function of temperature (-30-80 °C) at 2450 MHz using open-ended coaxial probe. They found that ε' decreases with increasing in temperature because the water in the potato puree is free water and ε'' increases with increasing in temperature for temperature above 0 °C. This is due to the fact that the temperature dependent behavior of $\varepsilon''$is determined by the amounts of free water and the dissolved ions. Dipole loss results from water dipole rotation, and its value decreases with increasing temperature at 2450 MHz, while ionic loss results from migration of ions and increases with temperature. For samples with salt, the increase of ionic loss with temperature exceeds the decrease of dipole loss with temperature, so the net loss factor increases with increasing temperature.

Ahmed et al., (2008) measured dielectric properties of commercial soy protein isolate (SPI) dispersions as a function of concentration (5, 10 and 15 g/100 g water), temperature (20-90 °C) and pH (4.5, 6.6 and 10). Over the frequency range of 200–2500 MHz by the open-ended coaxial probe method using a network analyzer. The dielectric constant (ε′) decreased with temperature (except at 90 °C) and frequency but increased with concentration. The loss factor (ε″) increased with frequency and concentration. The significant change in ε′ and ε″ at 90 °C was a result of protein denaturation which was identified by differential scanning calorimeter (DSC). Change in the association/dissociation behavior of SPI dispersions due to electrostatic attraction/repulsion among protein molcules on heating as a function of pH was assumed to be responsible for the significant increase in dielectric parameters.

Brinley et al., (2008) studied dielectric properties of sweet potato purees at 915 MHz as affected by temperature and chemical composition. An open-ended coaxial probe (HP 85070B, Agilent Technologies, Palo Alto, CA) and an automated network analyzer (HP 8753C, Agilent Technologies, Palo Alto, CA) were used to determine the dielectric properties of sweet potato purees. In microwave processing, dielectric properties have a major role in determining the interaction between purees and the electromagnetic energy. Results indicated that temperature, moisture, sugar and starch content had a pronounced effect ($p < 0.001$) on dielectric properties measured from 15 °C to 145°C at 915 MHz. Dielectric constant decreased with increasing temperature, while dielectric loss factor increased quadratic.

Ahmed et al., (2007) studied the dielectric properties of basmati rice flour slurry as a function of flour concentration and temperature was studied between 30 and 80 °C. And frequency range of 500–2500 MHz. The dielectric constants (ε') generally do not vary with frequency while the loss factors (ε'') show an increasing trend. A sharp change in dielectric parameters was note above 70 °C attributable to rice starch gelatinization, confirm by differential scanning calorimeter. An increase in flour slurry concentration systematically reduces ε' during the entire frequency range while variations in ε'' values are mixed. Addition of 1% salt markedly increases ε'' of slurries whereas butter result in significant reduction in ε' values. Rice flour slurry containing both salt and butter exhibits intermediate values of dielectric properties.

Everard et al., (2006) investigated the effects of frequency, temperature, moisture content and inorganic salt content on the dielectric properties of cheese 16 processes over the frequency range 0.3–3 GHz. The effect of temperature on the dielectric properties of process cheeses was investigated at temperature intervals of 10 °C between 5 and 85 °C. The dielectric constant (ε′) and the dielectric loss factor (ε″) decreased with increasing frequency, for all cheeses. ε′ is highest at 5 °C and generally decreased with increasing temperature. Dielectric loss factor (ε″) generally increased with increasing temperature for high and medium moisture/fat ratio cheeses. Dielectric loss factor (ε″) decreased with temperature between 5 and 55 °C and then increased, for low moisture/fat ratio cheese.

Lakshminarayana, (2006) studied effect on dielectric properties on Saskatoon berries under frequencies between 0.5 and 5 GHz and temperature (23 °C) using the HP 8510 that is a high performance microwave vector network analyzer (VNA) and HP software program provided the permittivity based on the measured reflection coefficient (Engelder and Buffler, 1991). The results show that the dielectric constants decreased with increasing solute concentration in the berries. The lower the moisture content, the lower the dielectric constant. And Dielectric loss factor of maple syrup also decreases with increasing moisture content (35 to 98%) at 240 MHz.

Fasina et al., (2003) studied dielectric properties of sweet potato puree, these properties were determined by HP 85070 dielectric probe kit (Hewlett Packard, Santa Clara,CA). The dielectric properties of sweet potato puree were measured at frequencies of 900 to 2500 MHz (at every 2MHz) and at temperatures of 5 to 80 °C. The kit consists of an open-ended, 3.6mm diameter, semi-rigid, Teflon-insulated coaxial line with copper conductors connected to a network analyzer (Model 8510B, Hewlett Packard, Santa Clara, CA). It was found that both temperature and frequency (900–2500 MHz) significantly affected the dielectric constant (60.5–73.0) and dielectric loss factor (16.5–29.5) of sweet potato puree. Dielectric constant exhibited the expected decrease with increase in both temperature and frequency. At temperatures of 5 and 20 °C, the loss factor initially decreased, reached a minimum, and then increased with increase in frequency. Nelson and Datta explained that this response is caused by ionic conductivities at the lower frequencies by bound water relaxation and by the relaxation of free water near the top of the frequency range. At 35 °C and higher, the loss factor only decreased with increase in frequency. This is an indication that at the higher temperature levels, ionic conductivity is predominantly responsible for loss factor of the puree.

Sipahiglu et al., (2003) studied dielectric properties of vegetables and fruits as a function of temperature, ash, and moisture content. The dielectric properties of 15 vegetables and fruits were measured at 2450 MHz from 5 to 130 °C. Equations were developed as a function of temperature, ash, and either moisture content or water activity, and compared to literature equations. Dielectric constant of vegetables and fruits decreased with temperature and ash content. However, ash was not a factor in the equations produced separately for fruits. Dielectric loss factor changed quadratic with increasing temperature: first decreasing and then increasing. This transition temperature decreased with ash content. Ash increased the dielectric loss factor. Garlic and potato gave unusual results, which could be explained by the behavior of solutions of Inulin and potato starch, respectively.

Liao et al., (2003) studied dielectric properties of a-D-glucose aqueous solutions at 2450 MHz measured at concentrations ranging from 10 to 60% in the temperature range of 0 –70 °C using the cavity perturbation technique, requiring a dielectric analyzer (Meda & Raghavan, 1998), a PC, a resonant cavity made of copper (Inside diameter = 90 mm; high =45 mm; TM 010 simplistic mode). The system was calibrated with distilled water. Dielectric constant increases with temperature in a quadratic manner while linearly decreasing with glucose concentration. Dielectric loss factor decreases with temperature in a quadratic way. The loss factor–concentration relationship depends on the temperature. At lower temperature, loss factor increases linearly with concentration up to a certain concentration then decreases. At temperatures higher than 40 °C, loss factor linearly increases with concentration at all concentration ranges studied.

Ikediala et al., (2000) studied dielectric properties of four apple cultivars and third and fifth instars codling moth (Cydia pomonella). They were measured between 30 MHz and 3000 MHz at 5°C to 55°C, using the open-ended coaxial-line probe technique. Dielectric constant of apples decreased with frequency and decreased slightly with increasing temperature. The dielectric loss factor increased linearly with temperature in the radio frequency range but was nearly constant at the microwave frequencies.

2.3 Rheological Properties

Rheology can be stated as the science dealing with the deformation and flow of bodies (Fredrickson, 1964). All materials ideally possess all the rheological properties, both as solid or fluid. Flow pertains to liquid matter, e.g., fruit juice, and deformation pertains to solids, e.g., hard cheese. Materials that are not solids or liquids but possess both properties are considered viscoelastics, e.g., yogurt. Measurement or prediction of the rheological properties of foods is very important in the design, operation, and optimization of processes, as well as the control of quality of food products.

Fluids are normally divided into two different groups according to their flow behavior: Newtonian fluids and non-Newtonian fluids. A fluid may exhibit Newtonian or non-Newtonian behavior depending on the nature of its continuous and dispersed phases, concentration of particles and chemical composition (Rao and Rizvi, 1986). The flow behavior of several foods can be classified by the viscosity function (η).

Viscosity

Viscosity is a liquid property that describes the magnitude of the resistance due to shear forces within the liquid. Viscosity is an important physical property related to liquid food products. The tendency of a fluid to flow easily or with difficulty has been a subject of great practical and intellectual importance to mankind for centuries. The SI unit for viscosity is N.s/m.

Apparent Viscosity

This is the viscosity of a non-Newtonian fluid expressed as if it was a Newtonian fluid. It is a coefficient calculated from empirical data as if the fluid obeyed Newton's law.

Apparent viscosity was defined as the viscosity of non-Newtonian fluid. Since, in a Newtonian fluid, the flow rate is directly proportional to the shear stress and the curve begins at the origin, a single-point measurement suffices to establish viscosity. One simply measures the shear stress at standard shear rate and by drawing a line from a particular shear rate to origin to obtain the true Newtonian viscosity from the slope of the line. This is known as the one-point test and it is quite satisfactory for specifying the viscosity of Newtonian fluid. The symbol η_a is used to donate apparent viscosity.

Shear Stress

Shear stress is the stress component applied tangential to the plane on which the force acts. It is expressed in units of force per unit area. It is a force vector that possessed both magnitude and direction. The SI unit for shear stress is Pascal (Pa) with units of Newton meter^{-2} (Nm^{-2}) and the symbol τ is used to donate apparent viscosity.

Shear Rate

Shear rate is the velocity gradient established in a fluid as a result of an applied shear stress ($\dot{\gamma}$). It is express in units of reciprocal second (s^{-1}).

2.3.1 Type of Viscous Behavior

Newtonian Fluids

For an ideal Newtonian fluid, the shear stress is a linear function of shear rate. Typical Newtonian fluid are water and water beverages such as tea, coffee, beer and carbohydrate beverages, sugar syrup, apple juice, orange juice, wine and most honeys, edible oils and milk. A simple equation to describe Newtonian fluid behavior is

$$\tau = \eta \dot{\gamma} \tag{2.7}$$

Where;

τ is the shear stress exerted by the fluid [Pa]

η is the fluid viscosity [Pa·s]

$\dot{\gamma}$ is the shear rate [s^{-1}]

Non-Newtonian Fluids

For most agricultural materials, including food products such as cream and salad dressing, the relationship between shear stress and shear rate shown a non-linear. Some of these materials have a yield stress. Non-Newtonian fluid is separated into Non-Newtonian fluid with time-independent behavior and Non-Newtonian fluid with time-dependent behavior.

Non-Newtonian fluid with time-independent behavior:

- Shear-Thinning behavior or Pseudo plastic fluid has viscosity decreases as shear rate increases for example coconut milk.

  The expression shear-thinning is preferred compared to pseudo plastic because it is an accurate of shear rate-shear stress curve, Shear-thinning may be through of being due to breakdown of structural units in a foods due to the hydrodynamic forces generated during shear. Most non-Newtonian foods exhibit shear-thinning behavior, including many salad dressing and some concentrated fruit juices.
- Shear-Thickening or Dilatant fluid has viscosity increases as shear rate increase for example 60%cornflour suspension. Dilatancy implies an increase in the volume of sample during the test. It is incorrect to use it to describe shear-thickening behavior. Strictly speaking, shear-thickening should be due to increase in the size of structural units as a result of shear.

- Bingham fluid does not flow until a critical shear stress is reached and then shear rate is either linear (Bingham plastic) or non-linear (quasi-plastic).

Non-Newtonian fluid with time-dependent behavior:

- Thixotropic fluid has viscosity decreases with time for which shearing force are applied. In the case of thixotropic foods, the material structure breaks down as shearing action continues. This type of food materials includes gelatin, cream, shortening and salad dressing, etc.
- Rheopectic fluid has viscosity increases with time for which shearing force are applied. In the case of rheopectic foods, the material structure build up as shearing action continues. This type of food materials is not common in food system but can occur in a highly concentrated starch solution over long period of time.
- Visco-elastic fluid, some fluids have elastic properties, which allow them to spring back when a shear force is released.

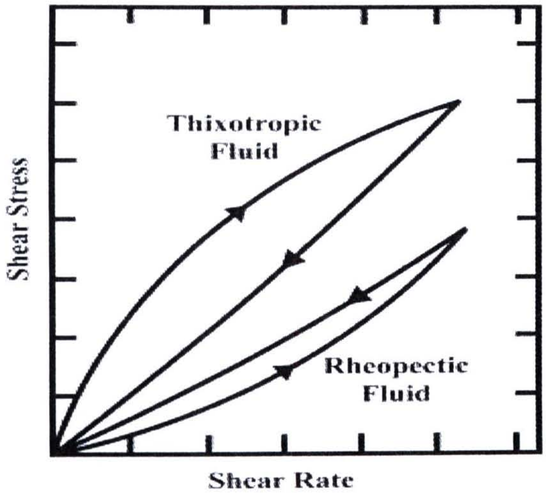

Figure 2.5 Shear stress-shear rate curves for thixotropic and rheopectic fluids (Chhabra, 2010)

From Figure 2.5 shows shear stress-shear rate curves for thixotropic and rheopectic fluids, the area between up and down curves is hysteresis loop.

Most foods that exhibit thixotropic behavior are heterogeneous system containing a dispersed phase that is very fine. At rest, the particles or molecules in foods are linked together by weak forces. When the hydrodynamic forces during shear are sufficiently high, the inter-particle linkages are broken, resulting in reduction in the size of the structural units that, in turn, offer lower resistance to flow during shear (Mewis, 1979). Thixotropic refers to the time dependent decrease in viscosity, due to shearing, and the subsequent recovery of viscosity when shearing is removed (Mewis, 1979). Irreversible thixotropic, called rheomalaxis or rheodestruction, is common in food products and may be a factor in evaluating yield stress as well as the general flow behavior of a material. Anti-thixotropic and negative thixotropic are synonyms for rheopectic. A rheopectic fluid can be described as a thixotropic fluid but with the important difference that the structure of the fluid will only recover completely if subjected to a small shear rate. This means that a rheopectic fluid will not rebuild its structure at the rest.

2.3.2 Rheological Models

2.3.2.1 Power Law Model

Many rheological models are used to describe the properties of material during flow and deformation. In most cases, the shear stress (τ) versus shear rate ($\dot{\gamma}$) curves for pseudoplastic and dilatants materials can be described using a simple power law model as shown in Equation (2.8).

$$\tau = K\dot{\gamma}^{n} \tag{2.8}$$

Where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (1/s), K is the consistency index (Pa.s^n) and n is the flow behavior index, which is unit less.

Tanking logarithms reduces Equation (2.9).

$$\log\tau = \log K + n\log\dot{\gamma} \tag{2.9}$$

A plot of log shear stress versus log shear rate is linear with a slope equal to n for those fluids that obey the power law equation.

For a Newtonian fluid, $n = 1$ and K becomes the viscosity. For n less than 1, it is used to describe pseudo plastic behavior and n more than 1 to indicate dilatants behavior.

2.3.2.2 Herschel-Bulkley Model

In the Herschel-Bulkley model (Equation 2.10), the yield stress term (τ_y) has been added to describe the data of thixotropic and rheopectic fluids (Herschel and Bulkley, 1926).

$$\tau = \tau_y + K\dot{\gamma}^{n} \tag{2.10}$$

By plotting log shear stress versus log shear rate, the values of K and n can be determined as intercept and slope, respectively. If plotting log of shear stress minus yield stress versus log shear rate, the values of K and n can be determined as intercept and slope, respectively too.

2.3.2.3 Casson Model

In the case of cusson model (Equation 2.11), this equation was developed printing ink by Casson (1995). The shear stress versus shear rate curve can be transformed into a straight line by plotting the square root of the shear stress and the square root of the shear rate. Chocolate is notable example of this type of fluid.

$$\tau^{1/2} = \tau_y^{1/2} + K\dot{\gamma}^{1/2} \qquad (2.11)$$

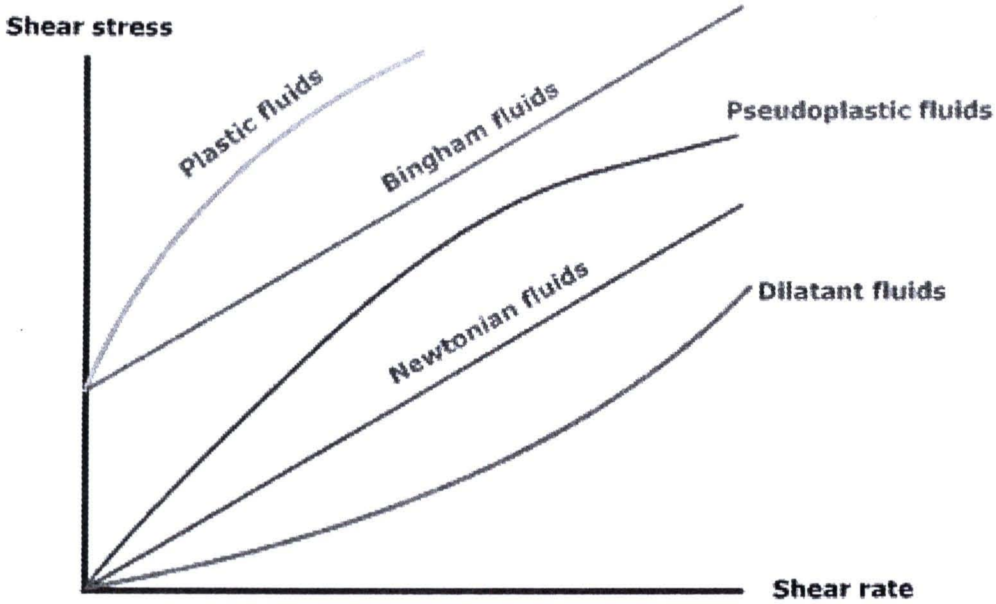

Figure 2.6 Rheological Behavior between Newtonian fluids and non-Newtonian fluid (Toledo, 1991)

The rheological properties of foods depend on several factors, such as shear rate, temperature and concentration (Marcotte et al., 2001 and Abu-Jdayil et al., 2002). The concentration and temperature are the parameters of interest in this research.

2.3.3 Effect of Temperature

Different temperatures are usually encounted during processing of hydrocolloid solutions; therefore, their rheological properties are studied as a function of temperature. The effect of temperature on both the consistency coefficient and the flow behavior index can be evaluated using the Turian approach (Turian, 1964 cited by Marcotte et al., 2001).

$$\log K = \log K_o - A_1 T \tag{2.12}$$

$$n = n_o - A_2 T \tag{2.13}$$

An Arrhenius-type equation is also frequently used to describe the effect of temperature on the viscosity of Newtonian fluids or apparent viscosity of non-Newtonian (Scott-Blair, 1969 cited by Rao, 1999). For some fruit juices, the temperature effect can be described using an Arrhenius-type relation as shown in Equation (2.14).

$$\eta_a = \eta_{\infty A} \exp(E_a / RT) \tag{2.14}$$

$$\ln \eta_a = \ln \eta_{\infty A} + \frac{E_a}{RT} \tag{2.15}$$

Where η_a is the apparent viscosity at specific shear rate (Pa.s), $\eta_{\infty A}$ is the frequency factor, E_a is the activation energy (kJ mol^{-1}), R is the gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature (K). The quantity E_a is the energy barrier that must be overcome before the elementary flow process can occur.

2.3.4 Effect of Concentration

In most foods, it is often possible to identify the components, called key components that play an important role in the rheological properties.

The effect of concentration of soluble or insoluble solids on apparent viscosity can be described by either exponential or power law relationships.

$$\eta_a = a \cdot C^b \tag{2.16}$$

$$\eta_a = d \exp(e \cdot C) \tag{2.17}$$

Where η_a is the apparent viscosity at specific shear rate (Pa.s), C is the concentration (°Brix) and *a, b, d* and *e* are constant s of the models.

2.3.5 Combined Effect of Temperature and Concentration

The combined effect of temperature and concentration on the apparent viscosity of power law model are described by;

$$\eta_a = a \cdot C^b \exp(E_a / RT) \tag{2.18}$$

Or

$$\eta_a = d \exp\left(\frac{E_a}{RT} + e \cdot C\right) \tag{2.19}$$

$$E_a = A \cdot C^B \tag{2.20}$$

Where η_a is the apparent viscosity at specific shear rate (Pa.s), C is the soluble solids content (°Brix), T is absolute temperature (K) and a, b, d, e, A and B are constants of the models.

2.3.4 Literatures Review for Rheological Properties

Yilmaz et al., (2011) studied steady and dynamic oscillatory shear rheological properties of ketchup–processed cheese mixtures: Effect of temperature and concentration using a controlled stress rheometer (Thermo-Haake, RheoStress 1, Germany) in the shear rate range of 1–100 s^{-1} at selected temperature range (10, 20, 30 40 and 50 °C). They found that all ketchup–processed cheese mixtures (including ketchup, 0% processed cheese) had non-Newtonian shear-thinning behavior with values of flow behavior index (n) ranging from 0.61 to 0.82, indicating that a general decrease in the shear-thinning nature as the processed cheese concentration and temperature increased.

Witczak et al., (2011) studied rheological behavior of heather honey using Rheostress RS 150 rheometer using a parallel plate system (35 mm. diameter). Viscosity curves of honeys were drawn in shear rate range 1–100 s^{-1} (180 second up and 180 second down) at 10, 20, 30 and 40 °C. All heather honey samples used in this study exhibited non-Newtonian, shear-thinning behaviour with tendency to yield stress and they were also thixotropic. Non-Newtonian behaviour was well described by the Herschel–Bulkley model. In this study the values of yield stress, consistency coefficient and flow behaviour index were decreasing when the temperature was increasing.

Augusto et al., (2010) studied rheological behavior of tomato juice with steady-state shear and time-dependent modeling. Rheological measurements were carried out in a

Haake RS 80 rheometer with controlled stress (σ), using a Couette geometry (concentric cylinder; Haake Z40-DIN). Temperature was maintained constant by using a water bath (Phoenix ThermoHaake C25P) with deviation lower than ±0.3 °C. The three evaluated models, as well as their modification as function of shear rate, described well the experimental data of tomato thixotropy. The Herschel– Bulkley and Falguera–Ibarz models have shown to be very adequate to describe the data from steady-state shear.

Izidoro et al., (2009) studied the rheological properties of emulsions stabilized by green banana (Musa cavendishii) pulp fitted by power law model. The emulsions were performed with a rotational Haake. The emulsion showed pseudo plastic behavior and were adequately described by power law model. Response surface methodology, described by quadratic model, showed that consistency index increased with the interaction between green banana pulp and soy oil concentration and the water fraction contributed to the flow behavior index increase for all emulsions samples.

Renowati et al., (2008) studied theological properties of tropical fruit juices. The flow properties of water extract of Noni fruit were determined using a concentric cylinders rotational viscometer for extract concentration of 35 and 65% total solid, temperature range of 30 - 60 °C and shear rate range of 2.5-950 s^{-1}. The measured shear stress was within 0.5 to 50 Pa, corresponding to viscosity range of 0.0015-1.6 Pa·s. Within the tested conditions, the extract exhibited a pseudo plastic behavior. The experimental results were well fitted by power law models.

Maceiras et al., (2007) studied the rheological properties of fruit puree: Effect of cooking. The rheological behavior of different fruits (Raspberry, strawberry, peach and prune) fresh or cooked, was determined using a rotational viscometer which allowed experiments to be conducted at different temperatures from 20 to 40°C and the shear rate values ranged from 17.8 to 445 s^{-1}. The results were analyzed by employing two different rheological models; Ostwald de Wale and Herschel-Bulkley. And both of them fitted reasonably well the experimental data at all temperatures.

Debjani et al., (2005) studied rheological characteristics of pumpkin puree over the temperature range of 60–100 °C using a rotational viscometer (Brookfield R/S–CC25 Rheometer, Middleboro, MA, USA) equipped with a Coaxial Cylinder Measuring Systems. Herschel–Bulkley model was found to fit adequately over the entire temperature range. Pumpkin puree exhibited yield stress, which decreased exponentially with temperature. With the increase in temperature, the puree was found to behave as a pseudo-plastic fluid. Arrhenius model gave a satisfactory description of the temperature dependence of apparent viscosity. The activation energy for apparent viscosity and consistency index of pumpkin puree were found; 13.3845 kJ/mol and 31.9394 kJ/mol, respectively.

Nindo et al., (2005) studied on rheological properties of blueberry puree for processing applications at shear rates 10-1000 s^{-1} with the objective to determining the influence of temperature and total soluble solids on the rheological properties, They found that blue berry juice is more Newtonian in nature, the puree showed shear-thinning behavior, E_a increased with total solids content from 11.4 to 17.1 kJ/mol for puree with 10% and 25% total soluble solids. Moreover, the apparent viscosity was also expressed as a function of solids content.

Kassama et al., (2003) studied physical and rheological properties of mango puree at different temperatures (20 and 70° C), concentrations (12 and 24 °Brix), and shear rates (300 and 800 1/s). A controlled stress rheometer (AR2000, TA Instruments LTD, Leatherhead, UK) with a standard steel parallel plate (40 mm) geometry coupled with a built-in plate temperature control was used. A response surface analysis was used in optimizing the rheological properties. The rheological behavior was thixotropic, and the yield stress was sensitive to increases in temperatures. The viscosity of the product was significantly influenced by the independent variables.

Guerrero et al., (1998) studied effect of pH, temperature and glucose addition on flow behavior of fruit purees; peach, papaya and mango purees. The flow behavior of purees measured over the temperature range 10-50 °C using a Rotovisco RV12 (Haake, Buchler Instruments, Inc., USA) viscometer equipped with M-500 measuring head and a MV1 profiled coaxial cylinder sensor system. The effect of glucose addition (soluble solids concentration in the range 12-52 °Brix) and pH (3.0 and natural) was also investigated. After eliminating time dependency, flow was adequately described by the Herschel-Bulkley model. In mango and peach purees, exponential equations were used to describe the combined effect of temperature and soluble solids content on the consistency coefficient. Temperature showed little influence over the flow index but a severe effect on the yield stress. For the three fruits, flow index and yield stress values were correlated with temperature and water activity by means of polynomial equations.