

**DEVELOPMENT OF AN AFFORDABLE
CUREMETER TO MONITOR CURE
CHARACTERISTICS OF UNSATURATED
POLYESTER RESIN**

by

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**Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science**

January 2019

ACKNOWLEDGEMENT

In The Name Of Allah, Most Gracious, Most Compassionate

I take this opportunity to express my gratitude to everyone who supported me throughout this project especially to my supervisors, Prof. Dr. Zulkifli bin Mohamad Ariff and co supervisor Prof Dr. Azlan bin Ariffin for the continuous support, for their patience, motivation and knowledge given to me throughout my study and completing this thesis. For Prof Dr. Zulkifli bin Mohamad Ariff, you are one of the best “tok guru” in my life who has introduced me the meaning of “rheo” and “life” with your own point of view and philosophy.

Besides my supervisors, I would like to thank my best colleague, Dr. Mohd Nazri bin Idris for his encouragement and insightful comments. Not forgotten to my new young friend who were accompanied me during running experiments and writing sessions, Wan Abdur Rahman Bin Wan Mohd Amin and also Mr. Ooi , the best fabricator so far, help a lot in fabrication work and always like to share his experience and knowledge.

Last but not the least, I would like to thank my parents who always pray and support me spiritually throughout my life. Also to my beloved wife, Wani and my two princess Azzahra and Azzalia who have always be my inspiration motivation to complete this project.

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LIST OF SYMBOLS

\emptyset	Shear strain
τ	Shear stress
n	Power law index
k	Power la
$\dot{\gamma}$	Shear rate
μ	Dynamic viscosity
η	Viscosity
h	Gap size
r	Spindle radius
φ	Deflection
M	Geometry factor
C	Total Torque
ω	Velocity angle
T	Torque
V_{\max}	Maximun Velocity
V_{\min}	Minimum Velocity

LIST OF ABBREVIATIONS

COV	Coefficient of Variance
MEKP	Methyl Ethyl Ketone Peroxide
NFC	Newly Fabricated Curemeter
SDOM	Standard Deviation of Mean
UPR	Unsaturated Polyester Resin

**PEMBANGUNAN MESIN PEMATANGAN MAMPU-MILIK
UNTUK MEMANTAU CIRI-CIRI PEMATANGAN
RESIN POLIESTER TAK TEPU**

ABSTRAK

Objektif kajian ini adalah untuk membangunkan mesin pematangan mampu-milik yang dilengkapi dengan perisian pemantauan masa-sebenar dan menilai potensi penggunaannya sebagai peralatan ujian untuk mengkaji sifat dan kelakuan reologi polimer termoset. Satu mesin pematangan baru dengan pergerakan ricih ayunan telah dibangunkan. Beberapa pengubahsuaian telah dilakukan pada rekabentuk asal bagi memenuhi keperluan sistem penderia arus (tork) dan kelajuan. Satu perisian khas telah dibangunkan bersama-sama dengan mesin pematangan tersebut sebagai sistem sokongan untuk menganalisa kelakuan reologi suatu polimer termoset. Data-data yang terjana dari sistem mesin pematangan tersebut telah dibandingkan dengan data yang diperoleh dari mesin komersil, reometer kon-dan-plat (Anton Parr model MCR 301). Ujian keboleh-ulangan telah dilakukan untuk mengukur tahap kebolehpercayaan data yang diperoleh dengan menggunakan analisis pekali varians. Bagi mengkaji ciri-ciri pematangan suatu polimer termoset, kajian kesan kandungan pengeras dalam resin poliester tak tepu telah dijalankan dengan menggunakan mesin pematangan baru ini. Corak perubahan data yang diperoleh adalah boleh dipercayai dan mampu dibandingkan dengan corak perubahan data yang diukur menggunakan reometer komersil. Didapati bahawa mesin pematangan yang baru difabrikasi ini mempunyai potensi yang besar sebagai alat untuk memantau ciri-ciri pematangan dan kelakuan reologi suatu polimer termoset.

DEVELOPMENT OF AN AFFORDABLE CUREMETER TO MONITOR CURE CHARACTERISTICS OF UNSATURATED POLYESTER RESIN

ABSTRACT

The objective of this study was to develop an affordable curemeter equipped with a real-time monitoring software and assess its potential as a rheological testing instrument to study the rheological properties and behaviour of thermoset polymer. A newly fabricated curemeter with an oscillation shearing movement was developed. A few modifications were made on the original design to suit the current (torque) and speed sensor systems requirement. Real-time monitoring software was also developed together with the newly fabricated curemeter as a supporting system to analyze rheological behaviour of a thermoset polymer. Data generated by the newly fabricated curemeter system were compared with data obtained from commercial oscillatory rheometer (Anton Parr model MCR 301). Repeatability test was carried out to measure the level of reliability of the recorded data by using coefficient of variance analysis. In order to study the cure characteristics of a thermoset polymer, evaluation on the effect of hardener content in unsaturated polyester resin was carried out by using this newly fabricated curemeter. The obtained data trend were quite reliable and able to match with the data trend generated by the commercial rheometer. It was found that the newly fabricated curemeter has big potential as a device to monitor the cure characteristics and rheological behaviour of a thermoset polymer.

CHAPTER 1

INTRODUCTION

1.1 Background

Thermoset polymers have found their importance in many critical applications. Although they are often over-shadowed by their thermoplastics counterpart in terms of superficial existence, thermoset polymers are still irreplaceable in applications such as structural adhesive, integrated circuit (IC) components, engineering and aerospace applications which demand enhanced structural as well as mechanical integrity (Prime,1997).

Unlike thermoplastics, thermoset polymers do not have a straight-forward processing procedure. In processing thermoset polymers, the cure characteristics (e.g. pot-life, scorch time, cure time) and the rheological behaviour (e.g. viscosity) are major factors that govern the success of the processing procedure and machinery maintenance. Solidified thermoplastics can be re-melted with application of heat however, solidified or cured thermosets inside processing equipment parts will either result in high maintenance and repair cost or permanent damage to the machinery. Therefore, prior to processing procedure of thermoset polymers, cure characteristics and rheological behaviour need to be evaluated and this is usually conducted using established commercial rheometer such as oscillating rheometers having geometries specifically designed to cater thermoset polymers. In view of this statement and the extremely high price of commercial oscillating rheometers, this work is proposed to design and developed an affordable oscillating rheometer to suit the increasing needs of characterisation instruments for thermosetting polymers. The development of the

rheometer is targeted to reduce dependency of imported instrument and promote utilisation of local expertise as well as give contributions to Malaysian industries especially in rubber processing and semiconductor die-packaging activities.

1.2 Problem Statements

According to Brummer (2006), the study of rheological polymer can be an expensive study due to the high price of the instruments used to measure the rheological properties. While, Liang and Zhong (2010) claimed in their study that usage of special extensional rheological instruments was very expensive. Due to this matter, it has become a main constraint of many researchers to venture into this field of study. From these statements, it can be claimed in general that research work and findings obtained were restricted to a limit due to instruments price available in the market which is relatively expensive ranging from about USD40,000 up to of USD200,000 depends on features fitted to the system.

Most institutions cannot provide more than one device to accommodate a large number of researchers. Often, purchase of a rheometer with high-end specifications are made by dedicated research laboratory where limited access to the instrument is imposed to ensure that its usage is properly supervised and monitored to prevent unnecessary damage. This situation will cause use of the machine to be restricted to high-level research work by senior researchers. Also, with restriction of laboratory's operation hour, only selected research project will be able to use the device and it is limited to research which do not involve instrument usage over a long period of time.

From the above issues, many researchers have come out with new methods and approaches to study the rheological behavior of polymer. In this study, the purpose of developing a newly fabricated curemeter was to provide alternatives and opportunity to young researchers among undergraduate students to engage in research work without interfering with high-level research works by senior researchers. It will create research flexibility in conducting rheological measurement without any technical restriction and there is no need to use and modify the existing commercial rheometer to fulfill their research needs which could be costly if something went wrong. Due to concern of damaging the expensive available curemeter, it has deterred many researchers from exploring unique experimental setup which could enable new findings in the related field of research especially those involving special materials like thermoset polymers

Therefore, a newly fabricated curemeter, with affordable maintenance cost and spare parts, was developed to give opportunities to researchers who need to expand their research work using unique experimental setup and material without having the risk of damaging expensive dedicated research instrument. Other than that, usage of the expensive instrument can be optimized and able to reduce maintenance cost of the institution if the basic rheological data such as curing time can be obtained by using newly fabricated rheometer.

1.3 Objectives

The objectives of this research are listed below:

- 1) To develop an affordable instrument that is able to measure cure characteristics of unsaturated polyester and has potential to be used as a rheometer for thermoset polymer.
- 2) To acquire measurement results from the instrument and develop supplemental software for data analysis.
- 3) To assess the potential of the developed instrument in characterizing unsaturated polyester resin as compared to a commercial rheometer
- 4) To investigate the effect of hardener content on curing time of unsaturated polyester resin using the newly developed curemeter.

1.4 Scope of Work

To develop the curemeter, unsaturated polyester resin has been selected as the thermoset polymer candidate to be used during assessing the potential of this curemeter. The scope of this study covers the following;

- 1) Design a mechanical system (with oscillation movement), electrical system (sensor) and software development for the curemeter which has capability to perform real-time monitoring and capture rheological data of unsaturated polyester resin.
- 2) Study the trend of curing behaviour for unsaturated polyester with varying MEKP amount (0, 1, 2,3,4,5 and 6 drops) using a commercial rheometer and the newly fabricated curemeter.
- 3) Compare the coefficient of variance (COV) between commercial rheometer and the newly fabricated curemeter as an indicator to evaluate the potential performance of newly fabricated curemeter.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Rheometer

Rheometer is a laboratory device used to measure flow and deformation of materials under force or in the other words, to measure the rheological behavior of material. It is crucial to characterize the rheological behaviour due to its direct effects on product handling and flow characteristics especially in manufacturing process procedure.






In polymer processing and application, the rheological behaviour greatly influences mixing, dispensing and flow control of a given process. For example, rheological behavior of a fluid can dictate how the material will be applied during processing or application. The processing method is significantly influenced by the trend of viscosity changes corresponding to the fluid structure or the process itself.

Rheological behaviour measurements are also employed for product characterization and quality control purposes. Such measurements are often used for examining and understanding the interaction of the different constituents of a multi-component or multiphase mixture and their influence on the flow and other properties of such materials (Shumigin et al., 2011)

There are many types of rheometer available in the market which serves different purposes. Generally, rheometer is a device which is capable to measure many rheological properties of thermoset polymer such as viscosity, cure time, shear stress, shear rate etc. If a device only have the capability to measure viscosity, it can

only be classified as a viscometer and if the device capable to measure cure-time, it can be categorized as a curemeter.

Table 2.1 List of several Brookfield viscometer models with their specific capabilities (Mezger, 2006)

Figure	Product Name /model	Measured parameter
	DV-E Low Cost Digital Viscometer	- Viscosity - Torque - Speed
	DV1 Viscometer	- Viscosity - Torque - Speed - Temperature
	DV2T EXTRA Viscometer	- Viscosity - Temperature - Shear Rate/Stress - Torque - Speed - Step Program Status
	High Shear CAP-2000+Cone & Plate System viscometer	Viscosity - Temperature - Shear Rate/Stress - Torque - Speed - Step Program Status
	KU-2 viscometer	- Viscosity - Torque - Speed

From the Table 2.1, it can be projected that the selection of types or model of viscometer depends on types of properties need to be measured by the user (researchers, engineer etc.) with consideration of the rheometer price offered by the suppliers.

2.2 Rheological properties

In order to the design and develop rheological testing equipment, fundamental of rheology will be discussed deeply in this thesis to show the influence the rheological behaviour towards the design of a particular rheometer.

Rheological study is a process of determining the relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) of the materials under flow conditions. The relationship is presented as follows:

$$\tau = k \cdot \dot{\gamma}^n \quad (2.1)$$

where,

n = power law index

k = power law constant

2.2.1 Shear Stress

Figure 2.1 shows the shear stress is defined as force, F, acting tangential to the surface area, A, of a material element.

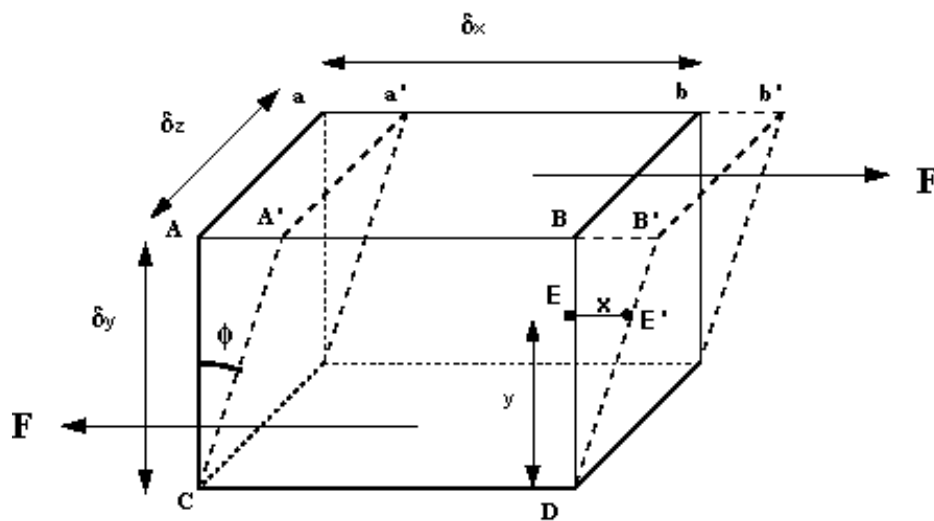


Figure 2.1 Deformation Diagram in the fluid element

Figure 2.1 shows the deformation in the fluid element is caused by shearing forces acts tangentially on the fluid's surface ($A = \delta_x \times \delta_z$) as shown in equation below.

$$\tau = \frac{F}{A} \quad (2.2)$$

Rectangular element ABCD is deformed into rhombus shape A'B'C'D. In other words, the fluid deforms continuously or flows, when subjected to shearing forces. Shear stresses will develop if the neighboring particles of the fluid move relative to one another.

The deformation is measured by the size of the angle ϕ , which is known as shear strain. If the particle at point E moves under the shear stress to point E' and it takes time, t to get there, (shear stress per unit time, τ /time) it has moved with a distance, x. For small deformations, the relationship can be written as:

$$\text{Shear strain, } \phi = \frac{x}{y} \quad (2.4)$$

$$\text{Rate of shear strain} = \frac{\phi}{t}$$

$$= \frac{x}{y} \cdot \frac{1}{t}$$

$$= \frac{x}{t} \cdot \frac{1}{y}$$

$$\text{Rate of shear strain} = \frac{u}{y} \quad (2.5)$$

$u = \frac{x}{t}$ is the velocity of the particle E also known as velocity gradient.

Shear stress is proportional to rate of shear strain,

$$\tau \propto \frac{u}{y}$$

$$= \text{constant} \times \frac{u}{y}$$

$$\tau = \mu \times \frac{du}{dy} \quad (2.6)$$

Where μ , is dynamic viscosity. This equation is also known as Newton's law of viscosity (Sleigh and Noakes, 2009)

2.2.2 Shear rate

To describe the shear rate term, Figure 2.2 is considered. A maximum flow speed, V_{\max} is found at the upper boundary. The speed drops across the gap size, y down to $V_{\min} = 0$ at the lower boundary contacting to the stationary plate. The difference between the flow speeds of the boundaries caused by the shear stress will result the liquid to flow in a specific pattern.

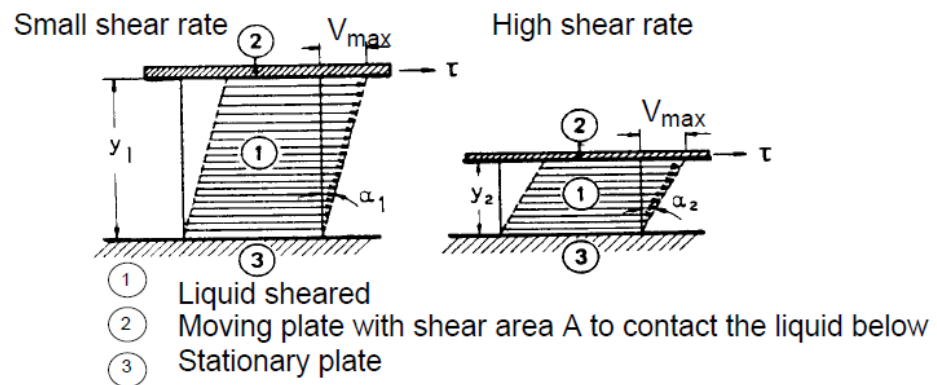


Figure 2.2 Flow between two parallel plate (Schramm, 1994)

To obtain the shear rate expression, the velocity, v of the upper stationary plate, in meters per second, is divided by the distance, y between the two parallel plates in meters. This gives the unit $[1/s]$ or reciprocal second $[s^{-1}]$.

$$\dot{\gamma} = \frac{v}{y} = \frac{v}{y} \left[\frac{m}{s.m} \right] = \left[\frac{1}{s} \right] = [s^{-1}] \quad (2.7)$$

2.2.3 Viscosity

Apart from the shear stress and shear rate, another fundamental rheological property of a fluid is its viscosity, which stands for the resistance of a fluid against flow. Mathematically, viscosity (η) is shear stress divided by shear rate as expressed in Equation 2.7

$$\eta = \frac{\text{shear stress}}{\text{shear rate}} = \eta = \frac{\tau}{\dot{\gamma}} \quad (2.7)$$

Viscosity can be considered as the most appreciated rheological parameters. Due to that fact it is quite common to find instrument called viscometer instead of rheometer. Viscosity is easier to be understood by practitioners and rheology beginners since it can be experimentally proven whether the fluid is thick and thin just by touching, stirring or squeezing the fluid. Hence, more viscometers are available in the market since their construction and principle are less complex than a rheometer.

2.3 Types of flow behaviour

From the rheological properties, the types of fluid flow can be graphically defined. Figure 2.3 shows various plots displaying several flow behaviors of fluids. The gradient of each line can also indicate relatively the differences of viscosity between the non-Newtonian fluids. From the graph, the viscosity for a Newtonian fluid is constant and is independent of shear rate. However, for non-Newtonian fluid, it has a viscosity that changes with the shear rate.

Viscosity of dilatant fluid increases with increasing shear rate, meanwhile viscosity of pseudoplastic fluid decreases with increasing shear rate. However, for Bingham plastic type fluid, it has unique properties where it inherits the Newtonian behavior but will only flow after reaching a certain stress value called yield stress. This behavior also occurred to the plastic type where it is exhibiting the pseudoplastic behaviour after a critical yield stress has been reached.

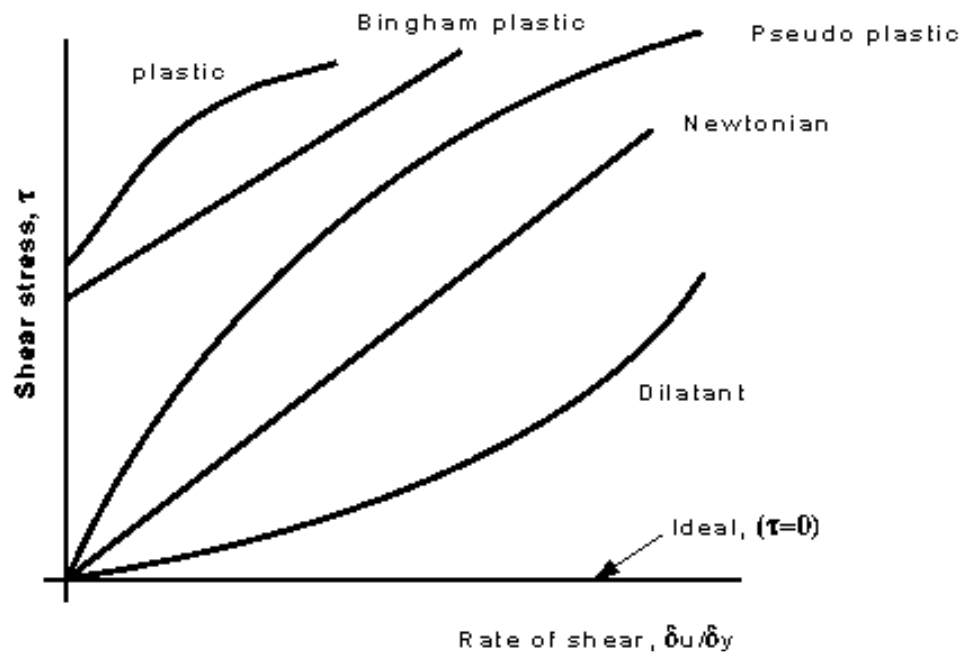


Figure 2.3 Shear stress vs. rate of shear strain (Schramm,1994)

Alternatively, the above shear stress-shear rate flow curve can be represented by plotting viscosity versus shear rate (Figure 2.4). As observed in the previous flow curve, viscosity change with regards to shear rate also can be used as a tool to identify the types of fluid flow or rheological behaviour.

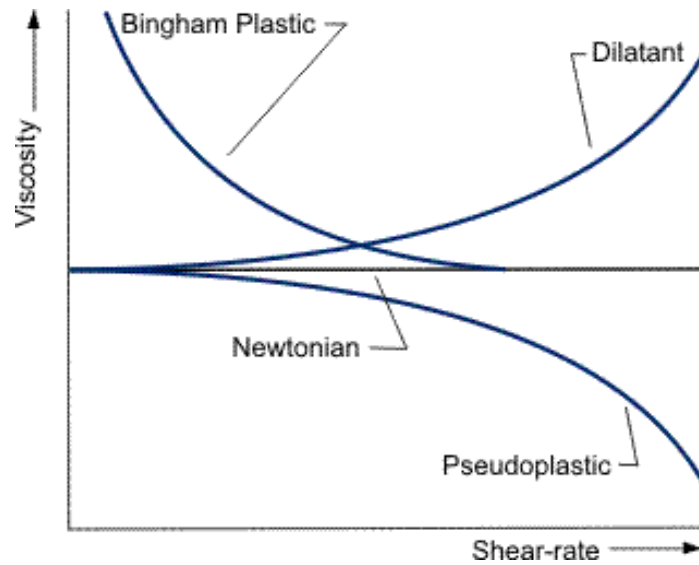


Figure 2.4 Viscosity versus shear rate flow curves for several types of fluids

Figure 2.5 shows the common phenomenon exhibited by different types of fluids in response to shear. When the fluids are stirred, they respond differently where the viscous fluid is thrown outwards and upwards on the container wall by the centrifugal force that is created during the rotation while for the elastic fluid is pulled upwards onto the shaft by the normal force which is exceeding the centrifugal force. This phenomenon can be explained by the normal stress value increase exceeding the shear stress values which force the liquid upwards onto the rotor shaft. This type of flow behavior is known as Weissenberg effect.

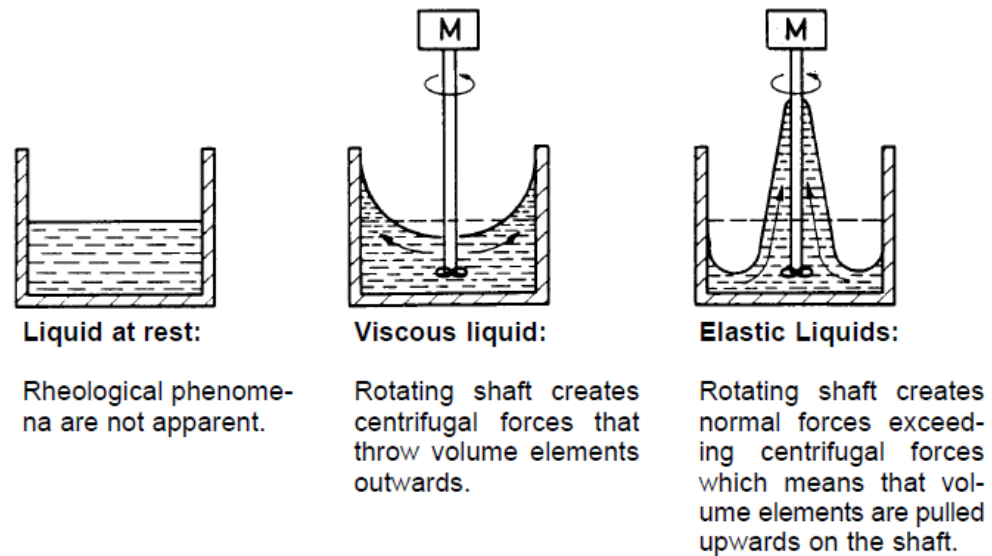


Figure 2.5 The difference in response to shear for viscous and elastic liquids (Schramm, 1994)

2.4 Thermoset resin

Thermosetting resins are the most widely used polymer resins in composite application and is defined as a plastic material which is initially a liquid monomer or oligomers or a pre-polymer, which then can be cured by either application of heat or catalyst to become an infusible and insoluble material. Thermoset polymers have covalent bonds linking the polymer chains. These links prevent the chains from sliding past one another resulting in higher modulus and improved creep resistance. Usually thermosets are more brittle than thermoplastics.

Prior to cure, the resin changes its physical state passing from a liquid to a rubbery and, then, transforming into a glassy material at the end of the processing cycle. Once cured, a tightly bound three dimensional network structure will be formed in the resin and hence the resin cannot be melted, reshaped and reprocessed by heating (Matthews and Rawlings, 1999). This clearly implies a significant variation of the resin mechanical and rheological properties as it experiences curing

process (Antonucci et al., 2006). Therefore, during composite manufacturing, the impregnation process followed by the shaping and solidification were done before the resin begin to cure.

According to Matthews and Rawlings (1999), cured thermoset resins are commonly brittle at room temperature and have low fracture toughness. Moreover, owing to its three dimensional cross linked structure, thermoset resins have high thermal stability, chemical resistance, high dimensional stability and also high creep properties. Thermosetting polymers also offered high electrical and thermal insulating properties that are important in electrical industries.

However, thermosets have the disadvantage of not being recyclable and, in general, having less variable processing technique. Among the most common thermosetting resins used in composite manufacturing are unsaturated polyesters, epoxies, vinyl esters, amino resin and phenolic

2.4.1 Unsaturated polyester resin

Unsaturated polyester resins consist of two main constituents, a short chain polyester containing polymerizable double bonds and a vinyl monomer. Polyester without the presence of vinyl monomer is called unsaturated polyester which is brittle at room temperature and rarely sold. Whenever this polyester is freshly synthesized in a plant, it is mixed with the vinyl monomer in the molten state and the mixture is viscous at room temperature.

2.4.1.1 Vinyl monomer

The most widely used vinyl monomer for unsaturated polyester is styrene. However according to the Environmental Protection Agency (EPA), the use of

styrene and methyl methacrylate are highly volatile and has been identified as a hazardous air pollutant by the environmental protection agency. Therefore, replacing styrene by some other vinyl monomer such as bio-based methacrylate has been reported by Johannes (2017). Several types of vinyl monomers for unsaturated polyester resins are shown in Table 2.2 and in Figure 2.6.

Table 2.2 Vinyl Monomers for Unsaturated Polyester Resins (Johannes, 2017)

Monomer	Remarks
Styrene	Most common, but carcinogenic
<i>p</i> -Vinyltoluene	Not really a substitute for styrene
<i>a</i> -Methylstyrene	Slower curing reaction to avoid thermal stress
Methyl acrylate	Good optical properties
Methyl methacrylate	
Diallyl phthalate	
Triallyl cyanurate	

The vinyl monomer serves as solvent/diluent for the polyester and reduces its viscosity to make it easier to process. The styrene monomer contains carbon double bonds which act as a curing agent by bridging adjacent polymer molecules at their unsaturation points. The curing or cross linking process is initiated by adding a small quantity of catalyst like organic peroxide which is also known as initiator.

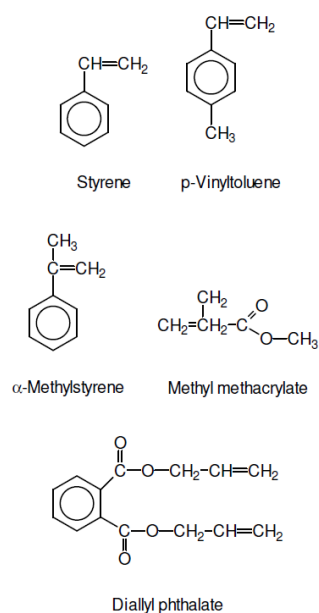


Figure 2.6: Chemical structure of several vinyl monomers for unsaturated polyester resins (Johannes, 2017)

2.4.1.2 Initiator and promoter

Initiator is also known as catalyst. The common initiator used to initiate the curing process of unsaturated polyester resin is peroxide. It can be used alone or can also be used in combination with two or more other reagent. Several peroxide initiators are shown in Table 2.3. Combination of initiator usage is very important. It depends on the process of curing itself. For an example, MEKP along with *tert*-butyl peroxybenzoate (TBPB) was used as a dual-initiator system. MEKP can only decompose into free radicals to initiate the curing process when the temperature is higher than 60°C but at ambient temperature the rate of decomposition is very slow and cannot successfully cure the unsaturated polyester without any promoter. In the presence of promoter such as cobalt octoate or naphthenate, MEKP decomposes rapidly and eventually reduce the processing cycle, increasing the final resin conversion while still maintaining sufficient pot life and gel time for mold filling for the low-temperature processes.

Table 2.3 Types of peroxides used as initiator for unsaturated polyester

Peroxide Type	Example
Ketone Peroxides	Methylethylketone peroxide
	Acetylacetone peroxide
Hydroperoxides	Cumene hydroperoxide
Diacyl peroxides	Dibenzoyl peroxide
Dialkyl peroxides	Dicumyl peroxide
	<i>tert</i> -Butylcumyl peroxide
Alkyl peresters	<i>tert</i> -Butylperoxy-2-ethylhexanoate
	<i>tert</i> -Butylperoxybenzoate
	<i>tert</i> -Amylperoxybenzoate
	<i>tert</i> -Hexylperoxybenzoate
Percarbonates	bis(4- <i>tert</i> -Butylcyclohexyl)peroxydicarbonate

2.4.2 Curing behavior

All the variables as discussed in Section 2.2 can be obtained or collected by application of a rheometer which usually presents a graph or table to predict the curing behavior of thermoset system. Table 2.4, summarized previous studies by researchers to investigate the measured rheological parameters of thermoset resin and the rheometers that were used in measuring the rheological behavior of thermosets which can be easily connected to their curing behavior.

Lin and Lee (1997) used Brookfield viscometer to monitor curing behaviors of polymer networks based on epoxy and acrylics. The results of the study are shown in Figure 2.7.

Table 2.4 Material and type of rheometry used to study rheological properties by researchers

Material used	Rheometer used	Studied rheological properties	Researcher
Fluoroelastomers (FKM)	MCR 302 Anton Paar rheometer.	Temperature dependence of elastic modulus and damping factor	Khajehpour et al., (2014)
Urethane	Physica MCR500	Storage modulus, loss modulus, and complex viscosity	Lee, et al., (2015)
Epoxy resin	A parallel plate SR5, a stress-controlled rheometer	Changes of viscosity G' and $G'' \tan \delta$	Calabrese and Valenza, (2003)
Epoxy-phenolic resins	viscometer (Brookfield Instruments, model DVII+)C.	Viscosity versus time	Chen, et al., (2012)
Epoxy and acrylics	Brookfield LVT viscometer.	Viscosity versus time	Lin and Lee, (1997)
Light-cured denture resin	cone and plate viscometer	Viscosity versus shear rate	Tulachka and Moser, (1989)
Cements mixed with polymeric lattices	coaxial cylinder viscometer using a grooved device	Shear stress versus time	Atzeni, et al., (1989)

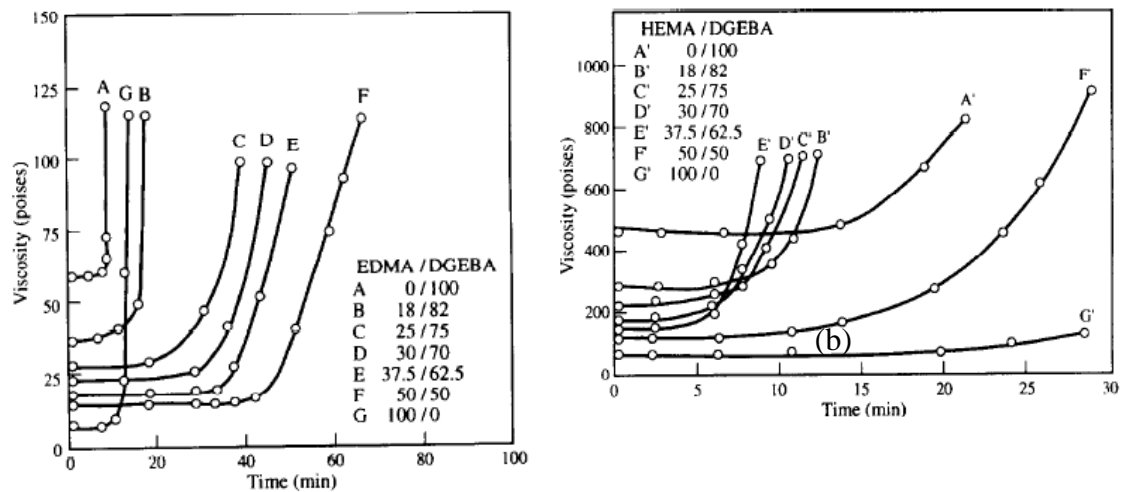


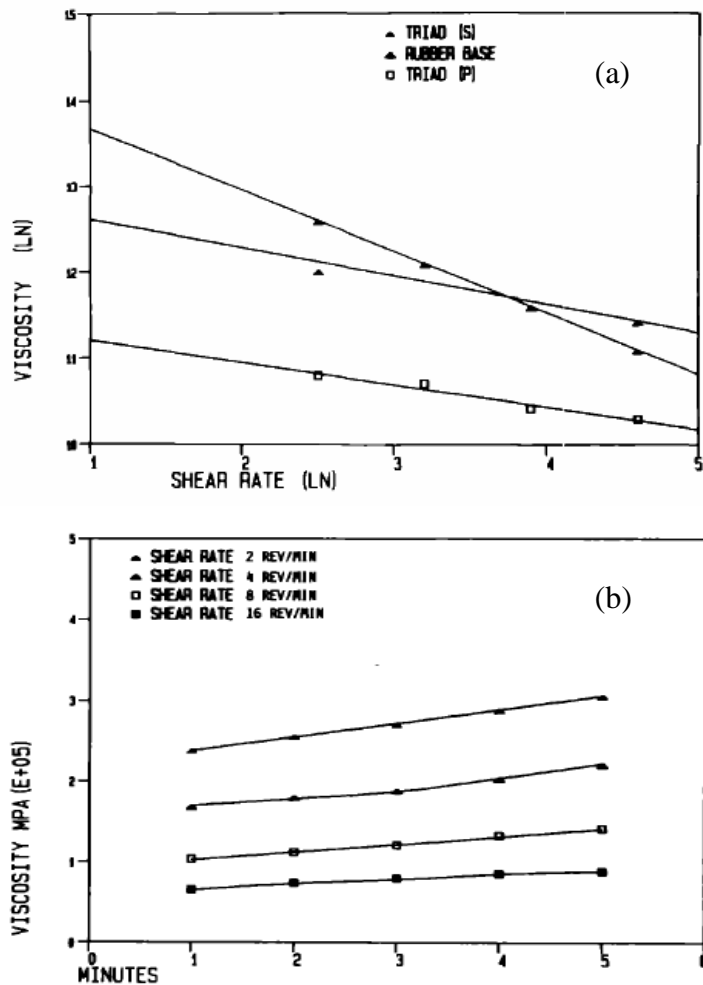
Figure 2.7 Viscosity changes of (a) Fully interpenetrating polymer networks (IPNs) based on ethylene dimethacrylate (EDMA) and diglycidyl ether of bisphenol A (DGEBA) (b) Semi interpenetrating polymer networks (IPNs) based on 2-hydroxyethyl methacrylate (HEMA) and diglycidyl ether of bisphenol A (DGEBA) (Lin and Lee, 1997)

When the results were constructed, it can be observed that the viscosity of the system changes with time, thus giving extra information such as cure time and cure rate of the tested thermoset resins. More advanced results such as storage and loss modulus, cannot be carried out due to constraint of viscometer's capability.

The study carried out by Tulachka and Moser (1989), on evaluation of viscoelastic behaviour of a light-cured denture resin, produced the following result (Figure 2.8) which was measured using a cone-and-plate viscometer. From the presented graph, Tulachka and Moser (1989) suggested that both types of resins are pseudoplastic in nature because both materials had a power law index that was less than 1. This implies that these materials displayed shear thinning properties, meaning that as the shear rate was increased, the viscosity of the materials decreased.

Similar trend of curing behavior can be expected for unsaturated polyester resin by monitoring the fluctuating value of viscosity. The trend and the movement

of viscosity value will represent the mechanism of curing. According to Varshney et al. (2017), the curing process of unsaturated polyester added with methyl ethyl ketone peroxide (MEKP)) is a free radical chain growth polymerization and caused exothermic reaction. Both of the chemical components cured under free radical chain-growth cross-linking copolymerization between the resin double bonds. In their study, the curing reaction was illustrated as shown in Figure 2.9.



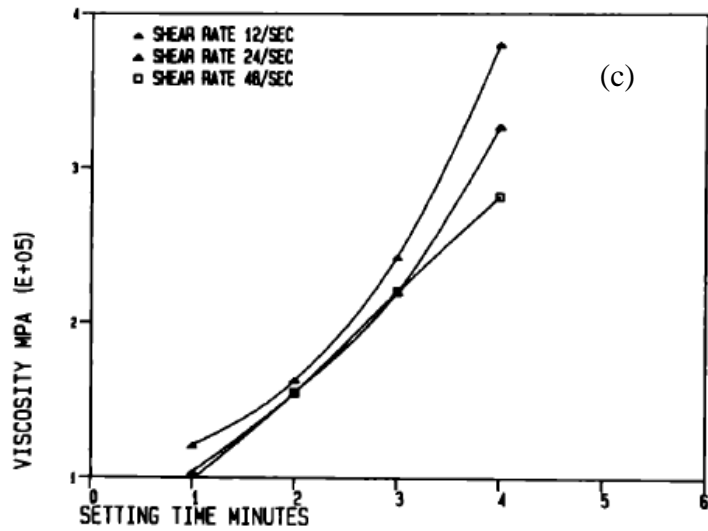


Figure 2.8 (a) Viscosity of investigated material as function of shear rate at 27°C (b) Viscosity of visible light-cured denture material in sheet form at varying low shear rates as function of time (c) Viscosity of rubber base at varying low shear rates as function of time (Tulachka and Moser, 1989)

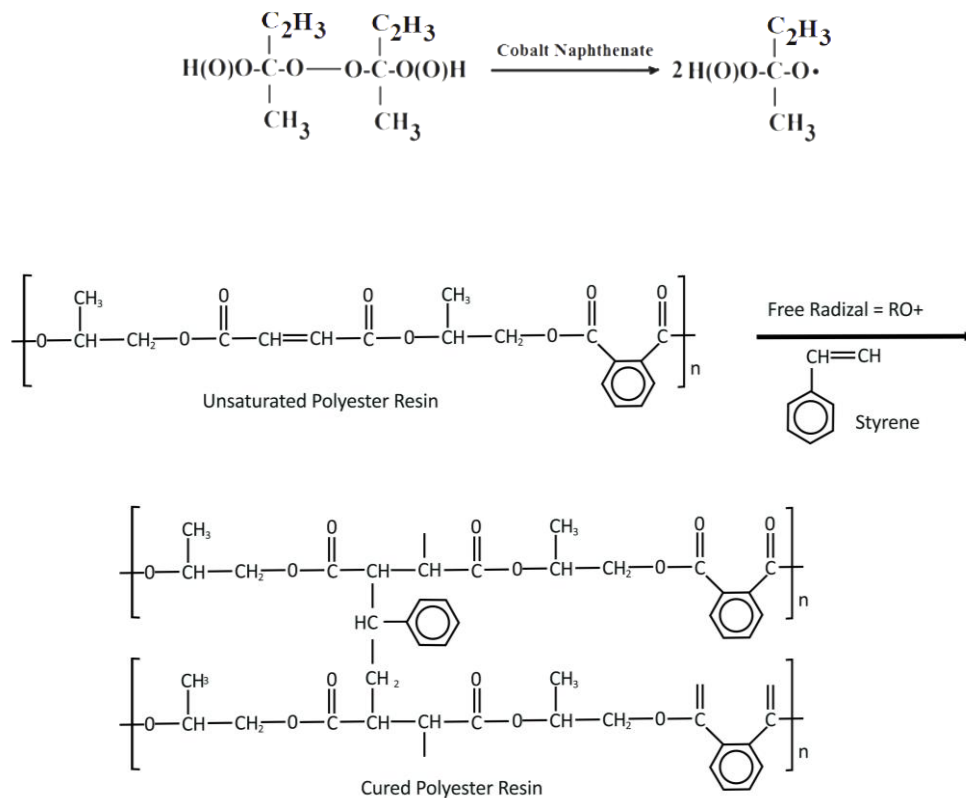


Figure 2.9 Curing reactions for unsaturated polyester with peroxide initiator (Varshney et al., 2017)

During polymerization, Suh et al. (2000) mentioned in their study that unsaturated polyesters can be dissolved in a polymerizable monomer, styrene which is dispersed in the methyl ethyl ketone peroxide. Unsaturated polyester is a long-chain linear polymer containing a number of reactive double bonds (C=C). The polymerizable monomer, styrene also contains reactive double bond (C=C) and acts as a curing agent by bridging adjacent polyester molecules at their unsaturation points. During this styrene–unsaturated polyester crosslinking copolymerization, styrene is decomposed and creates free radicals in the system. According to Atta et al. (2007), these free radicals initiate the exothermic copolymerization reaction. Long-chain molecules of unsaturated polyester connected by styrene monomers was formed which results in a rapid crosslinking and build up in viscosity. Thus, unsaturated polyester resin loses its fluidity and its viscosity becomes very high.

The time taken for the resin start to lose its fluidity is called gel time. Then, the resin start to cure until reach a maximum viscosity which it become fully solid and the time taken to reach this stage is called curing time.

The above findings explain the trend of graph plotted by Hanemann et al. (2010) in his study. The graph is shown in Figure 2.10.

Figure 2.10 shows the increase of MEKP content in the sample, will increase the amount of free radical in the polyester system coming from either the initiator (peroxide) or the styrene vinyl groups. This subsequently able to initiate a chain polymerization which yield a crosslinked styrene-polyester copolymer as described by Kosar and Gomzi, (2004) in Figure 2.11.

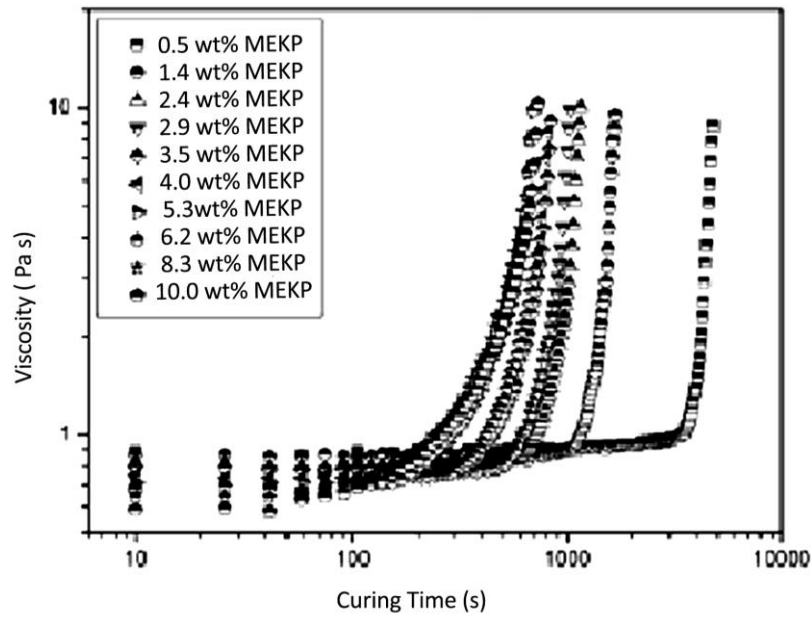


Figure 2.10 Viscosity changes over time for unsaturated polyester resin (65% wt% polymer, 35% styrene) having different MEKP concentrations (temperature 25°C, shear rate 100 s⁻¹) (Hanemann et al. 2010)

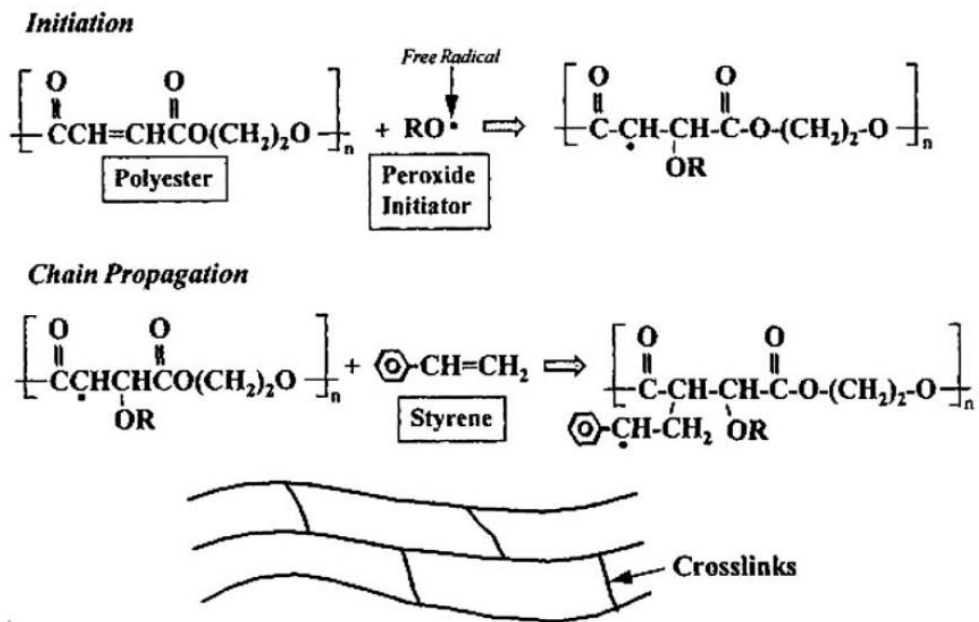


Figure 2.11 Formation of the crosslinked network via chain propagation reaction (Kosar and Gomzi, 2004)

2.5 Rheometer

Rheometer is an instrument for measuring flow which is also can be used to measure viscosity that is defined as “resistance towards flow” for given fluid.

Basically there three types of rheometer depending on the design of spindle used as shown below.

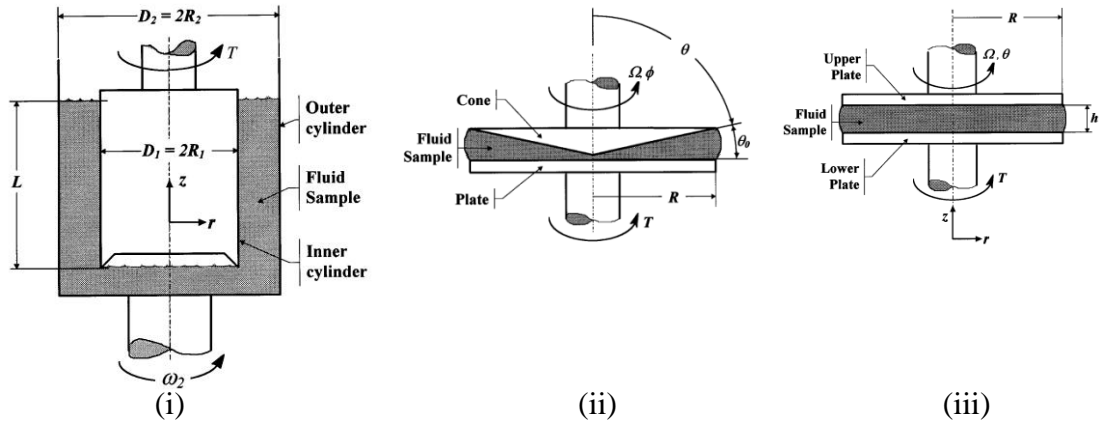


Figure 2.12 Spindle design (i) Concentric cylinders (ii) Cone-and-Plate (iii) Parallel Disc (Leblanc et al., (1999))

Selection of a rheometer depends on the material characteristic and in accordance with the requirements needed by the researchers. Table 2.5 shows the rheometer classification and its basic characteristic.

Table 2.5 Viscometer classification and basic characteristics (Leblanc et al., 1999)

Drag Flow Types:

Flow set by motion of instrument boundary/surface using external or gravity force.

Type/ Geometry	Basic characteristics/Comments
Rotating concentric cylinders (Couette)	Good for low viscosity, high shear rates; hard to clean thick fluids
Rotating cone and plate	Homogeneous shear, best for non-Newtonian fluids and Normal stresses; need good alignment, problems with loading and evaporation
Rotating parallel disks	Similar to cone-and-plate, but inhomogeneous shear: shear varies with gap height, easy sample loading
Sliding parallel plates	Homogeneous shear, simple design, good for high viscosity: difficult loading and gap control
Oscillating body.	Needs instrument constant, good for low viscous liquid metals

2.5.1 Rotational geometries – the parallel plate fixture

In this study, the rotational shearing mechanism of the parallel plate fixture will not be discussed because the mechanical drive for the spindle was designed for oscillation shearing mechanism instead of rotational.

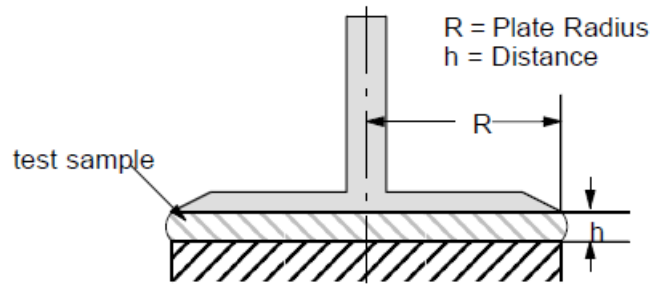


Figure 2.13 Parallel-plate sensor system (Schramm, 1994)

Parallel-plate geometries are chosen instead of cone-and-plate due to the fact that unsaturated polyester resin has high viscosity thus requires big separation distance between the shearing elements in order to measure its rheological properties. From the shear rate equation below:

$$\text{Shear rate, } \dot{\gamma} = M \cdot \Omega \left[\frac{1}{s} \right] = [s^{-1}] \quad (2.8)$$

$M = \text{geometry factor}$

$$= \frac{R}{h}$$

$R = \text{Outer plate Radius}$

$h = \text{gap size between plate [m]}$

The gap size, h is the critical part to be considered where its value should be between 0.3 and 3 mm and the size should be at least 3 times larger than the biggest particle size (Schramm, 1994).