University of Southern Queensland

Faculty of Engineering and Surveying

Shrinkage reduction of thermoset matrix particulate reinforced composites during hardening using low power microwave

A dissertation submitted by

Lee Wai Hung

In fulfillment of the requirements of

Course ENG 4111 and ENG 4112 Research Project

Towards the degree of

Bachelor of Engineering (Mechanical)

Submitted: November, 2007

Abstract

Reinforced composites have become one of the popular construction and manufacturing's materials used in various industries. In comparison to other materials such as ceramic and plastic, utilizes of composite materials such as Vinyl Ester will gives better quality in terms of strength and toughness. According to the research in Centre of Excellence in Engineered Fiber Composite (CEEFC) in University of Southern Queensland (USQ), it was found that Vinyl Ester shrinks significantly when it is solidified or cured under ambient condition. The main drawbacks of this shrinkage in a composite component are the stresses set up internally. To overcome this, microwave technology has been introduced to reduce its shrinkages by removing some of the stresses. Initially, mixture of VE/FLYASH (33%) was prepared before it is exposed to microwave irradiation, where it causes the shrinkages of VE/FLYASH (33%) to be reduced. In terms of engineering materials, shrinkage reduction in composites imply to less brittleness in within the microstructure of the composites. Consequently, the toughness and other mechanical properties of the cured composites will be improved. Direct Volume Measurement Technique (DVMT) was used to determine the percentage shrinkages before it is justified by Pycnometer Technique.

Declaration

University of Southern Queensland

Faculty of Engineering and Surveying

<div style="border: 2px solid black; padding: 10px;">

ENG4111 Research Project Part 1 &
ENG4112 Research Project Part 2

</div>

Limitations of Use

The Council of the University of Southern Queensland, its Faculty of Engineering and Surveying, and the staff of the University of Southern Queensland, do not accept any responsibility for the truth, accuracy or completeness of material contained within or associated with this dissertation.

Persons using all or any part of this material do so at their own risk, and not at the risk of the Council of the University of Southern Queensland, its Faculty of Engineering and Surveying or the staff of the University of Southern Queensland.

This dissertation reports an educational exercise and has no purpose or validity beyond this exercise. The sole purpose of the course pair entitled "Research Project" is to contribute to the overall education within the student's chosen degree program. This document, the associated hardware, software, drawings, and other material set out in the associated appendices should not be used for any other purpose: if they are so used, it is entirely at the risk of the user.

Professor F Bullen
Dean
Faculty of Engineering and Surveying

Certification

I certify that the ideas, designs and experimental work, results, analyses and conclusion set out in this dissertation are entirely my own effort, except where otherwise indicated and acknowledged.

I further certify that the work is original and has not been previously submitted for assessment in any other course or institution, except where specifically stated.

Lee Wai Hung
Student Number: 0050013907

_____ Signature

_____Date

Acknowledgments

I would like to thank Dr. Harry Ku for his time and guidance throughout the duration of this project. His patience and advice is greatly appreciated, and has led me to the completion of this project.

The moral support of my family throughout my years in USQ is also greatly appreciated and this encouragement has been the key to the completion of my course.

Table of Contents

List of Figures

List of Tables

Appendices

Chapter 1

Introduction

1.1 Project aim

The aim is to obtain the accurate percentage shrinkages of Vinyl Ester when it is cured under low power microwaves. Throughout the experiment, low power microwaves will be used to cure the composites before leaving them to harden in ambient conditions. Thirty three percent by weight of SLG reinforced vinyl ester resin, VE/FLYASH (33%) is poured up to 100ml and 150ml mark in empty beakers before curing them with specific exposure time in microwaves. Six beakers were used each time and subsequently the average percentage of shrinkages can be calculated.

To measure the shrinkages accurately, a different technique will be performed; Pycnometer will be employed to determine the density of the cured and uncured composites. This process consists of loading a sample of uncured, then later fully cured, resin into the machine. Accurate density will be determined from the machine. The procedure is repeated for each sample and the percentage shrinkages were calculated from the ratio of densities of cured to uncured resin.

1.2 Project Objectives

The objectives of the project include the following:

- Research on the theoretical background of the existing testing of VE/FLYASH (33%) with microwaves.

- Measure the height of the specimens accurately in beakers. This can be done by using digital vernier calipers. A fine marker pen is used to note the initial height of the specimens. After hardening, height reduction can be seen easily below the reference line.

- Carry out testing in Centre of Excellence in Engineered Fiber Composite (CEEFC).

- Evaluate the effect of environmental impact of curing the resins.

- Investigate the main reason of shrinkages. This can be done by calculations and graphs plotting.

- Compare and justify the results between the two techniques involved; Direct Volume Measurement Technique (DVMT) and Pycnometer Technique.

1.3 Dissertation Overview

This section will discuss the contents of each chapter in brief so that reader can picture the overall structure of the dissertation. There are seven chapters in total which includes introduction as the first and conclusion and recommendations as the last chapter.

Literature Review – This is mentioned in chapter 2. There are two important topics which will be mentioned, one being the machine; Pycnometer and secondly the background information of Vinyl Ester composites. Pycnometer is a precise machine used to determine the density of a material. The product features, technical specifications, the procedure for operation, calibration for better accuracy of Pycnometer is discussed. There are many types of composites used in manufacturing and construction; thermoset and thermoplastic are reinforced to become composites used commonly for various applications. The classifications and families of composites will be discussed.

The interaction of resins with microwaves – This is mentioned in chapter 3. Different type of radiations in terms of its frequencies and wavelengths are explained. To study the physical characteristics of the resins, the operation of a conventional microwave oven need to be understood. Microwaves can penetrate through most of the materials to a certain extent; the absorptions of radiated waves for different materials are not the same. In general, particles will heat up more quickly in fully operated power level. However, power level in microwave oven can be set to lower energy input per second, to suit the conditions necessary for the sample's exposure. This will result in lower temperature in the cured sample. The shrinkage reduction of composites is based on this principle.

Material characteristics of thermoset matrix particulate – This is mentioned in chapter 4. This chapter explains theory on engineering material. Movements of atoms are explained from diffusion to stability and then to solidification state. Activation energy is required for a particle to move and higher activation energy will tend to induce more movements to the particles. Vigorous movement of these molecules will cause the composite in the surface to expand and or evaporate especially when the medium is heated. Therefore, composites will shrinks differently with varying temperature. In high temperature heat treated medium, solidification defects are usually seen on the surfaces or within the composite. Consequently, fractures or cracks are obtained in two different modes; brittle and ductile.

Methodology – This is mentioned in chapter 5. As mentioned, two techniques are involved: DVMT (Direct Volume Measurement Technique) and Pycnometer Technique. Preparation of the composites is mentioned in details with pictures and figures. Consistency must be maintained for both techniques so that accurate results can be achieved. Procedure for the second technique must be followed accordingly as Pycnometer is a piece of sensitive equipment. Modification of microwave oven is crucial so that gases that are harmful to human beings can be removed quickly.

Results and discussions – Chapter 6 is the most important chapter throughout the whole dissertation. Two parts are involved with one technique discussed in each separate part. Equations to calculate cured volume and percentage shrinkage can be found in this chapter. Besides that, there are graphs and tables used to compare the two techniques; in theory the percentage shrinkages of both techniques are meant to close to one another. Uneven results are discussed and justified with reference to the graphs and standard deviations. The last section of this chapter is to compare the results with the previous findings.

Conclusion and recommendations – This is mentioned in chapter 7. Conclusion is based on the author findings with recommendations as a guide for future work in this area.

Chapter 2

Literature Review

2.1 Introduction to Pycnometer

Pycnometer is a device with a standard flask/ container enclosed, which is used to measure the density or specific gravity of materials. Figure 2.1 shows one type of pycnometer operate in the recent days; it gives precise measurement (up to 4 decimal places as displayed in the digital screen as shown in Figure 2.1) of the powder/ particulate placed in the enclosed container. In order to do so, crushed material is added to the container and it must ensure that the lid must be fully tightened before the analysis commences.

Before the powder/ particulate are loaded into the flask, the weight of the sample is obtained from a digital weight balance; one of which is shown in Figure 2.2. The reason of doing this is because the weight of the sample will be prompted into the screen by the key panel located just below the screen. The pycnometer is then filled with a liquid of known density, this happened in the small hole in which the powder is completely separated by the metal container. The weight of the displaced liquid can then be determined and hence the specific gravity of the powder.

In Figure 2.2, the weight of the empty container is displayed in the screen panel, 7.4426g. Glass block is built on top and at the edge of scale; this is to prevent any prevailing wind which could affect the reading. Results of samples and densities can be found in results and discussions section in chapter 6.

Figure 2.1: AccuPyc 1330 Pycnometer

Figure 2.2: Digital weight balance

2.1.1 Product features of AccuPyc 1330 Pycnometer

The AccuPyc 1330 Pycnometer is a fast, fully automatic density analyzer that provides high-speed, high precision volume and density measurements for various materials such as powers, slurries and aggregates. The AccuPyc performs its job by using a gas displacement technique for measurement. The product features includes:

- Measuring the absolute density of aggregates and powder with volumes from 0.1 to 100 ml

- Complete automatic operation

- Capable of measuring open and closed cell foam materials

- Multi volume option allowing analysis if a large variety of sample sizes

- Temperature control version allowing analysis at user selectable temperature range

- Glove box model allowing analysis in controlled environments (Micromeritics Instrument Corporation 1996-2007).

2.1.2 Technical specifications of AccuPyc 1330 Pycnometer

Pycnometer with model number AccuPyc 1330 is one of the instruments manufactured by Micromeritics Instrument Corporation. Its technical specifications are detailed in Table 2.1.   It can be noted that Helium gas is used throughout the analysis. A wire tube is connected to pycnometer and the other end is connected to a Helium gas cylinder, this is shown in the top section of Figure 2.1.

General	
Sample Chamber	Small, 1cm^3 model: 1.2 cm I.D. x 1.1 cm long (with insert: 0.9 cm I.D x 0.8 cm long) Standard, 10cm^3 Model: 1.82cm I.D. x 3.93 cm long (0.72 in. I.D. x 1.57 in. long) Large, 100cm^3 Model: 6.8 cm I.D. x 6.31 cm long (1.92 in I.D. x 2.48 in. long)
Precision:	Typical reproducibility to within 0.01% of the nominal full-scale sample chamber volume. Guaranteed reproducibility to within 0.02% of the nominal full-scale volume on clean, dry, thermally equilibrated samples.
Accuracy:	Accurate to within 0.03% of reading plus 0.03% of nominal full-scale sample chamber volume.
Gases:	Research grade helium is recommended. If unavailable, use helium with a dewpoint of 67 °C -88 °F or lower. Carbon dioxide, dry air, nitrogen, etc. can also be used for specific applications.
Electrical:	Voltage: 90 to 264 VAC Power: 30 VA Frequency: 50/60 Hz
Physical:	Width: 31 cm (12 in.) Height 18 cm (7 in.) Depth: 36 cm (14 in.) Weight 19 kg (38 lbs)
Miscellaneous:	ISO 9001 manufacturer CE certified

Table 2.1: Specifications of Pycnometer with model number AccuPyc 1330

(Micromeritics Instrument Corporation 1996-2007)

2.2 Application of AccuPyc 1330 Pycnometer

Density is calculated based on the Archimedes' principle. The basic definition of Archimedes's principle is that, a body immersed in a fluid is buoyed up by an upward force equal to the weight of the displaced fluid. In determining whether a given body will float in a given fluid, both volume and weight must be considered, the relative density. For a floating body, it has to be less dense than the fluid. On the other hand, it will sink if the body is denser than the liquid. In some circumstances, if the body is two thirds as dense as the fluid, then two thirds of its volume will be submerged.

With this principle in mind, the cured specimen density can be calculated. It is then followed by taking the ratio of cured and uncured resin to determine the shrinkage. Pycnometer is one way to measure the density of a sample. Other method includes using a hydrometer or gas Pycnometer. The density of cured and uncured VE/FLYASH (33%) can be calculated readily and easily from analysis performed with AccuPyc 1330 Pycnometer. Analysis was performed on samples of varying weight of crushed powders using the following procedure:

1. An instrument calibration was performed

2. A weighted amount of power was placed in the cup/ container of AccuPyc 1330.

3. An analysis was performed on the sample prepared in step 2 using the following parameters, and the results were recorded.

   Purges = 3

   Runs = 3

   Run Precision = No

4. Steps 1 to 3 were repeated several times for both 80W and 160W samples with 50 ml and 100ml of VE/FLYASH (33%).

5. The densities of the cured and uncured samples were noted and average value was taken within the 3 densities obtained from each sample.

6. The following equation was used to determine the density of the slurry.

$$\frac{Cured\ Density - Uncured\ Density}{Cured\ Density} \times 100\%$$

(2.1)

Note: Acetone liquid is used to clean the cup/container.

2.3 Sample weighting precision with AccuPyc 1330 Pycnometer

The AccuPyc 1330 series allows user to enter the sample mass (weight) determined to four decimal places. The weight balance as shown in Figure 2.2 does give the reading to four decimal places as well. Four decimals are sufficient even when working with small sample masses; it is not necessary to use additional decimal places.

Density of a sample is defined as the mass of the sample divide by unit volume. The operator enters the sample mass and the AccuPyc calculates the density, D, after measuring the volume, using the equation:

$$D = \frac{M}{V} \qquad\qquad (2.2)$$

where M is the sample mass measured using mass/weight balance, V is the sample volume measured by the AccuPyc

Since the density is calculated from two independent parameters, the expected error in the calculation results from a combination of errors in the two individual measurements. Division is used to calculate the density, thus individual relative errors of the two measured quantities are added to give the density relative error. Hence, the relative error is the actual error divided by the actual measured or calculated values, or

$$E_D = \left(\frac{E_M}{M} + \frac{E_V}{V}\right) x D \qquad\qquad (2.3)$$

where E_M is the maximum expected error in the measured sample mass, E_V is the maximum expected error in the measured volume, and E_D is the maximum expected error in the calculated density.

E_M and E_V are usually very small numbers when compare to M and V. The division of both fractions will yield a very small value; could be $\pm$ 0.001. When

this small value is multiplied to D, it will end up a small E_D. Again, AccuPyc series pycnometer is precise enough to perform its job.

2.4 Calibration for AccuPyc 1330 Pycnometer

Calibration is a technique used to give higher accuracy and precision to AccuPyc 1330 Pycnometers. This technique involves two parts:

1. Correcting for Residual Zero Offset
2. Correcting for Residual Scale Factor Errors

The AccuPyc 1330 pycnometer's automatic calibration routine typically achieves calibration to within ± 0.02% of true scale factor of the pycnometer. For a 10-cc pycnometer, this allows an uncertainty of ± 0.002 cc on an empty chamber which should read exactly zero. Also, the scale factor could cause a sample of exactly 10.000 cc to read between 9.998 cc and 10.002 cc, and if the zero error is included, the reading could be between 9.996 cc and 10.004 cc (Micromeritics Instrument Corporation 1996-2007).

Normally, calibration needs to be done when the machine has been used for a long period of time, or else the machine is accurate enough to perform its job. Due to the fact that this machine will give three values of density for each sample analyzed, within approximately 2-6 minutes. By calculate its average from the 3 readings obtained, it can be concluded that, the machine is accurate enough to analyze the samples of cured and uncured VE/ FLYASH (33%). For more information about calibration, user should look through the manual or hand book.

2.5 Pycnometer with VE/FLYASH (33%) samples

In the laboratory, beakers are crushed to obtain the cured VE/ FLYASH (33%) specimens. For the shrinkage reduction findings, there are two set of volumes to be analyzed (100 ml and 150 ml), each of them has 9 sets of power settings and time durations to be cured in an modified microwave oven. These are listed in the results and discussions section in Chapter 6.

For each set of power setting and exposure time from manual calculations in DVMT (Direct Volume Measurement Technique), one of the beakers with the closest to its average value is used to determine the density shrinkages. In another words, there are 18 beakers to be crushed for both set of volumes.

The step to prepare the samples into the cup/ container of the Pycnometer is as follows: first, rotten rag is used to cover or wrap up the beaker which is then placed in a bucket so that when the beaker is crushed from a hammer, glasses fragments will not scattered through out the work area. This step is required because the cured VE/FLYASH (33%) could not be removed from the beaker by just turning it upside down. This could be due to the irregular inner surface of the beaker.

Secondly, repeated hammering and drilling are used to crush the cured VE/FLYASH (33%) into powdery form which is shown in Figures 2.3 and 2.4. Both hammering and drilling techniques are used to get the aggregates. The reason to this is to observe the feasibility of the results obtained from both crushing methods. The flask/container must be filled up to at least two third by crushed aggregates. The procedure to carry out the analysis with Pycnometer has been described in previous section.

Figure 2.3: Crushed VE/FLYYASH (33%) by hammering

Figure 2.4: Crushed VE/FLYYASH (33%) by drilling

2.6 Introduction to Composite Materials

Composite materials are engineered materials made from two or more constituent materials, which has different physical and/ or chemical properties when combined. The new combined materials will significantly improved properties over the individual components. In this project, the materials to be analysed are Vinyl Ester resin and Flyash (Alumino Silicate). The composite is made from 33% by weight of Flyash with Vinyl Ester resin, VE/FLYASH (33%). Composites can be formed by combining resins and fibers to form polymer-based composites.

Composites are lighter, higher strength and stiffer than conventional materials. This is due to the adaptive nature of fibers, which can align themselves in the direction to carry the load. Composite polymers can be designed to minimize weight without sacrificing strength. This will be discussed later in this section. Further discussion and explanation of composite materials such as the type of composite materials, how it is formed, its classification and behavior under different environmental conditions will be introduced later. In thermosets section, the reader will be explained with commercially produced composites such as polyesters, vinyl ester and epoxy. Other commonly used composite such as Polyimide, Polyamide, Polypropylene and Peek will not be mentioned.

2.7 History of composites

The three key historical steps towards the finding of modern composites were (Schwartz 1997):

1. In 1935, fiberglass filaments were first made. Fiber- reinforced plastics (FRP) were used in construction of aircraft and produced commercially in United States in about 1942. By 1950s, the developments in fiber-reinforced plastic boat hulls, car bodies and truck cabs were introduced.

2. Strong carbon fibers were developed in the late 1960s and early 1970s. These developments parallel the developments of resins dating back to 1969 (Phenolics) and 1937 (epoxies) and of many other important thermosetting resins available today, which can be used to form special fiber-reinforced composites (e.g. Polyimides, Phenolics, Vinyl Esters etc).Thermoplastics development has been rapid. One of the reasons is because the development of thermoplastics was found before thermosets. In the case of resin development, it has increased in development since 1950s with the introduction of E-glass, R-glass, S-glass and special acid and alkali resistant glasses. Glass fiber has been the major reinforcement in the FRP industry. Due to other desires such as lighter, stronger, stiffer structures, carbon and Polyaramid fibers have been introduced.

3. After 1970s, fiber composites industry begun to expand. With the existence of new fibers and matrices, new commercial fabrication techniques were introduced. It was then stepped into next level of designs and developments where speed, maneuverability and weight of substructures of an aircraft need to be taken into consideration.

2.8 Classification of Composite Materials

Composite materials can be classified by Fiber Reinforced Polymers or FRPs, Reinforced carbon-carbon, Metal matrix composites or MMC, Ceramic matrix composites, Organic matrix/ceramic aggregate composites and many more. Generally, composites are polymer matrix, either thermoset or thermoplastic, reinforced with a fiber or other material with a sufficient aspect ratio (length to thickness) to provide a superficial reinforcing function in one or more directions. Not all plastics are composites. In fact, the majority of plastic materials today are pure plastic and not some form of composite. Many products such as toys, decorative products, household goods and similar applications require only the strength of the plastic resin to perform their functions. "Engineering-grade" thermoplastics can offer improved performance characteristics, such as increased

heat distortion temperatures, but usually at higher cost than general-purpose plastic resins. When additional strength is needed, many types of plastics can be reinforced with structural materials- usually reinforcing fibers to meet the demands for higher performance. Any thermoplastic or thermoset plastic resin that is reinforced is considered as a composite. Table 2.2 shows the classification of composites in brief.

FRPs are one type of polymer which is not shown in Table 2.2. It can be classified as fiber and matrix type. Classification by fiber type includes wood (cellulose fibers in lignin and hemicellulose matrix), carbon fiber reinforced plastic or CFRP, Glass-fiber reinforced plastic or GFRP.

	Matrix	Dispersed Phase
Purpose	Transfer to other phases	Enhance Matrix properties
	Protect phases from the environment	MMC: increase δy, Ts and creep
		CMC: increase Kc
		PMC: increase E, δy, Ts and creep
Classification	MMC, CMC, PMC	Particle reinforced and Fiber-reinforced lamellar

Table 2.2: The classification of composites.

Classification by matrix is more to our concern in the research as it includes thermoset and thermoplastic composites. These are usually reinforced with aligned ceramic fibers, such as glass or carbon. Details explanation will be discussed in thermoset and thermoplastic sections. Part of fiber composites properties are shown in Figure 2.5

Reinforced carbon-carbon or RCC is a composite material consisting of carbon fiber reinforcement in matrix graphite. It was developed for nose cones of ballistic missiles, and is widely known for the material used in the leading edges

of space shuttle. The benefits of using RCC are due to its high temperature and shock resistance.

Fiber Composite Properties

- Valid when fiber length $\gg 15\frac{\sigma_f d}{\tau_c}$

Elastic modulus in fiber direction:

$$E_c = E_m V_m + K E_f V_f$$

efficiency factor
aligned 1D: K=1 (anisotropic)
random 2D: K=3/8 (2D isotropy)
random 3D: K=1/5 (3D isotropy)

TS in fiber direction:
$$(TS)_c = (TS)_m V_m + (TS)_f V_f$$

Figure 2.5: The properties of fiber composites

Metal matrix composite (MMC) is another type of composite with at least two constituent parts, one being a metal. The other material may be a different metal or another material such as a ceramic or organic compound. In structural applications, the matrix is usually a lighter metal such as aluminum, magnesium or titanium and provides a strong support for the reinforcement. In high temperature applications, cobalt and cobalt-nickel alloy matrices are common.

Bone (hydroxyapatite reinforced with collagen fibers), cermet (ceramic and metal), concrete are examples of ceramic matrix composites. The physical properties are similar to MMC. The only different is that, ceramic is added to form the composites instead of metal. Organic matrix/ceramic aggregate composites such as asphalt concrete, mastic asphalt, dental composite, syntactic foam are used in different industries. One physical property which is common to all composites is its strength and toughness.

Composites have come into widespread recognition and acceptance among engineers, designers, manufacturers and management for their unique

combinations of performance benefits which these materials offer. Composite features translate into multiple benefits; designers, engineers, and others associated with turning design concepts into product realities can make their jobs easier and more effective.

In considering the formulation of a composite material for a particular type of application, it is important to consider the properties exhibit by the potential constituents. The properties of interest are the stiffness (Young's modulus), strength and toughness. Density is of great significance. Thermal properties such as expansivity and conductivity must also be taken into account. In particular, composite materials are subject to temperature changes (during manufacture and/ or in service), a mismatch between the thermal expansivities of the constituents leads to internal residual stresses. These can have a strong effect on the mechanical behavior. Some representative property data are shown in the Table 2.3 for various types of matrix and reinforcement, as well as for some typical engineering materials and a few representative composites. Inspection of these data shows that some attractive property combination (for example, high stiffness/strength and low density) can be obtained with composites.

Type of material	Density ρ (Mg m^{-3})	Young's modulus E (GPa)	Tensile Strength σ (MPa)	Fracture Toughness Kc (MPa m$^{-1/2}$)	Thermal conductivity K (W m^{-1}K^{-1})	Thermal expansivity α (10^{-6} K^{-1})
Thermosetting resin (epoxy)	1.25	3.5	50	0.5	0.3	60
Engine-ering thermosetting (nylon)	1.1	2.5	80	4	0.2	80
Rubber (polyurethane)	1.2	0.01	20	0.1	0.2	200
Construction ceramic (concrete)	7.8	208	400	140	60	17
Engineering ceramic (alumina)	3.9	380	500	4	25	8
General PMC (in-plane)	1.8	20	300	40	8	20
Adv. PMC (Load // fibres)	1.6	200	1500	40	200	0

Table 2.3: Overview of properties exhibited different classes of material

2.9 The advantages and disadvantages of using composite materials

The advanced in fiber reinforced composite materials is used to distinguish composite materials with high strength and stiffness fibers such as boron and graphite from some of the less capable fibers such as glass. Such advanced composite materials have two major advantages: improved strength and stiffness when compare with other materials on a unit weight basis. For instance, composite materials can be made that have the same strength and stiffness as high-strength steel, yet are 70% lighter! Other advanced composite materials are as much as three times as strong as aluminum, yet only weight 60% as much.

According to Jones (1999), the advantages of composite materials are

- **High strength** – Composites are among the most effective materials in delivering high strength. These materials can be designed to provide a wide range of mechanical properties including tensile, flexural, impact compressive strength. Unlike traditional materials, composites can have their strengths oriented or tailored to meet specific design requirements of an application.

- **Increased (or decreased) thermal or electric conductivity**- This depends on the type of composites use. Normally, metal reinforced composite has better conductivity than polymer type polymer. This also depends on the environment it is being placed, in a microwave environment for example.

- **Design Flexibility** - Composites can be formed into virtually any shape a designer may have in mind: complex or simple, large or small structural or appearance, decorative or functional. With composites, many choices are available to suit the buyer or user preference. Figure 2.6 illustrates the particle-reinforced of elastics modulus.
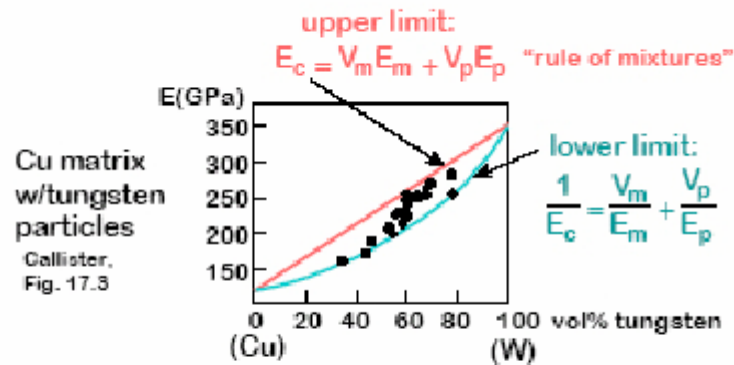
Figure 2.6: Particle-reinforced of elastics modulus

- **Light weight** –Composites deliver more strength per unit of weight than plastics without reinforcement, as well as most metals. This combination of high strength/light weight is powerful incentive for the effective use composites.

- **Dimensional Stability**- Under severe mechanical and environmental stresses, thermoset composites maintain their shape and functionality. Typically, composites do not exhibit the viscoelastic or "cold-creep" characteristics of unreinforced thermoplastics. The coefficient of thermal expansion is reduced. Generally speaking, the yield point of a composite is its break point.

- **Corrosion Resistance** – Composites do not rust or corrode. Even though many polymeric matrix composites are capable of absorbing moisture from the surrounding environment, which creates dimensional changes as well as adverse internal stresses within the material. There are a number of resin systems available, which provide long-term resistance to nearly every chemical and temperature environment. Properly designed composite have longer service life and requires minimum maintenance.

- **Inherent damping**- This has better vibrational energy absorption within the material and results in reduced transmission of noise and vibrations to neighboring structures.

- **Finishing**- In many composites applications color can be molded into the product for long lasting, minimum maintenance appearance. Low profile and low-shrink resin systems are compatible with most metallic painting operations.

The disadvantages are:

- **Cost of raw materials and fabrication**- Materials such as carbon and graphite for metal and Vinyl Ester and Phenolic for resin. These materials are costly to obtain. In process such as fabrication and sample preparations, many of the unused materials will turn into waste and eventually ended up in a dump truck.

- **Environmental degradation of matrix**- Climatic conditions such as wind, temperature, moisture will inevitably causes contraction and expansion in a microscopic level of the matrix. Over a period of time, crack starts to appear from the point where it has the higher stress concentration value.

- **Difficulty with analysis**- Composite materials has been used greatly for the past 50 years, thus it is still consider new to the society. Therefore, high number to testing and experiment need to be conducted to test its behavior under different conditions.

It was found that there are more advantages than disadvantages of using composite materials in industry. This makes the research and development of composite materials vital for the use in next generation.

2.10 The Basics of Polymers

The term polymer comes from "poly" meaning many and "mer", describing a unit. When combining the word "polymer", it simply means many repeating units. Monomers are single building blocks that when joined together form polymers. All polymers commonly used in composites are created from the product taking place in a chemical reaction. Before entering the world of polymers, it is helpful to have an understanding of the chemistry involved. This is part of organic chemistry. Chemists use a shorthand notation for various chemical elements. The significant elements which make up most of the plastics we will discuss here are:

C is carbon; H is hydrogen; O is oxygen; OH is hydroxide; CnH_2n belongs to Alkene's groups.

For example, using this shorthand, a typical polyester resin might be something like:

$$H - (OOC - C_6H_4 - COO - C_2H_4)n - OH$$
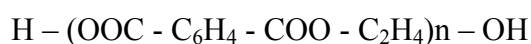
In this case the structure inside the brackets repeats itself many times, as designated by the number n. For a polymer, this would be a long chain and the value for n could be greater than 100.

Using the same shorthand, styrene would be shown as:

$$C_6H_5 - CH = CH_2$$

where - is a single covalent bond, whereas = is a double bond.

2.11 Fibers and Matrices

The role of matrix in a fiber-reinforced composite are:

1. to transfer stresses between the fibers,

2. to provide a barrier against an adverse environment, and

3. to protect the surface of the fibers from mechanical abrasion.

The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. Nevertheless, selection of a matrix has a major influence on the interlaminar shear as well as on in-plane shear properties of the composite material. The ease of processing composite material depends on the physical and thermal characteristics such as viscosity, melting point, and curing temperature of the matrix. Additional functions of a matrix are:

1. to keep the fibers in place in the structure,

2. to help distribute or transfer load, and

3. to carry interlaminar stress.

Some of the matrix materials that have been produced commercially or used in research are show in Figure 2.7.

Polymeric

▪ Thermoset polymers (resins)

    ▪ Epoxies

    ▪ Polyester; vinyl ester

    ▪ Phenolics

▪ Thermoplastic polymers

    ▪ Nylons (such as nylon 6 and 6.6)

    ▪ Polyester

Metallic

▪ Aluminum and its alloys

▪ Titanium alloys

▪ Magnesium alloys

Ceramic

▪ Aluminum oxide

▪ Carbon

▪ Silicon carbide

Figure 2.7: Matrix Materials

Due to the broad topic of composite materials, only polymeric matrix will be discussed in the report even though metallic and ceramic matrices play an important role in today's manufacturing world. Uses of thermoset and thermoplastic polymers will be discussed in the next sections.

2.12 Thermosetting Plastic/ Resin

There are two major groups of plastic or resin, one of them is known as thermoset. Thermosetting plastics are polymer materials that cured with the addition of energy to become a stronger matrix. The energy is in the form of heat energy (above 200 degree Celsius) through chemical reaction or irradiation. Before curing, thermoset materials are usually liquid, powder or malleable and designed to be molded into their final form. The most common thermosetting resins used in the composites industry are unsaturated polyester, epoxies, vinyl ester, polyurethanes and phenolics. There are few differences between these groups that must be understood to choose the proper material for a specific application. Thermoplastic is the second group of plastic which will be explained in next section.

2.12.1 Polyester Resins

Polyester resins are widely used as manufactured fiber in many countries including the United States. It accounts for approximately 75% of the total resins used in composite industries. Examples of products made from polyester are bed sheets, curtains, draperies, cotton, liquid crystal displays, film insulation for wire, insulating tapes and many more. These resins are also available, in different grades, for injection molding of both composite and non-composite parts. Thermosetting polyester resins are commonly used as casting materials, fiberglass laminating resins and non-metallic auto-body fillers. In such applications, polymerization and cross-linking are initiated through an exothermic reaction which involves an organic peroxide such as methyl ethyl ketone peroxide. In general, polyesters are produced by the condensation

polymerization of dicarboxylic acids and diayoric alcohols (glycols). In addition, unsaturated polyester contains an unsaturated material, such as maleic anhydride or fumaric acid, as part of the dicarboxylic acid component. The finished polymer is dissolved in a reactive monomer such as styrene to give a low viscosity liquid. When this resins cured, the monomer reacts with the unsaturated sites on the polymer converting it to a solid thermoset structure.

A range of raw materials and processing techniques are available to achieve the desired properties in the formulated or processed polyester resins because polyester is so versatile. The classical method to synthesis polyesters is by, an alcohol and a carboxylic acid to form carboxylic ester. In this case, the ester formed is usually a sweet smelling compound. Other synthesis technique includes alcoholic transesterification, acylation (HCL method), acetate method (esterification) and ring-opening polymerization. The principal advantage of these resins is a balance of properties (including mechanical, chemical, electrical), dimensional stability, cost and ease of handling or processing.

Unsaturated polyesters are divided into classes depending upon structures of their basic building blocks. Some common examples would be orthophthalic ("ortho"), isophthalic ("iso"), dicyclopentadiene ("DCPD") and bisphenol A fumarate resins. In addition, polyester resins are classified according to end use application as either general purpose (GP) or specialty polyester.

2.12.2 Epoxy Resin

Epoxy is a thermosetting polymer that cures (polymerizes and crosslinks) when mixed with a catalyzing agent. Generally, epoxies are cures by addition of an anhydride or an amine hardener. Each hardener produces different properties to the finished composite. Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A. The structure of the resin can be engineered to yield a number of different products with varying levels of performance. Epoxy resins can also be formulated with different materials or blended with other epoxy resins to achieve specific performance features. Cure

rates can be controlled to match process requirements through the proper selection of hardeners and/or catalyst systems.

The applications for epoxy based materials are extensive and include coatings, adhesives (a compound that bonds two items together) and composite materials such as those using carbon fiber and fiberglass reinforcement. To achieve high performance composites, epoxies are also used for fabricating composites with superior mechanical properties, resistance to corrosive liquids and environments, superior electrical properties, good performance at elevated temperatures or a combination of these benefits. Use of epoxies usually requires a critical application that can justify the use of superior performing but higher cost, resin systems. Epoxy resins are used in marine automotive electrical appliance and other composite parts and structures, although they are generally not cost effective in these markets unless special performance is required. Because their viscosity is much higher than most polyester resins and requires post cure to obtain ultimate mechanical properties, epoxies are more difficult to use.

Epoxies are also used as a matrix resins for "whiskers" such as tungsten, steel, boron carbide, silicon carbide, graphite and quartz. This latter group is of small volume, comparatively high cost and is usually used to meet high strength and/or high stiffness requirements. In aerospace applications, it is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include glass, carbon, Kevlar and boron. Epoxies are also used as structural glue. Epoxies are readily usable with most composite manufacturing processes, particularly vacuum-bag molding, autoclave molding, pressure-bag molding, compression molding, filament winding and hand lay-up.

However, the primary risk associated with epoxy is that, it can induce allergic reaction when used. The two compounds (epichlorohydrin and bisphenol A) used to form epoxy are suspected endocrine discruptors. According to some reports, Bisphenol A is linked to some physical chances in human body such as alteration of male reproductive organs, early puberty induction, shortened duration of breast feeding and pancreatic cancer.

2.12.3 Vinyl Ester

Vinyl Ester is a resin formed by the esterification of an epoxy resin with an unsaturated monocarboxylic acid, such as methacrylic or acrylic acid. The reaction product is then dissolved in a reactive solvent, such as styrene, to 35-45 percent content by weight. Vinyl Ester was developed to combine the advantages of epoxy resins such as low viscosity and fast curing. It can be used as a replacement to polyester and epoxy materials in matrix or composite materials, where its characteristics and strengths are superior to that of polyester, but not as high as epoxy in term of ranking. Vinyl esters are also cured with the conventional organic peroxides used with polyester resins.

In terms of chemistry, there are three families of vinyl esters. The first and most commonly used family is based on the reaction between methacrylic acid and diglycidylether of bisphenol A as shown in Figure 2.8. From corrosive standpoint, this family of ester can resist a wide range of chemicals well.
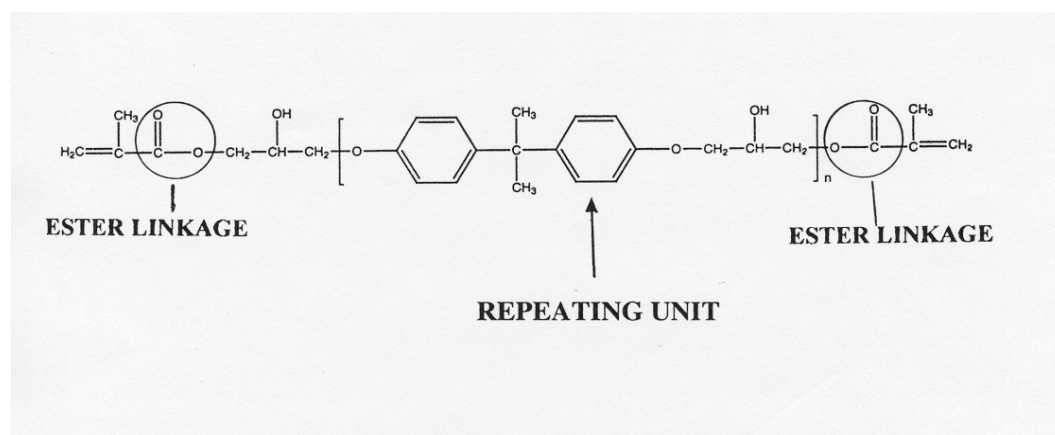
Figure 2.8: The structure of bishophenol A vinlyester

The second vinyl ester family uses a novolac epoxy resin as its starting point. The resulting epoxy vinyl ester resins have a higher crosslink density than the bisphenol A epoxy vinyl ester resins. This means that it is more difficult for chemicals to penetrate the matrix, and they have improved resistance to organic

solvents and mineral acids. The final category of vinyl ester resins is formed when tetrabromo bisphenol-A is used in the manufacture of the resin. Up to 20 percent of bromine is bound into its structure and is designed to have good fire resistance.

Vinyl ester offer mechanical toughness and excellent corrosion resistance. These enhanced properties are obtained without complex processing, handling or special shop fabricating practices that are typical with epoxy resins. The volumetric shrinkage of vinyl ester resins is in the range of 5-10%, which is higher than that of the parent epoxy resins. They also exhibit only moderate adhesive strengths compared with epoxy resins.

2.12.4. Crosslinking of Vinyl Ester

Crosslinks are covalent bonds linking one polymer chain to another. They are the characteristic property of thermosetting polymer materials. Crosslinking are formed by the chemical reactions that are initiated by heat and/or pressure, or by mixing of a non-polymerized resin with various chemicals. In most cases, cross-linking is irreversible, and the resulting thermosetting material will degrade or burn if heated, without melting.

Esters are susceptible to hydrolysis and this process is catalyzed by the presence of acids or bases. Vinyl esters contain substantially less ester groups than polyesters and contain only one at each end of the resin molecule. This is illustrated by the structure of bishphenol A vinyl ester in Figure 2.9. This means that vinylesters are similar to epoxies, where they both have few possible crosslink sites per molecule. Under similar conditions at room temperature, the crosslink of vinyl esters are faster in term of time duration.

The initiator (methyl ethy ketone peroxide, MEKP) used is a molecule that produces free radicals. The free radicals attack one of the double bonds on the ends of the resin and bonds to one of the carbon atoms, thus producing a new

free radical at the other carbon atom. The initiation and crosslinking processes are illustrated in Figure 2.9. This newly

REACTANTS

INITIATION STEP

BRIDGING STEP

CROSSLINKED POLYMERS
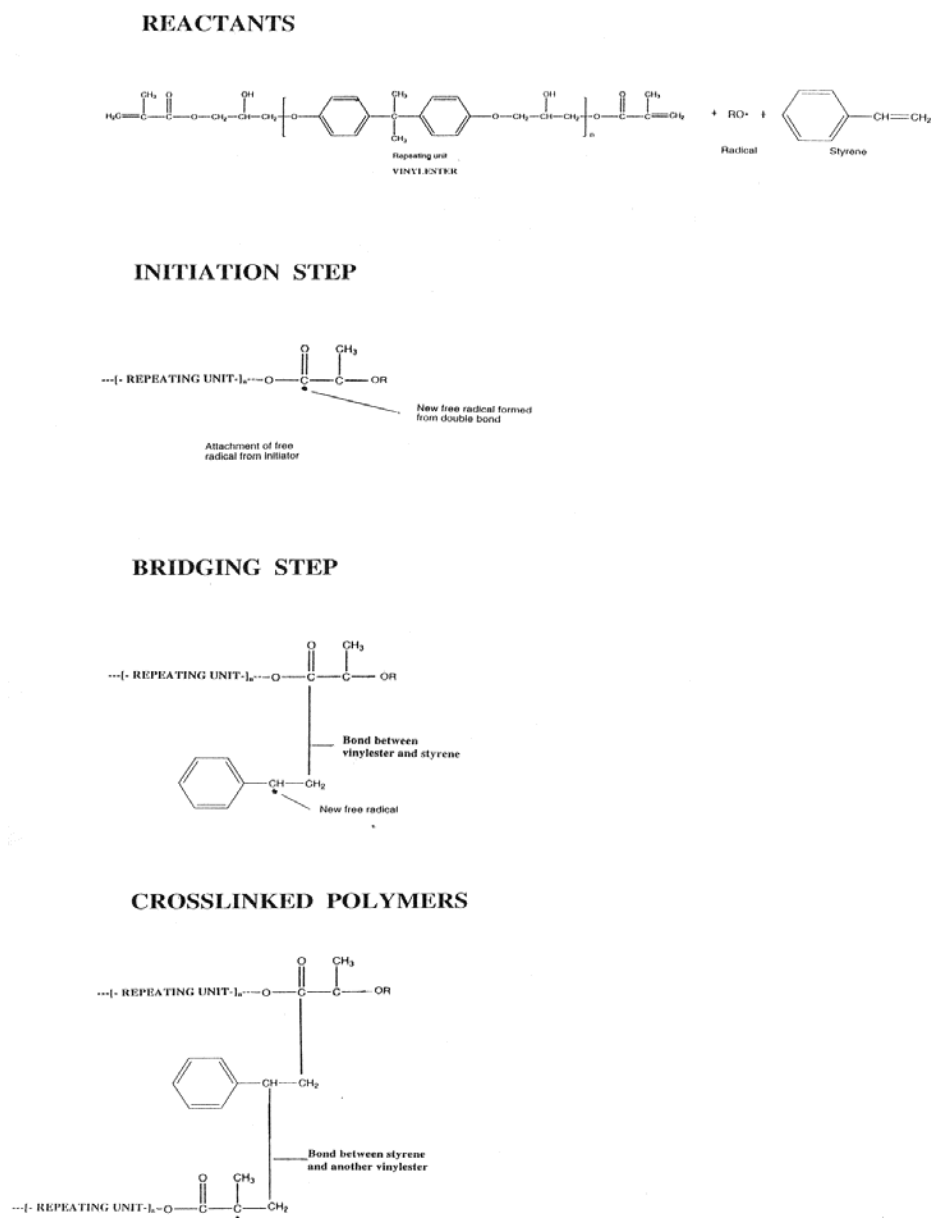
Figure 2.9: Schematic of addition or free radical crosslinking of vinyl ester

created free radical is then free to react with another double bond. Since the small monomer molecules and the styrene molecules move much more freely within the resin than the high molecular weight polymer molecules, this double

bond very likely belongs to a styrene molecule, as illustrated in the bridging step of Figure 2.9. The bridging step creates a new free radical on the styrene, which is then free to react with another double bond and so on.   Obviously the styrene is not only used as solvent, but actively takes part in the chemical reaction.

Figure 2.10 shows typical temperature time relations for crosslinking of a vinyl ester following addition of initiator (Astrom, 1997). The three solid curves on the right hand side of the figure represent room temperature crosslinking of vinyl esters. The different curves illustrate different amounts of initiator, inhibitor, accelerator, ambient temperature and humidity or volume of resin. A reduced amount of initiator and accelerator, as well as an increased amount of inhibitor, leads to later crosslinking at lower temperature. The temperature does not immediately increase after addition of an initiator despite free radicals being produced. Simultaneously, the crosslinking reaction does not start without increase in temperature until all inhibitor molecules have reacted with free radicals, which corresponds to inhibition time. As crosslinking commences, the resin becomes a rubbery solid quickly and the gel time is reached. On the other hand, the dashed line curve on the left hand side of the figure illustrates the hypothetical crosslinking as a result of the application of microwave to the resin. In this case, the inhibition time is short and maximum temperature is reached quickly. It is anticipated that the result of such a curing reduces the shrinkage of vinyl ester. This is because of its initial thermal expansion, which is observed by the initial rise of the level of the composite.
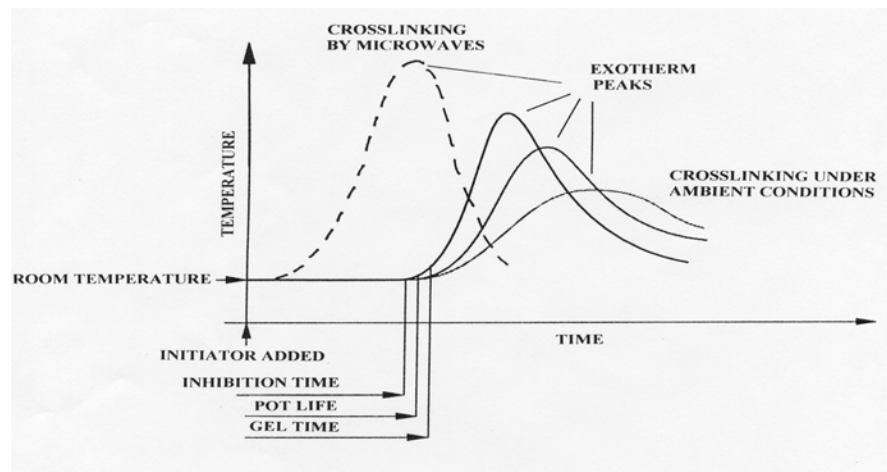
Figure 2.10: Temperature time relationships for crosslinking of vinylester (Ku ed. 2002)

2.13 Thermoplastic Resins

Thermoplastic is materials that can be easily deformed; it will melt to a liquid in the presence of heat and freezes to brittle state when cooled. Most thermoplastics are high molecular weight polymers, but there have weak Van der Waals forces between the chains. Thermoplastics resins have unique and advantageous properties, particularly when combined with reinforcing fibers to make composite materials. Increasingly, designer is capitalizing on the properties of thermoplastic composites to improve product performance and reduce manufacturing costs. Thermoplastic resins are inherently tough and provide superior impact resistance whereas thermoset resins are typically characterized as hard and brittle. Moreover, thermoplastic polymers can be remelted and remoulded unlike thermosetting polymers (Bakelite; vulcanized rubber).

It is the fact that thermoplastic resins do not undergo a time-consuming curing process to achieve final properties. This quality translates to shorter cycle times, increased productivity and lower part costs. In term of environment, composites made from thermoplastic resins can be readily recycled; this often applies to most automotive industries. In addition, thermoplastic are naturally impervious

to attack from harsh chemicals such as petroleum and other existing environmental elements.

Thermoplastic resins will soften and thus enabling the process of shaping or molding when it is heated. For thermoset resins, they are usually in liquid state or are low melting point solids in their initial form. In thermoplastic, post molding shrinkage may be severe due to slow crystallization. For thermoset, post curing often necessary for optimum properties. In term of cost, thermoplastic is a better solution and it provides toughness and less brittleness, whereas thermoset provides higher strength, modulus and average use temperature.

When both of these resins were first discovered, the growth of composites was in thermosets; primarily glass fiber reinforced unsaturated polyester resins. However, in the last couple of years, the growth has moved to reinforced thermoplastics and it is expected to go on expansion due to its improved properties and effective cost of thermoplastics. In order for the user to consider which composite to choose from, it is crucial for them to know the background information of the plastics. A list of comparison between thermoplastic and thermoset will enhance their selection which is shown in Table 2.4.

Property	Thermoset	Thermoplastic	Notes
Resin cost	Low to medium high, based on resin requirements	Low to high; premium thermoplastic prepregs cost more than thermoset prepregs	Decreases for thermoplastics as volume increases
Formulation	Complex	Simple	
Melt viscosity	Very low	High	High melt viscosity interferes with fiber impregnation
Fiber impregnation	Easy	Difficult	
Prepreg tack or drape	Good	None	Simplified by comingled fibers
Prepreg stability	Poor	Good	
Composite voids	Good	Good to excellent	
Processing cycles	Long	Short to long (long processing degrades polymer)	
Fabrication costs	High for aerospace, low for pipes and tanks with glass fibers	Low (potentially)	
Composite mechanical properties	Fair to good	Good	
Interlaminar fracture toughness	Low	High	
Resistance to fluids or solvents	Good	Poor to excellent (choose matrix well)	Thermoplastics stress craze
Damage tolerance	Poor to excellent	Fair to good	
Resistance to creep	Good	Not known	
Database	Very large	Small	
Crystallinity problems	None	Possible	Crystallinity affects solvent resistance

Table 2.4: Comparison between thermoplastics and thermosets (Schwartz 1997).

Chapter 3

The Interaction of Resins with Microwaves

3.1 Introduction

The basic theory of science or heat treated medium is that, particle will expands in the presence of heat, on the other hand particle will contracts when it is treated with low temperature in a medium. Most of the resins that can be found in a lab are in liquid form. When it is mixed with specific amount of fly ash (contains silicon dioxide, aluminium oxide and iron oxide) and accelerator such as MEKP (Methyl Ethyl Ketone Peroxide), it becomes a composite material. Before it is completely solidified, this composite material is being treated in a microwave, to observe its physical properties; after heat is imposed to the content.

The CEEFC Group of USQ had found out that, composites made from Vinyl Ester resins suffer considerable shrinkage during hardening. With this matter, research on the methods to reduce the shrinkage of the composites had been implemented. Ku (2002) claimed that by having Vinyl Ester composites cured under microwave condition, such shrinkage can be reduced.

Thermoset matrices such as unsaturated polyesters, epoxies and vinyl esters are the most common composite used in an industry. Unsaturated polyesters dominate the market due to the variation of matrix. Nevertheless, unsaturated polyester formulations have drawbacks in terms of poor temperature and ultra-violet tolerance. Most epoxies are preferred to use in high-performance applications and can reasonably withstand high temperature.

When epoxy resins are used to make composite structures, there are three main drawbacks (Pritchard, 1999):

i)   Because of their two-step hardening process, they are slow to cure, and they require a minimum post cure of 2 to 4 hours at 120^0C to achieve 70- 80% of optimal properties.

ii)   Their viscosity makes it difficult to wet the glass fibers efficiently.

iii)   The use of amine hardeners renders to cured resins susceptible to acid attack.

Due to these characteristics, the so-called epoxy vinyl ester range of resins (vinyl ester resins) was developed in the 1960s (Pritchard, 1999). Vinyl esters (VE) are chemically closely related to both unsaturated polyesters and epoxies and in most respects represent a compromise between the two. They were developed in an attempt to combine the fast and simple cross linking of unsaturated polyesters with the mechanical and thermal properties of epoxies (Astrom, 1997). To achieve the project objectives, i.e. to reduce the shrinkage of vinyl esters, it will be necessary to apply microwave energy in a multimode oven cavity to samples of vinyl ester resins under controlled conditions. A commercial 800W microwave oven will be used. The power inputs can be varied from 10% (80 W) to 100% (800 W) in steps of 80 W. However only power input of 80W and 160W will be used throughout the project.

3.2 Fundamentals of microwave

Microwaves are waves that have one of the longest wavelengths but relative short frequency in electromagnetic waves as shown below (Figure 3.1). Microwave generally refers to alternating current signals with frequencies range between 300 MHz and 300GHz.

Radio Waves	Microwaves	Terahertz Radiation	Infrared Radiation	Visible Light	Ultraviolet Radiation	X-rays	Gamma Rays
			Increase in frequency				
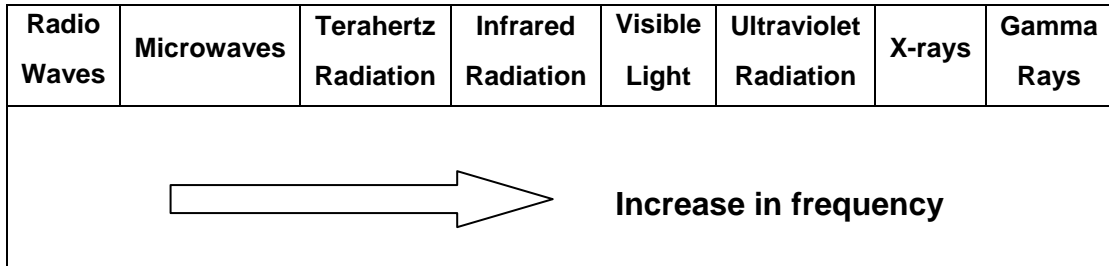
Figure 3.1: Electromagnetic spectrum

Electromagnetic (EM) spectrum is a range of all possible electromagnetic radiation. Radiations as shown above are arranged according to their wavelengths and frequency. In general, higher wavelength will lead to a shorter frequency for a particular radiation. Oppositely, radiation with shorter wavelength will have higher frequency. Frequency and wavelength are related according to the equations:

Wave speed (c) = frequency x wavelength, or

$$\lambda = c \, / \, f \tag{3.1}$$

Electromagnetic energy at a particular wavelength λ has an associated frequency f and proton energy E. Thus, the electromagnetic spectrum may be expressed equally well in terms of any of these three quantities:

$$E = hc \, / \, \lambda \tag{3.2}$$

Where h is Plank's constant (h $\approx 6.626069 \times 10^{-34}$ J.s)

Microwaves can sometime be regarded as radio waves as they lie next to each other in Electromagnetic spectrum. In the case of microwave ovens, the

commonly used radio wave frequency is roughly 2.5 GHz. Radio waves in this frequency range have an interesting property: they are be easily absorbed by water, fats and sugars. The conservation of energy states that energy cannot be created nor destroyed. With this theory in mind, the absorptions of these radiations will converts to another form of energy- heat energy. Apart from this, microwaves in this frequency range have another interesting property; they are not absorbed by most plastics, glass or ceramics. Metal reflects microwave, this is the reason why metal pans do not work well in microwave oven.

Technically, the radio frequency range is divided into bands as depicted in Table 3.1. Bands 9, 10 and 11 constitute the microwave range that is limited on the low-frequency side by Very High Frequency (VHF) and on the high- frequency side by the far infra red. The VHF and Ultra High Frequency (UHF) bands constitute a natural resource managed by three international organizations. These organizations (International Meteor Organization, International Civil Aviation Organization (ICAO) and International Maritime Organization (IMO)) delegate their power to national organizations for allocating frequencies to different users.

Band	Designation		Frequency limits		
4	VLF	very low frequency	3 kHz	-	30 kHz
5	LF	low frequency	30 kHz	-	300 kHz
6	MF	medium frequency	300 kHz	-	3 MHz
7	HF	high frequency	3 MHz	-	30 MHz
8	VHF	very high frequency	30 MHz	-	300 MHz
9	UHF	ultra high frequency	300 MHz	-	3 GHz
10	SHF	super high frequency	3 GHz	-	30 GHz
11	EHF	extremely high frequency	30 GHz	-	300 GHz

Table 3.1: Frequency Bands for Radio Frequency Range

3.3 The interactions of material with microwaves

The first law of thermodynamics states, "The increase in the internal energy of a system is equal to the amount of heat energy added to the system minus the work done by the system on the surroundings". The mathematical statement of the first law of a closed system is given by:

$$dU = \delta Q - \delta W \qquad (3.3)$$

where dU is the increase in the internal energy of the system, δQ is the amount of heat added to the system, and δW is the amount of work done by the system on the surroundings. When microwaves and material interacts, wave energy will convert to heat energy, thus it stores as an internal energy in the system.

The material properties of greatest importance in microwave processing of a dielectric are the complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and the loss tangent, $\tan \delta = \varepsilon''/ \varepsilon'$ (Metaxas and Meredith, 1983). The real part of the permittivity, ε', sometimes called the dielectric constant, mostly determines how much of the incident energy is reflected at the air-sample interface, and how much enters the sample. The most important property in microwave processing is the loss tangent, $\tan \delta$ or dielectric loss, which predicts the ability of the material to convert the incoming energy into heat. For optimum microwave energy coupling, a moderate value of ε', to enable adequate penetration, should be combined with high values of ε'' and $\tan \delta$, to convert microwave energy into thermal energy. Microwaves heat materials internally and the depth of penetration of the energy varies in different materials. The depth is controlled by the dielectric properties. Penetration depth is defined as the depth at which approximately 1/e (36.79%) of the energy has been absorbed. It is also approximately given by (Bows, 1994):

$$D_p = \left(\frac{4.8}{f} \right) \frac{\sqrt{\varepsilon'}}{\varepsilon''}$$

$$(3.4)$$

Where D_p is in cm f is in GHz and ε' is the dielectric constant.

Note that ε' and ε'' can be dependent on both temperature and frequency on the materials. The picture below (Figure 3.2) shows the penetration of microwave into and out of the material.
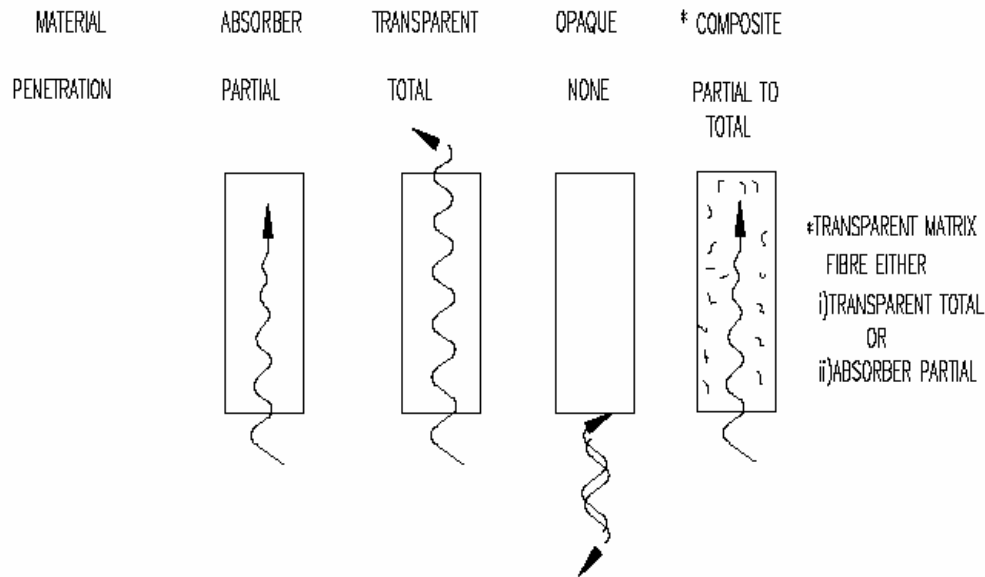
Figure 3.2: Interaction of microwaves with materials

When microwaves operate, microwave energy penetrates through the material. Some of the energy is absorbed by the material and converted into heat, which in turn raises the temperature of the material such that the interior parts of the material are hotter than its surface, since the surface loses more heat to the surroundings. This characteristic has the potential to heat large sections of the material uniformly. The reverse thermal effect in microwave heating does provide some advantages. These include:

- Rapid heating of materials without overheating the surface

- A reduction in surface degradation when drying wet materials because of lower surface temperature

- Removal of gases from porous materials without cracking

- Improvement in product quality and yield

- Synthesis of new materials and composites

Hence, it is crucial to know how much of its material is being heat up when microwaves are introduced to the material in a system. The heat energy imposed to the material will directly cause the material; especially in liquid or molten phase to expand. This is the reason of carrying out this research to explain the shrinkages of material.

3.4 VE and its behavior under low power microwave treatment

High power treatment such as 180W and above will cause pores in the cured sample. This is because when the composite was exposed to prolonged microwave irradiation, a large amount of gases were given off, resulting in a dramatic increase in volume. The presence of pores is to compensation for the volume increase. However, in low power microwave, the irradiation is low and hence it takes longer period of time for the composite to heat up. It this condition, the composite surfaces will remain normal despite its physical properties could alter. Pores trapped in between composites will lead to poor strength and this must be avoided it building and structure.

The tendency of a material to absorb microwave energy and convert it into heat depends on its relative complex permittivity and loss tangent. Ku et al. (2002) showed that liquid rapid Araldite (epoxy resin) has a dielectric constant of 2.81 and a loss tangent of 0.244 at 2.45 GHz at room temperature. High loss tangent imply that, epoxy resin used to form VE can also absorbs microwave irradiation easily.

A possible risk in applying microwave energy to the vinyl ester composite is the interaction of styrene in the resin with the high voltage (HV) transformer in the oven. The oven cavity used was spot welded together and is not necessarily

water/air/steam proof. Styrene is a flammable vapor and will be given off during the curing process of the composite. The gas may explode if it is affected by the heat of the HV components. The oven does not have an exhaust fan. A blower motor inside sucks air through the air filter at the front and cools the HV transformer as the air passes. The air from the fan is blown into a duct and cools the magnetrons. Some air is forced into the cavity at the back and then out of the steam exhaust outlet at the back.

However, only 10 and 20 percents of commercial 800W oven were used in the experiment. This reduces the risk factor by at least 6 by comparing to setting the power level to normal (800W). In this case, it is obvious that the penetrations of wave energy into the contents are not as much as normal power setting. Therefore, the heat energy that can be transmitted through to the core of the content will be minimal. As an unsupportive saying, it is expected the heating of the contents are not as great as what it usually does.

As a precaution, a beaker of 10 ml of the composite was exposed to microwave irradiation for 30 seconds for trial. The power used was 180 W. There was no arcing at all. Longer exposures (1 to 2 minutes) of microwaves were tried for the same composite, again there was no arching. It seems either the forced air can blow out some of the styrene out of the cavity or the cavity is shielded from the HV transformer.

3.5 Low and high power microwaves

In fact, the differences of curing composite in low and high power microwaves are still under research. The microwave that is used in our experiment consists of a high voltage transformer, which passes energy to the magnetron, a magnetron control circuit, a wave guide, a cavity magnetron and a cooking chamber. Modification is made in the microwave so that an extra duct is used with the exhaust fans to remove the air accumulate in the cooking chamber.

A microwave oven works by passing non-ionizing microwave radiation through the substances placed in the cooking chamber. VE/FLYASH (33%) in the beaker absorbs energy from the microwaves in a process called dielectric heating. Many molecules are electric dipoles, which mean they have both negative and positive charges at the end. These molecules rotate as they try to align themselves with the alternating electric field created by the microwaves. Therefore, the rotating motions of the molecules create heat which is then passes to the following molecules and eventually the liquid heats up. Microwave heating can also be explained as a rotational resonance of water molecules.

3.5.1 Duty cycle of Magnetron

Magnetron is a high powered vacuum tube that generates coherent microwaves. It is commonly found in conventional ovens and also various radar applications. The power setting of a microwave oven can be set from 0-100 percent. However the common power settings used in a controller system were: 100%, 80%, 50% and 30%, which were achieved by modifying the duty cycle during a 12 seconds period. The magnetron operation involved two (2) phases. The first was a transient phase and consisted of the cathode warming up, which took around one (1) second after which electrons were emitted.

The next phase was a steady state phase when microwaves were generated. The duty cycle comprised two phases: "ON" phase and "OFF" phase. The "ON" phase of a duty cycle involved the transient phase (TP), plus the steady state operation (SS), plus the shut down period (SP) of the magnetron, the latter of which was very rapid and approached zero. The "OFF" phase meant power was not supplied to the magnetron.

At the 30% power setting, and for 15 seconds duration, the operation was as follows:

"ON" phase: TP + SS + SP; TP = one (1) second; SS = 30% x 12 seconds = 3.6 seconds; SP = 0 second. Therefore, the heating cycle composed of five (5)

seconds "ON" followed by seven (7) seconds "OFF" and followed by three (3) seconds "ON". The total time was fifteen (15) seconds and the last three (3) seconds were merely a fragment of the next duty cycle. For the experiment in this project, the 10% and 20% power setting tested are based on the same explanations from the 30% power setting.

The 30% setting therefore referred to a percentage of the duty cycle and not the continuous microwave output power. It was 100% power delivered 30% of the time, but the average power was 30% of the full power. Over longer duration, the time average power output would approach 30%, but for short programme times, the researcher has to be aware of the difference between continuous wave output power and the duty cycle approach. The time weighted average power output between the two approaches could differ by as much as 70%.

3.6 Rheology of curing Vinyl Esters

Rheology is the study of the deformation and flow of matter under the influence of an applied stress. The scope of Rheology is shown in Table 3.2 to ease the understanding of the term to reader.

	Solid mechanics or strength of materials	Elasticity	
Continuum Mechanics		Plasticity	Rheology
	Fluid mechanics	Non-Newtonian Fluids	
		Newtonian Fluids	

Table 3.2: The continuum mechanical scale (Wikipedia 2007)

Figure 3.3 depicts the degree of cure for vinyl ester against time at various isothermal cure temperatures. It is found that if the cure temperature is 60°C, the

curing completes in 11 minutes after the inhibition time and the degree of cure is 0.69. Similarly, if the cure temperature is 40°C, the curing completes in 13 minutes after the inhibition time and the degree of cure is 0.36.

To achieve a completely cured VE/FLYASH (33%), the degree of curing must be equal to 1.0. From the graph in Figure 3.3, the temperature require to do so must be higher than 60 for time duration of 11 minutes. Conversely, the test specimen can leave in ambient condition for longer duration so that it will turn completely hardened. This can be justified by looking at Figure 3.3 once again, the threes lines are moving upwards or increase towards the degree of cure axis as the time duration gets longer.
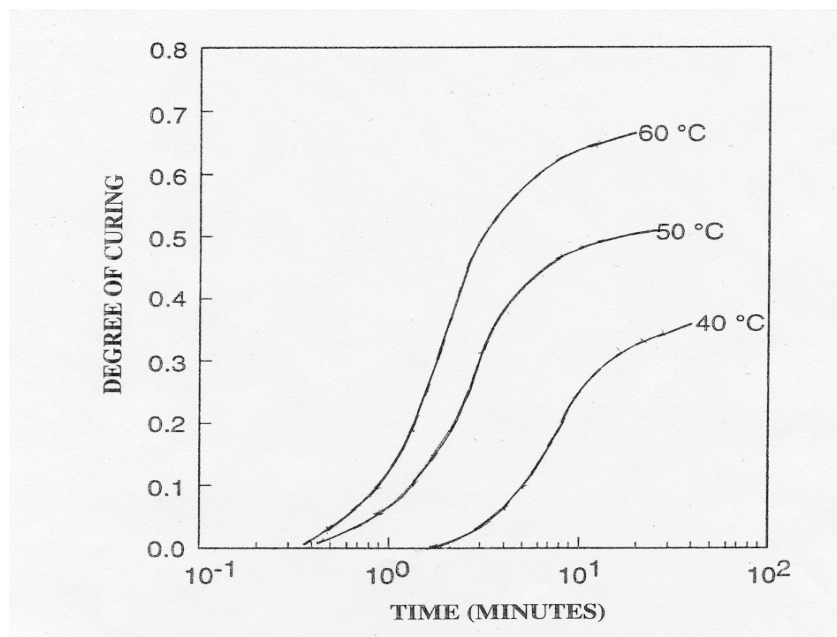
Figure 3.3: Degree of cure of VE at different curing temperatures

Chapter 4

Materials Characteristics of Thermoset Matrix Particulate

4.1 Introduction

Particulate composites contain large amounts of coarse particles that do not effectively block slip. The particulate composites are designed to produce unusual combinations of properties rather than to improve strength.

Rule of mixtures: Certain properties of a particulate composite depend only on the relative amounts and properties of the individual constituents. The rule of mixtures can accurately predict these properties. The density of a particulate composite is

$$\rho_c = \sum (f_i \cdot \rho_i) = f_1 \cdot \rho_1 + f_2 \cdot \rho_2 \dots + f_n \cdot \rho_n \, ,$$

(4.1)

where ρ_c is the density of the composite, $\rho_{1,} \rho_{2,} \dots_{,} \rho_n$ are the densities of each constituent in the composite, and f_1, f_2, …, f_n are the volume fractions of each constituent (Askland & Phule 2003).

Many engineering polymers that contain fillers and extenders are particulate composites. Extender such as Flyash and various clays are added so that a smaller amount of more expensive polymer is required. The extenders may stiffen the polymer, increase the hardness and wear resistance, increase thermal conductivity, or improve resistance to creep. However ductility normally decreases as shown in Figure 4.1.
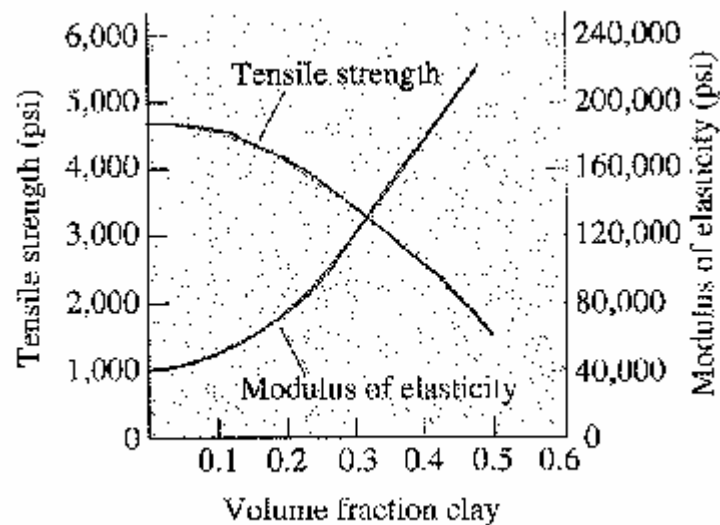
Figure 4.1: The effect of clay on the properties of polyethylene

VE/FLYASH (33%) is the thermoset particulate used to analyze the shrinkages. The shrinkages are crucial to researcher as well as builder so that correct amounts of aggregates are use to avoid catastrophic failure. Being treated in a conventional microwave is one way to reduce its shrinkages as material or particulate expands when it is heated.

Experiments carried out previously shows that conventional microwave oven do affect the mass behavior of this thermoset particulate. This chapter will look into the detail of the material properties such as residual stresses built up within the particulate, the stability of atoms and ions, diffusion, activation energy and other factors that might cause the shrinkages to happen. Moreover, topics such as

factors affecting the solidification structure, fracture analysis and hardness of the thermosetting polymer will be mention in this chapter.

4.2 Stability of Atoms and Ions

Imperfections or defects in a crystalline material are of three general types: point defects, line defects or dislocations, and surface defects. However, in normal situation, these imperfections in ions or atoms are not stable or at rest in the crystal structure. Instead, the atoms or ions posses' thermal energy and they will move, even without introduction of microwave energy. The movement depends on the amount of energy gained. Low power microwaves will gradually increase the thermal energy and the movement of atoms or ions which can be vigorous if it is placed for a long period of time.

For instance, an atom may move from a normal crystal structure location to occupy a nearby vacancy. An atom also moves from one interstitial site to another. Atoms or ions may jump across a grain boundary, causing the grain boundary to move. The ability of atoms or ions to diffuse increases as the temperature possessed by the atoms or ions increases. The rate of atom or ion movement is related to temperature or thermal energy by the Arrhenius equation:

$$Rate = c_o \exp\left(\frac{-Q}{RT}\right)$$

(4.2)

where c_o is a constant, R is the gas constant (1.987 cal/mol.K), T is the absolute temperature (K), and Q is the activation energy (cal/mol) required to cause an Avogadro's number of atoms or ions to move.

4.3 Diffusion of particles

The classic definition of diffusion is the movement of particles from area of higher concentration to area of lower concentration until equilibrium is reached. However, in mechanic of material perspective, the diffusion of particles can be movement of particles within the surrounding fluid or lattice. Regardless of which, both definitions are still governed by the same diffusion equation. This equation is derived from Fick's law, which states that the net movement of diffusing substance per unit area of flux, J is proportional to the concentration gradient and is toward lower concentration. Fick;s first law explains the net flux of atoms:

$$J = -D\frac{dc}{dx}$$

(4.3)

where J is the flux, D is the diffusivity or diffusion coefficient and dc/dx is the concentration gradient. Depending upon the situation, concentration may be expressed as atom percent (at%), weight percent (wt%), mole percent (mol%), atom fraction, or mole fraction. The units of concentration gradient and flux will also change respectively. However, Fick's law assumption that may not hold for a given diffusive system such as the diffusion may depend on concentration in addition to concentration gradient (Askland & Phule 2003).

4.3.1 Activation Energy for diffusion

A diffusing atom must squeeze past the surrounding atoms to reach its new site. In order for this to happen, energy must supply to force the atom to its new position. This is illustrated schematically for vacancy and interstitial diffusion in Figure 4.2. The atom is originally in a low-energy, relatively stable location. In order to move to a new location, the atom must overcome an energy barrier. The energy barrier is the activation energy Q.
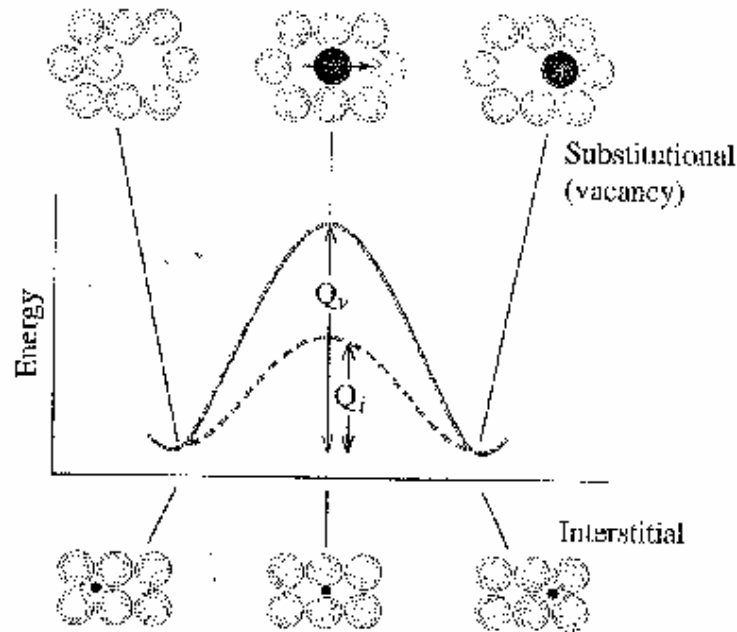
Figure 4.2: Activation energy is required to squeeze atoms past one another during diffusion.

Normally, less energy is required to squeeze an interstitial atom past the surrounding atoms; consequently, activation energies are lower for interstitial diffusion than for vacancy diffusion. Vacancy diffusion is defined as diffusion involving substitutional atoms, an atom leaves its lattice site to fill a nearby vacancy. As diffusion continues, we have countercurrent flows of atoms and vacancies. Interstitial diffusion is where a small interstitial atom or ion present in the crystal structure, the atom or ion moves form one interstitial site to another. No vacancies are required for this mechanism. This is because there are more interstitial sites than vacancies. Interstitial diffusion occurs more easily than vacancy diffusion. The two important mechanisms are shown in Figure 4.3 (Askland & Phule 2003).

.
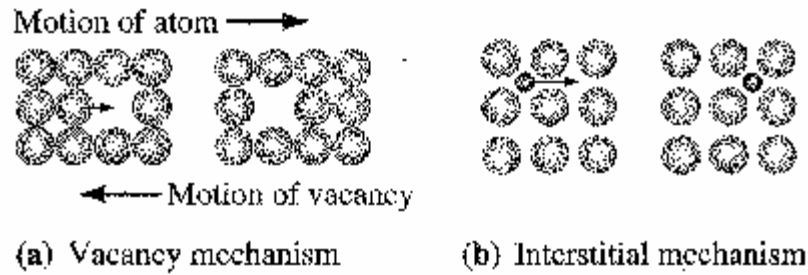
Figure 4.3: Diffusion mechanisms in materials

Shrinkage of VE/FLYASH (33%) happens partly because of this movement of the atoms and ions. The movement is large when external energy such as microwave energy is introduced to the atoms and ions which enhance them to move. In this situation, both mechanisms will occurs which causes pores or voids to form in between the lattice. The increase of pores or voids can be seen with an increase in time duration placed in a microwave. This is shown in Figure 4.4. The present of pores or voids will essentially reduce the shrinkage in VE/FLYASH (30%).
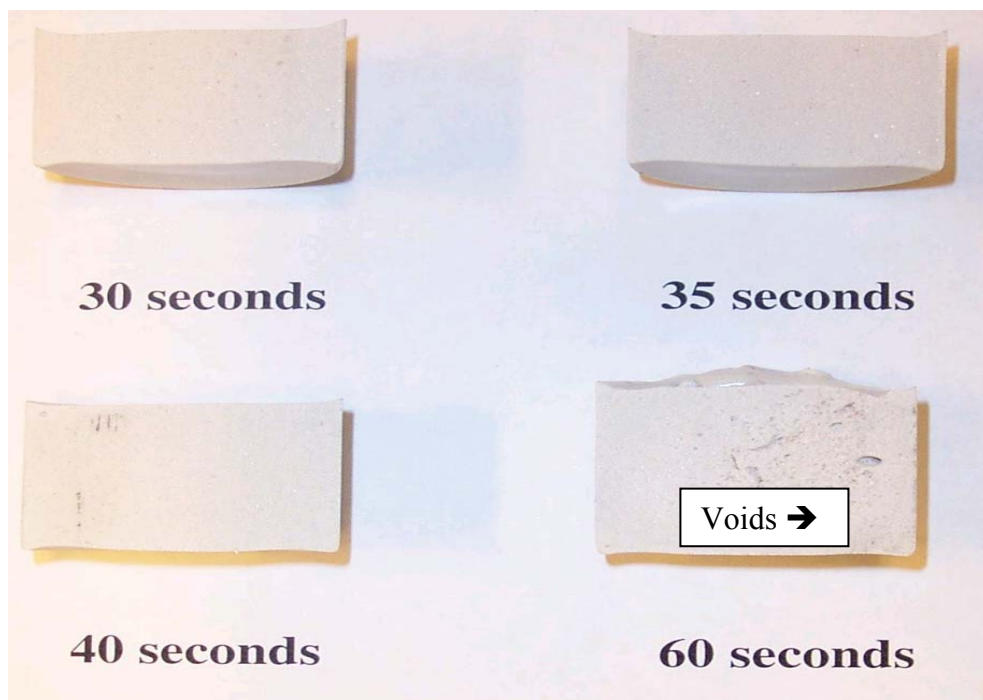
Figure 4.4: The cross sections of 4 composite samples exposed to different duration of microwave irradiation

4.3.2 Factors affecting diffusion

Temperature and the diffusion coefficient are the main factors affecting diffusion. The kinetics of the process of diffusion is strongly dependent on temperature. The diffusion coefficient D is related to temperature by an Arrhenius type equation,

$$D = D_0 \, \exp\left(\frac{-Q}{RT}\right)$$

(4.4)

where Q is the activation energy, T is the temperature in absolute, D_0 is the pre-exponential term. Depending on the material D_0 can be found in most material handbook and it is given in (cm/s^2). For instance, the D_0 for aluminum in face-centre-cubic is $0.10 \, cm/s^2$.

In ionic materials such as oxides which are one of the components present in flyash, a diffusion ion only enters a site having the same charge. In order to reach that site, the ion must physically squeeze past adjoining ions, pass by a region of opposite charge, and move a relatively long distance (Figure 4.5). Consequently, the activation energies are high and the rates of diffusion are lower for ionic materials than those for metals (Figure 4.6) (Askland & Phule 2003).

.
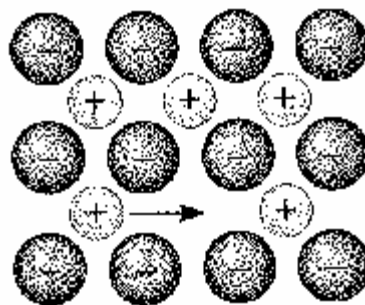
Figure 4.5: Diffusion in ionic compounds

In Figure 4.6, since most of the temperature taken in the experiment for a short period of time with low power microwave exposure is less than 100^0C. It is obvious that flyash which contains silicon dioxide, aluminium oxide and iron oxide with lower temperature (below 100^0C) does not show on the graph. Extrapolation of line can be made to get the value of D. For example Fe in $Fe_{0.95}O$ can be extrapolated to 100^0C and then D can be found to be approximately 10^{-13} cm/s^2.
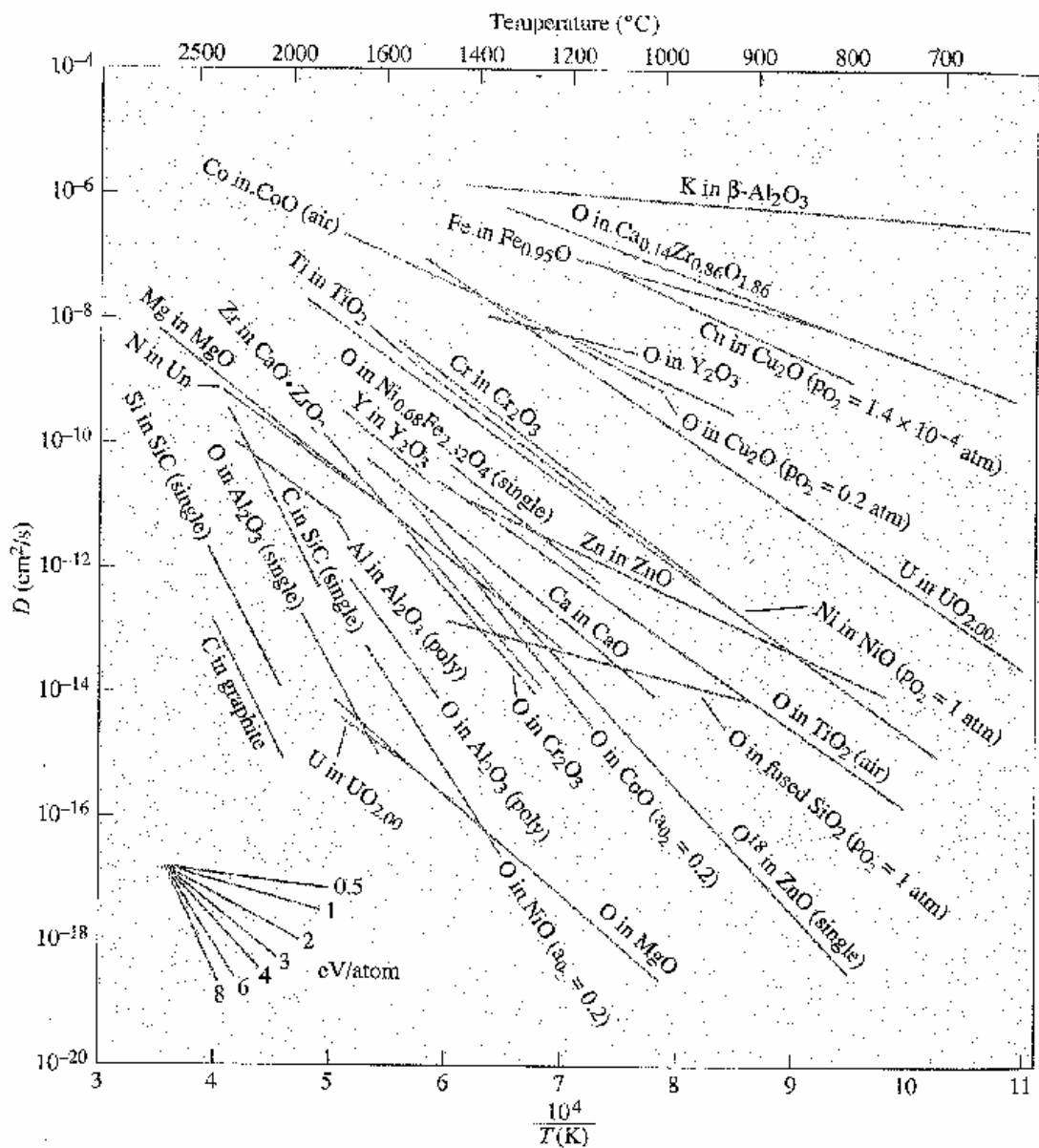
Figure 4.6: Diffusion coefficients of ions in different oxides

4.4 Solidification of particles

Nucleation is another term used to precisely describe the solidification of particles. In atomic physics sense, it refers as the formation of the first nano-sized crystallites from molten material. However, in a broader sense, the term refers to initial stage of formation of one phase from another phase. In general, we expect a material to solidify when the liquid cools to just below its freezing (or melting) temperature, because the energy associated with the crystalline structure of the solid is then less than the energy of the liquid. It must be noted that the Methyl ethyl ketone peroxide (MEKP) used in the experiment to act as a catalyst which initiates the polymerization of polyester resin. Its application is to speed up the chemical reactions between the reactants and it has nothing to do with how the particle solidified. MEKP is a catalyst and thus will remain physically unchanged in the end of the reaction.

4.4.1 Grain size strengthening

Grain size strengthening is an application of controlled nucleation, when the VE/FLYASH (33%) freezes, impurities in the melts and walls of the beaker serve as heterogeneous nucleation sites. This statement is valid only if high temperature (more than 100^0C) is used. Despite this experiment is carried out with low temperature, high temperature usage needs to take into consideration as it is important in civil applications. Heterogeneous nucleation is defined as nucleation on preexisting surfaces. The process is dependent on the contact angle for the nucleating phase and the surface on which nucleation occurs. Grain refinement or inoculation is the term used to describe the intentionally introduce nucleating particles into the liquid. Similarly, in our experiment, chemical such as MEKP added to molten particulates to promote nucleation and hence, finer grain size, are known as grain refiners or inoculants. Grain refining or inoculation produces a large number of grains, each beginning grow from one nucleus. The greater grain boundary area provides grain size strengthening not only in metallic materials but also in polymer such as vinyl ester.

4.4.2 Solidification defects

Shrinkage of particulate is one type of defects occurs during solidification. This shrinkage and the porosity can be harmful to builders and designers as it may result it catastrophic failure in load bearing application such as turbine blades. Practically, materials are denser in the solid state than in the liquid state. The results of shrinkages of VE/FLYASH (33%) are tabulated in Appendices B and C , however Table 4.1 illustrate the percentage shrinkages of some other materials and the shrinkage of material may go up to 7%.

Material	Shrinkage (%)
Al	7.0
Cu	5.1
Mg	4.0
Zn	3.7
Fe	3.4
Pb	2.7
Ga	+3.2 (expansion)
H_20	+8.3 (expansion)
Low Carbon Steel	2.5-3.0
High Carbon Steel	4.0
White Cast Iron	4.0-5.5
Grey Cast Iron	+1.9 (expansion)

Table 4.1: Percentage Shrinkage during solidification for various materials

Normally, the bulk of shrinkage occurs as cavities, if solidification begins at all surfaces during curing or casting. Simultaneously, if one surface solidifies more slowly than the others, pipe or cavity will be formed. The presences of pipes and cavities can pose problems. For instance we take production of aluminum as an example, when the shrinkage pipes remains in the ingots, water vapor can

condense in it. This water can lead to an explosion if the ingot gets introduced in a furnace in which aluminum is being remelted for such applications as hot dip galvanizing. Moreover, the presence of water vapor enhanced corrosions such as rust in the presence of oxygen. This corrosion will increase gradually in the pipes or cavities which can eventually change the mechanical behavior of curing or casting component.

4.4.3 Interdendritic shrinkage

Dendrite is the tree-like structure of the solid that grows when an undercooled liquid solidified. Basically, "inter" mean in between and combining the word "interdendendrite" simply mean in between or within dendrites. Interdendritic shrinkage consists of small shrinkage pores between dendrites. This defect is known as micro shrinkage or shrinkage porosity. This defect is difficult to prevent even with the use of risers. Fast cooling rates may reduce problems with interdendritic shrinkage; the dendrites may be shorter, permitting liquid flow through the dendritic network to the solidifying solid interface. Additionally, any shrinkage remains may be finer and more uniformly distributed (Askland & Phule 2003). This type of shrinkage is shown in Figure 4.7.
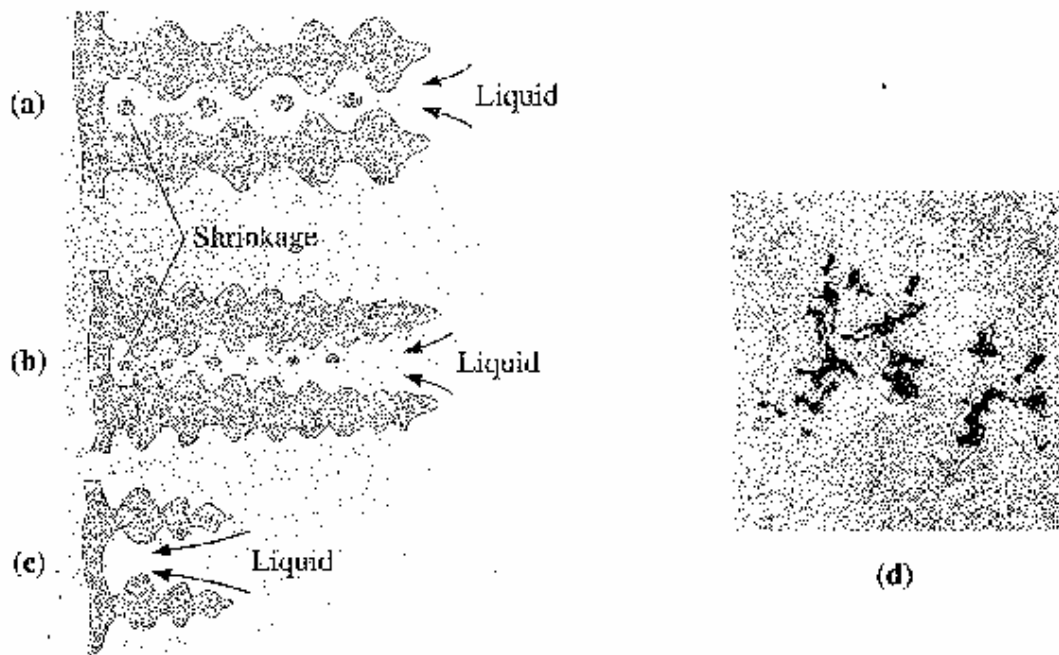
Figure 4.7: Shrinkage in between dendrites

4.5 Microstructural features of fracture in composites

Fracture mechanics can be defined as a field of solids mechanics that deal with the behavior of cracked bodies subjected to stresses and strains. Determine the severity of a pre-existing defect in term of its tendency to initiate a fracture which would cause failure is the aims of fracture mechanics.

In fracture of polymers, it can fail either by ductile or brittle manner. For thermoplastic polymers, it usually fails in a brittle manner. Likewise, the hard thermoset polymers, whose structure consists of inter-connected long chains of molecules, fail by a brittle mechanism. Some plastics whose structure consists of tangled but not chemically cross-linked chains, however, fail in a ductile manner. The ductile behavior is a result of sliding of the polymer chains, which is not possible in thermosetting polymers. Thermosetting polymers have a rigid, three dimensional cross-linked structure. In simple, both glass fibers and epoxy are brittle; thus the composite as a whole should display little evidence of ductile fracture.

For fracture in fiber- reinforced composite materials, it is more complex. Typically, these composites contain strong, brittle fibers surrounded by a soft, ductile matrix such as in boron-reinforced aluminum. When a tensile stress is applied along the fibers, the soft aluminum deforms in a ductile manner, with void formation and eventually producing a dimpled fracture surface. As the aluminum deforms, the load is no longer transmitted effectively to the fibers. Thus, the fibers will break up as brittle manner.

4.5.1 Brittle Fracture

Brittle fractures generally occur with slight plastic deformation. The strain rates within the material are regularly high because of the stress systems. Brittle fractures occur with little warning because the crack knows how to grow at the speed of sound. Excessive overloading or an impact force can cause a brittle fracture.

Macroscopic analysis of a brittle material failure shows that the materials fail differently which depends on whether it was in tension or compression. When the material fails in tension, the crack is perpendicular to the applied load. If the sample fails in compression the fracture will occur at 45 degrees to the applied load.

The crack is usually initiated from flaws of the material; these can be caused by either surface finish or impurities within the material. The cracks can be intergranular or transgranular depending on the material. A truly brittle fracture is caused by cleavage, which means transgranular. Cleavage occurs when the material is under high constraint conditions (Baddeley, D T and Ballard J, 1991).

4.5.2 Some characteristics of Brittle Fracture

Refer to Figure 4.8, according to New Hampshire Materials Laboratory, INC, 2000-2006, the characteristics of brittle fracture are as follows:

- The surface of the brittle fracture tends to be perpendicular to the principal tensile stress although other components of stress can be factors.

- There is no gross, permanent deformation of the material.

- Characteristic crack advance markings frequently point to where the fracture originated.

- The path the crack follows depends on the material's structure. In metals, transgranular and intergranular cleavage are important. Cleavage shows up clearly in the SEM (Scanning Electron Microscope).

4.5.3 Ductile Fracture

A ductile fracture is the result of plastic deformation prior to failure. A ductile fracture usually occurs when the sample is in strain. Overloading usually causes ductile transgranular fractures. It can be sometimes recognized from macroscopic test of the failed specimen. Usually the specimen is thin size and there is contraction of the sample before failure occurs.

At a microscopic level, most of the structural materials fail by a process called microvoid coalescence. Microvoid coalescence caused the fractured surface to have a dimple appearance with both large and small dimples. The shape of the dimple is influenced by the type of loading which is applied to the sample. Failures caused by shear will produce extended shaped dimples that point in the opposite directions on the matching fracture surfaces. Tensile tearing produces

extended dimples that point in the same direction on matching fracture surfaces (Baddeley, D T and Ballard J, 1991).

4.5.4 Some characteristics of Ductile Fracture

Refer to Figure 4.8, according to New Hampshire Materials Laboratory, INC, 2000-2006, the characteristics of ductile fracture are as follows:

- There is permanent deformation at the tip of the advancing crack that leaves distinct patterns in SEM images.

- As with brittle fractures, the surface of a ductile fracture tends to be perpendicular to the principal tensile stress, although other components of stress can be factors

- In ductile, crystalline metals and ceramics is microscopically resolved shear stress that is operating to expand the tip of the crack.

- The fracture surface is dull and fibrous.

- There has to be a lot of energy available to extend the crack.

An illustration of how the crack, ductile and brittle fracture can be seen in Figure 4.9.
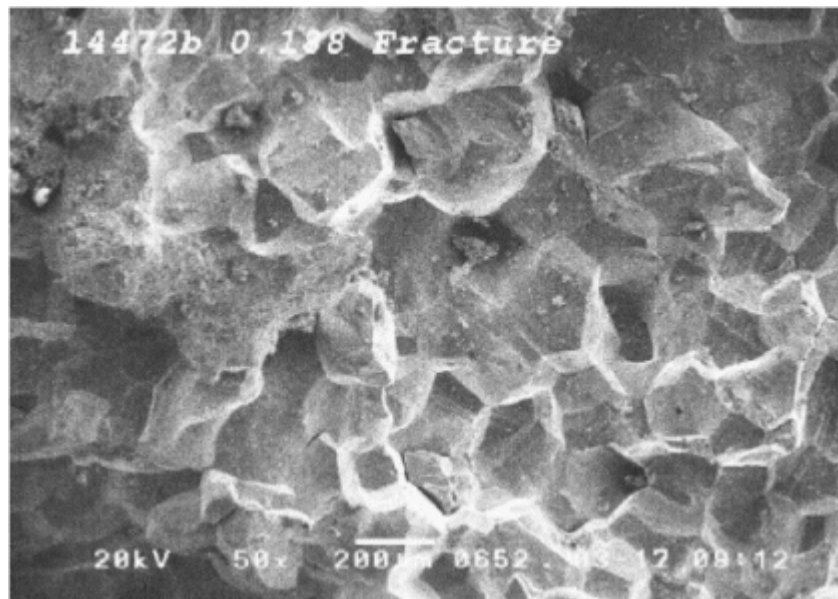
Figure 4.8: Intergranular fracture in a nickel-cromium alloy, viewed under the scanning electron microscope. (New Hampshire Materials Laboratory, INC, 2000-2006).
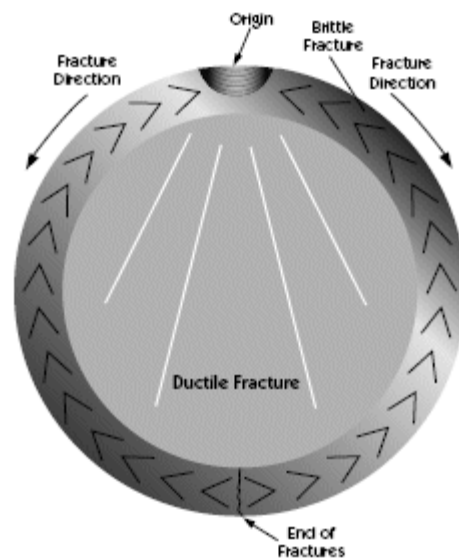
Figure 4.9: Ductile and Brittle Fractures

4.5.5 Theories of Mechanics and Fracture Toughness

The development of the field of fracture mechanics was lead by the modifications to Griffith's theory. Fracture mechanics deals with facture initiation and crack propagation, and provides quantitative methods for characterizing the behavior of an intact material as it fractures due to crack growth. The extension of fracture mechanics to rock is understandable since rock masses contain cracks and discontinuities. States of stress around these flaws cannot be predicted using macroscopic failure criteria. In order to deal with crack propagation, particularly in terms of "intentional" fracturing as in size reduction processes, fracture mechanics must be used.

Although fracture mechanics has an undeniable place in mechanics applications, it was not developed for geomaterials. It should be recognized that differences exist between fracture mechanics for man-made materials (metals) and rock fracture mechanics, particularly in basic material response and engineering application. Whittaker et al., (1992) gave a comprehensive list and explanation of these differences, which can be summarized as:

- **Stress state** – Many rocks structures are subjected to compressive stresses as opposed to tensile stresses. However, in crushing the induced stress state is tensile (from point-load compression) and thus tensile fracture is seen in rock.

- **Rock fracture** – Rock materials usually fracture in a brittle or quasi-brittle manner and usually do not exhibit plastic flow.

- **Fracture process zone (FPZ)** – Non-elastic behavior ahead of a crack tip in rock takes the form of micro-cracking as opposed to excessive shear stresses and the resultant plastic process zone seen in metals. If the size of the FPZ is small then linear elastic fracture mechanics applies.

- **Crack surface** – Crack surfaces in rock can be non-planar with friction and inter-locking occurring, but linear elastic fracture mechanics assumes that no forces are transmitted across the surface of a smooth planar crack

- **Crack propagation** – In rocks there is a tendency for crack propagation to "wander" along grain boundaries or planes of weakness. The area of newly created surface is then larger then the assumed fracture area.

- **Rock fracture mechanics applications** – In rock mechanics, as in (man-made) materials engineering, the prevention of failure by fracture growth is a concern. But the optimizing the generation and propagation of cracks is also a concern as in size reduction processes. Thus the application dictates how material parameters should be determined and used.

- **Influence of scale** – Due to the complicated geologic nature of rock masses, the characterization of a rock mass is high. For the prevention of crack growth and failure, parameters measured experimentally are of secondary importance but for rock fragmentation applications, experimentally measured properties are of primary importance.

- **Heterogeneity** – Changes in local structure and strength ahead of a crack tip affects the continuity of crack growth.

- **Presence of discontinuities** – Pre-existing discontinuities affect the local stress states and crack propagation.

- **Anisotropy** – Rocks can be anisotropic affecting measured fracture parameters as a function of crack orientation.

There are more practical and developed concepts of fracture mechanics was lead by the recognition of these variations as it applies to behavior, with principles of linear elastic fracture mechanics being extended even to rocks that behave non-linearly and much of the focus centering on the measurement of fracture toughness.

The most fundamental aspect of rock fracture mechanics is the establishment of a relationship between rock fracture strength and the geometry of the flaws that result in fracture. Through this relationship an intrinsic material property that describes a materials' resistance to crack propagation can be measured. This property is called fracture toughness. The application of fracture toughness in size reduction processes is clear. Fracture toughness represents a critical level above which crack extension and fracture occurs. When individual rock particles are subjected to the applied forces of size reduction, it is most likely that the intrinsic tensile property measured as the fracture toughness will control breakage (Bearman, 1998). Since the amount of energy input into a size reduction process and the amount of size reduction achieved (i.e., the fractured size distribution) are related to the type of loading and the crack pattern in the material, there should be a relationship between these parameters and fracture toughness.

Chapter 5

Methodology

5.1 Introduction

There are two techniques involved: The first technique is known as the DVMT (Direct Volume Measurement Technique) and second technique uses a machine which is known as the Pycnometer Technique. In theory results obtained from Pycnometer technique are more accurate than DVMT as the accuracy of within 0.03% of a reading can be achieved. Whereas results obtained from DVMT can result in human error such as parallax, uncertainties etc. The procedure of taking the measurements, preparation of samples, compositions of mixtures will be discussed in this section.

5.2 Preparing VE/FLYASH (33%)

The best know weight of Flyash to be mixed with the resin is 33 percent of the total weight of the entire mixture which comprise of Vinyl Ester resin, Flyash (or Alumino Silicate) and MEKP (Methyl Ethyl Ketone Peroxide). MEKP acts as an accelerator to the process. Table 5.1 depicted the approximate compositions of mixture to make 500ml of composite. In order to make 500ml of composite

301.8 grams of resin, 154 grams of flyash as well as 5.6grams of accelerator are required.

	Resin	Accelerator	Flyash	Composite
Relative density	1.1	1.0	0.7	---
Percentage by volume	56	---	44	100
Percentage by weight	67	---	33	100
Weight for 500 ml of composite	301.8 (g)	5.6 (g)	154 (g)	---

Table 5.1: Mass of materials required to make 500 ml of VE/FLYASH (33%)

Initially, an empty container is placed on a weight balance and it is set to zero as a start. While the container is still on the balance, flyash are poured gradually into the container until the correct amount is reached. The procedure to measure the resin is the same as flyash. The next step is to mix both the contents together thoroughly with MEKP accelerator. The steps of mixing is shown in Figure 6.1

1   2

3

4
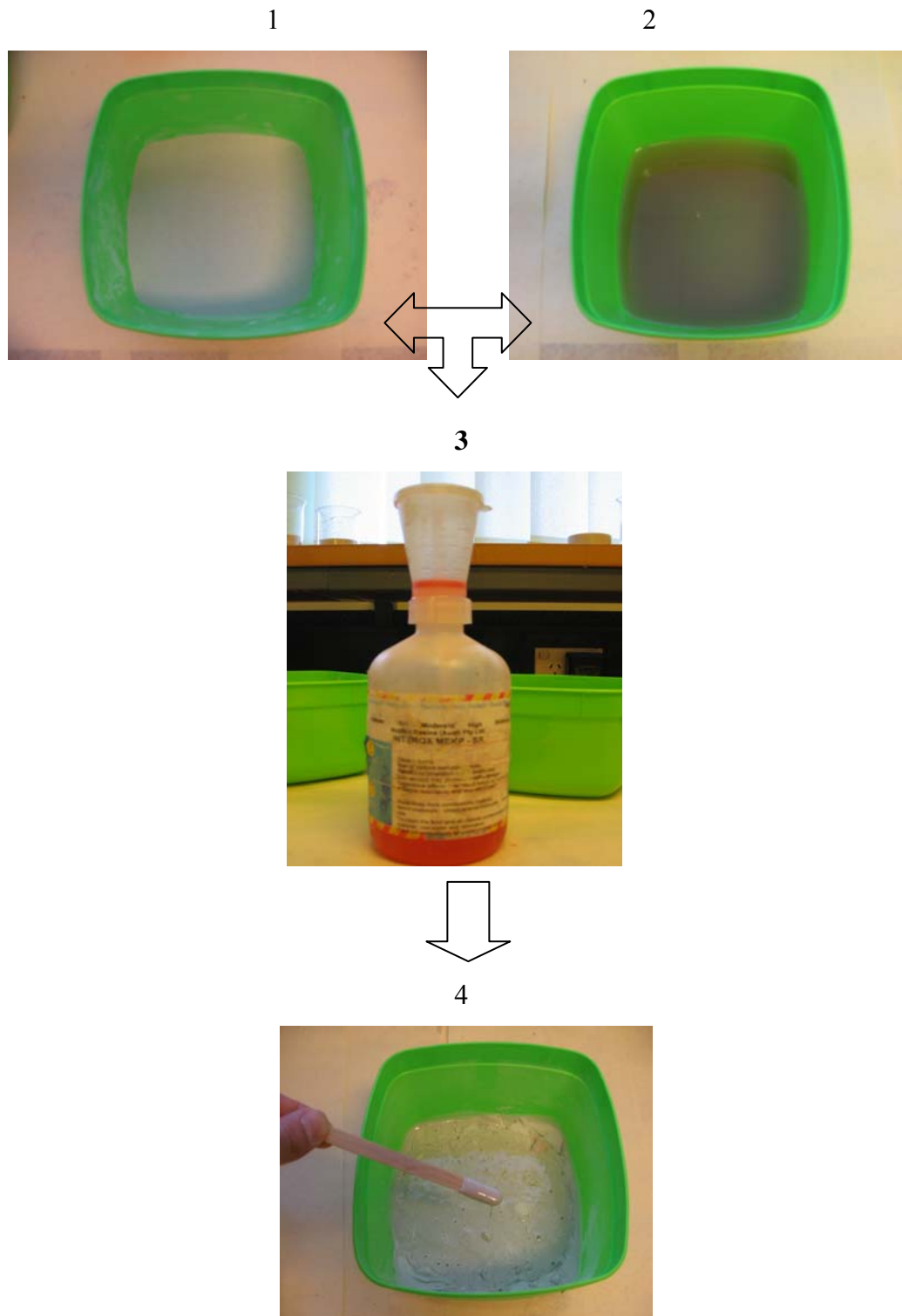
Figure 5.1: Preparation of VE/FLYASH (33%) with picture: 1. Flyash, 2. Resin, 3. MEKP and 4. Uncured VE/FLYASH (33%)

5.3 Procedure for DVMT

Six beakers are used for each set of power setting and time duration. The power settings are:

80W 50Sec	80W 60Sec	80W 70Sec	80W 80Sec
160W 30Sec	160W 35Sec	160W 40Sec	160W 45Sec

Table 5.2: Power level and different exposure time

Moreover, sample of ambient conditions are prepared to compare and justify the shrinkages with the samples placed in a microwave oven. Once the mixture of uncured VE/FLYASH (33%) is prepared, it is follow by pouring them in each beaker into the 100ml mark. The next critical step is to take the measurements of the uncured height and temperature. Beakers are numbered so that it can be identify when the next measurement is taken. To ensure higher accuracy in measurement, the uncured height is mark with a marker pen so that any shrinkage occurs in the beakers can be measured with a Vernier's calliper. After the first set of readings is obtained from 100ml, the same procedure applied to 150ml with the same power level and exposure time. The specifications of typical 200ml beaker are shown in Table 5.3.

Capacity (ml)	200
Diameter (mm)	65
Height (mm)	90
Graduation Interval (ml)	25
Graduation Range	25ml-175ml
Material	Borosilicate Glass
Weight (lbs)	4

Table 5.3: Specifications for a 200ml beaker

A commercial 800W microwave oven is used. In the built in function of microwave oven, the power inputs can be varied from 10% (80W) to 100% (800W) with a step interval of 80W. Once the samples are prepared, it is cured in the oven according to the placement shown in Appendix E inside the microwave chamber. Cured temperature is immediately taken once it is pulled out from the microwave. It is followed by the measurement of the cured height after the samples are solidified. Thus, cured volume and percentage shrinkages can be determined; from Equations 6.1 and 6.2. Figure 5.2 shows all the solidified beakers used for the VMT.

Figure 5.2: 108 Beakers with solidified VE/FLYASH (33%)

5.4 Procedure for Pycnometer technique

This technique is newly developed technique to calculate the shrinkages by comparing the ratio between the cured and uncured densities. This experiment was carried out in CEEFC (Centre of Excellence in Engineered Fiber Composite), which is one of the research facilities in USQ. Derived from VMT, one beaker is chosen from each set of power setting and time duration. The percentage shrinkage of this particular beaker must be close or similar to the average percentage shrinkage calculated for the 6 beakers.

The next step is to break the beakers so that the harden VE/FLYASH (33%) can be obtained. Due to the size of the samples, it cannot be fitted into the flask/container which is shown in Figure 2.1. To overcome this problem, the harden samples needs to break into fragment or powdery form so that it can fit into the 35cm^3 flask. This is shown in Figure 5.3 (a) and (b).

Figure 5.3 (a): Composite fragment for 100ml sample

Figure 5.3 (b): Composite powder for 150ml sample

Crushed materials are then poured into the container/flask which is then inserted into the hole of the pycnometer. The procedure of using a pycnometer is mentioned in chapter 2. Nevertheless, one thing should be noted, Helium gas is

supplied into the pycnometer chamber which assisted in the analyzing process, thus the density of the material can be determined.

5.5 Risks associated with the resins

The risks involved with VE resins are two chemical elements; styrene and Methyl ethyl ketone peroxide (MEKP), which are commonly known for its biological effect on human body. At room temperature, styrene is a volatile gas that can evaporates easily which can cause inhalation hazard. MEKP is a colorless, oily liquid at room temperature. However it belongs to organic peroxide group which can be high explosive similar to acetone peroxide.

5.5.1 Risk of styrene

Styrene is one of the products that dissolved in a reactive solvent during the esterification of an epoxy resin with an unsaturated monocarboxylic acid- where VE resins are formed. Styrene will be produced to 35-45 percent content by weight. At concentrations in the range of 20-100 parts per million (ppm), styrene is consider mild, temporary irritant to eyes and respiratory tract. Above 200 ppm styrene has the potential to cause irritation to central nervous system (CNS), and above 500 ppm it is a severe irritant.

The risk of styrene poisoning through inhalation is low since the human nose is extremely sensitive to the very sharp and unpleasant styrene smell; the odour threshold is approximately 0.1 ppm Long term occupational exposure to styrene increases the frequency of chromosome damage in one type of blood cells and may possibly cause brain damage at concentrations as low as 10 ppm. Styrene is classified as a possible human carcinogen by the Environmental Protection Agency (EPA) and by the International Agency for Research on Cancer (IARC).

Under normal conditions, the aromatic hydrocarbon is an oily liquid. In terms of personal protection equipment (PPE) it is important to note that, wearing gloves can significantly reduce the contact of styrene with skin, as it may cause irritation. Apart from that, Styrene can be highly flammable; explosion can occur if the vapour concentration is high. Styrene vapour has a higher density than air and there is always a misconception that styrene flows along the floor. This is true in theory, but in practical the density differences between the styrene-containing air and the uncontaminated air is very little.

The potential health effects of styrene in vinyl ester resins on human beings are:

- **Ingestion.** Even though small amount of styrene can be found in foods such as fruits, vegetables, nuts, beverages and meats. However, ingested large amount of Styrene may be harmful. Symptoms may include nausea, vomiting, diarrhea, lethargy, drowsiness and sleepiness.

- **Eye.** Prolong exposure can cause irritation and corneal damage. Symptoms may include tearing, stinging and swelling.

- **Skin.** Exposure can cause skin irritation. Prolonged or repeated exposure may dry the skin. Symptoms may include redness, itching, pain, drying and cracking, skin burns and skin damage. Skin absorption is possible which may produce blisters.

- **Inhalation.** Inhaling small amounts of styrene during normal handling is not likely to cause harmful effects. Oppositely, inhaling large amounts may be harmful as it causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. It can also cause a build-up of fluid in the lungs.

The first aid measure for styrene in the resin will be:

- **Ingestion.** Seek medical attention. If an individual is drowsy or unconscious, do not give anything by mouth. Contact a physician, medical facility, or poison control centre for advice about whether to induce vomiting. If possible, do not leave individual unattended.

- **Eyes.** If symptoms develop, immediately move individual away from exposure and into fresh air. Flush eyes gently with water for at least 15 minutes while holding eyelids apart; seek immediate medical attention.

- **Skin.** Remove contaminated clothing and shoes. Immediately flush exposed area with plenty of soup and water for at least 15 minutes. If skin is damaged, consult doctor immediately. Thoroughly clean clothing and shoes before reuse.

- **Inhalation.** If symptoms develop, move individual away from exposure into area with fresh air. If symptoms persist, seek medical attention. If breathing is difficult, administer oxygen. Keep person warm and quiet; seek immediate medical attentions.

5.5.2 Risk of MEKP

MEKP is less encounters in daily life if one does not work in factories or industries. These organic peroxide initiators are toxic in nature, which may led to severe irritants that causes progressive corrosive damage or blindness if the concentration is high. In preparation of VE/FLYASH (33%), dilute solution of 30 to 60 percent MEKP are used to catalyst the hardening process. Consequently, this brings down the potential damaging effect of MEKP to human beings.

The storage of MEKP is crucial as it can cause damages to both human and the environment. MEKP originally come with closed plastic bottle, it should be kept

in a cool place, which is away from all source of heat such as sparks, flames, and direct sunlight. Exposure to high temperatures or contamination with foreign materials may result in explosive decomposition. Besides that, MEKP is not advises to store in area where food and drink are placed. The container must dispose responsibly to avoid reuse of container occurs. It must note that the maximum storage temperature of MEKP is 38 $^{\circ}$C.

In term of health effect with MEKP such as ingestion, inhalation and other direct contact with any part of the body. It is similar to that of styrene. Therefore, direct contact with MEKP is absolutely inadvisable. For instance, if MEKP is contact to any part of the body, the immediate action such as wash affected skin thoroughly with soap and water, and dispose clothes and shoes must follow. If accidentally ingested, take large quantities of milk or water is advice. All the above action would not occurs if a proper safety measure is applied and reinforced. Safety precautions are wearing goggles, gloves, protective clothing, and a respirator. Keep an "eyewash bottle" anywhere with MEKP in a room as it can provide instant first aid to user.

Additionally, when preparing VE/FLYASH (33%), it is necessary to ensure that all promoters and accelerators are thoroughly mixed into the resin before adding MEKP. These agents should not be mixed directly with MEKP. This is because violent chemical reaction and fire could result from such action. If spilling occurs, it should be absorbed in inert material such as vermiculite or sand and then wet with water. All contaminated materials should be placed in double polyethylene bags and away from combustibles until it is removed by qualified hazardous waste personnel. In case of fire, tap water preferably with a fog nozzle, or carbon dioxide or foam should be sprayed from a safe distance. Dry chemical or other extinguishers may be effective against a very small fire.

In catalyses MEKP to VE resins, uses of MEKP dispenser is recommended. It operates by applying pressure to the plastic bottle, thus measurable amount of

MEKP is flow upward to the upper phial. This method is one way to reduce the possibility of direct contact with the chemical.

5.6 The Modified Microwave Oven

There are two microwave ovens shown in Figure 5.4. The maximum power level for, the silver microwave oven is 1800W whereas 800W for the other one lie on the bottom of the cart. The microwave ovens were modified for use in this experiment. The main purpose is to direct the styrene gas evolved to exhaust rapidly. Modification was made on the microwave lie on lower level of the cart with pipe and exhaust (not shown), which is the same as the one shown with the silver microwave oven. This modification will reduce the inhalation hazards bring to human being.
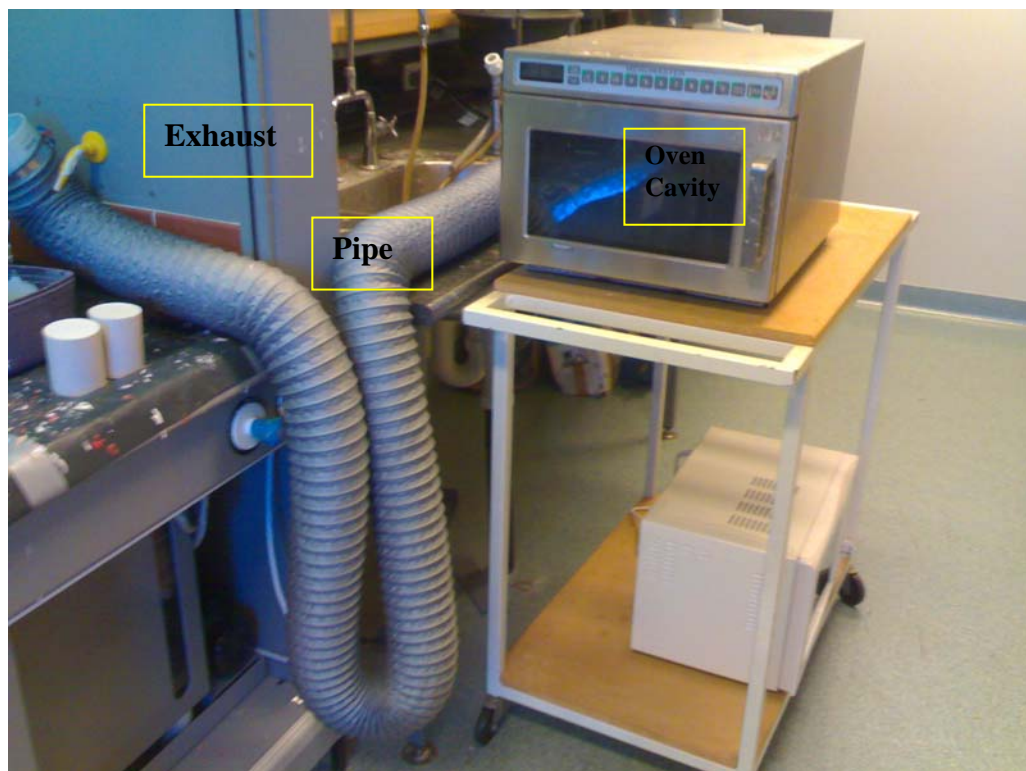
Figure 5.4: The modified oven and its peripherals (Ku, H S 2002)

Chapter 6

Results and Discussions

6.1 Introduction

The main objective of this project is to obtain the results from two different methods and make comparisons between them. In the results, there are two parts to be analyzed; one being Direct Volume Measurement Technique (DVMT) and the other part being Pycnometer technique. Previously, DVMT has been performed by other researchers with high power microwaves. Using Pycnometer to obtain the shrinkages of the composite is a fairly new technique; it is achieved by comparing the densities of cured and uncured material. In this chapter, not only results obtained from both techniques will be mentioned, but also results obtained from high power microwaves. The power levels and exposure times of low power microwave for this experiment are shown in Table 6.1. Firstly, testing is performed with 100ml of composite in a beaker. It is then repeated with 150ml beaker. It is followed by justifications and discussions of the results.

6.2 Part 1: Direct Volume Measurement Technique (DVMT)

6.2.1 Background

Refer to Appendix B are results tabulated for the DVMT. There are 18 tables in total with the first 9 tables for 100ml of VE/FLYASH (33%) and the second half for 150ml beakers. There are 6 beakers used in each power level and exposure time in microwaves. However, columns highlighted in grey are not taken into calculations of average value and standard deviation. This is due to the inconsistency of its percentage shrinkage to the batch of percentage shrinkages in the same table. The equations to calculate the final volume of the cured sample and percentage shrinkage of VE/FLYASH (33%) are:

$$V_{cured} = V_{uncured} \times \left(1 - \frac{\Delta h}{h}\right)$$

(6.1)

$$\% \, Shrinkage = \frac{V_{uncured} - V_{cured}}{V_{uncured}} \times 100\%$$

(6.2)

where Δh is the change in height and h is the original height.

Using equations (6.1) and (6.2), the final volume, V_{cured} and the percentage shrinkage (first column in Appendix B, ambient condition) can be calculated as follows:

From (6.1),

$$V = 100 \times \left(1 - \frac{32.5 - 31.2}{32.5}\right)^3$$

$$V = 88.47$$

From (6.2),

$$\% \ Shrinkage = \frac{V_{uncured} - V_{cured}}{V_{uncured}} \times 100\%$$

$$\% \ Shrinkage = \frac{100 - 88.47}{100} \times 100\%$$

$$\% \ Shrinkage = 11.53$$

6.2.2 Graphs and results

The procedure is repeated to find out the least percentage shrinkages and tabulated in the tables shown in Appendix B. Eight Graphs are plotted as shown in Figure 6.1 to Figure 6.4. However, there are parts (a) and (b) for each figure, with part (a) being the line connected to all the values obtained, whereas part (b) is the trend line or line of best fit within the values. The graphs are drawn with y-axis being average percentage shrinkage and x-axis being exposure time in microwave. These values are obtained from Appendix B and it is summarized in Table 6.1 to Table 6.4.
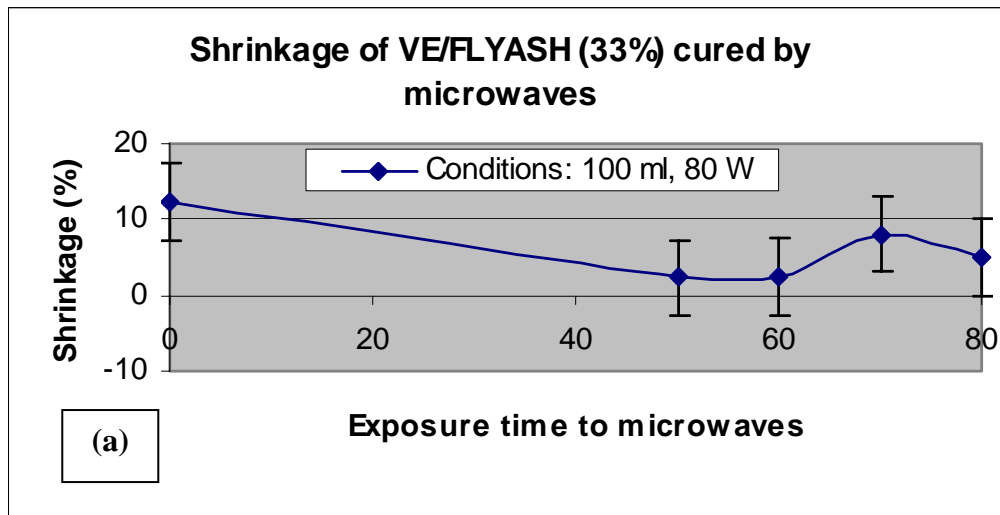
Figure 6.1 (a): Shrinkages of 100 ml of VE/FLYASH (33%) cured by different exposure times in 80W microwave
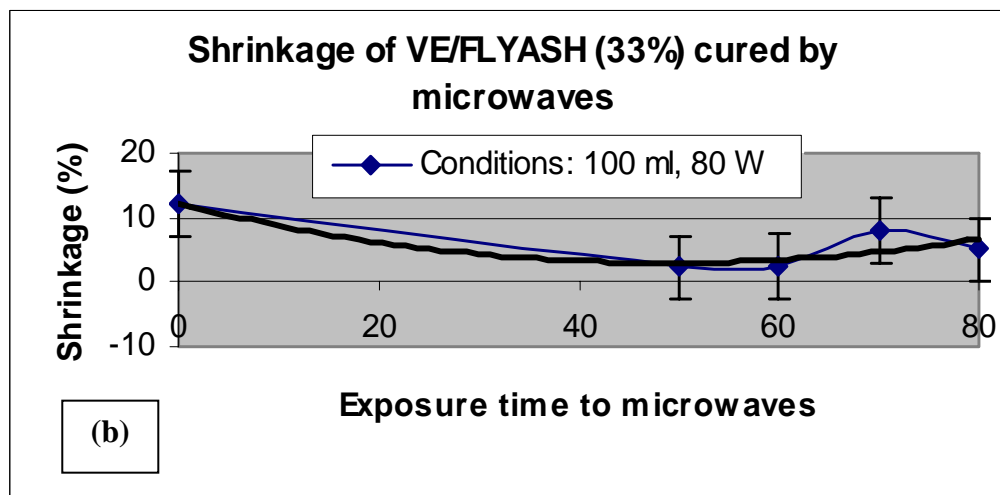
Figure 6.1 (b): Shrinkages of 100 ml of VE/FLYASH (33%) cured by different exposure times in 80W microwaves with trend line added.
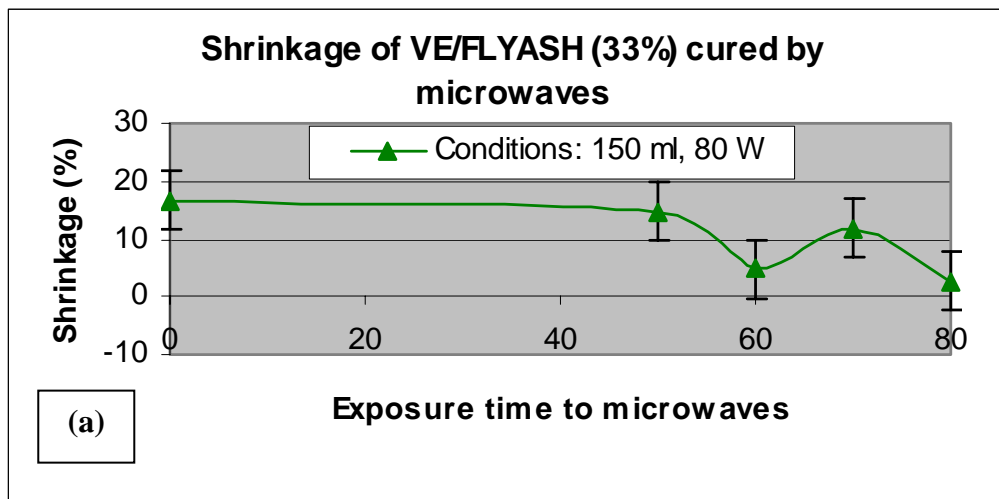
Figure 6.2 (a): Shrinkages of 150 ml of VE/FLYASH (33%) cured by different exposure times in 80W microwave
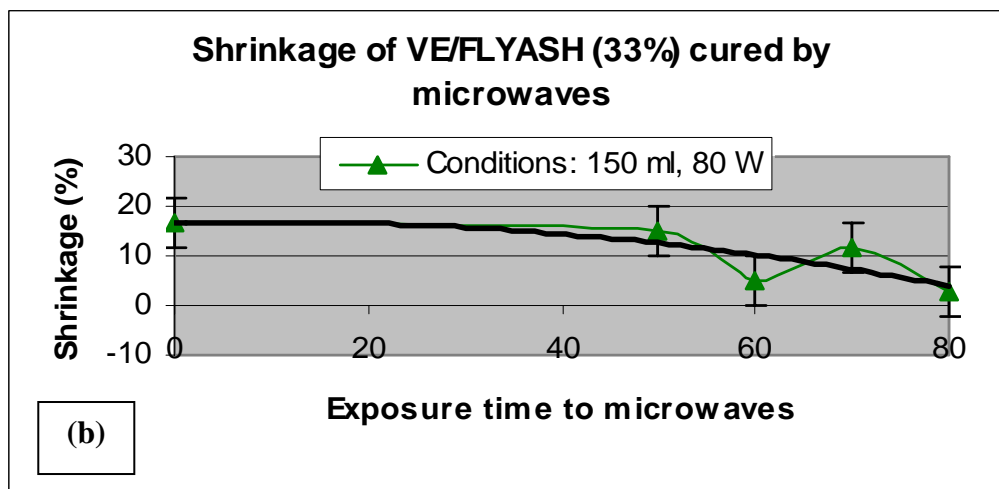
Figure 6.2 (b): Shrinkages of 150 ml of VE/FLYASH (33%) cured by different exposure times in 80W microwave with trend line added.
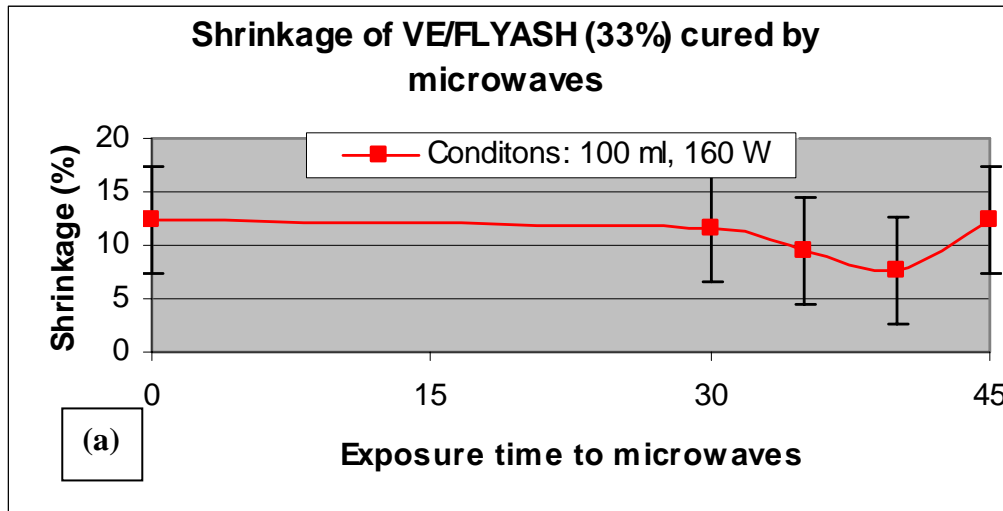
Figure 6.3 (a): Shrinkages of 100 ml of VE/FLYASH (33%) cured by different exposure times in 160W microwave
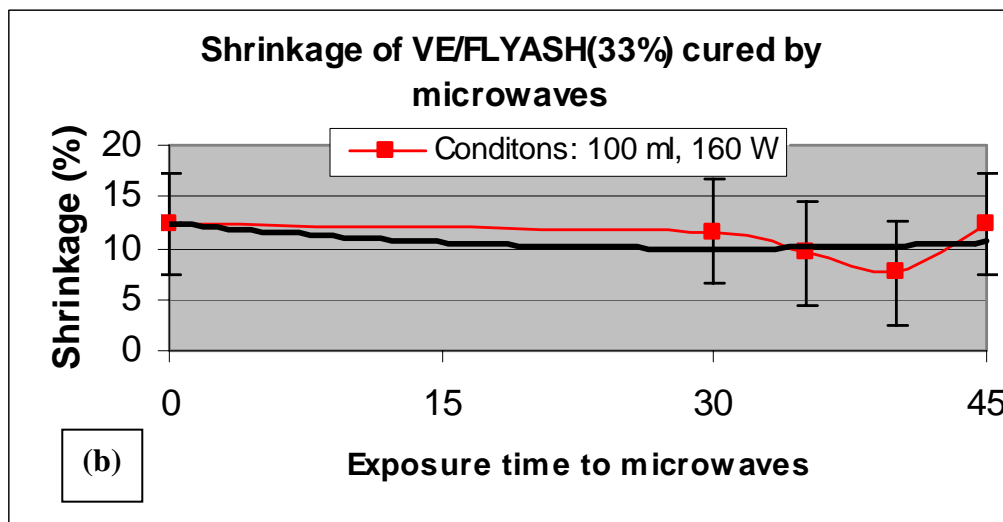
Figure 6.3 (b): Shrinkages of 100 ml of VE/FLYASH (33%) cured by different exposure times in 160W microwave with trend line added.
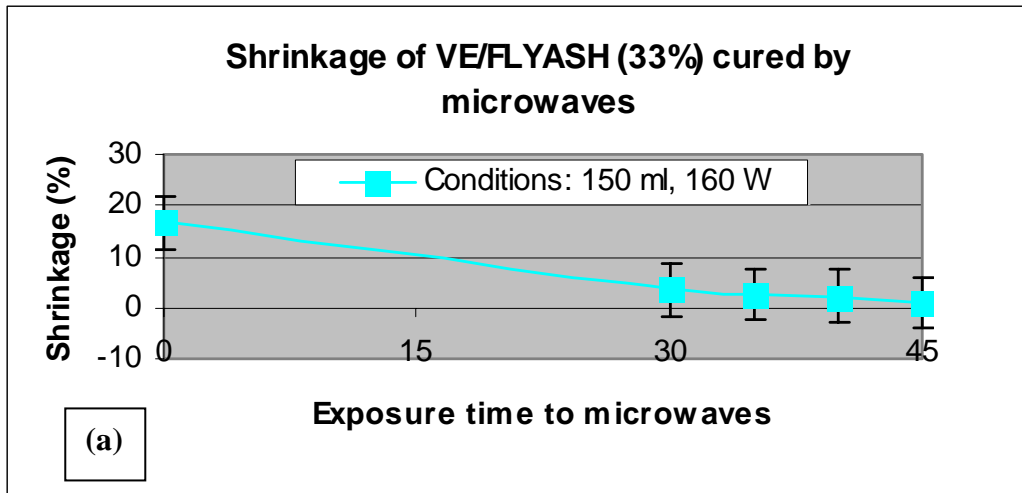
Figure 6.4 (a): Shrinkages of 150 ml of VE/FLYASH (33%) cured by different exposure in 160W microwave
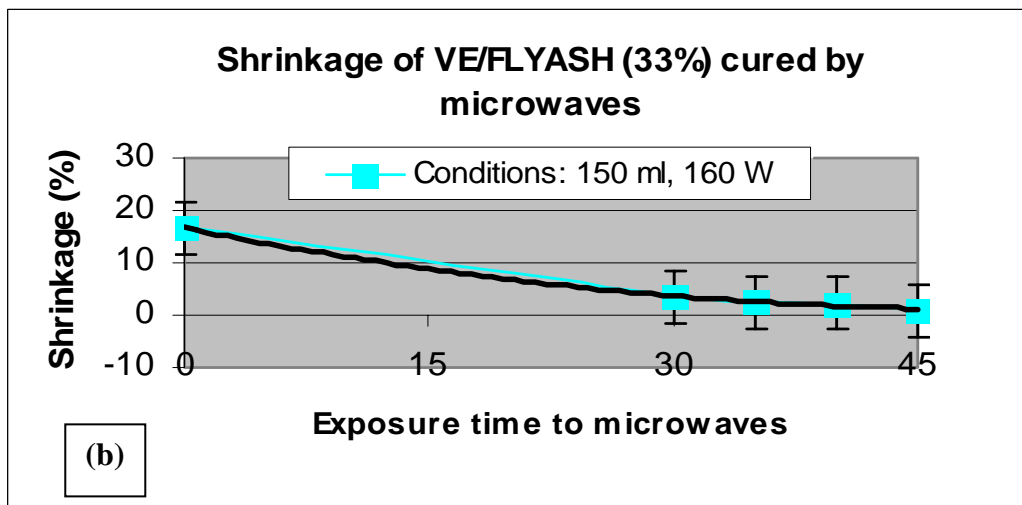
Figure 6.4 (b): Shrinkages of 150 ml of VE/FLYASH (33%) cured by different exposure times in 160W microwave with trend line added.

Table 6.1: Shrinkage of 100 ml of VE/SLG (33%) cured under microwaves of 80 W and its standard deviation

Volume of composite = 100 ml; power level = 80 W					
Exposure time (s)	0 (ambient cured)	50	60	70	80
Shrinkage	12.29 (2.83)[#]	2.26 (2.92)	2.40 (1.13)	8.05 (3.36)	5.04 (2.55)

Table 6.2: Shrinkage of 150 ml of VE/SLG (33%) cured under microwaves of 80 W and its standard deviation

Volume of composite = 150 ml; power level = 80 W					
Exposure time (s)	0 (ambient cured)	50	60	70	80
Shrinkage	16.60 (4.23)[#]	14.78 (2.46)	4.86 (3.05)	11.75 (2.98)	2.69 (1.56)

Table 6.3: Shrinkage of 100 ml of VE/SLG (33%) cured under microwaves of 160 W and its standard deviation

Volume of composite = 100 ml; power level = 160 W					
Exposure time (s)	0 (ambient cured)	30	35	40	45
Shrinkage	12.29 (2.83)[#]	11.58 (3.28)	9.49 (1.82)	7.54 (2.65)	12.33 (3.29)

Table 6.4: Shrinkage of 150 ml of VE/SLG (33%) cured under microwaves of 160 W and its standard deviation

Volume of composite = 150 ml; power level = 160 W					
Exposure time (s)	0 (ambient cured)	30	35	40	45
Shrinkage	16.60 (4.23)[#]	3.44 (2.12)	2.60 (3.08)	1.77 (2.30)	0.89 (0.35)

6.2.3 Discussion of graphs and results

Figure 6.1 (a) shows the shrinkages of 100 ml of VE/FLYASH (33%) particulate composite cured by different exposure times in 80W microwave irradiation. The shrinkage was large (12.29%) when it is cured under ambient conditions. For 50 seconds of exposure time, the shrinkage was 2.26%. The shrinkage increased slightly to 2.40% when the composite was exposed to microwave radiations of 60 seconds.   In the next 10 seconds, it increased further to 8.05%. However, it dropped back to 5.04% when it was exposed to microwave radiations of 80 seconds. Referring to Table 6.1, it was found that the standard deviation (σ) of 3.36 with respect to the exposure time of 70 seconds was the highest amongst the σ values in the table. It can be argued that the shrinkage of composite which has been exposed to microwaves radiation of 70 seconds was not too reliable. Therefore, a trend line was added and the resulting graph was plotted in Figure 6.1 (b). From the graph, it was found that the minimum shrinkage of the composite was attained when it has been exposed to microwave radiations for roughly 55 seconds. The trend was further supported by the fact that, the shrinkage of composite exposed to microwave radiations of 70 seconds is within the upper 5 percent marker of shrinkage.

Figure 6.2 (a) shows the shrinkages of 150 ml of VE/FLYASH (33%) particulate composite cured by different exposure times in 80W microwave irradiation. The shrinkage was large 16.60% when it is cured under ambient conditions. For exposure time of 50 seconds, the shrinkage was 14.78%. The shrinkage dropped further to 4.86% when the composite was exposed to microwave radiations of 60 seconds. It increased again to 11.75% when it was exposed to microwave radiations of 70 seconds.   However in the last 10 seconds, it dropped back to 2.69%. In general, the shrinkages of the composite in Figure 6.2 is more than the shrinkages shown in Figure 6.1 for the same period of exposure time to microwave radiations because the amount of composite is 50% more; the power input per ml of composite is one third less than in Figure 6.1.

Referring to Table 6.2, the SD (3.05) with respect to the exposure time of 60 seconds was large and it can be argued that the shrinkage obtained in that

particular time interval was not too reliable. Similarly after observations, the SD (2.98) obtained from exposure time of 70 seconds was not reliable as well. To explain this phenomenon, a trend line was added and the resulting graph was plotted in Figure 6.2 (b). From the graph, the minimum composite shrinkage seems to happen after the exposure time of 80 seconds; it can be argued that the exposure time will not surpass 120 seconds, for which the energy input per ml will be the same as the case in Figure 6.1. By extrapolation, it can be found that the exposure time for minimum shrinkage will be at 100 seconds and the shrinkage will be 2.03%.

For VE/FLYASH (33%), the shrinkages occurred during curing is due to polymerization of resin and this happens at microscopic level. These shrinkages happen because of the closer pack of atoms within a molecule. The drop in percentage shrinkage by exposing the composite to microwaves for a shorter period of time prior to curing in ambient conditions is the result of initial expansion of the composite at macroscopic level; the composite shrinks but to a lesser extent, resulting in the closer pack of molecules within the composite. For cases in Figures 6.1 and 6.2, shrinkages of composites will reduce from a maximum (which is in ambient curing) to a minimum when it is exposed to microwave irradiations for a certain period of time. This depends on the duration of exposure and power level of microwaves; the decrease in percentage shrinkages is due to the fact that the initial volume expansion is large, thus the differences between the cured and uncured volume become smaller. Hence the resulting shrinkage will be less than expected.

Figure 6.3 (a) shows the shrinkages of 100 ml of VE/FLYASH (33%) particulate composite cured by different exposure times in 160W microwave irradiations. The behavior of this graph is similar to the case in Figure 6.1(a). A trend line (Figure 6.3 (b)) was added and it was found that a minimum shrinkage (10%) was attained when the exposure time to microwaves was 30 seconds. Table 6.3 shows the shrinkages of 100 ml of VE/FLYASH (33%) and its standard deviation cured under 160W microwave radiations. It can be argued that both the shrinkages and their standard deviations were reasonable.

Figure 6.4 (a) shows the shrinkages of 150 ml of VE/FLYASH (33%) particulate composite cured by different exposure times in 160W microwave irradiation. A trend line (Figure 6.4 (b)) was added and it was found that the minimum percentage shrinkage has not been reached even after exposing the composites to 45 seconds. By extrapolation, the minimum shrinkage found is 0.53%; when the duration of exposure is 60 seconds. Table 6.4 shows the shrinkage of 150 ml of VE/FLYASH (33%) and its standard deviations cured under microwaves of 160 W. It can be argued that both the shrinkages and their standard deviations were reasonable.

By comparing Figures 6.1 and 6.2, the higher the volume of the composites, the larger will be the shrinkages in ambient curing; the shrinkage at ambient curing of Figure 6.1 (100ml) was 12.29% while that of Figure 6.2 (150ml) was 16.60%. The minimum shrinkage of Figure 6.1 was 2.26 % (exposure time was 50 seconds and energy input per ml = 40W) while that of Figure 6.2 was 2.03% (exposure time was 100 seconds and energy input per ml = 53 W). With reference to Figures 6.3 and 6.4, the minimum percentage shrinkage of Figure 6.3 was 10% (exposure time was 30 seconds and energy input per ml = 48W) and 0.53% for Figure 6.4 (exposure time was 60 seconds and energy input per ml = 64 W).

From the finding in the last paragraph, it can be argued that the minimum percentage shrinkage will be small when the applied microwave energy per ml of composite is high. By comparing Figures 6.1 and 6.3, the percentage shrinkage of Figure 6.1 was 3.39% corresponds to exposure time of 60 seconds (energy input per ml = 48W) while that of Figure 6.3 was 10% corresponds to exposure time of 30 seconds (energy input per ml = 48W). The minimum percentage shrinkage of Figure 6.1 was 2.26% (exposure time was 50 seconds and energy input per ml = 40W) while that of Figure 6.3 was 10% (exposure time was 30 seconds and energy input per ml = 48W).

By comparing Figures 6.2 and 6.4, the percentage shrinkage of Figure 6.2 was 2.71% corresponds to exposure time of 90 seconds (energy input per ml = 48W) while that of Figure 6.4 was 1.32% with corresponds to exposure time of 45

seconds (energy input per ml = 48W). The minimum percentage shrinkage of Figure 6.2 was 2.03% (exposure time was 100 seconds and power per ml = 80W) while that of Figure 6.4 was 0.53% (exposure time was 60 seconds and power per ml = 64W).

Referring back to Figures 6.1 and 6.2 (maximum power level of 80W) with the same amount of energy input at 48W, the percentage shrinkage of Figure 6.1 was 3.39% (exposure time was 60 seconds) and that of Figure 6.2 was 2.71% (exposure time was 90 seconds), it was found that the shrinkage is less with longer duration of exposure given that the volume of the composite in Figure 6.2 was 150 ml and that of Figure 6.1 was 100 ml.

Referring back to Figures 6.3 and 6.4 (maximum power level of 160W) with the same amount of energy input, 48W, the percentage shrinkage of Figure 6.3 was 10% (exposure time was 30 seconds) and that of Figure 6.4 was 1.32% (exposure time was 45 seconds), it was found that the shrinkage is less with longer duration of exposure given that the volume of the composite in Figure 6.3 was 100 ml and that of Figure 6.4 was 150 ml.

From the finding in the last two paragraphs, it can be argued that it is more efficient to expose the composites to longer duration with lower power setting rather than the opposite. In this case the shrinkages will be reduced. The other way to reduce the percentage shrinkage in this situation is to increase the power level with larger volume of composites.

6.3 Part 2: Pycnometer Technique (PT)

6.3.1 Background

This is one of the sophisticated techniques used to explore the shrinkages by finding the densities ratio between cured and uncured sample, an equation similar to that of (6.2) was used. The equation to calculate the percentage shrinkage is shown in equation (6.3):

$$\% \ Shrinkage = \frac{\rho_{cured} - \rho_{uncured}}{\rho_{cured}} \times 100\%$$

(6.3)

This technique cannot be performed without the use of technique 1. As it has been mentioned previously in Chapter 2 and 5, one of beaker out of the six in each set of power setting and exposure time, which is closest to its average value, was taken to perform this experiment. In order to do this, beaker must be break to obtain the cured VE/FLYASH (33%) in a beaker before it is crushed into smaller fragment which can be fitted into the $35cm^3$ metal container for the analysis of densities. In theory, both the percentage shrinkages obtained from techniques 1 and 2 must be close to one another. However in practice, discrepancy occurs and it is shown in Appendix C.

6.3.2 Mathematical calculation of percentage shrinkages

The percentage shrinkage obtained from column 2 (80W & 50 seconds) and row 8 (% shrinkage obtained from Part 2) of Table D in Appendix C can be calculated as follows:

Using equation (6.3),

$$\% \ Shrinkage = \frac{1.1313 - 0.9124}{1.1313} \times 100\%$$

$$\% \ Shrinkage = 19.349$$

If Flyash is used instead of VE/FLYASH (33%), refer to Table C, the density, ρ obtained from Pycnometer is 0.7654, the percentage shrinkage will be:

$$\% \ Shrinkage = \frac{1.1313 - 0.7654}{1.1313} \times 100\%$$

$$\% \ Shrinkage = 32.343$$

This results in a higher value of the percentage shrinkage when compare to the value obtained from VE/FLYASH (33%) alone.

If vinyl ester resin is used instead of VE/FLYASH (33%), refer to Table B, ρ obtained from Pycnometer is 1.0621, thus the percentage shrinkage will be:

$$\% \ Shrinkage = \frac{1.1313 - 1.0621}{1.1313} \times 100\%$$

$$\% \ Shrinkage = 6.117$$

6.3.3 Discussion with graphs and results

This value (the neat resin) is closer than the percentage shrinkage obtained from Part 1 with the same condition. Using the resin instead of VE/FLYASH (33%) will give closer results between the two techniques. Hence, the following figures (Figure 6.5-6.9) are plotted to compare the results between the two techniques. In the plots, one must know the abbreviations P1 and P2 stands for technique 1 and 2, which are DVMT and PT.
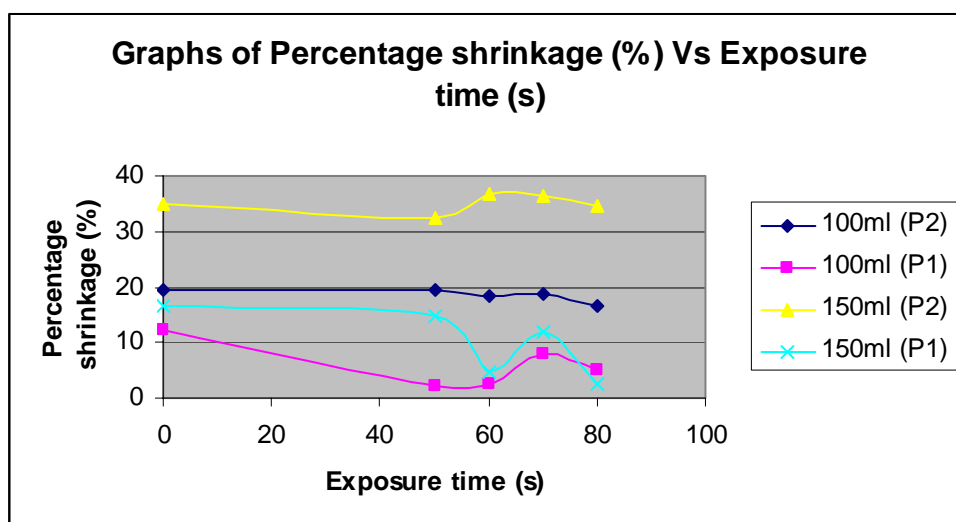
Figure 6.5 (a): Shrinkages of 100ml and 150ml composite for both techniques in 80W

Figure 6.5 (a) are plots of percentage shrinkage against exposure time for 100ml and 150ml of VE/FLYASH (33%) for both techniques in 80W of microwave radiations. It can be found that, technique 2 has recorded higher value of shrinkages. Technically, shrinkages obtained from higher volume; 150ml should be higher. In theory, the shrinkage in ambient conditions will generally be more than the cured samples which have been exposed to microwave radiations. The reason for this is because, when the uncured sample was heated up, it tended to expand and then solidify to become a cured sample. This can hardly be seen by our naked eyes as it happens in a microscopic level. The expansions of composites obtained from microwave exposure will lead to smaller shrinkages when compare to ambient conditions.

By comparing 100 ml (P2) and 100ml (P1) lines, the shrinkages were reduced when the exposure time was increased; when it came to the fourth value, 18.601% for 100ml (P2) and 8.044% for 100ml (P1), its shrinkages increased again before it dropped back. This proves that, the results obtaining from both techniques are matched even though both lines should come closer to one another for the same batch of samples. Same explanations apply for the 150ml samples; the yellow and teal lines should be closer to one another. However the sudden drop in shrinkages (4.86%) of 150ml (P1) and sudden rise in shrinkages (36.744% onwards) of 150 (P2) proves that, the results obtained from these two volumes are not reliable.
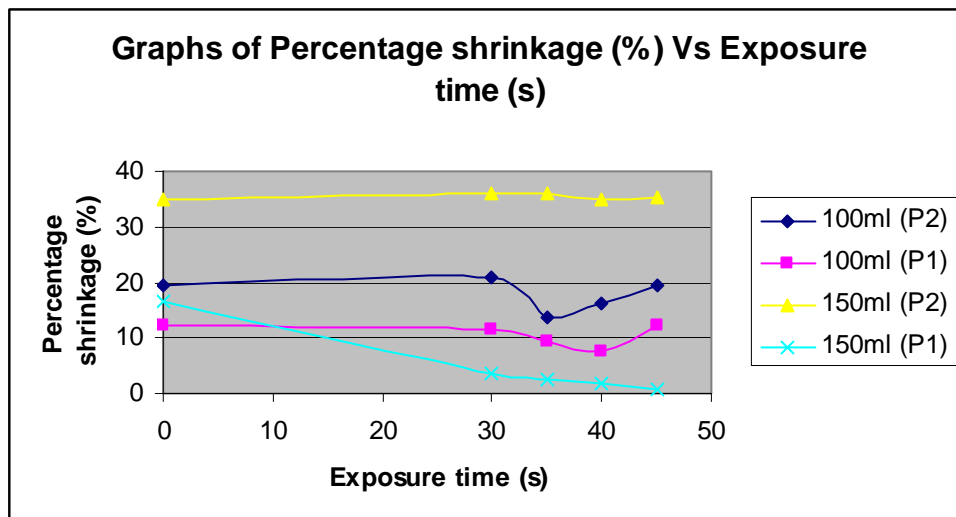
Figure 6.5 (b): Shrinkages of 100ml and 150ml composite for both techniques in 160W

Figure 6.5 (b) are plots of percentage shrinkage against exposure time for 100ml and 150ml of VE/FLYASH (33%) for both technique in 160W of microwave radiations. Inconsistency can also be observed from this graph, as from theory, the values taken from specimens placed under microwave exposure cannot be greater than the ambient conditions. These values can be found from the purple curve (12.334%) and also the P2 curves in this graph; 21.079% for navy blue curve and all the values of shrinkage between 30 to 45 seconds of exposure time for yellow line. When heat is imposed to a medium, it will expand before it solidified. This is not true in this case. To justify this, it can be argue that, when

uncured sample is heat up in a microwave, the molecules in the surfaces of VE/FLYASH (33%) will heat up faster which initiate molecules with lower activation energy to evaporate as a form of vapor (Styrene gas). This results in lesser content of VE/FLYASH (33%) in the beaker, which significantly reduces the percentage shrinkages of the sample.

Comparing technique 1 (P1) curves, these curves yielded a better results than the one shown in Figure 6.5 (a) except that the last value (12.334%) of the purple curve in Figure 6.5 (b) should be lowered. With reference to the previous paragraph, this value (12.334%) also existed in the discussion. It can be justified that, the batch of samples made for the 45 seconds of exposure time are not reliable. However to a researcher of this experiment, the teal curve (150ml (P1)) yielded a better result for this finding as it shrinkages decreases with respect to increase exposure times. It is also anticipated the rest of the results to be similar or close this curve. Somehow, these two curves contradict the justification made earlier as the shrinkages of VE/FLYASH (33%) for 150ml samples is less than 100ml samples for technique 1 of 160W finding. Nevertheless, the justifications of higher percentage shrinkages for 150ml in technique 2 still hold.

The closest results obtained from this finding can be observed by comparing the 100ml samples in 160W for both techniques; the navy blue and purple curves in Figure 6.5 (b). The largest difference between the two percentage shrinkage is only 9.5% (30 seconds exposure time) whereas the smallest difference is only 4.5% (35 seconds of exposure time), compare to the highest possible percentage shrinkage difference of all time (34.604%) which lies on 45 seconds for 150ml sample in Figure 6.5 (b).

To compare the results more closely, the following graphs (Figure 6.6 to Figure 6.9) are shown below with the line/curve of best fit drawn in within the points/values to analyze the trend of the graphs, so that more accurate discussion and justification can be drawn. It is realized that, the ambient conditions are not included in the graphs below. The reason to this is because of, finding the feasibility of using microwaves and pycnometer to compare the results;

including the percentage shrinkages of ambient condition might affect the trend of the graphs.
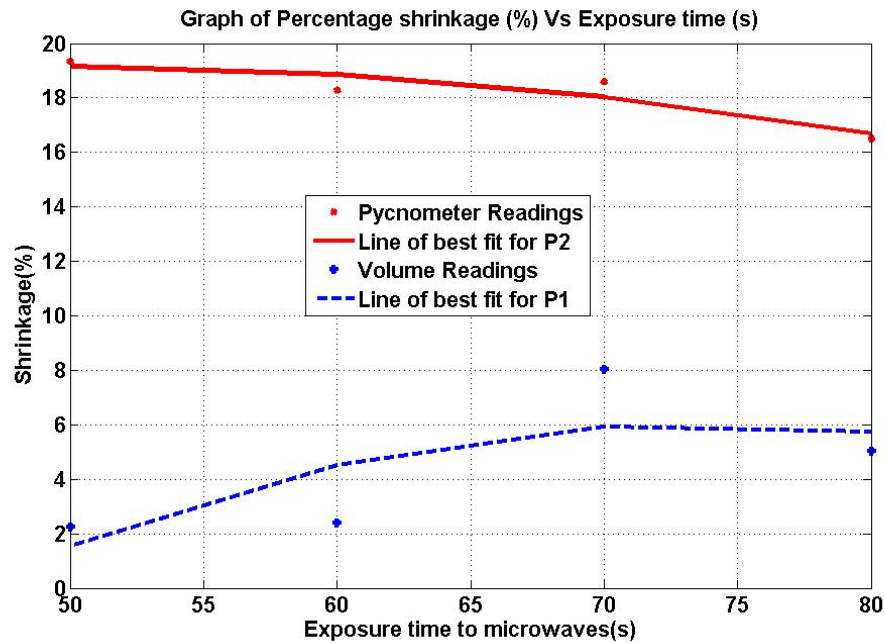
Figure 6.6: Comparison of shrinkages between P1 & P2 for 100ml of composite in 80W microwaves

Figure 6.6 is the graph of percentage shrinkage against exposure time for 100ml of composite in 80W microwaves. No similar trend is observed here as one of the line decreases (P2) and the other one increases (P1) as they go along the x-axis. In this graph, it can be argued that, shrinkages obtained from P2 are more reliable as its percentage shrinkages reduce as the exposure time to microwaves increases. For the dotted line (P1), the percentage shrinkages range from 2.255% to 8.044% within an exposure time of 30 seconds. The maximum final temperature recorded for 80W and 100ml finding is 43°C which is at 70 seconds of exposure time (Appendix B). Compare to the final average temperatures recorded, the average temperature for 60 seconds of exposure time is 29.3^{o}C, it rise to 33.5^{o}C at 70 seconds of exposure time and drop back to the same and exact value of 29.3^{o}C for 80 seconds of exposure time. This could be the reason of sudden jerk of percentage shrinkages from 2.404% to 8.044%. Somehow, the

94

duty cycle of the microwaves (as discussed in chapter 3) brings some inconsistencies for the last 3 values of the dotted line.
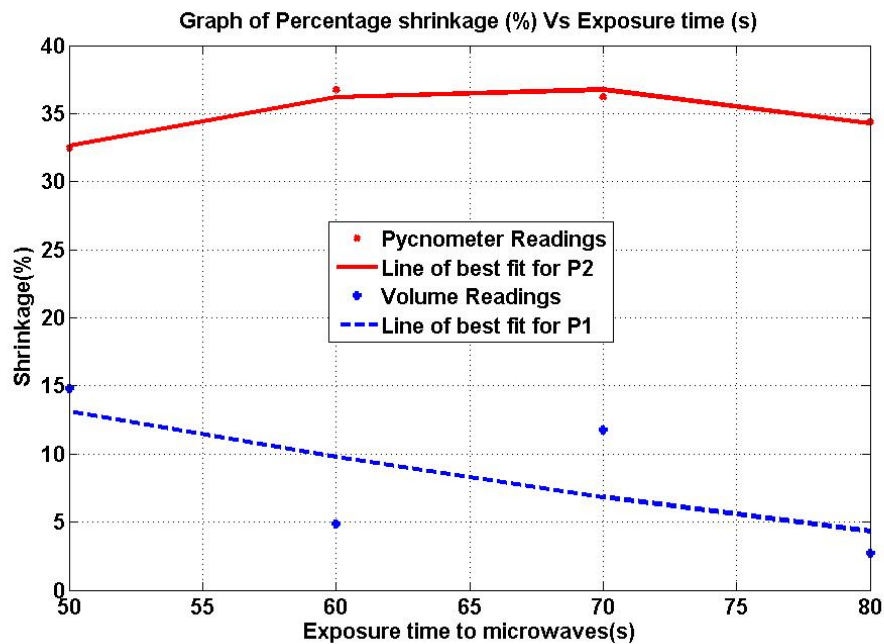
Figure 6.7: Comparison of shrinkages between P1 & P2 for 150ml of composite in 80W microwaves

Figure 6.7 is the graph of percentage shrinkage against exposure time for 150ml of composite in 80W microwaves. When compared to the 100ml graph (Figure 6.6), it can be found that, the percentage shrinkages obtained from 150ml samples are higher in overall. The blue dotted line shows an expected results; percentage shrinkages decreases with increased exposure times. However, the result obtained from P2 which is plotted in red solid line is out of expectation. The densities of the cured samples vary from 1.3436g/cm^3 to 1.1194g/cm^3 which are shown in Table F of Appendix C. One way to solve this phenomenon is to perform it with other beakers. No similar trend is observed in this graph although both of the lines mean to be close to one another.
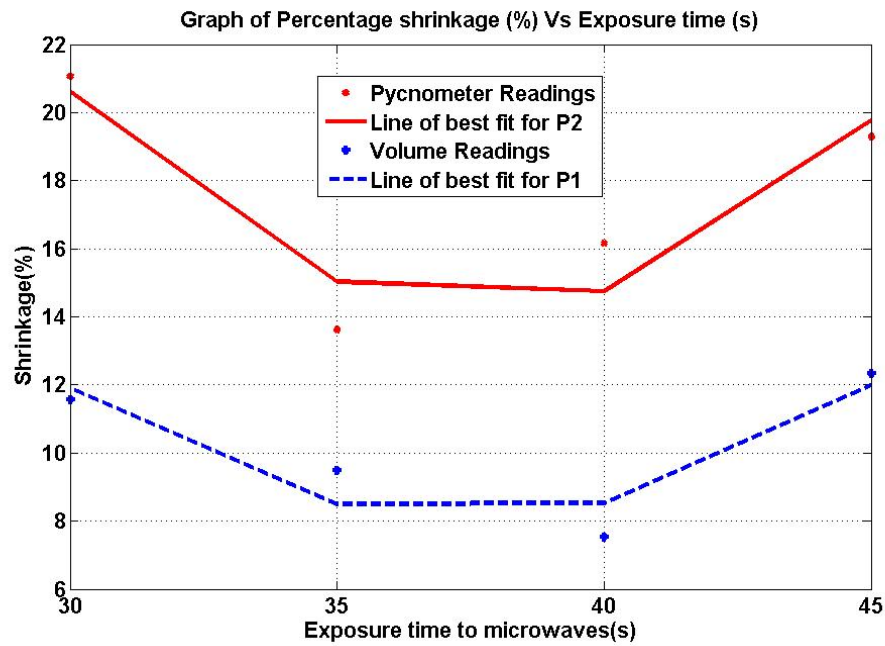
Figure 6.8: Comparison of shrinkages between P1 & P2 for 100ml of composite in 160W microwaves

Figure 6.8 is the graph of percentage shrinkage against exposure time for 100ml of composite in 160W microwaves. After the line of best fit has been drawn, similarity can be observed. Both curves decreases from 30 seconds to 35 seconds of exposure time and then remain constant for the next 5 seconds before it increases again in the last 5 seconds. As the same as the previous two graphs, the percentage shrinkages obtained from technique 2 (P2) is unexpectedly a lot higher than technique 1 (P1). However, this graph gives a closer difference (with less than 10% differences) between the two techniques. These set of data are regarded as more accurate and reliable and the values obtained from both techniques can be used in future researches.
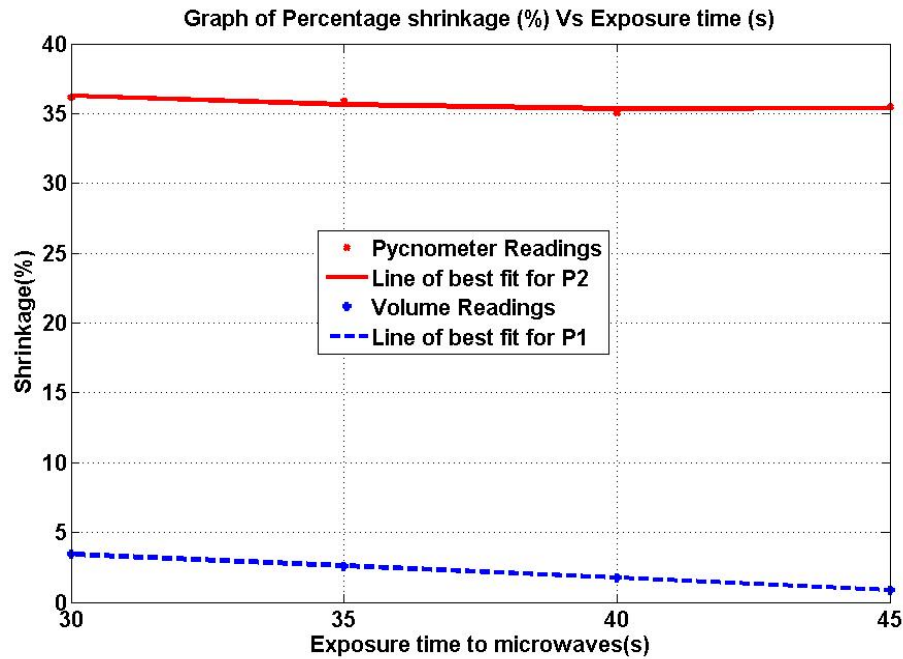
Figure 6.9: Comparison of shrinkages between P1 & P2 for 150ml of composite in 160W microwaves

Figure 6.9 is the graph of percentage shrinkage against exposure time for 150ml of composite in 160W microwaves. Similarity can be observed here, both line drops as the exposure time to microwaves increases. This graph obeys the rules stated in theory which says, increase in exposure times will result in smaller shrinkages in the samples. However there is a bigger gap in between both lines which is not a good sign for a researcher. The differences in percentage shrinkages between the two lines are more than 30% which realistically cannot be correct. As a researcher, I would say the data obtained from technique 1 (dotted line) is more accurate than technique 2 (solid line) as shrinkages of composite can hardly go beyond 20% when cured in microwave.

In summary, it is unfortunate to obtain such results where increase in exposure time in microwave does not vary linearly with the shrinkages in VE/FLYASH (33%). By comparing the line of best fit graphs, I would say composite treated in 160W (Figure 6.8 and Figure 6.9) gives a similar trend between the two techniques although the lines are still further apart from one another. For the

80W graphs (Figure 6.6 and Figure 6.7), I would suggest the results obtained can be used as raw data because of inconsistencies and fluctuation in values.

6.4 Comparison with high power microwaves level

Previously, similar experiment was conducted with high power microwaves (Ku, 2002). The experiment was carried out with 50ml, 200ml and 400ml of VE/FLYASH (33%) in 180W of microwave with technique 1. Three beakers instead of six beakers were used for each set of microwave exposure time in specific volume. The microwaves exposure time chosen are listed below:

- 50ml samples for 0, 30, 35 and 40 seconds,
- 200ml samples for 0, 30, 35, 40 seconds, and
- 400ml samples for 0, 55, 60, 65 seconds.

Three tables are listed in Appendix D with its percentage shrinkages for specific volume of VE/FLYASH (33%). Figure 6.10 is the plot of the three graphs with x axis being the exposure time ranges from 0 to 70 seconds and y axis being the percentage shrinkage ranges from 0 to 10 percent. The figure shows obvious drop in percentage shrinkages when the exposure time to microwave increases. Also, the percentage shrinkages in ambient condition for the three set of volumes is higher that those sample that is cured in microwave. The graphs in this figure obeyed the theory behind the shrinkage of composite. Despite overlapping can be observed between the blue and the red lines, each new value obtained is still lower than the previous one when it goes along the right of x axis. It is also noted that, the percentage shrinkage of this set of data can never reach more than 10%. Nevertheless, higher percentage shrinkages will be obtained from larger volume of VE/FLYASH (33%) is one similarly that can be justified between high power and low power findings.
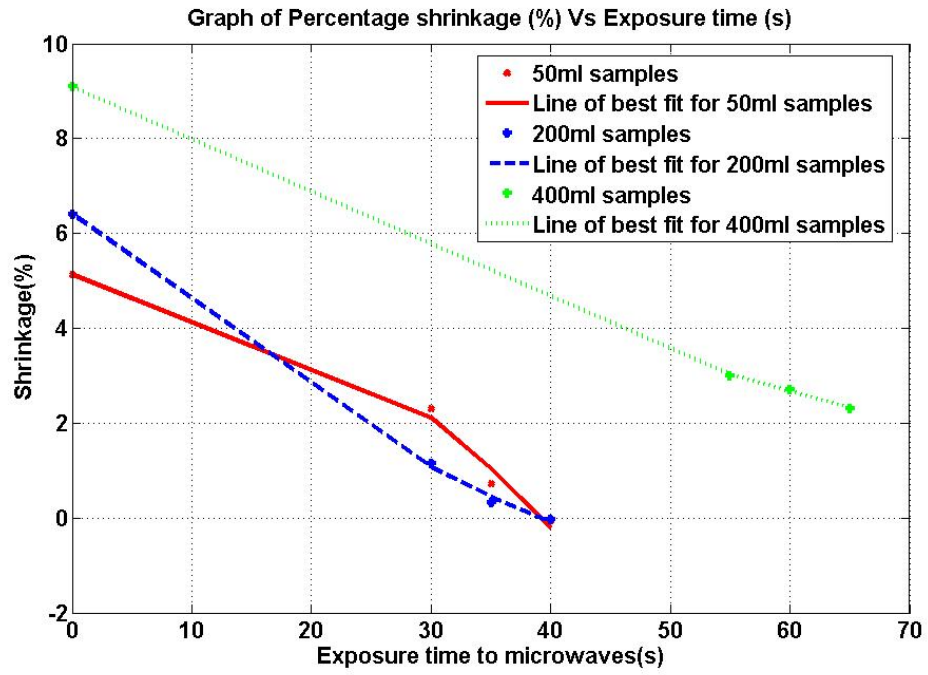
Figure 6.10: Results obtained from High power microwaves (180W)

Chapter 7

Conclusion and Recommendations

7.1 Conclusion

In this study, the percentage shrinkages obtained from both techniques are high when compared to the previous findings. This may due to many factors, one of which being uneven mixture of sample. The other factor which is responsible for the high percentage shrinkages is due to the fact that, the initial heights of each beaker are different (refer to Appendix B). Thus, it will directly affect the initial volume of the samples and hence its percentage of shrinkages. By Comparison of both techniques, it can be argued that Pycnometer is not a good technique to determine the shrinkages of VE/FLYASH (33%) as the percentage shrinkages can never be less than 20%.

Furthermore, increase in exposure time does not vary linearly with the percentage shrinkages in low power microwave application. This can be justified by the analyzing the results obtained from both techniques. However, this statement is not true when it comes to high power level applications.

Compare with the final temperature of the readings (refer to Appendix B), it can be argued that the duty cycle of microwaves bring some inconsistencies in

heating up the sample, even though the initial temperature of the samples remains within $1^{o}C$ of difference. This could be the other reasons of having numerous fluctuating results.

However, in this work, most results obtained have proven that 150ml samples shrink more than 100ml samples. This situation is the same as using high power microwave to cure the samples. Overall it can be concluded that, having VE/FLYASH (33%) cured in low power microwave level is not a good idea to reduce its shrinkages as it gives enormously high and scattered results, this is obvious especially with 80W power level.

7.2 Recommendations

The results can be improved from the following efforts:

- To overcome the inconsistencies (duty cycle) in heating up the sample, future research should start off with temperature interval of 20 seconds instead of 10 seconds.

- For pycnometer technique, other samples of the same batch should be analyzed and not average sample only.

- To ensure the raw materials are mixed thoroughly, electrical stirrer can be used, so that the mixture of resins, SLG and accelerator are mixed evenly before it is pour into each beaker.

- Use electron microscope to view the cut surfaces so that better discussions and conclusions can be drawn from the cured sample.

- Repeat the 80W power level experiment with 40s, 60s, 80s and 100s of exposure time, as results obtained from both techniques for exposure at 80W power level are not very reliable.

- Use nodal analysis section from heat and mass transfer to explain the temperature distributed in within the composite as this might impact the shrinkages of the material.

- Viscosity of the fluid does not really affect the shrinkages. However, during solidification process, the viscosity will change from low to high.

- Collect all the preliminary information such as viscosity, forces, temperatures etc. This information is needed to input into simulation software such as ANSYS. More discussions and justifications can be made from finding out the maximum residual stress within the composite. Software such as ANSYS is recommended because it is user friendly and it can be incorporated with PRO-ENGINEER.

References

Measuring Percent solids of slurry with AccuPyc 1330, Micromeritics Instrument Corporation 1996-2007, viewed 05/07/2007, <http://www.micromeritics.com/products/article_percent_solids.aspx?id=140>

AccuPyc 1330 Pycnometer Fully Automatic Density Analyzer- Supplier Data By Micromeritics, The AZo Journal of Materials online 2000-2007, viewed 08/07/2007, <http://www.azom.com/details.asp?ArticleID=3216>

AccuPyc 1330 Pycnometer, Technical Specifications, Micromeritics Instrument Corporation 1996-2007, viewed 05/07/2007, <http://www.micromeritics.com/products/accupyc_specs.aspx?id=76>

Sample-Weighting Precision with the AccuPyc 1330, 1cm^3 Capacity, Application note Page 113, Micromeritics Instrument Corporation 1996-2007, viewed 05/07/2007, <http://www.micromeritics.com/pdf/app_notes/ap113.pdf>

Composite material, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 08/08/2007, <http://en.wikipedia.org/wiki/Composite_material>

Reinforced Carbon-carbon, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 08/08/2007, < http://en.wikipedia.org/wiki/Reinforced_carbon_carbon>

Metal Matrix Composite, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 09/08/2007, <http://en.wikipedia.org/wiki/Metal_matrix_composite>

Thermosetting Plastic, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 09/08/2007,
<http://en.wikipedia.org/wiki/Thermoset>

Thermoplastic, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 09/08/2007,
<http://en.wikipedia.org/wiki/Thermoplastic>

Polyester, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 09/08/2007,
<http://en.wikipedia.org/wiki/Polyester>

Vinyl Ester, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 20/08/2007,
<http://en.wikipedia.org/wiki/Vinyl_ester>

Rheology, Wikipedia-The free Encyclopedia, Wikimedia Foundation, Inc, US, viewed 18/09/2007,
<http://en.wikipedia.org/wiki/Rheology>

Marshall Brain, 2005, How Microwave Cooking Works, 1998-2007 How StuffWorks, Inc, US, viewed 15/09/2007,
<http://www.howstuffworks.com/microwave1.htm>

Ductile and Brittle Fracture, NHML Resources, New Hampshire Materials Laboratory Inc 2000-2006, viewed 16/009/2007,
<http://nhml.com/resources_NHML_Ductile-Brittle-Fracture.php>

L. Xu and L.T.Drzal, 2005, Influence of Cure Volume Shrinkage of Matrix Resin on the Adhesion between Carbon Fiber and Vinyl Ester Resin, Composite Materials and Structure Center, Department of Chemical Engineering and Materials Science, Michigan State Univeristy, viewed, 18/09/2007,
<http://www.frpbbs.com/bbs/simple/index.php?t2866.html>

Vinyl Ester and Polyester Resins, Last updated 26th December 2002, Sweet Composites, Betesda, USQ, viewed 30/09/2007,
<http://www.sweetcomposites.com/resinfo.html>

Fibergate Composite Structures Inc, MSDS: Structural shapes- VEFP, viewed, 30/09/2007,
<http://www.fibergrate.com/fileshare/ProductFiles/msds/vefr.pdf>

Mel M. Schwartz 1997, Composite Materials, Volume 1: Properties, Nondestructive Testing and Repair, PTR Prentice Hall, Upper saddle River, New Jersey.

Robert M. Jones 1999, Mechanics of Composite Materials, 2nd edition, Taylor and Francis, Philadelphia.

Ang, S F, 2004, Evaluation Impact Strength on Particulate Reinforced (25% and 30%) Vinyl Ester Composite Cured Under Microwave Conditions, University of Southern Queensland.

Astrom, B T, Manufacturing of polymer composites, Chapman and Hall, United Kingdom.

Osswald, T A and Menges, G, Materials science of polymers for engineers, Hanser publishers, New York, USA, 1995:103-5,229-31

Thuery, J, Microwaves: Industrieal, Scientific and Medical Applications, Artech House, Inc, USA

National Research Council, Microwave Processing of Materials, National Materials Advisory Board, Commission on Engineering and Technical Systems, National Academy Press, USA

Bows, JR, Variable Frequency Microwave Heating of Food, Journal of Microwave Power and Electromagnetic Energy, USA, 1999:34:4:227-38

Sheppard, L M, Manufacturing Ceramics with Microwaves: Potential for Economic Production, Ceramic Bulletin, United Kingdom

Ku, H S, Siores, E, Ball, J A R and Horsfield, B, Permittivity measurement of thermoplastic composites at elevated temperature, Journal of Microwave Power and Electromagnetic Energy, USA, 2001:36:2:101-111.

Peters, S T, Handbook of Composiites, Chapman and Hall.

Ku, H S, Siores, E, Ball, Microwave Processing and Permittivity Measurement of Thermoplastic Composites at Elevated Temperatures, Journal of Materials Processing Technology, USA, 1999:89-90:419-24.

Ku, H S, Siores, E, Ball, J A R, Microwave Facilities for Weldoing Thermoplastic Composites, and Preminary Results, Journal of Microwave Power and Electromagnetic Energy, USA, 1999:34:4:195-205.

Ku, H S, Risks involved in curing Vinly Ester Resins using microwave irradiation, Journal of Material Synthesis and Processing, USA, 2002

G. Pritchard (Editor), Reinforced plastics durability, Woodhead publishing Ltd, US.

A C. Metaxas, and R. J. Meredith, Industrial microwave heating, Institution of Electrical Engineers, London, U.K., Peter Peregrinus Ltd.

R. J. Meredith, Engineers' Handbook of Industrial Microwave Heating, Short Run Press Ltd.,United Kingdom.

Fox, McDonald & Prichard 2004, Introduction to Fluid Mechanics, Sixth Edition, USA

Askeland & Phule 2003, The Science and Engineering of Materials, Fourth Edition

Appendix A

Project specification

University of Southern Queensland
Faculty of Engineering and Surveying

ENG 4111/4112 Research Project
PROJECT SPECIFICATION

Project title: **Shrinkage reduction of thermoset matrix**
                                  particle reinforced composites during
                                  hardening using low power microwaves

Student: LEE Wai Hung - 0050013907

Supervisor: Dr. Harry Ku
Co-Supervisor:

Sponsorship:

Project Synopsis:

The project involves the production of number of vinyl ester resin specimens
which is then tested with low power microwave. After each Specimen is mixed
accurately with VE/FLYASH (33%), it is follow by exposing them to cure with
a nominated time-scale. The chosen microwave powers for curing are 80W,
160W, 180W and 240W. Measurements will be conducted before and after the
uncured/cured specimens to evaluate the shrinkage reduction. However, formula
will be used with the measurements taken, to calculate the volume shrinkage.
Equipment such as pycnometer will be used to measure the density of the cured
vinyl ester composites accurately. Additionally, mass of the total resin shrinkage
can also be determined.

Timelines:

1. Familiarization of equipment and literature reviews.

   Begin   : 4th March 2007
   Completion   : 20th March 2007
   Approx. Hours   : 30 hours

2. Mix, measure, produce and record cured and uncured specimens.

   Begin   : 20th March 2007
   Completion   : 11th May 2007
   Approx. Hours   : 60 hours

3. Calculate and evaluate the volume reduction with different power
   settings.
   Begin   : 14th May 2007
   Completion   : 31st May 2007
   Approx. Hours   : 20 hours

4. Use pycnometer to test and calculate density of specimens.

   Begin   : 31th May 2007
   Completion   : 15th June 2007
   Approx. Hours   : 20 hours

5. Analysis of results.
   Begin   : 2nd July 2007
   Completion   : 13th July 2007
   Approx. Hours   : 20 hours

6. Repeat testing for unsatisfying results.
   Begin   : 13th July 2007
   Completion   : 20th July 2007
   Approx. Hours   : 10 Hours

7. Software package analysis- Use FEA to analyse the rate of heat transfer.
   Begin   : 23st July 2007
   Completion   : 14th August 2007
   Approx. Hours   : 30 hours

8. Discussion of dissertation outline with supervisors.
   Begin   : 14th August 2007
   Completion   : 24th August 2007
   Approx. Hours   : 20 hours

9. Start dissertation write-up and prepare for PP2 presentation.
   Begin   : 24th August 2007
   Completion   : 14th September 2007
   Approx. Hours   : 30 hours

10. Dissertation initial drafting– Draft each chapter and shown to supervisors.

    Begin   : 17th September 2007
    Completion   : 30th September 2007
    Approx. Hours   : 40 hours

11. Final draft of dissertation, to incorporate modifications suggested by supervisor.

    Begin   : 1st October 2007
    Completion   : 20th October 2007
    Approx. Hours   : 40 hours

12. Compile the dissertation in requested format.

    Begin   : 20th October 2007
    Completion   : 31st October 2007
    Approx. Hours : 30 hours

AGREED:

_____ (Student)   _____ (Supervisor)

    (Date)___/___/___

Appendix B

Tables for DVMT

100ML of VE/FLYASH (33%)

Ambient Condition

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25	25	25.5	26	25	25
Initial height, h_1	32.5	32.6	29.8	31.5	33.4	32
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	25.5	25	25	25	25	26
Final Height, h_2	31.2	30.98	29	30.1	31.7	31.6
Final volume, v_2	88.47	85.16	92.2	87.25	85.49	96.2
Shrinkage (%)	11.53	14.84	7.84	12.75	14.5	3.8

Average: 12.292
STDEV 2.827

Power Level= 80W   Duration of exposure= 50 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25.5	24	25	25	25.5	26
Initial height, h_1	33.7	33.1	32	33.2	33	32.4
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	27.5	27.5	26	28.5	28.5	27
Final Height, h_2	33.3	33	31.8	33	32.7	32.1
Final volume, v_2	96.48	99.1	98.14	98.2	97.3	97.25
Shrinkage (%)	3.52	0.9	1.86	1.8	2.7	2.75

Average: 2.255
STDEV 0.921

Power Level= 80W   Duration of exposure= 60 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	27.5	27.5	26.5	26.5	27.5	26.5
Initial height, h_1	29.6	29.5	29.8	29.6	29.7	29.6
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	29.5	30.5	29	27	32	28
Final Height, h_2	28.4	29.4	29.6	29.3	29.5	29.2
Final volume, v_2	88.32	98.99	98	96.99	97.99	96
Shrinkage (%)	11.6	1.01	2	3.01	2.01	3.99

Average: 2.404
STDEV 1.134

Power Level= 80W   Duration of exposure= 70 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25.5	28.5	24.5	27	25	25.5
Initial height, h_1	28.6	29.9	29.4	29.9	28.1	29.5
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	33.5	35.5	28	43	29	34
Final Height, h_2	28.3	27.6	28.6	28.7	27.4	28.4
Final volume, v_2	96.89	78.65	92.06	88.44	92.71	89.23
Shrinkage (%)	3.11	21.35	7.49	11.56	7.29	10.77

Average: 8.044
STDEV 3.355

Power Level= 80W   Duration of exposure= 80 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25	24.5	24.5	24.5	24.5	25
Initial height, h_1	32.2	33.7	32.3	32.8	33.2	33.6
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	32.5	28.5	32.5	27	25.5	30
Final Height, h_2	32	32.7	31.6	32.1	32.7	33.3
Final volume, v_2	98.15	91.36	93.64	93.73	95.55	97.35
Shrinkage (%)	1.85	8.64	6.36	6.27	4.45	2.65

Average: 5.037
STDEV 2.548

Power Level= 160W   Duration of exposure= 30 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25.5	26	25.5	24.5	24	24.5
Initial height, h_1	33.2	32.9	31.9	33.7	32.5	32.2
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	32	32.5	32	27	27	30
Final Height, h_2	32.5	31.5	30.2	32.3	31.1	31.9
Final volume, v_2	93.81	87.77	84.85	88.05	87.63	97.23
Shrinkage (%)	6.19	12.23	15.15	11.95	12.37	2.77

Average: 11.578
STDEV 3.278

Power Level= 160W   Duration of exposure= 35 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24	24	24	25	24.5	25
Initial height, h_1	32.5	32.2	32.5	32.8	33.9	32.5
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	28.5	28	27	31.5	30.5	32
Final Height, h_2	31.3	31.3	31.7	31..6	31.6	31.5
Final volume, v_2	89.32	91.85	92.79	89.42	88.61	91.05
Shrinkage (%)	10.67	8.15	7.2	10.58	11.39	8.95

Average: 9.49
STDEV 1.815

Power Level= 160W   Duration of exposure= 40 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	26	26	26	25	25.5	25.5
Initial height, h_1	31.9	32.8	31.4	32	31.9	32
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	35.5	35.5	33	29.5	31	31.5
Final Height, h_2	31.1	31.7	31	30.9	31.8	31.2
Final volume, v_2	92.66	90.27	96.23	90.04	99.06	92.69
Shrinkage (%)	7.34	9.73	3.37	9.96	0.94	7.31

Average: 7.542
STDEV 2.652

Power Level= 160W   Duration of exposure= 45 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25	25	25	25.5	25	25
Initial height, h_1	32.9	33	33.4	34.1	34.1	34.7
Initial volumn, v_1	100	100	100	100	100	100
Final temperature, t_2	30	30	27.5	27	27	27.5
Final Height, h_2	31.9	31.8	33.3	32.4	32.8	32.6
Final volume, v_2	91.16	89.48	99.1	85.78	88.99	82.92
Shrinkage (%)	8.84	10.52	0.9	14.22	11.01	17.08

Average: 12.334
STDEV 3.291

150ML of VE/FLYASH (33%)

Ambient Condition

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24	24	24	24	23.5	24
Initial height, h_1	41.5	40.8	41.8	41.5	41.4	41.4
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	21.5	21.5	21.5	21.5	21.5	21.5
Final Height, h_2	38.4	38.3	38.8	39.7	39.9	38.6
Final volume, v_2	118.83	124.66	119.97	131.32	134.28	121.58
Shrinkage (%)	20.78	16.89	20.02	12.46	10.48	18.95

Average: 16.597
STDEV 4.228

Power Level= 80W   Duration of exposure= 50 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	23	23.5	24	23.5	25	24
Initial height, h_1	40.9	40.9	40.7	42.1	40	41.9
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	23.5	23.5	25.5	25.5	30.5	23.5
Final Height, h_2	38.5	39.1	38.3	40.5	37.9	39.4
Final volume, v_2	125.11	131.05	124.99	133.54	127.59	124.72
Shrinkage (%)	16.59	12.63	16.67	10.97	14.94	16.85

Average: 14.775
STDEV 2.462

Power Level= 80W   Duration of exposure= 60 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24	24	24	25	25	25.5
Initial height, h_1	40.7	40.8	40.6	40.6	40.4	40.6
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	24.5	26	25.5	27	27.5	29.5
Final Height, h_2	40.6	40.3	40.3	39.3	40	39.7
Final volume, v_2	148.89	144.55	146.7	136.04	145.59	140.24
Shrinkage (%)	0.74	3.63	2.2	9.03	2.94	6.5

Average: 4.86
STDEV 3.050

Power Level= 80W   Duration of exposure= 70 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24	24	24	24	24.5	24.5
Initial height, h_1	42.1	42.3	42.1	41.1	41	40.9
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	25.5	25.5	25.5	25.5	24.5	25.5
Final Height, h_2	40.1	40.2	41.1	39.8	39	39.1
Final volume, v_2	129.62	128.75	139.56	136.21	129.1	131.05
Shrinkage (%)	13.59	14.17	6.96	9.19	13.93	12.63

Average: 11.745
STDEV 2.975

Power Level= 80W   Duration of exposure= 80 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	25	25.5	25.5	25.5	25.5	26
Initial height, h_1	48.6	47.1	47.4	48.2	48.1	48.3
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	28	27.5	28	27	27.5	27
Final Height, h_2	48.1	46.5	46.6	47.9	48	48
Final volume, v_2	145.42	144.34	142.53	147.22	149.06	147.22
Shrinkage (%)	3.05	3.77	4.98	1.85	0.624	1.85

Average: 2.687
STDEV 1.563

Power Level= 160W   Duration of exposure= 30 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24.5	24.5	24.5	24.5	23.5	24
Initial height, h_1	46.1	47.2	46.8	47	47.7	47.6
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	28.5	29	28	28.5	25	26.5
Final Height, h_2	46	46.3	46.3	46.7	47.2	46.6
Final volume, v_2	149.03	141.58	145.24	147.15	145.33	140.74
Shrinkage (%)	0.65	5.61	3.17	1.9	3.11	6.17

Average: 3.435
STDEV 2.121

Power Level= 160W   Duration of exposure= 35 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	23	23.5	23	23	23.5	23
Initial height, h_1	47.2	47.6	48	48.7	47.4	46.9
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	25.5	23.5	23.5	24	24	26.5
Final Height, h_2	46.1	27.3	47.6	48.4	47.7	46.5
Final volume, v_2	139.76	147.18	146.28	147.24	152.87	146.19
Shrinkage (%)	6.83	1.88	2.48	1.84	-2.87	2.54

Average: 2.595
STDEV 3.083

Power Level= 160W   Duration of exposure= 40 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	23.5	23.5	23	23	22.5	23
Initial height, h_1	46	47.6	50.1	47.2	47.2	46.7
Initial volumn, v_1	150	150	165	150	150	150
Final temperature, t_2	25	23.5	24	25.5	24	24.5
Final Height, h_2	46	46.7	50.4	46.8	46.8	46.7
Final volume, v_2	0	141.65	167.98	146.22	146.22	0
Shrinkage (%)	0	5.57	-1.81	2.52	2.52	0

Average: 1.768
STDEV 2.303

Power Level= 160W   Duration of exposure= 45 secs

Specimen number	1	2	3	4	5	6
Initial temperature, t_1	24	24	24	24	23.5	23.5
Initial height, h_1	47.4	46.8	47.4	47.4	47.3	47.7
Initial volumn, v_1	150	150	150	150	150	150
Final temperature, t_2	26	27.5	26.5	26	25	26
Final Height, h_2	46.7	46.6	47.2	47.3	47.2	47.6
Final volume, v_2	143.45	148.07	148.11	149.05	149.05	149.06
Shrinkage (%)	4.37	1.28	1.26	0.632	0.633	0.628

Average: 0.887
STDEV 0.350

Appendix C

Tables and MATLAB Codes for PT

PART 2: PYCNOMETER TECHNIQUE

Table A: Uncured VE/FLYASH (33%)

Mass (g)	24.995
Temperature ©	26.8
Density 1 (g/cm^3)	0.9123
Density 2 (g/cm^3)	0.9122
Density 3 (g/cm^3)	0.9126
Average	0.9124

Table B: Vinyl Ester Resin

Mass (g)	15.4655
Temperature ©	28
Density 1 (g/cm^3)	1.0628
Density 2 (g/cm^3)	1.0619
Density 3 (g/cm^3)	1.0615
Average	1.0621

Table C: FLYASH

Mass (g)	6.0503
Temperature ©	28
Density 1 (g/cm^3)	0.7659
Density 2 (g/cm^3)	0.7649
Density 3 (g/cm^3)	0.7655
Average	0.7654

Table D: 100ML of cured VE/FLYASH (33%) for 80W & Ambient

	Ambient	80W 50Sec	80W 60Sec	80W 70Sec	80W 80Sec
Mass (g)	10.0141	10.1666	11.2641	11.2421	11.0048
Temperature ©	28	28.1	28.1	28.1	28.2
Density 1 (g/cm^3)	1.1327	1.1321	1.1171	1.1215	1.0943
Density 2 (g/cm^3)	1.1329	1.1312	1.1172	1.1206	1.0921
Density 3 (g/cm^3)	1.1325	1.1307	1.1158	1.1206	1.0918
Average	1.1327	1.1313	1.1167	1.1209	1.0927
% Shrinkage from Part 2	19.449	19.349	18.29	18.601	16.5
% Shrinkage from Part 1	12.292	2.255	2.404	8.044	5.037

m

Table E: 100ML of cured VE/FLYASH (33%) for 160W Power Level

	160W 30Sec	160W 35Sec	160W 40Sec	160W 45Sec
Mass (g)	10.6035	10.3589	10.1773	9.7144
Temperature ©	28.2	28.3	28.6	29
Density 1 (g/cm^3)	1.1562	1.0571	1.088	1.1309
Density 2 (g/cm^3)	1.1569	1.0561	1.0884	1.1303
Density 3 (g/cm^3)	1.1552	1.0558	1.0882	1.1303
Average	1.1561	1.0563	1.0882	1.1305
% Shrinkage from Part 2	21.079	13.623	16.155	19.292
% Shrinkage from Part 1	11.578	9.49	7.542	12.334

Table F: 150ML of cured VE/FLYASH (33%) for 80W & Ambient

	Ambient	80W 50Sec	80W 60Sec	80W 70Sec	80W 80Sec
Mass (g)	3.014	3.5813	3.6102	2.7515	2.9388
Temperature ©	26.1	26.3	26	25.8	25.7
Density 1 (g/cm^3)	1.4078	1.359	1.4494	1.4329	1.3919
Density 2 (g/cm^3)	1.3995	1.3508	1.4395	1.4333	1.3897
Density 3 (g/cm^3)	1.3909	1.3436	1.4384	1.4255	1.3928
Average	1.3994	1.3511	1.4424	1.4306	1.3915
% Shrinkage from Part 2	34.801	32.469	36.744	36.222	34.43
% Shrinkage from Part 1	16.597	14.775	4.86	11.745	2.687

Table G: 150ML of cured VE/FLYASH (33%) for 160W Power Level

	160W 30Sec	160W 35Sec	160W 40Sec	160W 45Sec
Mass (g)	4.5374	4.9467	4.9828	4.506
Temperature ©	25.7	25.6	25.5	25.5
Density 1 (g/cm^3)	1.4373	1.4269	1.4099	1.4174
Density 2 (g/cm^3)	1.428	1.4262	1.4009	1.4115
Density 3 (g/cm^3)	1.4228	1.4179	1.4039	1.414
Average	1.4294	1.4237	1.4049	1.4143
% Shrinkage from Part 2	36.169	35.913	35.056	35.488
% Shrinkage from Part 1	3.435	2.595	1.768	0.887

```matlab
% Script for Figure 6.6 (MATHLAB)
%
% Values taken from Table D
s1=[19.349 18.29 18.601 16.5];
s2=[2.255 2.404 8.044 5.037];
% Set time interval
t=[50 60 70 80];
% Draw line of best fit for s1
coeffs=polyfit(t,s1,2);
% calculate output from model
Y=polyval(coeffs,t);
% Plot Graph for s1
plot(t,s1,'rx',t,Y,'r','LineWidth',3);
hold on
% Draw line of best fit for s2
coeffs=polyfit(t,s2,2);
% calculate output from model
Z=polyval(coeffs,t);
% Plot Graph for s2
plot(t,s2,'b*',t,Z,'b--','LineWidth',3);
grid on
% Set X-axis
xlabel('Exposure time to microwaves(s)','Fontsize',16,'FontWeight','bold');
% Set ylabel
ylabel('Shrinkage(%)','Fontsize',16,'FontWeight','bold')
% Set Title
title('Graph of Percentage shrinkage (%) Vs Exposure time (s)',...
    'Fontsize',16,'FontWeight','bold')
hold on
% Set legend
legend('Pycnometer Readings','Line of best fit for P2',...
    'Volume Readings','Line of best fit for P1')
% Set Font
set(gca,'Fontsize',16,'FontWeight','bold');
%
% EOF
```

```
% Script file for Figure 6.7 (MATHLAB)
%
% Values taken from Table F
s1=[32.469 36.744 36.222 34.430];
s2=[14.775 4.86 11.745 2.687];
t=[50 60 70 80];
% Use polyfit and polyval functions to get line of best fit for Pycnometer
coeffs=polyfit(t,s1,2);
Y=polyval(coeffs,t);
% Plot graphs for Pycnometer Readings
plot(t,s1,'rx',t,Y,'r','LineWidth',3);
hold on
% Use polyfit and polyval functions to get line of best fit for Volume
% measurement
coeffs=polyfit(t,s2,2);
Z=polyval(coeffs,t);
% Plot graphs for values taken from volume measurement technique
plot(t,s2,'b*',t,Z,'b--','LineWidth',3);
% Set grid line
grid on
% Set xlabel
xlabel('Exposure time to microwaves(s)','Fontsize',16,'FontWeight','bold');
% Set ylabel
ylabel('Shrinkage(%)','Fontsize',16,'FontWeight','bold')
% Set Title
title('Graph of Percentage shrinkage (%) Vs Exposure time (s)',...
    'Fontsize',16,'FontWeight','bold')
hold on
% Set Legend
legend('Pycnometer Readings','Line of best fit for P2',...
    'Volume Readings','Line of best fit for P1')
% Set font
set(gca,'Fontsize',16,'FontWeight','bold');
%
% EOF
```

```matlab
% Script file for Figure 6.8 (MATHLAB)
%
% Values taken from Table E
s1=[21.079 13.623 16.155 19.292];
s2=[11.578 9.49 7.542 12.334];
t=[30 35 40 45];
% Use polyfit and polyval functions to get line of best fit for Pycnometer
coeffs=polyfit(t,s1,2);
Y=polyval(coeffs,t);
% Plot graphs for Pycnometer Readings
plot(t,s1,'rx',t,Y,'r','LineWidth',3);
hold on
% Use polyfit and polyval functions to get line of best fit for Volume
% measurement
coeffs=polyfit(t,s2,2);
Z=polyval(coeffs,t);
% Plot graphs for values taken from volume measurement technique
plot(t,s2,'b*',t,Z,'b--','LineWidth',3);
% Set grid line
grid on
% Set xlabel
xlabel('Exposure time to microwaves(s)','Fontsize',16,'FontWeight','bold');
% Set ylabel
ylabel('Shrinkage(%)','Fontsize',16,'FontWeight','bold')
% Set Title
title('Graph of Percentage shrinkage (%) Vs Exposure time (s)',...
    'Fontsize',16,'FontWeight','bold')
hold on
% Set Legend
legend('Pycnometer Readings','Line of best fit for P2',...
    'Volume Readings','Line of best fit for P1')
% Set font
set(gca,'Fontsize',16,'FontWeight','bold');
%
% EOF
```

```matlab
% Script for Figure 6.9 (MATHLAB)
%
% Values taken from Table G
s1=[36.169 35.913 35.056 35.488];
s2=[3.435 2.595 1.768 0.887];
t=[30 35 40 45];
% Use polyfit and polyval functions to get line of best fit for Pycnometer
coeffs=polyfit(t,s1,2);
Y=polyval(coeffs,t);
% Plot graphs for Pycnometer Readings
plot(t,s1,'rx',t,Y,'r','LineWidth',3);
hold on
% Use polyfit and polyval functions to get line of best fit for Volume
% measurement
coeffs=polyfit(t,s2,2);
Z=polyval(coeffs,t);
% Plot graphs for values taken from volume measurement technique
plot(t,s2,'b*',t,Z,'b--','LineWidth',3);
% Set grid line
grid on
% Set xlabel
xlabel('Exposure time to microwaves(s)','Fontsize',16,'FontWeight','bold');
% Set ylabel
ylabel('Shrinkage(%)','Fontsize',16,'FontWeight','bold')
% Set Title
title('Graph of Percentage shrinkage (%) Vs Exposure time (s)',...
    'Fontsize',16,'FontWeight','bold')
hold on
% Set Legend
legend('Pycnometer Readings','Line of best fit for P2',...
    'Volume Readings','Line of best fit for P1')
% Set font
set(gca,'Fontsize',16,'FontWeight','bold');
%
% EOF
```

r

Appendix D

Previous Results

Table A: Volume shrinkage and other parameters for 50 ml of VE/FLYASH (33%) exposed to 180-W microwaves at different duration

Microwave exposure time (seconds)	0	30	35	40
Oven cavity Temperature (^{o}C)	20	28	25	25
Temperature after microwave exposure	NA	44	40	45
Original volume (ml)	50	50	50	50
Final volume (ml)	47.36	48.85	49.64	51.43
Volume shrinkage (%)	5.13	2.3	0.72	-0.06

Table B: Volume shrinkage and other parameters for 200 ml of VE/FLYASH (33%) exposed to 180-W microwaves at different duration

Microwave exposure time (seconds)	0	30	35	40
Oven cavity Temperature (^{o}C)	20	28	25	25
Temperature after microwave exposure	NA	41	45	52
Original volume (ml)	200	200	200	200
Final volume (ml)	187.2	202.32	199.36	200.06
Volume shrinkage (%)	6.4	1.16	0.32	-0.03

Table C: Volume shrinkage and other parameters for 400 ml of VE/FLYASH (33%) exposed to 180-W microwaves at different duration

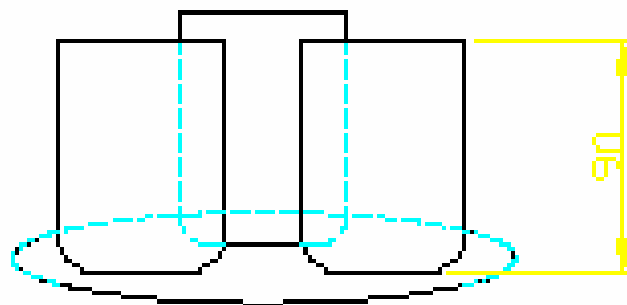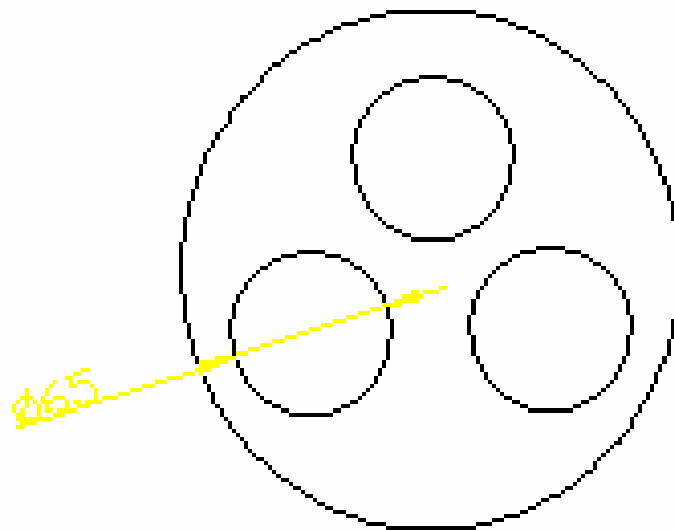| Microwave exposure time (seconds)	0	55	60	65
Oven cavity Temperature (^{o}C)	16	24	22	22
Temperature after microwave exposure	NA	30	32	34
Original volume (ml)	400	400	400	400
Final volume (ml)	363.64	387.69	389.26	390.81
Volume shrinkage (%)	9.09	3.00	2.70	2.30

(H Ku 2002, p.27, 28)

```matlab
% Script for Figure 6.10 (MATHLAB)
%
% Values taken from the Table above
s1=[5.13 2.3 0.72 -0.06];
s2=[6.4 1.16 0.32 -0.03];
s3=[9.09 3 2.7 2.3];
%
% Set time interval
t1=[0 30 35 40];
t2=[0 55 60 65];
%
% Draw line of best fit for s1
coeffs=polyfit(t1,s1,2);
%
% calculate output from model
Y=polyval(coeffs,t1);
%
% Plot Graph for s1
plot(t1,s1,'rx',t1,Y,'r','LineWidth',3);
hold on
%
% Draw line of best fit for s2
coeffs=polyfit(t1,s2,2);
%
% calculate output from model
Z=polyval(coeffs,t1);
%
% Plot Graph for s2
plot(t1,s2,'b*',t1,Z,'b--','LineWidth',3);
hold on
%
% Draw line of best fit for s3
coeffs=polyfit(t2,s3,2);
```

```matlab
% calculate output from model
X=polyval(coeffs,t2);
%
% Plot Graph for s3
plot(t2,s3,'G+',t2,X,'G:','LineWidth',3);
hold on
%
grid on
% Set X-axis
xlabel('Exposure time to microwaves(s)','Fontsize',16,'FontWeight','bold');
% Set Y-axis
ylabel('Shrinkage(%)','Fontsize',16,'FontWeight','bold')
% Set Title
title('Graph of Percentage shrinkage (%) Vs Exposure time (s)',...
    'Fontsize',16,'FontWeight','bold')
hold on
%
% Set legend
legend('50ml samples','Line of best fit for 50ml samples','200ml samples',...
    'Line of best fit for 200ml samples',...
    '400ml samples','Line of best fit for 400ml samples')
% Set Font
set(gca,'Fontsize',16,'FontWeight','bold');
```

Appendix E

Placement of Beakers in Microwave Oven

TOP VIEW

⌀65

SIDE VIEW

90