University of Southern Queensland

Faculty of Engineering and Surveying

Micrographs of the Fracture of Vinyl Ester Composites Cured by Microwaves

A dissertation submitted by

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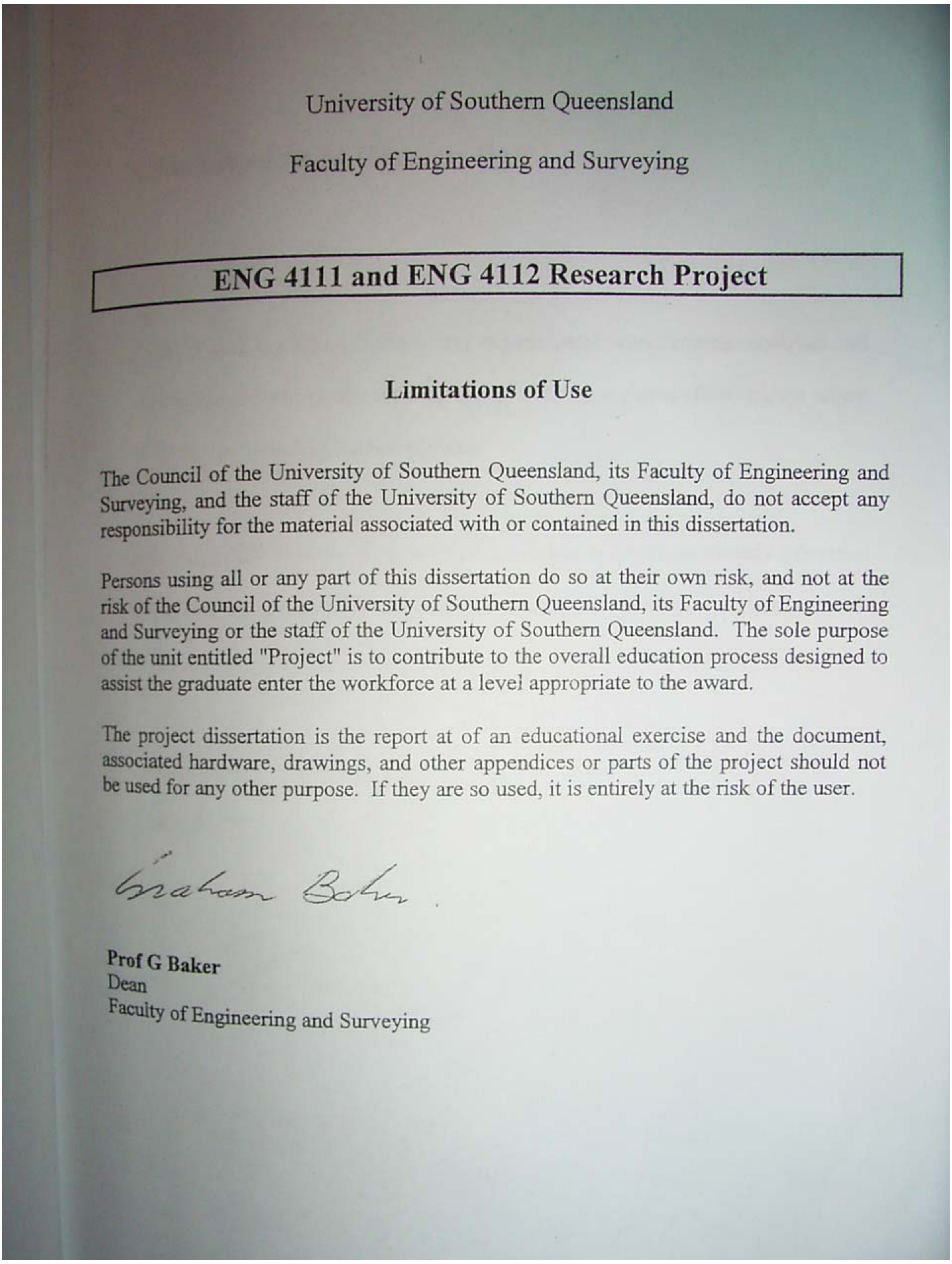
Abstract

Vinyl esters (VE) in production exhibit shrinkage upon hardening which may be up to 10%. Shrinkage inherently sets up internal stresses within a material which are usually tensile in the core of the material and compressive on the surface (Ku, 2002). When these stresses act together with an applied load, they may cause premature failure of the composite component. Initial research by Ku has identified microwave technology as a possible solution to the shrinkage problem with initial tests revealing overall shrinkage results of around 1%. This has been achieved by selecting an optimum combination of initiator, input power of microwave energy and low profile additives. The aim of this project was to investigate the fracture behaviour of particulate reinforced vinyl ester composites cured by microwaves. To achieve this, a number of specimens were produced. These specimens were 33% by weight of the ceramic hollow spheres (envirospheres).

Two types of tests have been performed, the drop weight impact test and the short bar fracture test. The drop weight impact and short bar tests yield fracture samples which were viewed under a scanning electron microscope (SEM) to investigate the mechanics of fracture. These SEM images or micrographs will provide further material and information on the fracture mechanics of VE/FLYASH cured under microwave conditions and will build on the knowledge base for this composite.



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Chapter 1

Introduction

1.1 Project Aim

The aim of this project was to investigate the fracture behaviour and mechanics of particulate reinforced vinyl ester resins cured under microwave conditions, using a scanning electron microscope. The percentage by weight of flyash (reinforcement) will be 33%.

1.1.1 Specific objectives

The specific objectives of this project were:

1. To produce specimens of VE/FLYASH (33%) cured under microwave conditions at various intensities and duration of exposure.
2. To investigate the impact strength of VE/FLYASH (33%)
3. To investigate the fracture toughness of VE/FLYASH (33%)
4. To investigate the fracture behaviour and mechanics of VE/FLYASH using micrographs taken using a scanning electron microscope.

1.2 Dissertation Overview

In this section, the reader will be introduced to a very brief overview of the material presented in each chapter of the dissertation.

Chapter Two

Chapter two presents background information on the polymer composite. This is followed by a discussion of the polymer material family. A brief overview of the composite constituents and their characteristics is given.

Chapter Three

Chapter three discusses the interaction between microwaves and the materials used in this project. The concept of microwave curing of composites is introduced. The advantages and risks involved with using microwave curing are also discussed. This is accompanied with a presentation of the safety measures that need to be considered when using this method of curing.

Chapter Four

Chapter four introduces the concept of fracture mechanics and the fracture toughness and the application of these concepts to engineering problems. The two types of tests used in this project are presented.

Chapter Five

Chapter five gives an overview of the experimental design used in the project.
Specimen production and related safety issues are discussed.

Chapter Six

This chapter discusses the of testing of specimens

Chapter Seven

Microscopy is discussed in this chapter. The techniques used in the investigation of fracture surfaces are discussed. A detailed description of the scanning electron microscope technique is provided.

Chapter Eight

Interpretation of surface topography is discussed in this chapter. This chapter discusses the findings from the investigation of micrographs of fractured samples.

Chapter Nine

This chapter presents the findings of the project.

Chapter Ten

Conclusions from the findings and recommendations for further work is given in this section.

Chapter 2

Composite Materials

2.1 Introduction

This chapter introduces the concept of composite materials and the potential for these materials cured under microwave condition to exhibit little or no shrinkage. A brief outline of the constituent materials of the composite under investigation in this project has also been highlighted.

2.2 Background

Composite materials have been in use for thousands of years, a common composite material being concrete. There are many composite materials available on the market today and the more advanced composites, predominantly developed for use in the aerospace industry, have shown great potential and use in the transportation and civil engineering areas. Research undertaken at the University of Southern Queensland (USQ) by the Fibre Composites Design and Development Group (FCDD) has focused on possible applications of these advanced composite materials in these areas.

Fibre composites and particulate filled resins (PFRs), which are composites by themselves were used in much of the early composites developed at the university. The PFRs were used to form the bulk of the composites. These PFRs were comprised of ceramic hollow microspheres dispersed throughout a thermosetting polymer matrix.

These PFRs possess different material properties attributable to the type of polymer resin used, the proportion of particulate to resin, method of manufacture and curing conditions.

This project is an extension of the earlier work carried out in 1999 by visiting Dutch students Rauol van Loon and Rene Ubachs who studied various aspects of the fracture of PFR composites. The project also encompasses much of the work presently being conducted in the Faculty of Engineering and Surveying, USQ by lecturers and undergraduates. The project aims to investigate the fracture behaviour and mechanics of particulate reinforced vinyl ester resins cured under microwave conditions, using a scanning electron microscope (SEM). The percentage by weight of fly ash (reinforcement) will be 33%. The data collected may be useful in supporting the FCDD group in the future.

Considerable research and development in the area of fibre composites has been undertaken at the USQ. The (FCDD) group has been using particulate filled vinyl ester resins as a component for their fibre composites. The PFR has been applied as a core material, with extremely promising results.

The advantages of this PFR core include high strength, damage tolerance and its ability to support screws and bolts. It is castable, which means any type of cross-section is able to be produced. It has been suggested by Van Erp and Ayers (2000) that the cost associated with this filled resin system depends heavily on the filler and base resin used. However, as pointed out in *Materials Australia,* by Van Erp and Ayers (2000, p.17), ‘at an average cost of \$2500-\$5000 per m^3 it is significantly cheaper than steel and allows for the design of competitive fibre composite structures’.

The high strength to weight ratio of the fibre composite systems being developed is attributed to the very low densities of the constituent materials (fibres, particulates and matrix) and the orientation and location of the fibres within the structural member. This is a deliberate manipulation of the components in the design of such systems so as to achieve the efficiencies in the use of these materials. These efficiencies may produce cost benefits in the areas that these systems are applied and these will be discussed later. There are currently no Australian design standards for fibre composites and in particular, fibre composites using PFRs. The design of fibre composites has largely been based on the macro mechanics level with much of the design work being done on a permissible stress approach. This is because the micro mechanics of constituent materials, i.e. the mechanical behaviour of the constituent materials is not yet fully understood. It is envisaged that as more knowledge of PFRs and fibre composites is gained, a limit state approach to fibre composite design will be adopted. Here lies the importance of the study of the properties and mechanics of composites.

One has presented some advantages that fibre composites possess. However, composites do have disadvantages. These include production and health and safety issues. One serious problem associated with the use of vinyl esters in production is the shrinkage of this material upon hardening (may be up to 10%). Shrinkage inherently sets up internal stresses within a material. The stresses are usually tensile in the core of the material and compressive on the surface (Ku, 2003). When these stresses act together with an applied load, they may cause premature failure of the composite component.

Currently the FCDD group has solved the problem of shrinkage by casting smaller components which are then joined together to form the overall structure (see Figure

2.1). However by doing this, the manufacturing lead-time and costs are significantly increased.

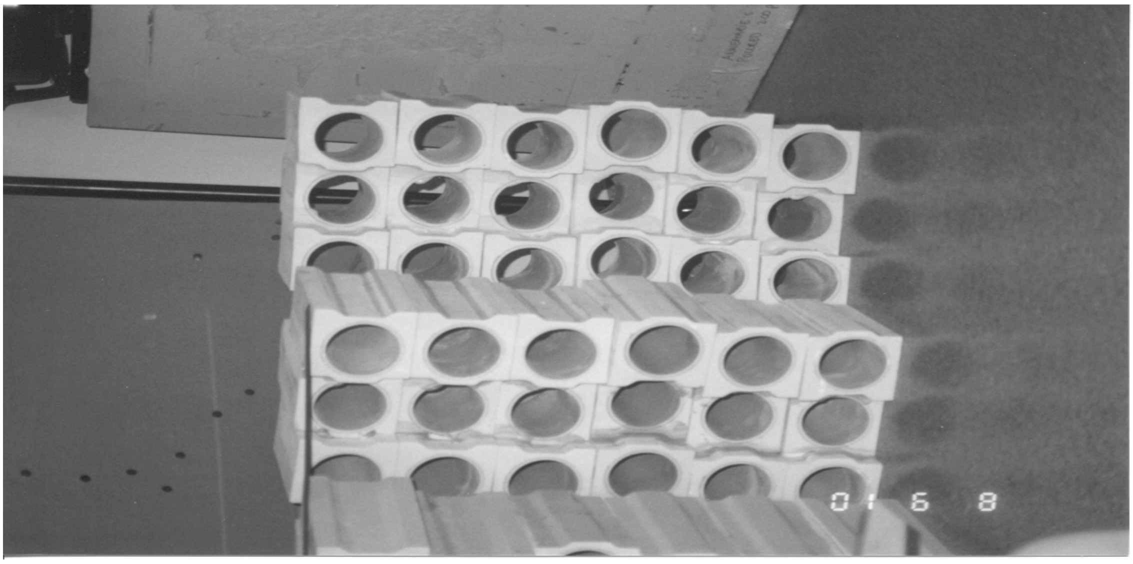


Figure 2.1: Small cast components joined by epoxies and cured in ambient conditions (Ku. et al., 2002).

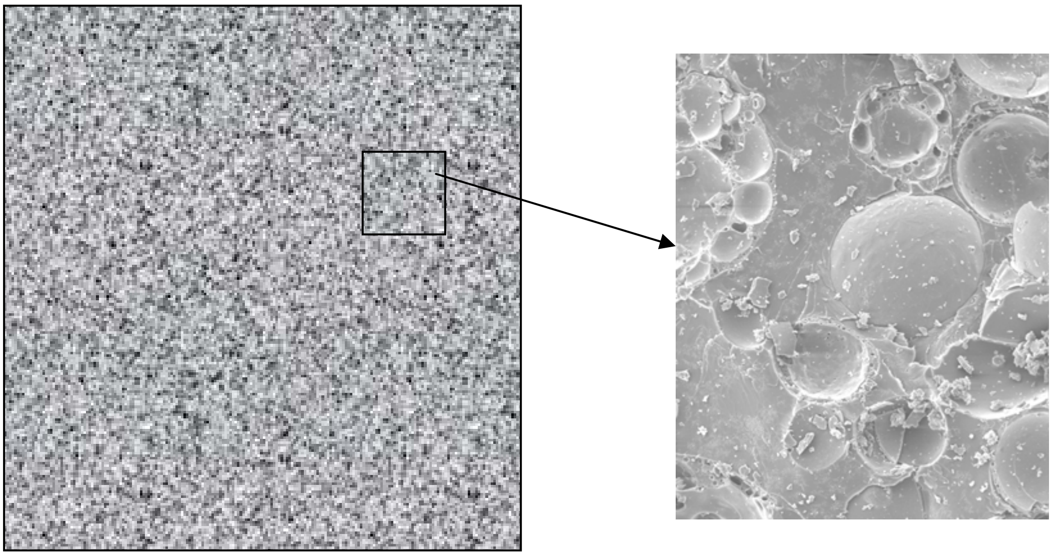
Further research has been undertaken by Ku (2003) and microwave technology has been identified as a possible solution to the shrinkage problem. Initial tests have revealed overall shrinkage results of around 1%. This has been achieved by selecting an optimum combination of initiator, input power of microwave energy and low profile additives.

To summarize, microwave curing of vinyl ester composites has been shown to reduce shrinkage but not much is known about the effect of this type of curing on the fracture properties of such composites. This project shall attempt to contribute to the greater understanding of the fracture properties of particulate filled resins cured by microwaves by investigating the mechanisms of fracture failure using micrographs produced from a scanning electron microscope. VE/FLYASH (33%) by weight of flyash has been selected so that a comparison may be made. The significance of the 33% by weight of flyash is that it has been advised by the FCDD group that this is the optimum composition for strength and viscosity and may be referred to in Van Erp and Ayers (2000) article 'Particulate Filled Resin Core Materials for Fibre Composites in Civil Engineering Applications'. Inclusively, fracture tests methods to be performed shall be the drop weight impact test and short bar test, for comparison to work conducted by undergraduates Cheng and Chew in 2003.

2.3 Composites

A composite material is defined as a combination of two or more materials exhibiting properties distinctively different from those of the individual materials used to make the composite. Composite materials have been developed so that certain desirable properties of a material may be obtained. Many naturally occurring materials are composites. Wood for example, consists of long cellulose fibres held together by amorphous lignin, while bone is a composite of the strong but soft protein, collagen, and a hard and brittle mineral consisting essentially of the carbonate and phosphate of lime.

The composite we are dealing with is the particulate filled resin or PFR type. This composite is comprised of hollow allumino silicate microspheres dispersed randomly throughout a vinyl ester resin matrix. This PFR was developed primarily as a core material to support the advanced fibre composite structures at the USQ.



Macroscopic view of PFR (a) **Microscopic view of PFR (b)**

Figure 2.2: Schematic diagram of the constituents of the PFR composite, the microscopic view (b) clearly showing the hollow spheres within the resin matrix.

In essence the PFR is a polymer matrix resin with discontinuous particle reinforcements. Reinforcements are introduced in many materials as a strengthening mechanism. For example, steels containing bainite, tempered martensite and precipitation-hardened aluminum alloys are strengthened by the presence of fine particles of harder phases, as the fine hard particles serve to block the movement of dislocations in the matrix. The effect of the silica particles will be discussed in greater detail in later chapters.

2.4 Constituent Materials

The selection of constituent materials is important in obtaining a composite that satisfies one's needs. The individual constituent materials bring inherent properties that combine together within a composite to produce another set of properties. The constituent materials of the PFR are the vinyl ester resin and the hollow silica microspheres (envirospheres). This section shall present a discussion of the two materials with mention of their individual mechanical, physical and chemical properties.

2.4.1 Polymers and Vinyl Esters

Polymers are a large group of naturally occurring and synthetic materials. The term polymer itself is derived from the two Greek words *poly*, meaning “many” and *meros*, meaning “parts”. There are many polymers on the market today however, three major classes of polymers have been identified as candidate matrix materials for composites in the infrastructure industry:

- Unsaturated polyesters and vinyl esters
- Epoxy resins
- Phenolic resins

(Riffle et al., 1998)

These classes of polymers have been identified on the basis of the application requirements of civil structures such as bridges and highways, off shore oil platforms, and industrial construction, as well as polymer-concrete composites for highway reinforcement and repair.

Materials for such applications must be able to be manufactured rapidly and easily to enable the production of cost-effective parts. The resultant composites must be able to maintain stability to outdoor environments for many years (50-75yrs). The combination of such factors requires polymer matrix resins to be low viscosity materials which cure to strong, tough networks. Hence the precursor resins should be hydrophobic, stable to freeze-thaw cycles, and durable in the presence of UV light (sunlight).

The most common class of polymer used for infrastructure is the thermosetting polymers. Thermosetting polymers or thermosets harden quickly while in a hot state and cannot be softened and reworked once the curing process has gone to completion.

Thermosetting materials are characterized by the formation of an infusible network structure as its final form. The thermoset resin is a low viscosity reactive starting resin which cures (reacts) to form an insoluble, infusible network solid. Initially the resin is comprised of low molecular weight species which begin to grow and branch. As the polymerization process continues, the branched molecules begin to bond together and an insoluble gel begins to form. This stage is characterized by a gelled fraction (“gel”) and a soluble fraction (“sol”) (Figure 2.3). Unreacted functional groups may be present as low molecular weight monomer, on branched low molecular weight species which have not yet become incorporated into the gel, and as pendent unreacted groups on the gel. As the reaction continues toward its final stage, the gel becomes larger and the sol correspondingly smaller. During this latter stage, low molecular weight soluble species can react with unreacted pendent groups on the gel (Riffle et al., 1998).

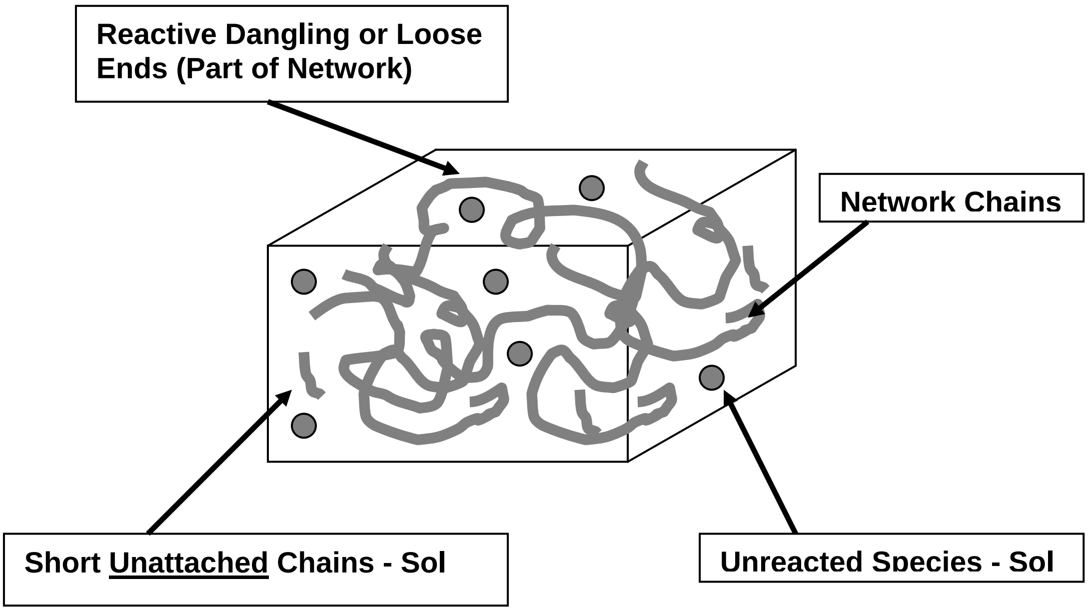


Figure 2.3: Components of the soluble fraction ("sol") and gelled fraction ('gel") during network formation of a polymer.

The extent of reaction of functional groups is essentially dictated by the temperature used in the curing reaction. As the initially low molecular weight species begin to polymerize, the glass transition temperature (T_g) of the mixture begins to rise. This is the result of the exothermic reaction as the chemical bonds are broken and the molecules revert to a lower energy state. When the T_g rises to meet the reaction temperature, the mixture will become relatively immobile and the reaction will essentially stop (even though reactive groups still remain in the resin). This is known as vitrification (Figure 2.4). Normally if the reaction temperature is increased, the mixture will react further until the T_g again rises to meet the new curing temperature. If the cure temperature is low, unreacted groups (such as styrene monomer) may be present in the final network. An incomplete cure affects mechanical properties, swelling behaviour in solvents, and probably also moisture susceptibility. On the other hand, an incomplete cure results in an increased distance between crosslinks and can result in improved flexibility and toughness. From a fundamental point of view, it is relatively meaningless to study network or composite mechanical or environmental properties without specifying the degree of cure (percentage of functional groups which have reacted) of the network.

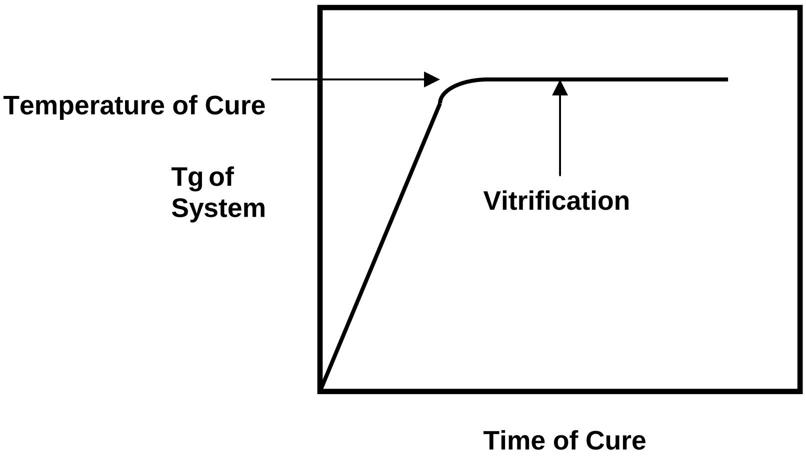


Figure 2.4: The glass transition temperature of a thermosetting reaction mixture corresponds to the degree of cure. The T_g will increase until it approximately reaches the cure temperature. At this point, the mixture solidifies into a partially gelled glassy structure and further reaction becomes infinitely slow. This solidification is referred to as vitrification.

The distance between crosslink junctions is important to obtain desirable mechanical properties (Figure 2.5). In general, the greater the distance between crosslink points, the more flexible and tough the final network will be. At full cure, the distance between crosslinks will be controlled by the molecular distance between functional groups in the starting materials. This is probably the major reason why vinyl ester-styrene resins cure to produce tougher networks relative to their cousin unsaturated polyester-styrene resins. The vinyl ester starting materials have been designed with their functional groups only at chain ends while unsaturated polyester starting materials have functional double bonds distributed throughout the middle of the molecules in a random sequence

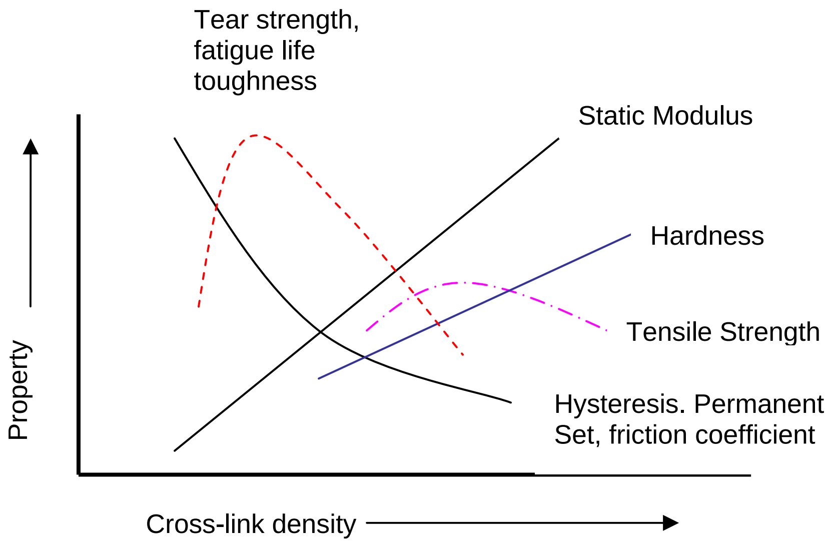


Figure 2.5: Effect of cross-link density on properties of cured polymeric thermoset networks.

There are two fundamental mechanisms by which polymers form: step growth and chain growth polymerizations. Unsaturated polymers and vinyl esters cure by chain growth polymerization whereby an initiator is introduced which begins a chain and thus, will only be at the ends of the final polymer chains. Since these polymer chains have high molecular weights, only a very small amount (usually between 1% and 2%) of initiator will be used. The molecular size distribution of the chains and the extents of reaction at the onset of gelation is not understood for chain growth networks.

Vinyl esters were developed in response to a need for a resin class with superior corrosion resistance and mechanical properties relative to the unsaturated polyesters which could be cured by the same facile type of free radical copolymerization as the unsaturated polyester resins. These materials are comprised of low molecular weight polyhydroxyether chains with reactive groups specifically placed at the chain ends diluted with styrene monomer. A notable difference between unsaturated polyester chains and vinyl ester chains is the distance between reactive double bonds. The reactive double bonds in vinyl esters are spaced at greater intervals which results in an increased distance between crosslinks and thus a tougher, more impact resistant, network.

Some of the interesting properties of vinyl esters are outlined below:

- The chemical structure of the backbone of the vinyl ester chain is the same as the most common epoxy resin backbones.

- The aromatic ring–oxygen bond in the chain is known to impart low temperature damping in many materials which contributes to material toughness.

- The pendent hydroxyl groups provide polarity which may be important for improved adhesion to various fillers, fibres and substrates.

The vinyl esters are commonly diluted with approximately 30 – 50 percent by weight of styrene. Since styrene is hydrophobic, there is a corresponding lower uptake of moisture in these systems (Figure 2.6). There is also significantly higher volume shrinkage upon cure as a result of this styrene (Figure 2.7).

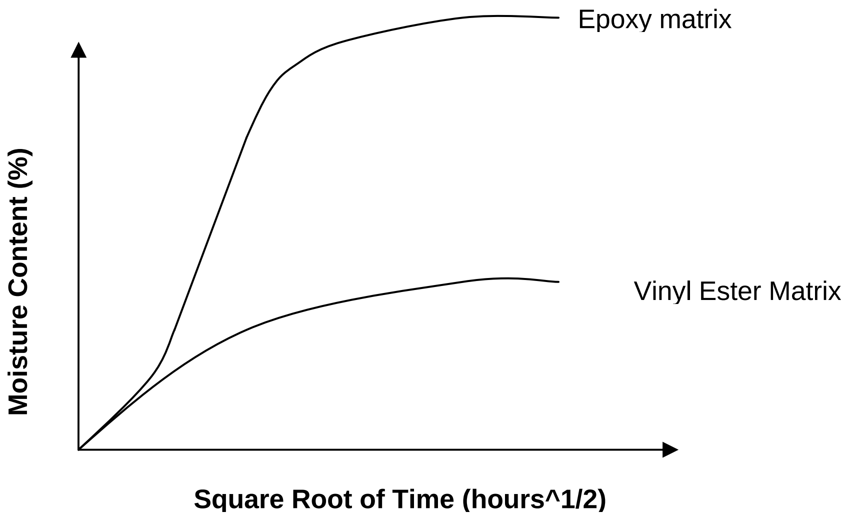


Figure 2.6: Typical graph for moisture uptake of epoxy vs. vinyl ester diluted with styrene

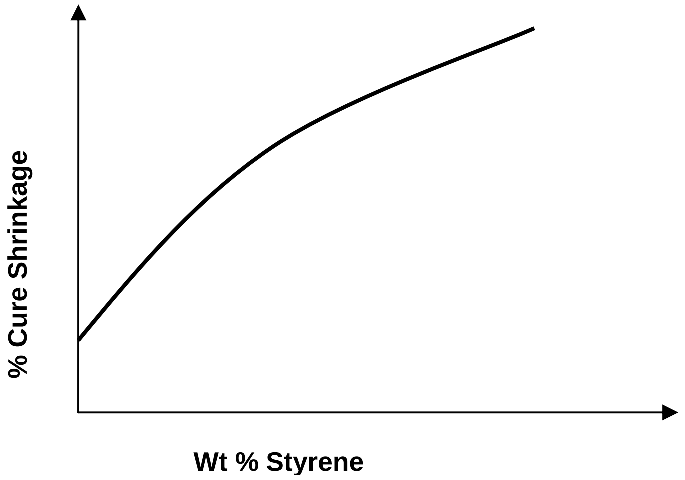


Figure 2.7: Typical graph for volume contraction of vinyl ester resins during cure as a function of the level of styrene in the resin.

As summarized by Astrom (1997), in most respects, vinyl esters are a compromise between epoxy and unsaturated polyesters. The vinyl ester resin used in this project is a thermosetting polymer known commercially as Hetron 922 PAW of the diglycidylether of bisphenol A (DGEBPA) family of vinylesters.

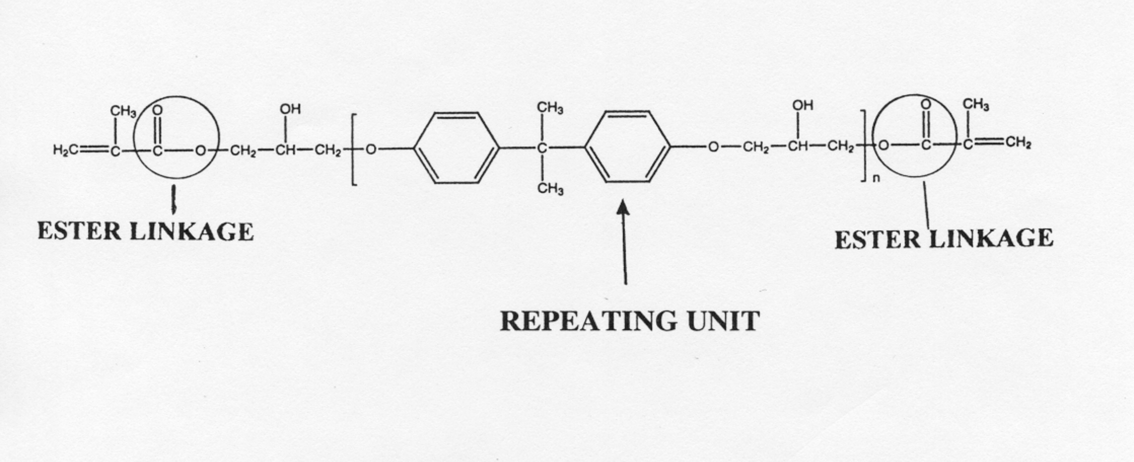


Figure 2.8: The structure of bisphenol A vinyl ester (Ku et al 2002, p. 179).

2.4.2 Crosslinking of Vinyl Esters

Ku et al. (2002) have presented the fundamentals of the crosslinking process specific to this vinyl ester. The following is a summary of the key points outlined in their work:

- Hetron 922 PAW has 50% by weight of styrene and exists as a highly viscous liquid at room temperature. The chain growth polymerization or addition reaction is initiated by an organic peroxide, methylethy ketone peroxide (MEKP). This reaction between Hetron 922 PAW and the initiator is essentially a copolymerization addition process whereby the styrene dilutent takes part in the reaction. The added amount is usually 1 to 2 percent by weight.

- Free radicals are produced by the initiator (MEKP) which attack one of the double bonds at the ends of the polymer and bonds to one of the carbon atoms, thus producing a new free radical at the other carbon atom. Figure 2.9 illustrates the whole cross linking process.

- The newly created free radical is then free to react with another double bond most likely belonging to the free moving low molecular weight styrene molecules within the resin, 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.

- The crosslinking reaction is intimately linked to temperature. Free radical production stimulated by the increase in temperature also promotes molecular mobility. Exothermic new bond formation increases temperature and as a result, this promotes further bond formation. Figure 2.10 shows typical temperature time relations for crosslinking of a vinyl ester following the addition of initiator. The three solid curves on the right hand side of the figure represent room temperature crosslinking of vinyl esters of different amounts of initiator, inhibitor (styrene), accelerator or volume of resin. The volume of resin is a factor in curing due to the heat generation and retention of the resin and the diffusional mobility of the molecules. The temperature does not immediately increase once the initiator is added. Crosslinking does not start and the temperature does not increase until all inhibitor molecules have reacted with free radicals, which corresponds to inhibition time. As crosslinking commences, the pot life is over. The resin becomes a rubbery solid quickly and the gel time is reached. The crosslinking activity now accelerates very rapidly until the increasing molecular weight of the crosslinking polymer starts restricting molecular movement. This occurs around the maximum temperature. The crosslinking then gradually tapers off.

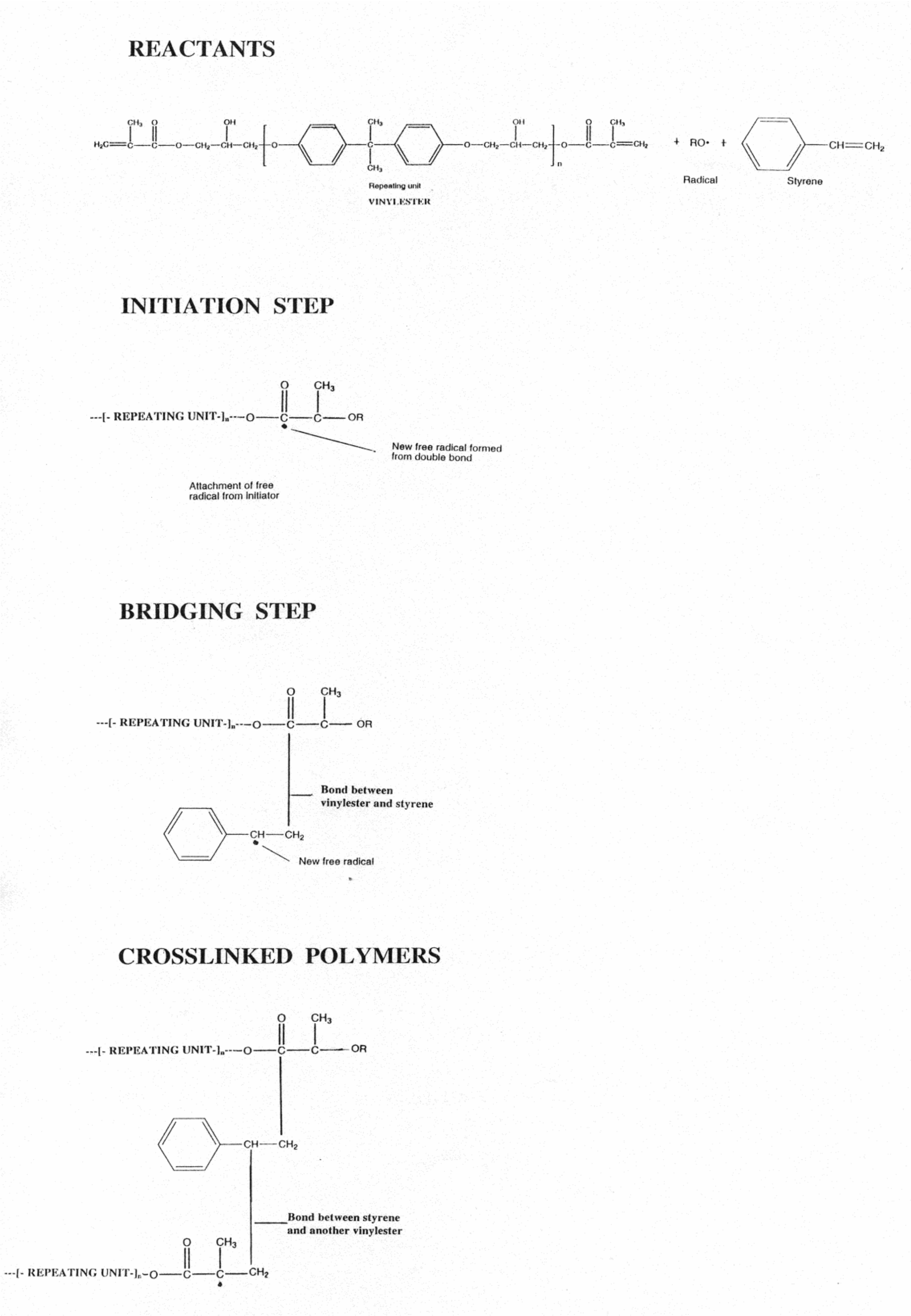


Figure 2.9: Schematic of addition of free radical crosslinking of vinyl ester (Ku et al., 2002, p. 179).

- The dashed curve on the left hand side of Figure 2.10 illustrates the addition of heat to the system by the application of microwaves. In this case the inhibition time is short and the maximum temperature is reached quickly.

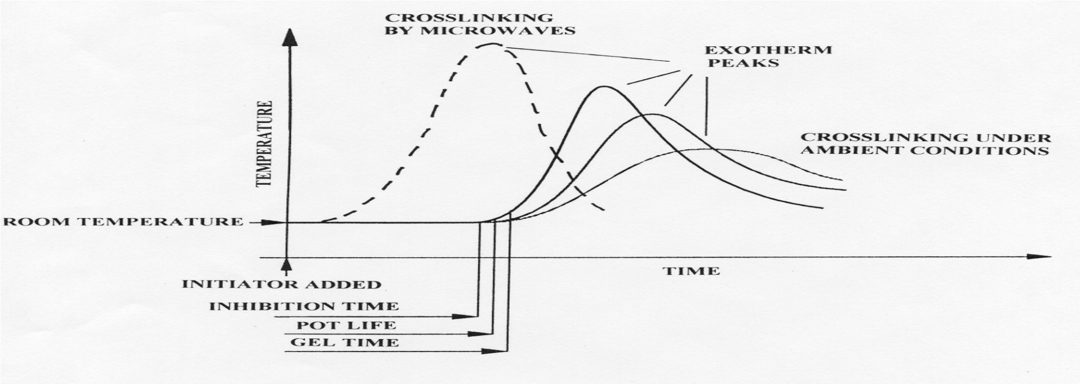


Figure 2.10: Temperature time relationships for crosslinking of vinyl ester (Ku et al., 2002, p. 180).

One hypothesizes that the resultant reduction in shrinkage of this vinylester by using microwaves is attributable to the:

- reduced loss of styrene in the resin as a result of a rapid curing process achieved by increasing the temperature of the system;
- limited time available for a significant level of hydrolysis to occur;
- decrease in the volumetric density when the system is heated coupled with a rapid cure. That is, when subjected to microwaves, there is an appreciable expansion of the resin which is counteracted by a rapid solidification of the resin which suffers from shrinkage. The presence of voids created by entrapped styrene gas could also be a contributing factor.

Therefore one has established the fundamentals of polymers and vinyl esters. In essence the vinylester produced in this project is a gigantic 3-D molecule formed by the crosslinking of styrene with bisphenol A vinyl ester via a free radical. The crosslinks formed are spaced at regular intervals at the ends of the vinylester polymer, which possibly makes this material tougher. The application of microwaves to this resin has been shown to be a method for reducing shrinkage upon cure of this resin.

2.4.3 Fillers and Envirospheres

Fillers have been incorporated in composites for many reasons. Factors influencing the selection of a particular type of filler to be used may be economic, aesthetic and material property related. The filler used in this project is flyash, known commercially as Envirospheres. Flyash, a by-product of coal burning powers stations is a pozzolanic material which can be described physically as hollow ceramic microspheres.

The major reason for the inclusion of flyash in the PFR is economic. Organic resins are produced from the petrochemical industry and oil is a highly expensive commodity. However, the inclusion of this brittle particulate reinforcement may serve a dual purpose by improving the material toughness property of the PFR. One obvious strengthening mechanism of these particles could be crack path diversion; which hinders the propagation.

One should state that it has been identified that the amount of filler used should not exceed 44% by weight of filler because it has been shown that the flexural strength begins to taper off beyond this level.

Chapter 3

Microwave and Materials Interaction

3.1 Introduction

The following information provided has been extracted from Ku's work as published in the *Journal of Composite Materials*, Vol. 37 in 2003 and serves as a brief overview of microwave-material interactions relevant to the curing process of vinyl ester particle-reinforced composites using microwaves.

Microwaves form part of a continuous electromagnetic spectrum that extends from low-frequency alternating currents to cosmic rays. In this continuum, 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 infrared (Thuery, 1992). These microwaves propagate through empty space at the velocity of light and their frequency range from 300 MHz to 300 GHz. The high frequency (HF) and ultra high frequency (UHF) bands constitute a natural resource managed by three international organisations. These organisations delegate their power to national organisations for allocating frequencies to different users. Industrial microwaves are generated by a variety of devices such as magnetrons, power grid tubes, klystrons, klystrodes, crossed-field amplifiers, travelling wave tubes, and gyrotrons (NRC, 1994).

Table 3.1: Frequency bands for radio frequency range.

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 – 3MHz
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

Frequency bands reserved for industrial applications are 915 MHz, 2.45 GHz, 5.8 GHz and 24.124 GHz. At the customary domestic microwave frequency of 2.45 GHz, the magnetrons are the workhorse. Material processing falls into this category (NRC, 1994). Magnetrons are the tubes used in conventional microwave ovens found almost in every kitchen with a power of the order of a kilowatt. Industrial ovens with output to a megawatt are not uncommon. Huge sums of money and effort have been spent in developing microwave-processing systems for a wide range of product applications. Most applicators are multimode, where different field patterns are excited simultaneously.

3.2 Microwaves/Material Interactions

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, $\tan\delta = \varepsilon''/\varepsilon'$. 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 δ, 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 $\frac{1}{e}$ (36.79%) of the energy has been absorbed. It is also approximately given by (Bows, 1994):

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

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, the extent of which depends on the materials. The results of microwaves/materials interactions are shown in Figure 3.1.

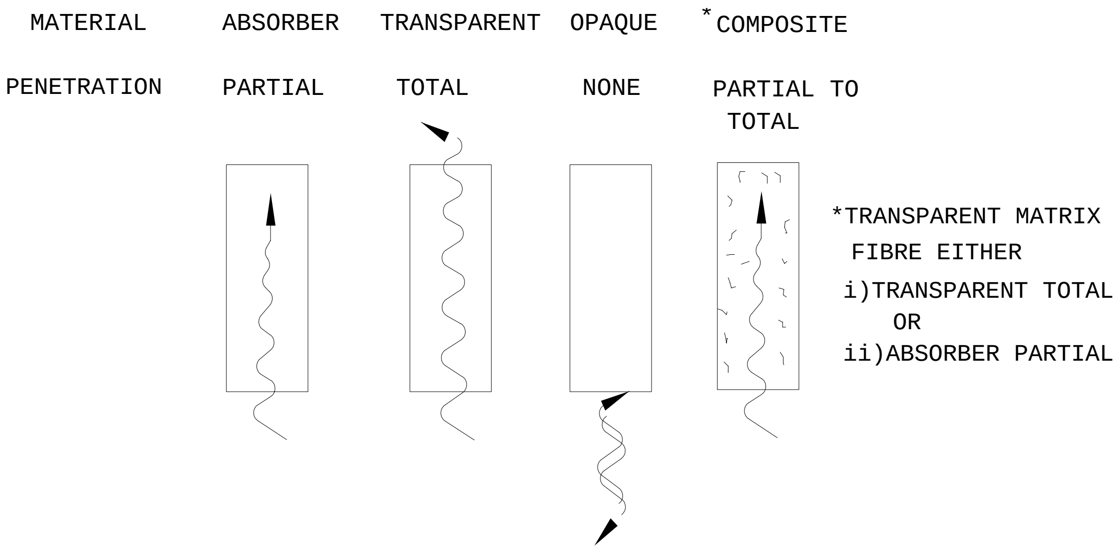


Figure 3.1: Interaction of microwaves with materials.

During microwave processing, 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.

(Ku, 2003, p.2029)

The afore mentioned microwave-material interactions have been well documented by Ku and in past studies conducted by Cheng and Chew in 2003 of vinyl ester composites cured by microwaves. The essence of their findings on microwave-material interactions in relation to the composite may be summarized as:

- Rapid cure of vinyl ester is achieved by the rapid heating of the composite; raising the temperature close to the glass transition temperature T_g to speed up the polymerization process which in turn is exothermic and generates more heat and contributes to the curing process.

- The amount of energy absorbed by any material subjected by microwaves is determined by two governing equations; the complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and the loss tangent, $\tan \delta = \varepsilon''/ \varepsilon'$ of the moulding materials. This is important in the design and selection of materials for the construction of the composite mould and has implications on the composite itself. Inclusion of an investigation into the dielectric constant ε' and the complex relative permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and the loss tangent, $\tan \delta = \varepsilon''/ \varepsilon'$ of the moulding materials and constituents of composite is recommended so that the on the amount of energy that is absorbed and reflected by the moulding material can be determined. This in turn affects the amount of energy able to be absorbed by the composite material one is trying to dielectrically cure. Coupled with the depth of penetration D_p one can select appropriate materials for mould construction and obtain satisfactorily microwave cured materials, a microwave cured particulate filled vinyl ester resin. An obvious example of an inappropriate material that cannot be used as moulding material is a metal due to the arcing effect (microwaves are reflected) when metals are subjected microwaves. Paper, cardboard, glass and plastics are generally accepted vessels for microwave heating.

- As mentioned before, ε' and ε'' can be dependent on both temperature and frequency, the extent of which depends on the materials. Therefore, curing of composites using microwaves is a complex interaction process with many variables: temperature, duration, frequency, power and specimen configuration and thermal properties of the material. A composite possessing specific mechanical properties could thus be reproduced by the strict adherence to a "recipe" that includes all the above variables. However, one would suggest that there are a number of “recipes” to obtain a composite with a specific mechanical property value with differing levels of input variables including composite constituent materials. From a holistic point of view, one would suggest that there are also a number of “recipes” with varying levels of inputs that could possibly yield a similar composite material with respect to mechanical properties. Figure 3.2 illustrates the argument.

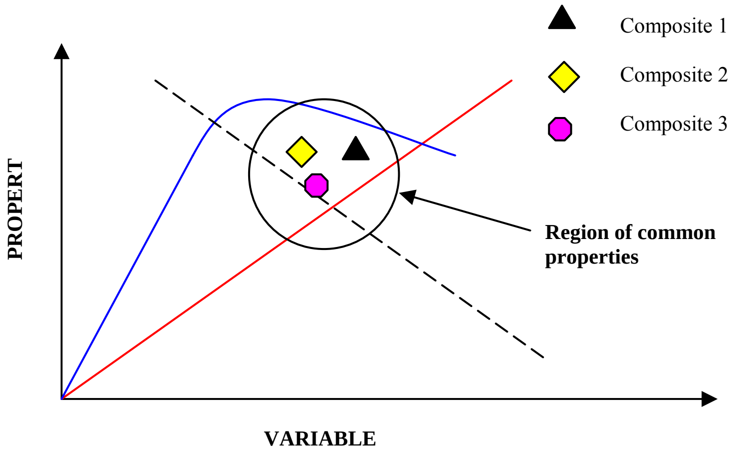


Figure 3.2: Graphical illustration of the similarity of mechanical properties of different composites manufactured with different inputs.

- In Ku’s paper ‘Curing Vinyl Ester Particle-reinforced Composites using Microwaves’, he points out that his four 50mL samples of VE/FLYASH (33%) cured under microwave conditions at different durations of exposure exhibited a notable change in cross-sectional surface texture. The cross-sections were revealed by sawing each of the samples. Samples with exposure duration of 30, 35 and 40 seconds were smooth and no pinholes were visible to the naked eye. These samples showed very little or no curing shrinkage. For the cured sample with exposure duration of 60 seconds, there was some degree of expansion and the presence of blowholes. Figure 3.3 shows the sample cross-sections.

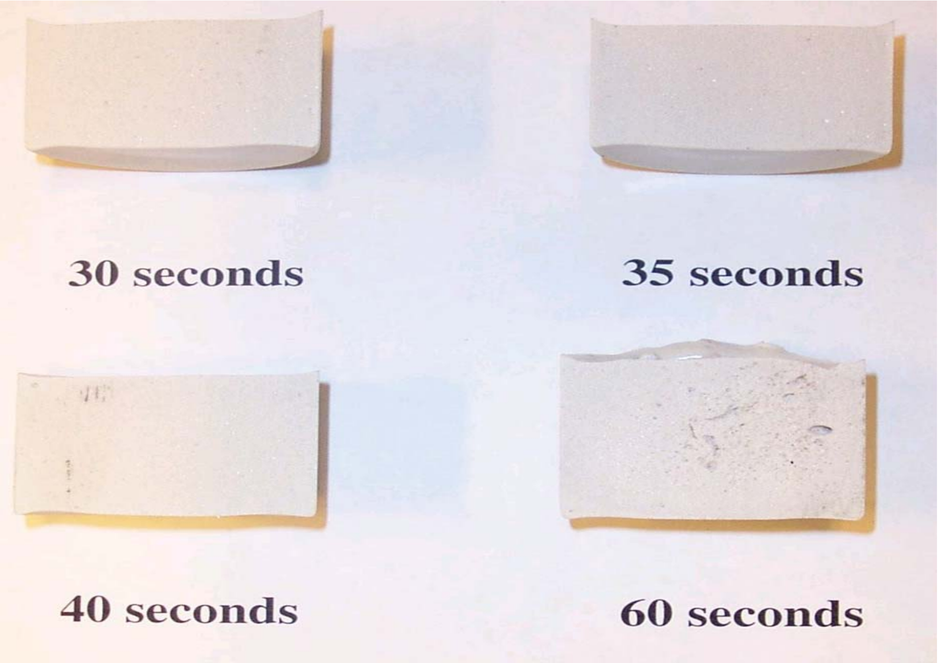


Figure 3.3: Four cross-sectional surfaces of cured samples of VE/FLYASH(33%) with different exposure durations of 30, 35, 40 and 60 seconds (source: Ku, 2003)

3.3 Risks in Curing Vinyl Ester Resins using Microwave Irradiation

Experiments carried out by Ku et al. (2002) to cure vinyl ester particle-reinforced resins using microwaves to reduce shrinkage have yielded very promising results. Vinyl ester composites can be produced with little or no shrinkage. Unfortunately though, there are inherent risks in the process which are common to the manufacture of plastics and also risks specific to the use of microwaves.

The risks associated with curing of vinyl ester resins using microwaves have been well documented by Ku, Cheng and Chew. The polymerization reaction is exothermic which presents a potential fire hazard. The materials themselves are also hazardous and should be handled appropriately.

The risks associated with the curing of vinyl ester resins can be classified into four groups; they are risks of the styrene, risks of the hardening agent MEKP, risks of the hollow spherical filler and risks of microwave and vinyl ester resin interactions

3.3.1 Risks of Styrene

The resin used in this project is Hetron 922 PAW which is diluted by 50% by weight of styrene. Styrene is volatile and evaporates easily and poses an inhalation hazard. Vinyl ester resin (Hetron 922 PAW) is potentially a sensitizer and can cause a more serious form of dermatitis. This is because they can cause an allergic reaction in some people. People who are allergic to these sensitizers can get dermatitis if they work near these products, even if there is no obvious contact with them. The styrene is a reactive diluent, i.e. it produces a low viscosity resin; which when mixed with an initiator (MEKP) produces vinyl ester. One of the by products of the reaction between the resin and the initiator is styrene fumes. Styrene can enter the lungs or through the skin. The fumes can irritate the eyes, nose and throat. Breathing in styrene fumes can cause headaches, nausea, and drowsiness. Long term damage can include memory loss and mood and personality changes (neurotoxic effects). Styrene can also cause liver damage. Styrene fumes are also very flammable.

The Fibre Glass Development Corporation lists the potential health effects of styrene in vinyl ester resins in their Material Safety Data Sheet (MSDS) which shall be provided below:

- **Skin.** Exposure can cause skin irritation. Prolonged or repeated exposure may dry the skin. Symptoms include redness, burning, cracking, skin burns and skin damage. Although skin absorption is possible, under normal conditions of handling and use, harmful effects are not expected.

- **Breathing.** Breathing of vapour or mist is possible. Inhalation of small amounts of styrene during normal handling is not likely to cause harmful effects; inhalation of large amounts may be harmful. Symptoms usually occur at air concentrations higher than the recommended exposure limits.

- **Symptoms**. Symptoms of exposure to this material through breathing, swallowing, and/or passage of the material through the skin may include: metallic taste, stomach or intestinal upset (nausea, vomiting, diarrhea), irritation (nose, throat, airways), central nervous system (CNS) depression (dizziness, drowsiness, weakness, fatigue, nausea, headache, unconsciousness) and other CNS effects, loss of coordination, confusion and liver damage.

- **Eye.** Exposure can cause eye irritation. Symptoms include stinging, tearing, redness and swelling.

- **Swallowing.** Swallowing small amount during normal handling is not likely to cause harmful effects; swallowing large amount may be harmful. This material can enter the lungs during swallowing or vomiting. This results in lung inflammation and other lung injury.

3.3.1.1 Styrene Risks Safety Measures

In the previous section, various risks of styrene to human beings has been discussed. This section will then discuss the safety measures that should be undertaken by individuals involved in activities where styrene is present. The MSDS of Fibre Glass Development Corporation suggested that the following first aid measures should be taken when styrene in the resin is exposed to:

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

- **Swallowing.** Seek medical attention. If an individual is drowsy or un-conscious, do not give anything by mouth; place individual on the left side with a head down. Contact a physician, medical facility, or poison control centre for advice about how to induce vomiting. If possible, do not leave individual unattended.

- **Skin.** Remove contaminated clothing. Flush exposed area with large amount of water. If skin is damaged, seek immediate medical attention. If skin is not damaged and symptoms persist, seek medical attention. Launder clothing before reuse.

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

The highly flammable nature of styrene in high vapour concentrations may cause explosions. Due to this, it is important to consider the fire fighting measures for the material. The Fibre Glass Development Corporation (2003) MSDS lists the following fire fighting measures for the vinyl ester resin.

- **Flash point**: 26.6 – 32.2 ^{o}C

- **Explosive limit (for component)**: Lower = 1.1 %, Upper = 6.1%.

- **Auto-ignition temperature**: No data.

- **Fire and explosion hazards**: Vapours are heavier than air and may travel along the ground or may be moved by ventilation and ignited by lights, other flames, sparks, heaters, smoking, electric motors, static discharge, or other ignition source locations distant from material handling point. Never use welding or cutting torch on or near drum (even empty) because product (even just residue) can ignite explosively.

- **Extinguishing media**: Regular foam, water fog, carbon dioxide and dry chemical.

- **Fire fighting instructions**: Wear a self-contained breathing apparatus with a full face piece operated in the positive pressure demand mode with appropriated turn-out gear and chemical resistant personal protective equipment. Polymerization will take place under fire conditions. If polymerization occurs in a closed container, there is a possibility it will rupture violently.

3.3.2 Risks of MEKP

Organic peroxide initiators or hardeners are used to produce vinyl ester polymers. Methyl ethyl ketone peroxide or MEKP in dimethyl phthalate, with 9% active oxygen is a colourless toxic solution and may be a severe irritant and sensitizer to skin and eyes and may be corrosive if concentration is high. This organic peroxide is also highly flammable and may decompose with explosive violence if not handled correctly. Exposure to high temperatures or contamination with foreign materials could result in explosive decomposition. The maximum storage temperature is 38°C and the decomposition temperature is 68°C. Therefore MEKP should be kept and stored properly:

- away from heat, sparks or flames, and out of direct sunlight
- stored in original closed container in a cool place
- not to be stored in unvented glass container
- do not store in vicinity of cobalt napthenate, dimethyl aniline, or other promoters, accelerators, acids, bases, or strong reducing agents
- do not store in the vicinity of food or drink

If promoters or accelerators are used, these should be thoroughly mixed into the resin before the addition of MEKP. These agents should never be mixed directly with MEKP. Violent decomposition and fire could result from such mixing or contamination. MEKP should be stirred into the resin slowly and carefully to avoid splashing. In the event of a spillage, an inert material such as vermiculite or sand should be used to absorb the material and the area wetted with water. All such contaminated waste material should be placed in double polyethylene bags and kept outdoors away from combustibles until it can be removed by qualified hazardous waste personnel. In the case of fire, spray with water or with carbon dioxide or foam from a safe distance. Dry chemical or other extinguishers may be effective against a very small fire (Cheng, 2003).

It is recommended that the MEKP dispenser is used for the pouring of the solution. The dispenser is adjustable to accurately dispense 2.5 to 35cc. Squeezing of the bottle until the upper vial is full then the release of pressure on the bottle leaves a precisely measured amount of catalyst in the vial. This is then poured out with no dripping. By doing this, the risk of skin contact with the chemical is much reduced (Chew, 2003).

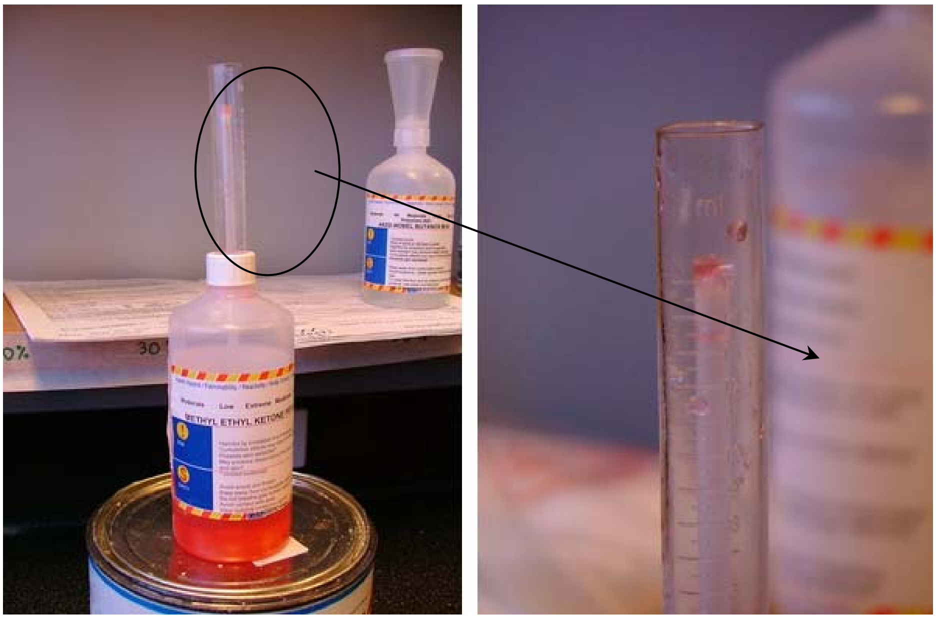


Figure 3.4: MEKP dispenser

MEKP is a strong irritant. Ingestion of the chemical can be fatal. Contaminated clothing should be discarded. All measures should be taken to avoid swallowing and contact with the skin and eyes. Personal protective equipment (PPE) should be worn. These include goggles, gloves, protective clothing, and a respirator. Care must be taken when handling MEKP. Courses of action that should be followed in the event of contact with MEKP are outlined below:

- If swallowed – take large quantity of milk or water followed by immediate consultation with a physician.
- Contact with the eye, even if flushed out with water presents the very serious risk of irreversible blindness occurring – flush the eyes immediately with water for 30 minutes, get urgent medical attention. Keep an ”eye wash bottle” handy anywhere MEKP is used to provide instant first aid while one gets to sink with running water.

3.3.3 Risk of Envirospheres

The ceramic hollow spheres can pose a health hazard and should be handled with care. If it comes into contact with the eyes, it could be a serious irritant. If inhaled, respiratory problems are very likely. The use of PPE, that is glasses and respirator required for handling of the resin would also serve to protect one from these potential hazards.

3.3.4 Risks of Microwave and Vinyl Ester Resins Interactions

A possible risk in applying microwave energy to the vinyl ester is the interaction of vapourized styrene in the resin with the high voltage (HV) transformer of the oven (Ku, 2002). As mentioned in section 3.3.1.1 the flash point of styrene is around 26.6 – 32.2°C. An experiment conducted by Ku (2003) where by a 200mL sample of VE/FLYASH (33%) was cured in a microwave oven at a power level of 180W for 40 seconds produced an oven cavity temperature of 52°C without explosion occurring. This implies that the styrene vapour concentration in the oven cavity was sufficiently low and below the threshold value for explosion to occur (Cheng, 2003).

Ku (2003) modified the microwave oven to prevent the styrene vapours from escaping through the back of the oven and being heated up by the high voltage resistor at the back of the facility. Figure 3.5 shows the modified oven and its peripherals. An exhaust outlet was fitted to the oven and the airflow was measured. The readings obtained from an airflow meter confirmed that all air from the oven cavity was being discharged and redirected away through the pipes. The outlet of the pipe may be directed outside to open space where the styrene can be safely dissipated.

Figure 3.5: Modified microwave and its peripherals (source: Cheng, 2003)

3.4 Personal Protection

Having highlighted the safety issues associated with the production of vinyl ester composites, it is imperative that personal protective equipment (PPE) is used at all times when dealing with these materials. PPE should include overalls, aprons, safety goggles and two pairs of gloves (latex gloves and at least 1 pair of nitrile).

Other items related to safe working practices are:

- Never wash work clothes with other items.
- Uses approved respirators and keep them fitted properly and in good condition.
- Work in a well ventilated area.
- Read and understand material safety data sheets.
- Store resins, hardeners and promoters in separate flammable liquids storage cabinets. Never store them together.
- Suitable fire extinguishers and warning signs are needed in these areas.

(WorkCover Authority of New South Wales (1992), *Working with fiberglass reinforced plastics*)

Chapter 4

Fracture and Fracture Tests

4.1 Introduction

A brief discussion of the mechanics of fracture will be presented in this chapter followed by an overview of the experimental methods used to obtain fracture samples in this research project. Two separate types of tests were performed to obtain fracture toughness results. They were the drop weight impact test and the short bar fracture tests. These tests were used by past students Cheng and Chew in their research projects to determine the fracture toughness of various samples of VE/FLYASH (33%).

4.2 Fracture Mechanics

Fracture mechanics may be defined as the field of solid mechanics that deals with the behaviour of cracked bodies subjected to stresses and strains. Many engineering failures have been caused by the pre-existing cracks or other defect. Fracture mechanics aims to determine the severity of a pre-existing defect in terms of its tendency to initiate fracture. It is also concerned with resistance to crack propagation and with crack growth rates in fatigue and stress corrosion cracking.

Fracture mechanics is a tool which relates the size of a flaw to the likelihood of it causing fracture in a given material under a given stress regime. The larger the flaw, generally, the lower the stress at which failure will occur. Conversely, the lower the service stress the larger the flaw which may exist without endangering the structure (AWRA, 1980).

The loading mode is important with respect to the state of stress at a flaw and consequently the crack propagation. Cracks move through 3-D space, the crack path is dictated by the microstructure and the state of stress at any point ahead of the crack, hence the appreciation of the state of stress and modes of loading must be included in any fracture analysis. The three basic loading modes are (a) mode I, crack opening, (b) mode II, in-plane shear, and (c) mode III, anti-plane shear or tearing (Figure 4.1)

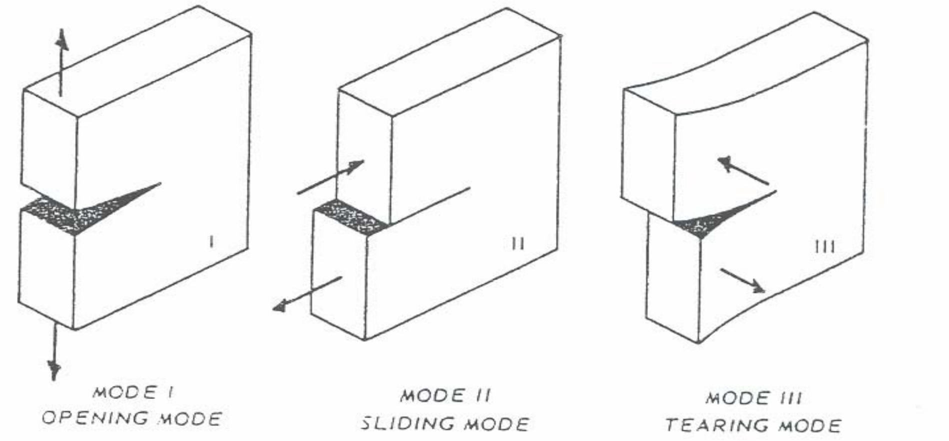


Figure 4.1: Three modes of loading.

4.2.1 Fracture Toughness

Toughness is the ability of a material to absorb energy when being deformed and thus resist deformation failure. If a material is tough, it is able to absorb a lot of energy before it fails under load. Fracture toughness can be measured and expressed in a number of ways such as Joules or stress intensity factor K depending on the nature and method of the test and end use of the results of these tests.

The concept of stress intensity factor K comes from Linear Elastic Fracture Mechanics (LEFM) and is strictly applicable only to materials in which cracks can grow with very little plastic deformation. That is cracks can grow within the linear elastic range of the material so that linear elastic analysis may be applicable. This implies that LEFM is particularly relevant to brittle materials since brittle materials undergo little or no plastic deformation before fracture or rupture.

A sharp crack-like defect of length = 2a is assumed to be present in an infinite plate and the stress intensity factor, K, at the tip of the crack is calculated from

$$K=f\,\sigma\sqrt{\pi a}$$

Where σ is the elastic stress acting on the structure, and $f = 1$ for an infinite plate.

In the configuration shown in figure 4.2, where the crack is being opened by a tensile stress normal to it, the stress intensity factor is known as K_C.

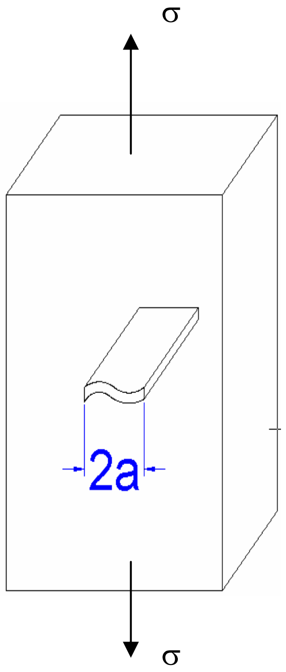


Figure 4.2: Rectangular through-thickness crack in finite plate.

Adopting a fracture mechanics approach to the design and selection of materials in engineering allows one to compensate for the inevitable presence of flaws. Three variables to consider in this approach are: The material property (K_C or K_{IC}), the stress σ that the material must withstand and the size of the flaw a. If we know two of these variables, the third can be determined. Chew (2003) summarized the importance of fracture mechanics in relation to the inevitable presence of flaws as follows:

- Selection of a material: If we know the maximum size a of flaws in the material and the magnitude of the applied stress, we can select a material that has a fracture toughness K_C or K_{IC} large enough to prevent the flaw from growing.

- Design of a component: if we know the maximum size of any flaw and the material (and therefore its (K_C or K_{IC}) has already been selected, we can calculate the maximum stress that the component can withstand. Then we can design the appropriate size of the part to ensure that the maximum stress is not exceeded.

- Design of a manufacturing or testing method: If the material has been selected, the applied stress is known, and the size of the component is fixed, we can calculate its fracture toughness.

The above concept of stress intensity factor, K, has been provided for completeness. There are numerous issues involved in the use of the stress intensity factor:

- The stress intensity factor or toughness is obviously different for different materials.

- Toughness is a function of thickness of the specimen. Thicker more rigid materials have lower fracture toughness than thin materials. As thickness increases, fracture toughness K_C decreases to a constant value K_{IC}. This is the plane strain fracture toughness which is normally reported as the property of a material.

- Toughness is dependent upon temperature, increasing the temperature generally increases the fracture toughness of a material. In the case of metals this could mean raising the temperature above the brittle-ductile transition temperature changes the material behaviour from brittle to ductile.

- Toughness is sensitive to the rate of stress and strain applied to a specimen, this relates to state of stress on a specimen and how a material behaves under these stress conditions. An example is that of corn flour mixed with water which exhibits some degree of rigidity when subjected to a relatively high impact force. On the other hand when the same mixture is subjected to a low force, the mixture is easily deformed.

- Large flaws reduce the permitted stress. Manufacturing techniques can reduce flaw size and improve fracture toughness.

- The ability of a material to deform is critical. In ductile metals, the material near the tip of the flaw can deform, causing the tip of any crack to become blunt, changing the stress conditions in the material. Let's consider a blunt notch as depicted in Figure 4.3. Broek (1997) states that at a blunt tip, the plane stress condition changes into a plane strain condition very rapidly with respect to distance from the crack tip. The resultant tri-axial stress condition which is complimentary to a plane strain condition means that a higher axial force is required to initiate crack propagation, assuming the material fails under shear.

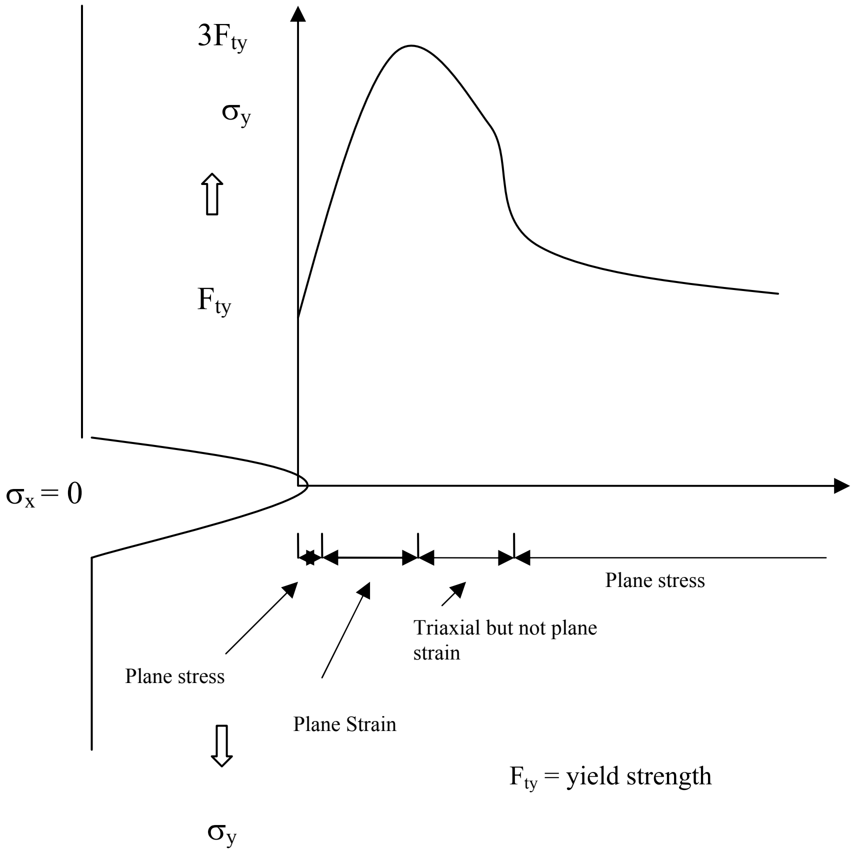


Figure 4.3: **Progress of yield at a blunt notch.**

In this project, the area of interest has focused on the mechanics of fracture in relation to fracture of VE/FLYASH (33%) by impact and tensile loading at the crack tip. That is, much emphasis has been placed on crack propagation. Limited attention has been placed on the critical defect or flaw size, states of stress and strain leading to plastic collapse.

The term toughness is the capacity of a material to absorb energy by deforming plastically before fracture. It is determined by the combined strength and ductility of a material and usually is measured by the amount of work absorbed during the propagation of a crack. Toughness can be measured in a variety of ways, but this project focuses on two:

- Area under a standard stress-strain curve taken to fracture; short bar test
- High strain–rate loading condition; impact test.

Fractures are usually classed as brittle or ductile, depending on the amount of plastic deformation preceding failure. Brittle fractures occur suddenly with little or no prior deformation. The type of fracture in a material is often related to the temperature. With regards to steel, it has been observed that brittle fracture occurs at low temperatures whereas ductile fractures occur at higher temperatures.

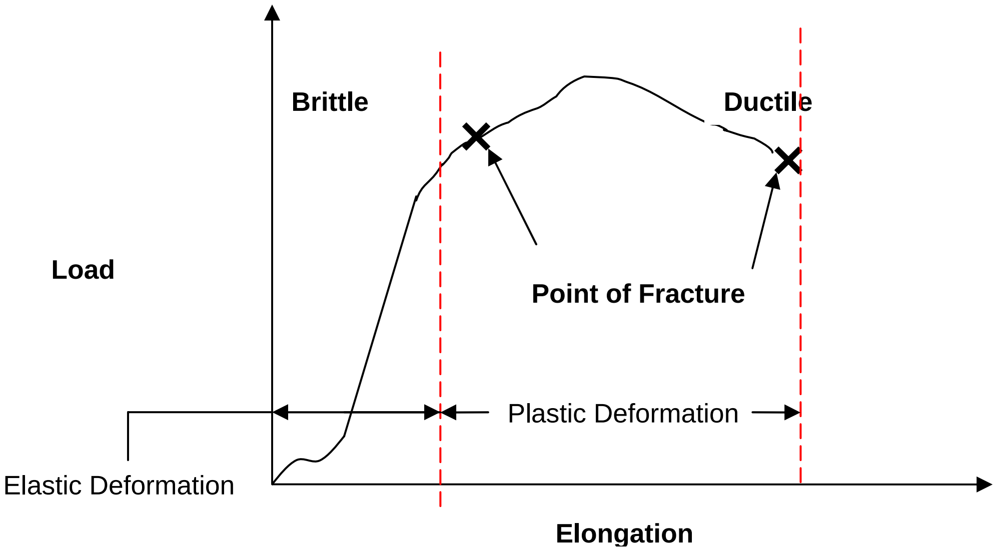


Figure 4.4: Typical stress-strain graph of a metal showing points at which brittle and ductile fracture occur.

4.2.2 The Drop Weight Impact Test

The drop weight impact test uses a drop weight or a falling weight which impacts the specimen. This impact striker is known as a tup which falls through a vertical guide tube that directs it to the centre of the specimen. The guide tube must be perpendicular to the impact surface for results to be valid. More about the test can be obtained in the

American testing standards (ASTM, 1990). The energy released from the drop weight test is:

$$E = mgh - l$$

Where E: energy (Joules)

m: mass of tup (kg)

g: gravity (m/s^2)

h: height (m) and

l: losses incurred by friction and other sources (Joules), which is negligible in this case.

This test has several advantages over other impact tests. The biggest advantage is it ability to simulate the multidirectional impact stresses that a part would be subjected to in actual service. Another advantage is the flexibility to use specimens of different sizes and shapes including an original part. Drop weight impact tests introduce multi-axial stresses into the specimen and measure toughness as opposed to the Izod test.

Impact energy in a drop weight test can be imparted by varying the height at which the tup is dropped or varying the weight of the tup. However care must be taken when using this test on plastics since they are viscoelastic and usually strain rate sensitive and therefore may be sensitive to changes in the velocity of the weight falling on their surface (Ubachs, 1999, p.14). In essence, the equivalence between constant weight - variable height and constant height-variable weight methods should be considered carefully. Past experiments show that VE/FLYASH (33%) fractures at around 400mm.

Ubachs points out that the drop weight test can lead to different failure modes. Therefore the test method must suit the intended end-use application for test results to be meaningful. Since this test is geometrically sensitive, generally results cannot be directly compared.

Incorporation of instrumentation gives more information about the impact event.

4.2.3 The Short Bar Test

The short bar or short rod test is a simple test that measures the force required to initiate crack propagation and cause complete fracture.

> *Barker's testing method used simple fracture toughness concepts to test sample configurations exhibiting crack growth even when loaded by a controlled force machine. Once calibrated for specimen configurations, the only parameter required for fracture toughness values was the peak force required to completely fracture the sample. This new test method used samples of a circular or rectangular cross section, which were called short rod/bar samples accordingly (Barker, 1977).*

(Chew, 2003, p.53)

By using the MTS machine, load-time or load-elongation information may be gathered for the entire fracture event.

Chapter 5

Experimental Methods

5.1 Introduction

This chapter will give an overview of the experimental design used in this research project. The beginning of the chapter will discuss the production of the specimens and the related safety issues. A brief discussion of the drop weight impact test and the short bar fracture test specimen production methods will be presented. Much of the information related to the afore mentioned tests may be obtained from the dissertations of Cheng, 2003 and Chew, 2003.

5.2 Specimen Production

In this project, 33% by weight of flyash particulate reinforced vinyl ester [VE/FLYASH (33%)] microwave cured test specimens had to be produced for each test type. One should point out that the term cure has been used loosely. It is actually a process used to elevate the temperature of the thermoset to achieve a rapid polymerization process. A diagram of the specimen production scheme for both types of tests is illustrated overleaf.

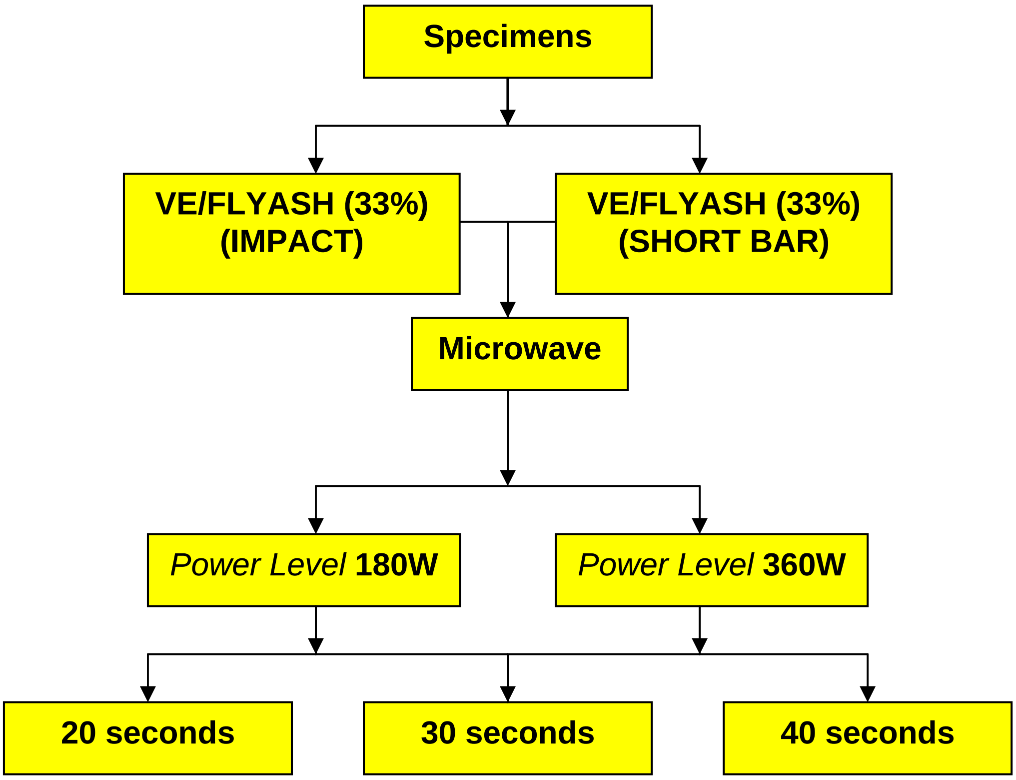


Figure 5.1: Grouping of production of specimens.

5.2.1 Casting Moulds

Specimens must be cured in a multimode oven cavity thus only non-metallic materials can be used to construct moulds. The two types of tests require specimens of different configurations.

5.2.1.1 The Drop Weight Impact Test Specimen

The drop weight impact test specimen was made using a PVC pipe which would produce a smooth finish on the specimens. The moulds for these test specimens are readily available and consist of a PVC pipe with an internal diameter of 21mm and length of 55mm, each having a cut down the side, allowing for expansion and ease of removal after curing and sealed with masking tape at one end of the pipe.

The actual test specimen is a cylinder, 21mm in diameter and 45mm long. The 55mm long mould is for ease of handling and pouring of the uncured composite mix. Figure 5.2 shows the mould used to cast the specimen.

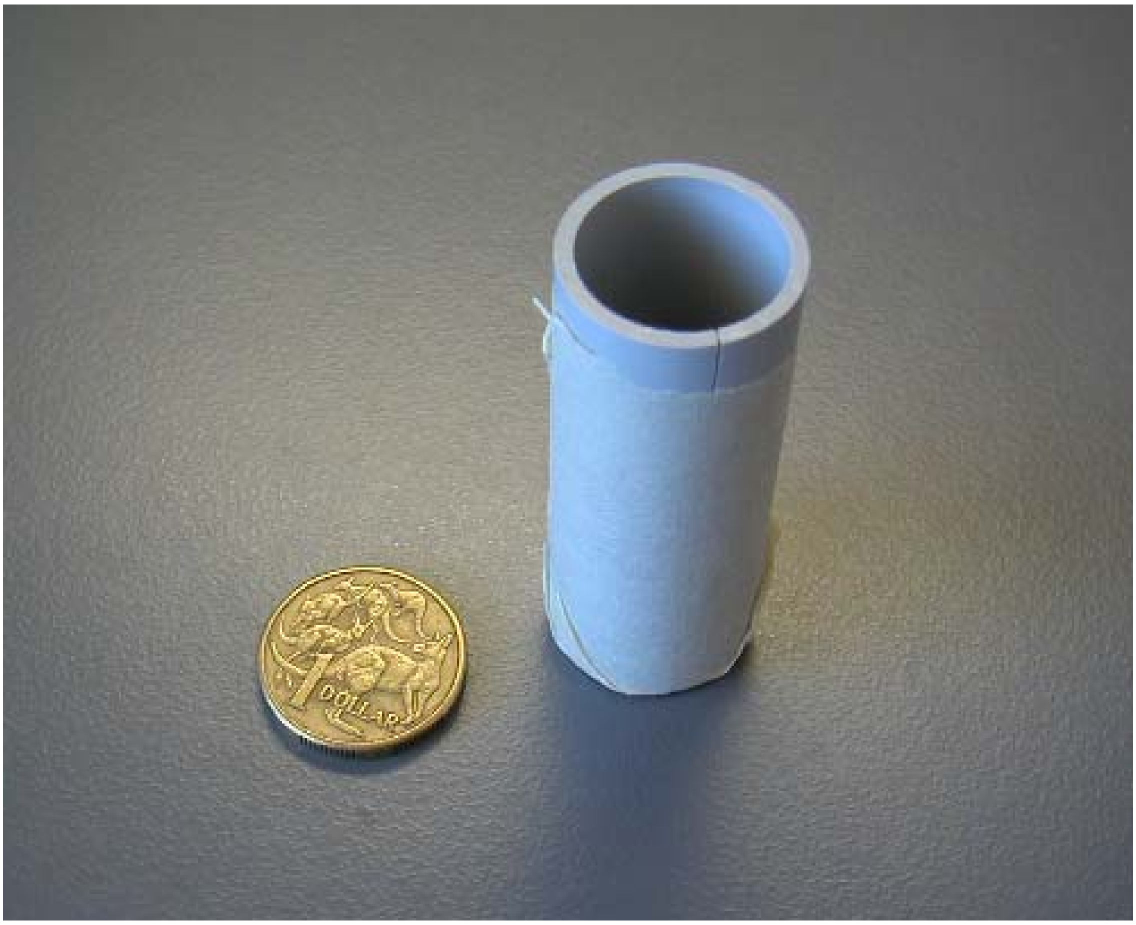
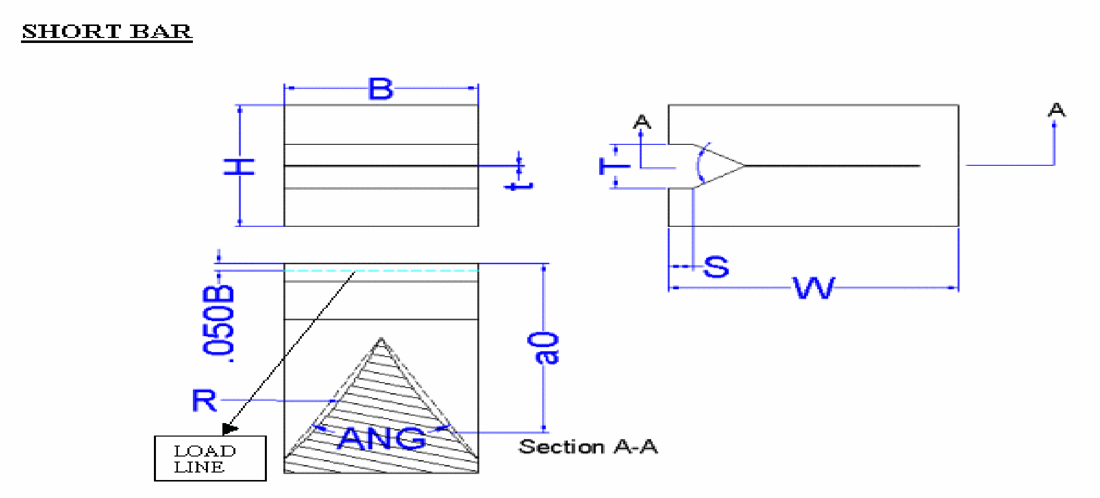


Figure 5.2: The Drop weight impact test.

5.2.1.2 The Short Bar Test Specimen

The mould for this specimen as described by Chew (2003) is rather complex. One adopted the same specimen geometry but instead of using manila folders, one used wood as a tongue to form the groove for the gripers of the test rig and a sheet of polypropylene to form the chevron slot. Similar to Chew, transparency paper shall be used to form a smooth and non adhesive coat between the composite and the mould, with canola oil also being employed as a release agent. The exterior walls of the mould were constructed from balsa wood, which were held together by packing tape, the concentration of this approximate 1/3W from the bottom to account for hydrostatic bursting pressure as would be the case when constructing false work for concrete columns (Figure 5.6). Figure 5.3 illustrates the geometry of the test specimen.



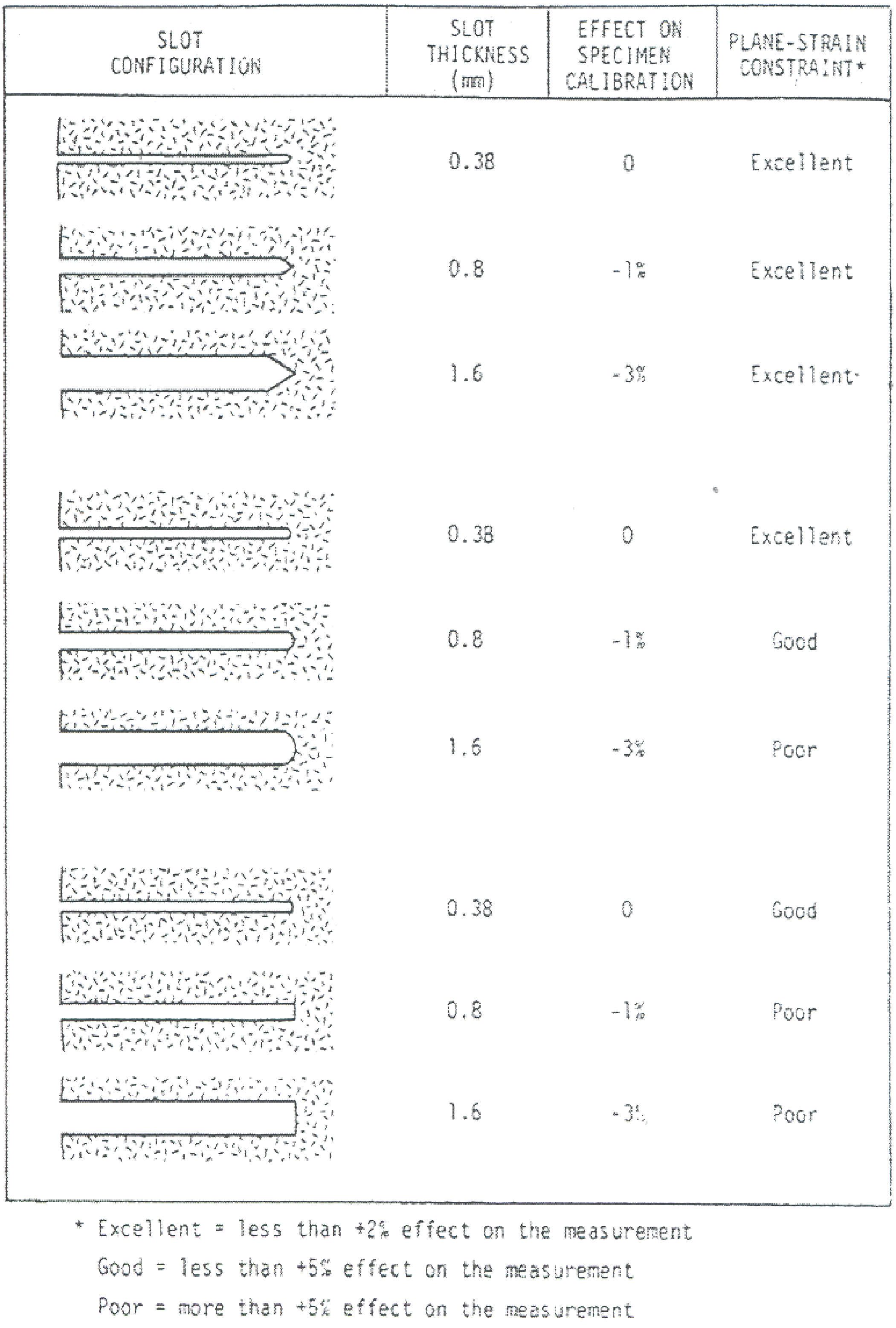
SYMBOL	DEFINITION	VALUE	TOLERANCE
B	BREADTH	B	
W	LENGTH	1.5B	±.010B
H	HEIGHT	.870B	±.005B
a_0	INITIAL CRACK LENGTH	.513B	±.005B
ANG	SLOT ANGLE	55.2°	±1/2°
τ	SLOT THICKNESS	SEE FIGURE 5.1.3	
S	GRIP GROOVE DEPTH	.130B	±.130B
T	GRIP GROOVE WIDTH	.313B	±.313B
R	RADIUS OF SLOT CUT	SEE FIG 5.1.4	±2.5B

Figure 5.3: Short bar specimens with curved chevron slots.

Where B = 51mm　　a_0 = 26.2mm　　T = 16

W = 76.5mm　　ANG = 55.2°

H = 44.4mm　　S = 6.6mm



SLOT CONFIGURATION	SLOT THICKNESS (mm)	EFFECT ON SPECIMEN CALIBRATION	PLANE-STRAIN CONSTRAINT*
	0.38	0	Excellent
	0.8	-1%	Excellent
	1.6	-3%	Excellent
	0.38	0	Excellent
	0.8	-1%	Good
	1.6	-3%	Poor
	0.38	0	Good
	0.8	-1%	Poor
	1.6	-3%	Poor

* Excellent = less than ±2% effect on the measurement

Good = less than ±5% effect on the measurement

Poor = more than ±5% effect on the measurement

Figure 5.4: List of tables for the grade of slot thickness (Baker L M, 1981).

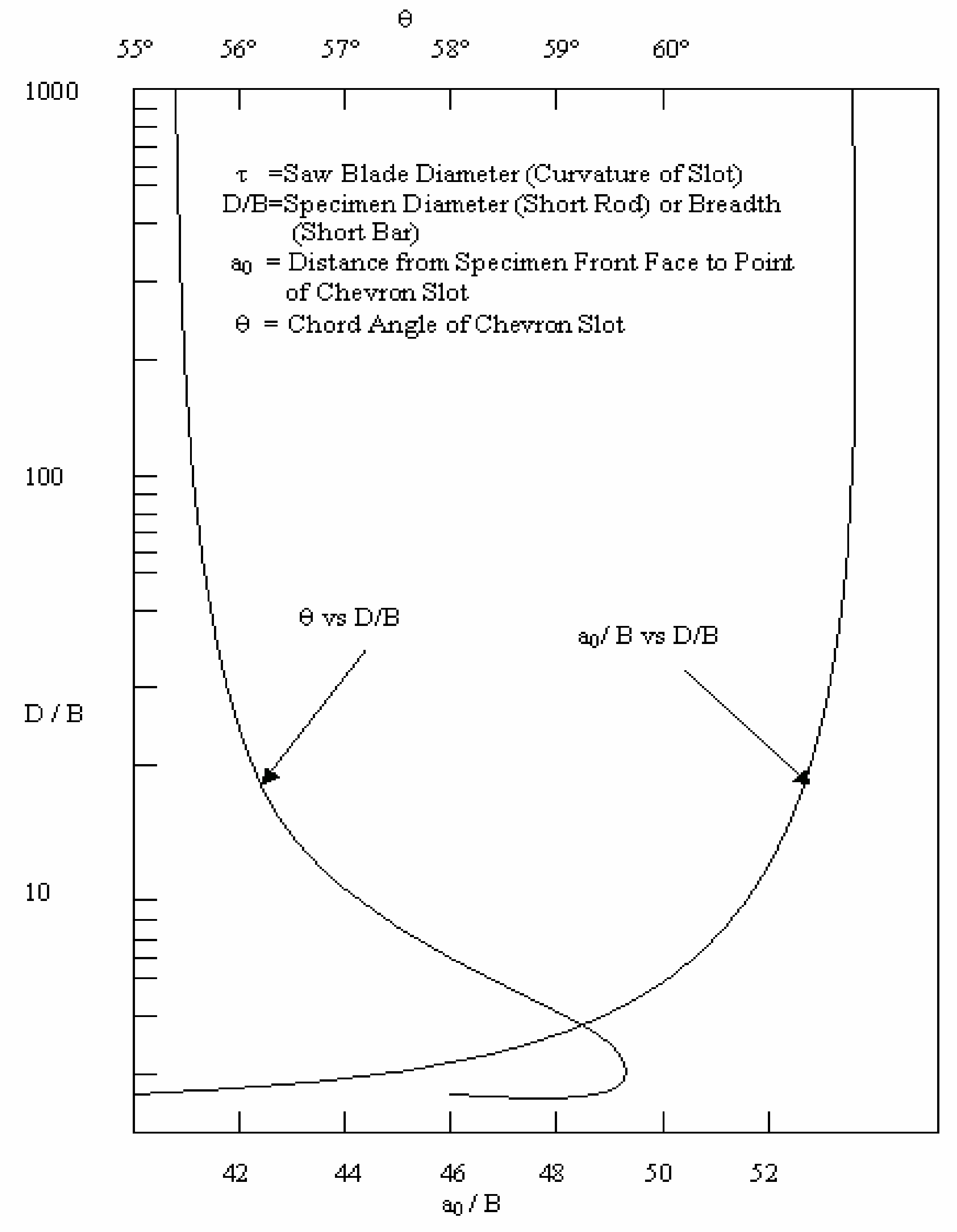


Figure 5.5: The equivalence for curved chevron slots.

Figure 5.6: Internal view of the short bar specimen mould showing the wooden tongue in the foreground and the transparent polypropylene chevron slots.

The materials used in the construction of the mould were selected on the basis of:

- ease of construction,
- microwave safety,
- microwave penetration and hence completeness of cure,
- ready removal of specimens from the mould and
- the strength of the construction materials being able to withstand the hydrostatic forces applied when resin was poured into the mould.

5.3 Chemical Formulation of the Specimens

The constituent materials of the composite are the vinyl ester thermosetting resin, initiator and filler. They are:

- Vinyl Ester Resin (Hetron 922 PAW)
- Methylethy Ketone Peroxide (MEKP)
- Flyash (ceramic hollow sphere)

Tables 5.1 shows the weight of materials required to make 500cm^3 (500ml) of VE/FLYASH (33%) (Ku 2003):

Materials	Resin	Initiator	Flyash
Parameters			
Relative Density	1.1	1.0	0.7
Percentage by weight (%)	67	---	33
Weight for 500cm^3 of composite (grams)	301.8	5.6	154

Table 5.1: Weight of materials required to make 500cm^3 of VE/FLYASH (33%)

The procedure to produce the composite is listed below:

1. Weigh the amount of resin required on an electric balance

2. Add the flyash and mix thoroughly as outlined previously

3. Add the MEKP and mix thoroughly with a plastic spoon, being careful to ensure that air bubbles are not entrained in the mixture

4. Spray canola oil on mould surfaces (release agent)

5. Pour the composite into the mould and place in the microwave at the required input energy and duration.

6. Remove from oven and allow curing in ambient surroundings for at least 24 hours before testing.

The chemicals used are hazardous and if not handled properly could cause serious harm or injury, and damage to equipment and facilities. As mentioned in chapter 3, it is important that all personal protective equipment used and precautions adhered to.

Short bar specimens where produced in batches of six at the required power level and duration of exposure. Impact specimens were also produced in batches of six. This was for efficiency, however as will be discussed in the recommendations, there may be a problem with this process with respect to specimen and results reproduction.

Chapter 6

Testing

6.1 Introduction

This chapter shall briefly discuss the testing apparatus used to obtain the fractured specimens. As mentioned before, the testing methods adopted were those adopted by Chew for the short bar test and Cheng for the impact test. The reader should refer to these two dissertations for greater detail on these testing methods.

6.2 Short Bar Testing Apparatus

The MTS 810 testing system was used for the short bar tensile testing in mode I loading. This system was more appropriate for small size specimen testing. The fracture toughness of the short bar specimen was tested by an opening tensile loan applied at the opening of the specimen by grippers shown in Figure 6.1.

Figure 6.1: MTS 810 Material Testing System.

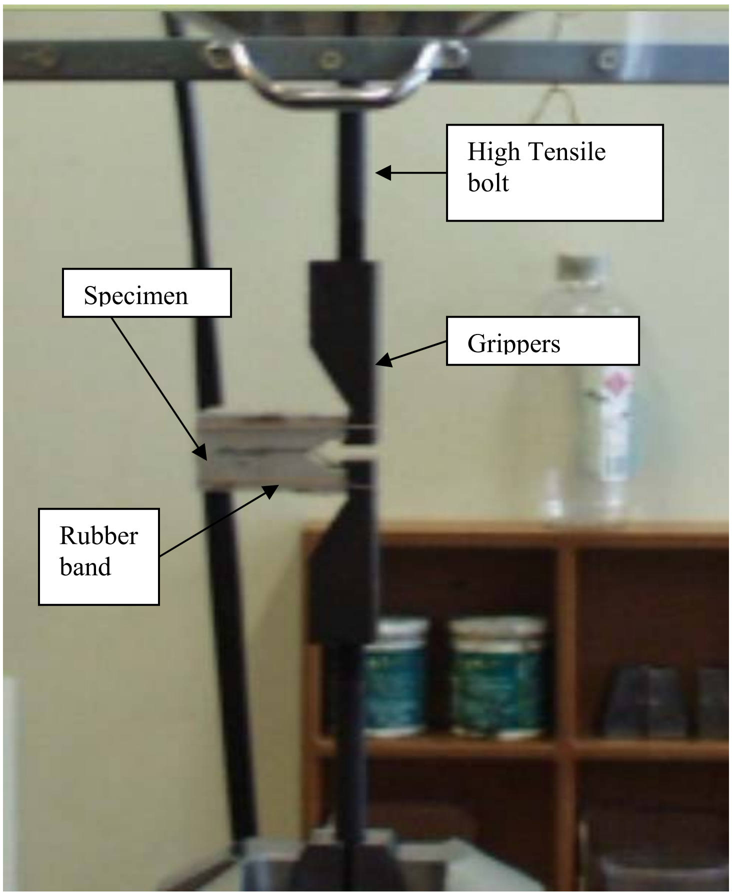


Figure 6.2: Test rig with specimen in position.

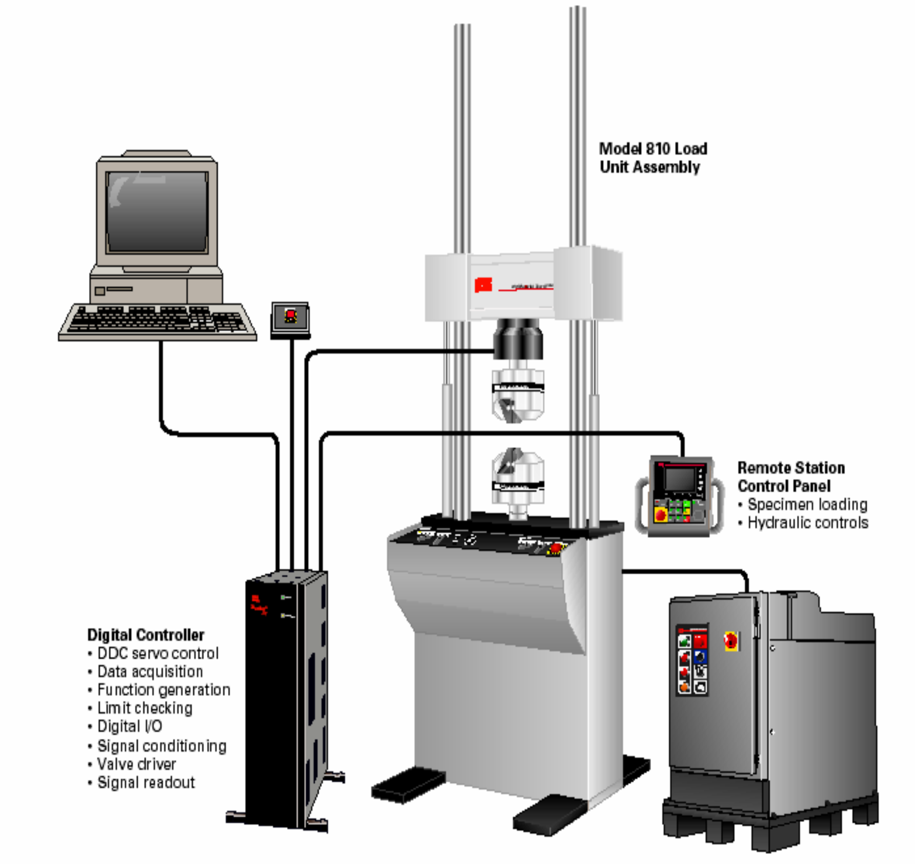


Figure 6.3: The operating systems of MTS 810 Material Testing Systems (MTS 810 Material Testing Systems, 2003).

6.3 Impact Testing Apparatus

The testing apparatus used in this test was developed by Cooper in 2002. A diagram of the test set up and accompany photograph of the test rig has been presented to show the general set up of this test method. Cheng later modified the test rig so that data related to the impact event could be recorded using a piezoelectric accelerometer, charge amplifier and a two channel digital real-time oscilloscope.

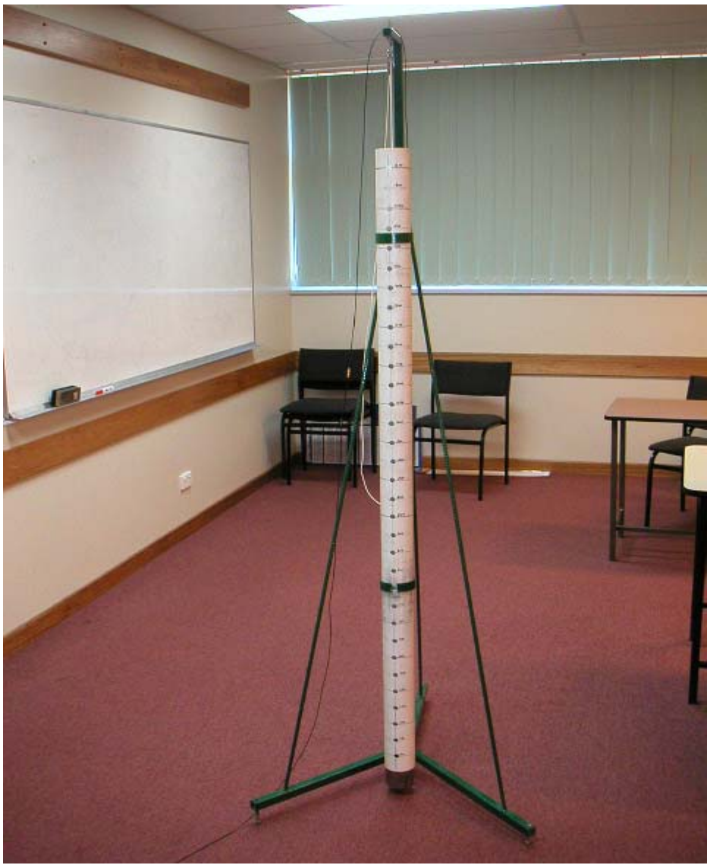


Figure 6.4: Test rig used for testing.

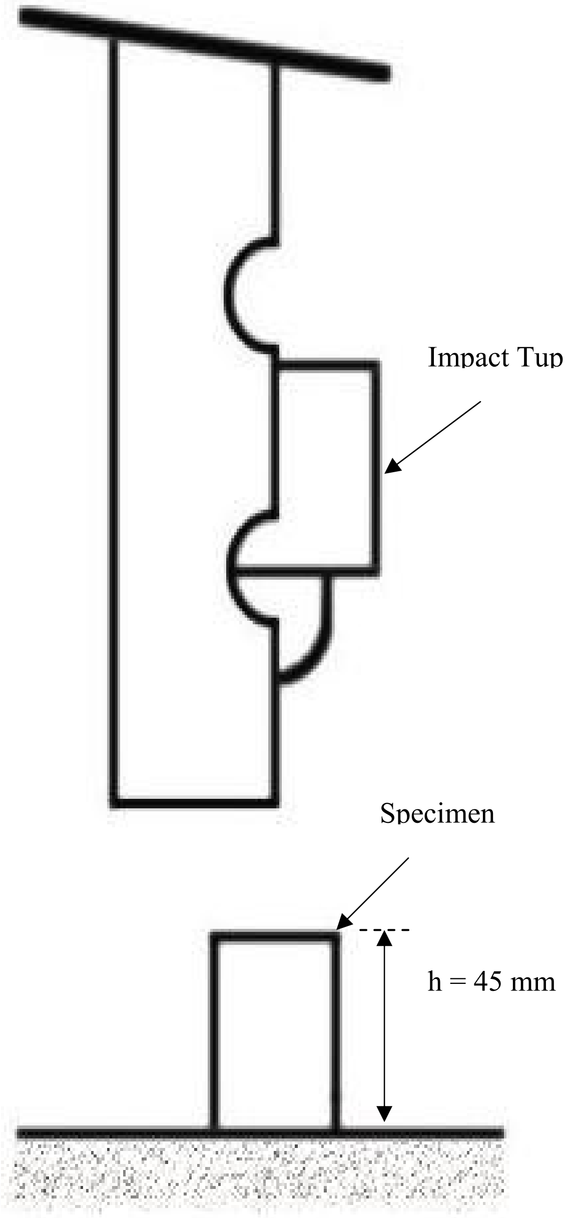


Figure 6.5: Test rig setup.

Chapter 7

Microscopy

7.1 Introduction

The study of fracture mechanics has been facilitated by advances in microscopy. The advent of the scanning electron microscope (SEM) in the 1950s enabled detailed structural analysis of samples to be conducted. Scanning electron microscopes image the surface of samples. A focused beam of electrons is used to scan the surface of the sample and images of up to 50, 000 times magnification can be obtained. Photographic or digital cameras allow recording of images and hence the production of micrographs.

Images captured from an SEM are termed micrographs. However, micrographs of fractured surfaces are termed fractographs. Consequently in this dissertation the use of the word micrograph and fractograph shall be used synonymously.

7.2 Observing

The observation and investigation of surface fractures should be undertaken at various levels of magnifications. The range of observations should begin with the naked eye, to identify any macroscopic features and end with possibly a SEM investigation. The use of the naked eye or hand lens should not be under-estimated as important features may be found and then a decision may be made as to whether or not the feature warrants further detailed investigation.

The range of observations may be illustrated by a schematic representation of the different methods of observation with increasing magnification (Figure 7.1).

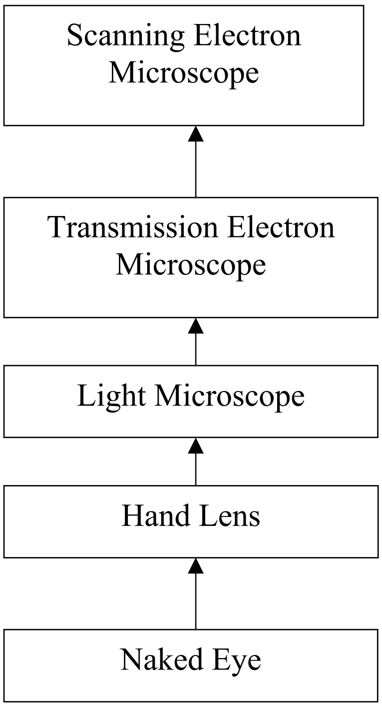


Figure 7.1: Schematic diagram of increasing magnifications of observation techniques.

In this project an initial examination of the fracture surface was conducted visually with the naked eye and then with a stereoscopic binocular microscope (Figure 7.2). The skill involved with the use of the stereoscopic microscope was difficult to master and involved focusing and controlling illumination. Shadows were induced by adjusting the level of illumination for better viewing. It should be noted that the composite was transparent and opaque with a vitreous nature when viewed under the stereomicroscope (Figure 7.3). The images from the stereomicroscope were subsequently captured using a CCTV camera in connection with a TV and a computer program called AlGotcha!95.

Live images of samples are broadcast through a coaxial cable to a TV. Once satisfied, still images were able to be captured using the AlGotcha!95 software and saved to disk.

The stereomicroscope had a maximum magnification of 20X and this was sufficient for preliminary work. The availability of the SEM facility was limited due to cost and time factors. The SEM facility cost $150 an hour which is very expensive and one specimen could possibly take hours to investigate.

Figure 7.2: Stereo microscope set up at USQ with lamps for illumination and a CCTV for image capture.

Figure 7.3: Image captured from a stereomicroscope showing multiple cleavage steps.

7.3 Scanning Electron Microscope

Images taken from the SEM, also called micrographs, or more specifically fractographs when images are of fractured materials; have been captured at 20X magnification and upwards to 5000X magnification.

The samples were systematically viewed initially at 20X magnification to identify specific areas of interest. Then subsequently these areas of interest were zoomed in on to capture greater detail at these specific locations.

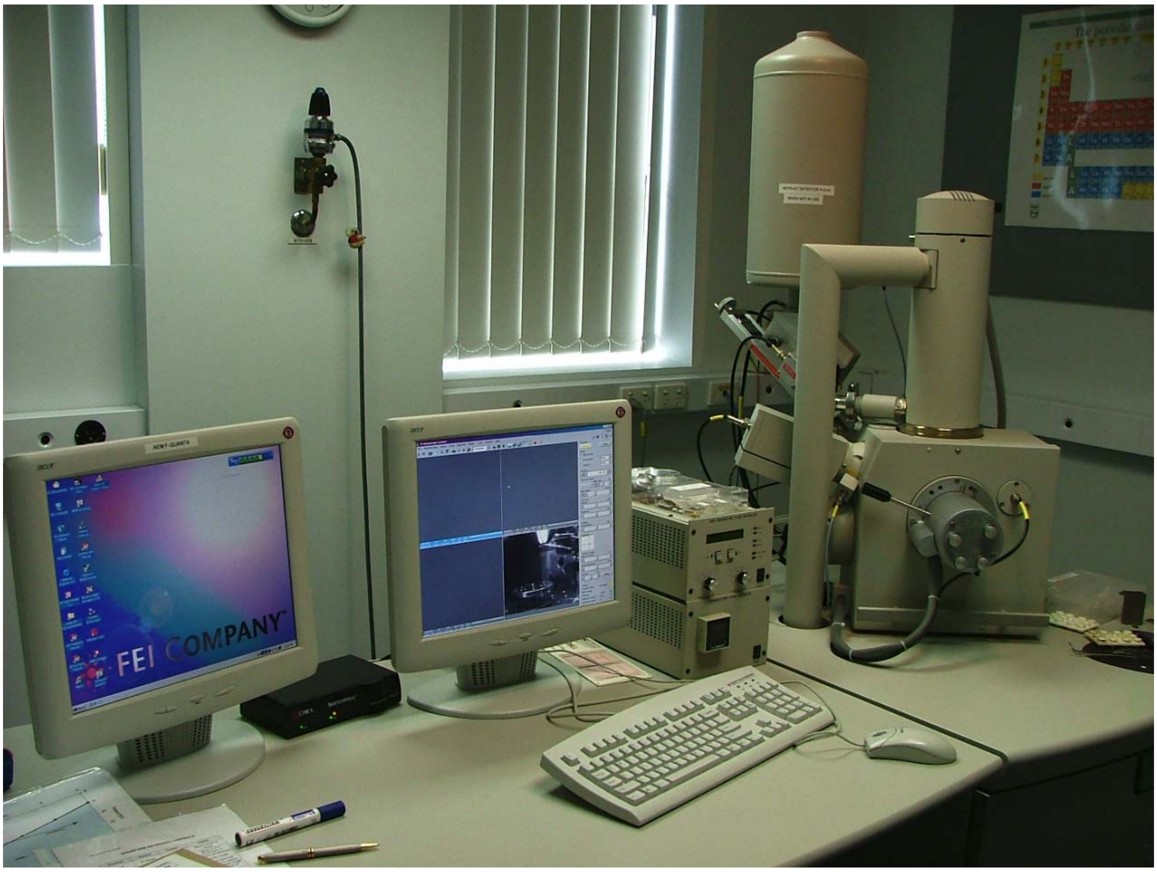


Figure 7.4: The scanning electron microscope (SEM) at QUT.

Scanning electron microscopy is by far the most popular technique for fractographic studies (Hull, 1999). It has many advantages over light microscopy but must not be used in isolation as scanning electron microscopy is complementary to light microscopy. The advantages afforded by a SEM are high resolution, magnification and depth of field.

- Resolution is controlled by a number of factors that are outside the scope of this project, but has been mentioned for completeness and give the reader an idea of the quality of images captured.

- The range of magnifications is very wide from about 20X to 250,000X. For fractographic work 20,000X is generally the maximum magnification due to limitations of resolution and subsequently the usefulness or effectiveness of images greater than 20,000X begins to deteriorate. A powerful feature of the SEM is the ability to zoom the magnification range so that the detail identified at low magnification can be further explored without having to adjust the specimen.

- Finally the most important feature of the SEM is the large depth of field which means image sharpness is maintained over a large area.

The basic set up of the SEM is the integration of a number of systems:

- illumination,
- vacuum,
- sample manipulation and
- signal detection and imaging.

Scanning electron microscopes image the surface of samples. A focused beam of electrons (approximately 2 – 50nm diameter) is used to scan the surface of the sample. Several types of detectors are used to obtain information from the sample and generate an image of the surface. The secondary electron detector provides high resolution topographical details.

The most common method of viewing samples in a SEM is a magnified image, which appears three-dimensional. The backscattered electron detector can show areas in the sample with different average atomic numbers, indicating differences in composition. X-ray detectors may be used to determine the elemental composition of the sample.

Photographic or digital cameras allow recording of the images. Other detection systems may be used to collect and process other signals arising from the sample.

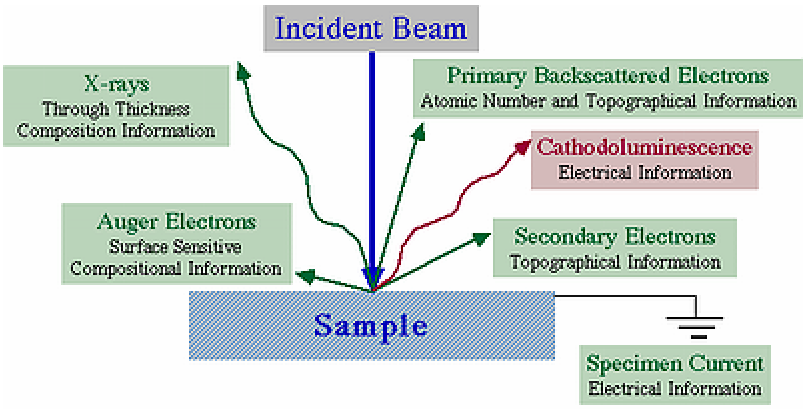


Figure 7.5: Electron and Specimens Interaction.

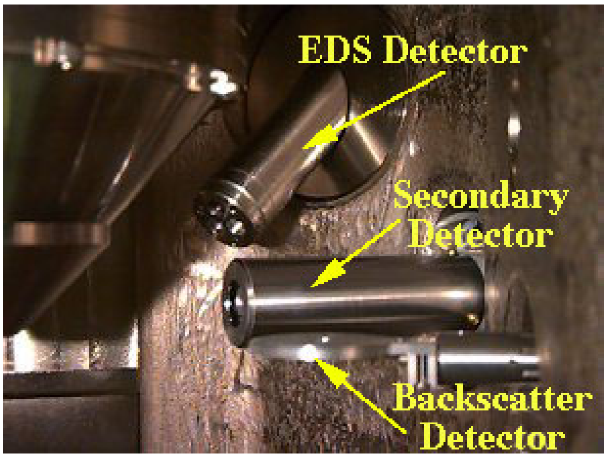


Figure 7.6: The lens and detectors located inside the sample chamber.

The scanning electron microscope used at Queensland University of Technology (QUT) was actually an environmental scanning electron microscope. The environmental scanning electron microscope (also known as ESEM, variable pressure SEM or low vacuum SEM) requires a specially constructed electron microscope. It has some advantages for some applications, namely less sample preparation, and samples may be examined without the removal of all water or solvent.

7.3.1 Sample Preparation

Although less sample preparation is required when using an ESEM, generally samples usually need some preparation before they can be successfully imaged and analysed. Samples must be dry, clean, able to generate a signal and conductive. To improve conductivity, samples are coated in gold and to aid this samples are limited to approximately 1 – 2 cm in diameter. A low vacuum chamber is used to eliminate moisture and samples go through a process called sputter coating.

This method is used to gold coat samples for secondary electron imaging (topographical imaging). It is a non directional coating method where by all surfaces of the sample are coated. The conductivity is improved and discharge of electrons is eliminated. The coating grounds the sample via the stub and dissipates heat from the sample.

A sputter coater is used at a relatively low vacuum (10^{-3}Torr/10^{-1}Pa); an inert gas (argon) is introduced into a high voltage (1-3kV) field. The gas molecules are ionized (Ar^+) and are accelerated into a metal “target”. For gold coating, the target is a gold plate. Gold atoms are dislodged from the target, and the dislodged atoms continue to interact with the argon, producing a “cloud”. Gold atoms preferentially deposit on the sample (due to the configuration of the sample chamber), and build up a metallic coating on the sample.

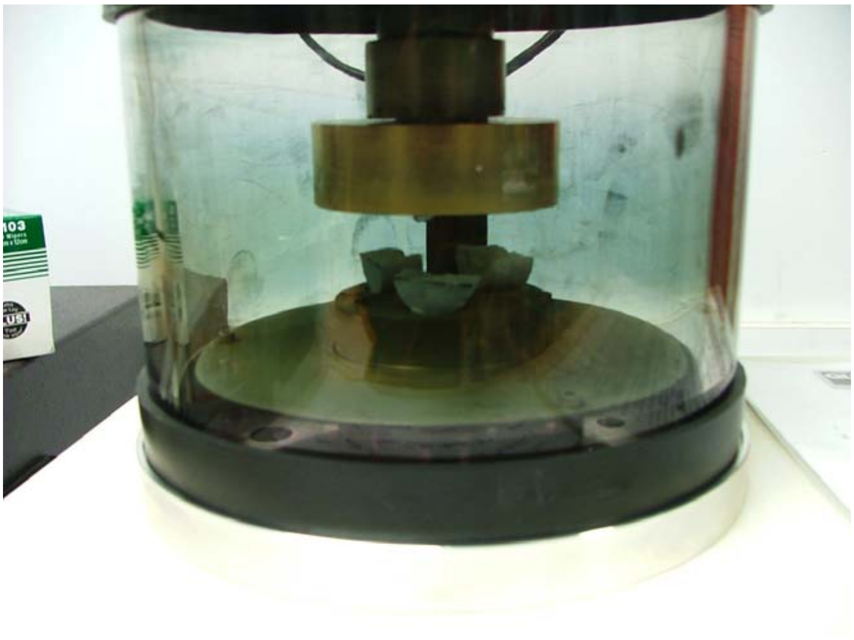


Figure 7.7: Samples are placed in a sputter coater.

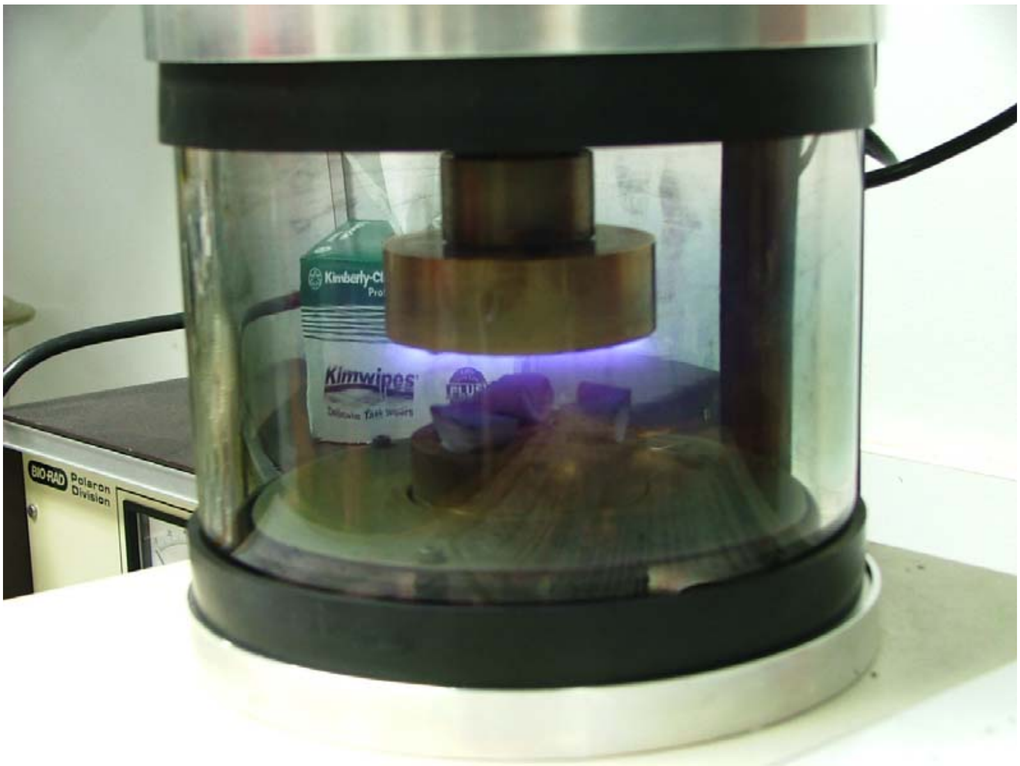


Figure 7.8: Argon gas molecules are ionized and are accelerated into the gold plate. Gold atoms are preferentially deposit on the sample.

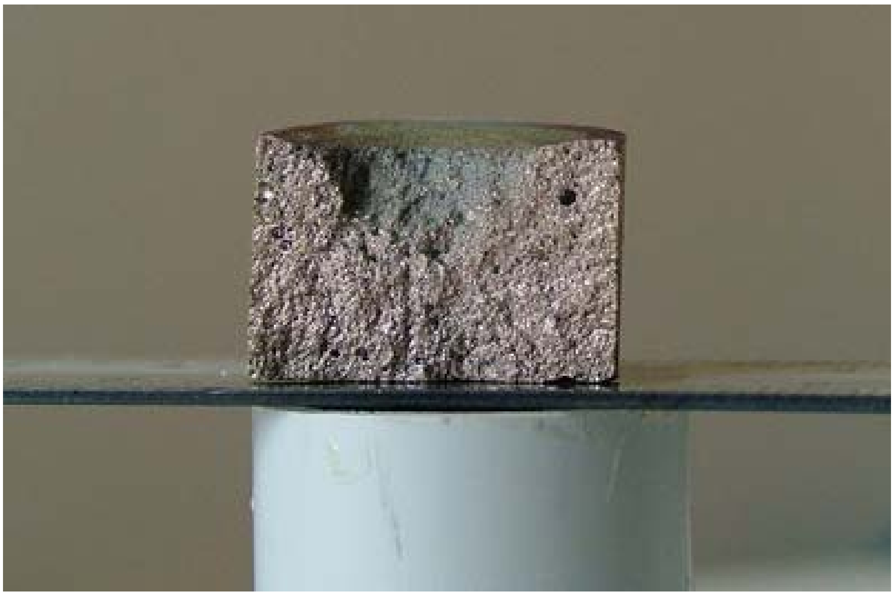


Figure 7.9: Photograph of an impact specimen thinly coated with gold.

7.3.2 Mounting of Samples

Samples must be mechanically stable in the scanning electron microscope and this was achieved by directly attaching the specimen to a stub. Stubs are usually metallic for conductivity and graphite tape used to attach the sample to the stub. The samples on the stub were then placed into specimen chamber for viewing.

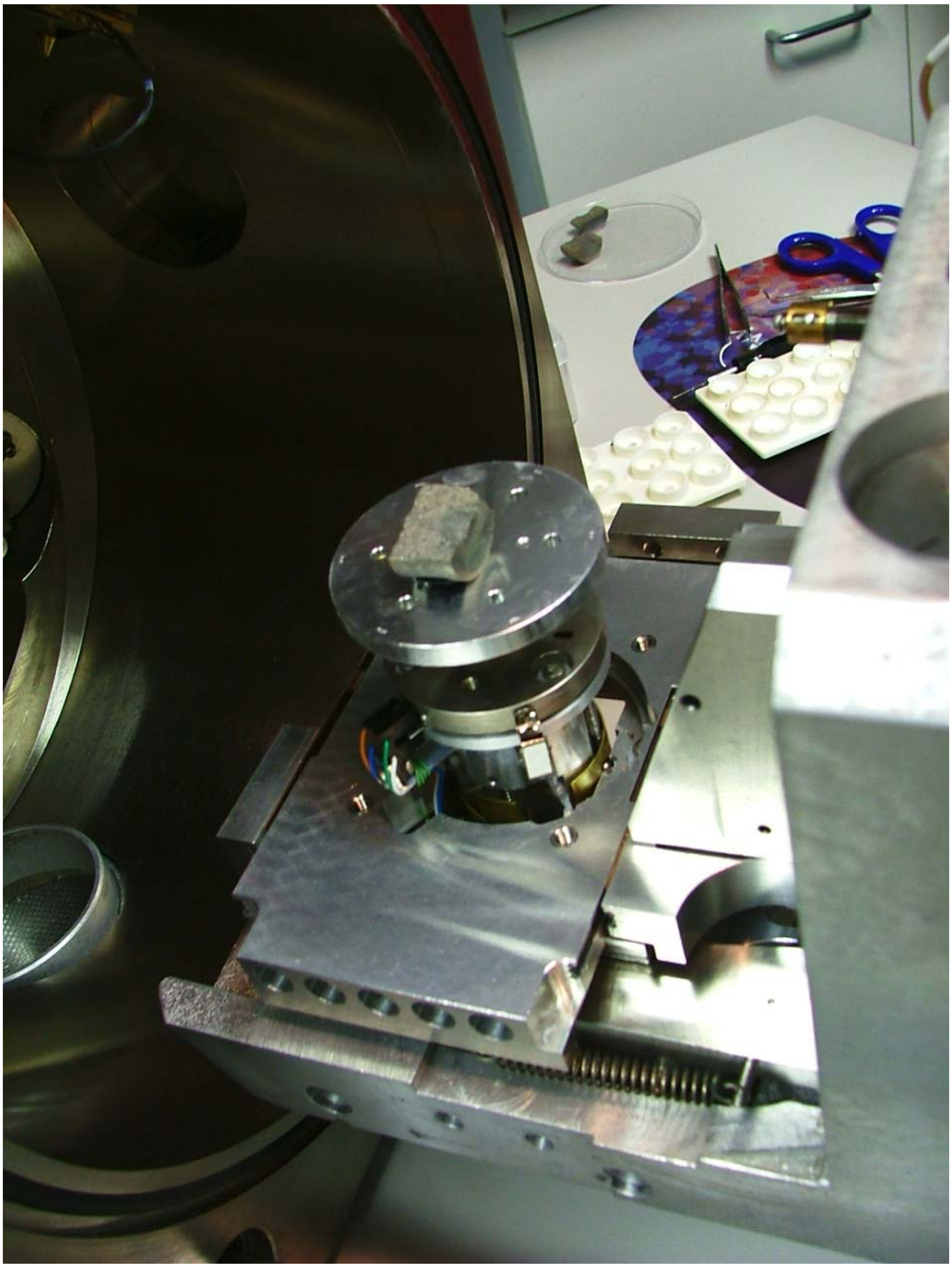


Figure 7.10: Gold coated fracture sample mounted on a sample stub is placed on the specimen stage within the specimen chamber of the SEM.

Chapter 8

Fractography and Fracture Failure Analysis

8.1 Introduction

The science of studying fracture surfaces is called fractography. Fractography is employed as a production-line evaluation tool and as a research tool in controlling and understanding the properties that metals exhibit in service, in addition to its use in failure analysis.

Certain patterns in fractographs/micrographs correlate to different modes of failure and to the trained eye a picture really does say a thousand words. The presence of dimple shapes on metal fracture surfaces reveals ductile failure. Dimple shapes in a fracture can also be used to determine the direction of local crack propagation.

Other microscopic fracture features include transgranular fracture by micro void coalescence, micro void initiation, and transgranular fracture by cleavage and transgranular fracture by quasicleavage and intergranular fracture. The afore mentioned fracture features relate to the crack propagation leading to failure of the material.

The subject of fractography and fracture analysis in metals is exhaustive, however by understanding the fundamentals of fractography and how it relates to fracture mechanics one is in a good position to apply this to the PFR of the project and further ones understanding of the properties of this material.

8.2 Observing and Describing Surface Topography

Micrographs of fractured samples reveal various features which to the trained eye can explain how a material behaves under certain conditions. As mentioned before in section 7.3, micrographs should not be used in isolation, which implies knowledge of conditions under which fracture occurred and microstructure of the material is required in order that a proper conclusion of the events that lead to crack growth and fracture may be drawn. The following is a presentation of a number of features that have been observed in the impact test and short rod samples. All samples viewed have exhibited both brittle and ductile fracture characteristics. That is features characteristic of brittle behaviour and ductile behaviour but this does not necessarily mean that the material as a whole will fracture in a ductile or brittle manner.

8.2.1 Crystallographic cleavage

The composite is a combination of two materials; the resin and the ceramic hollow spheres. It has been observed that a considerable level of cleavage behaviour occurs in both the impact and tensile fracture tests (Figure 8.1). The presence of this feature leads one to believe that the resin possess some degree of crystallinity and cracks that grow through some weak plane within the crystal structure of the resin due to the induced state of stress.

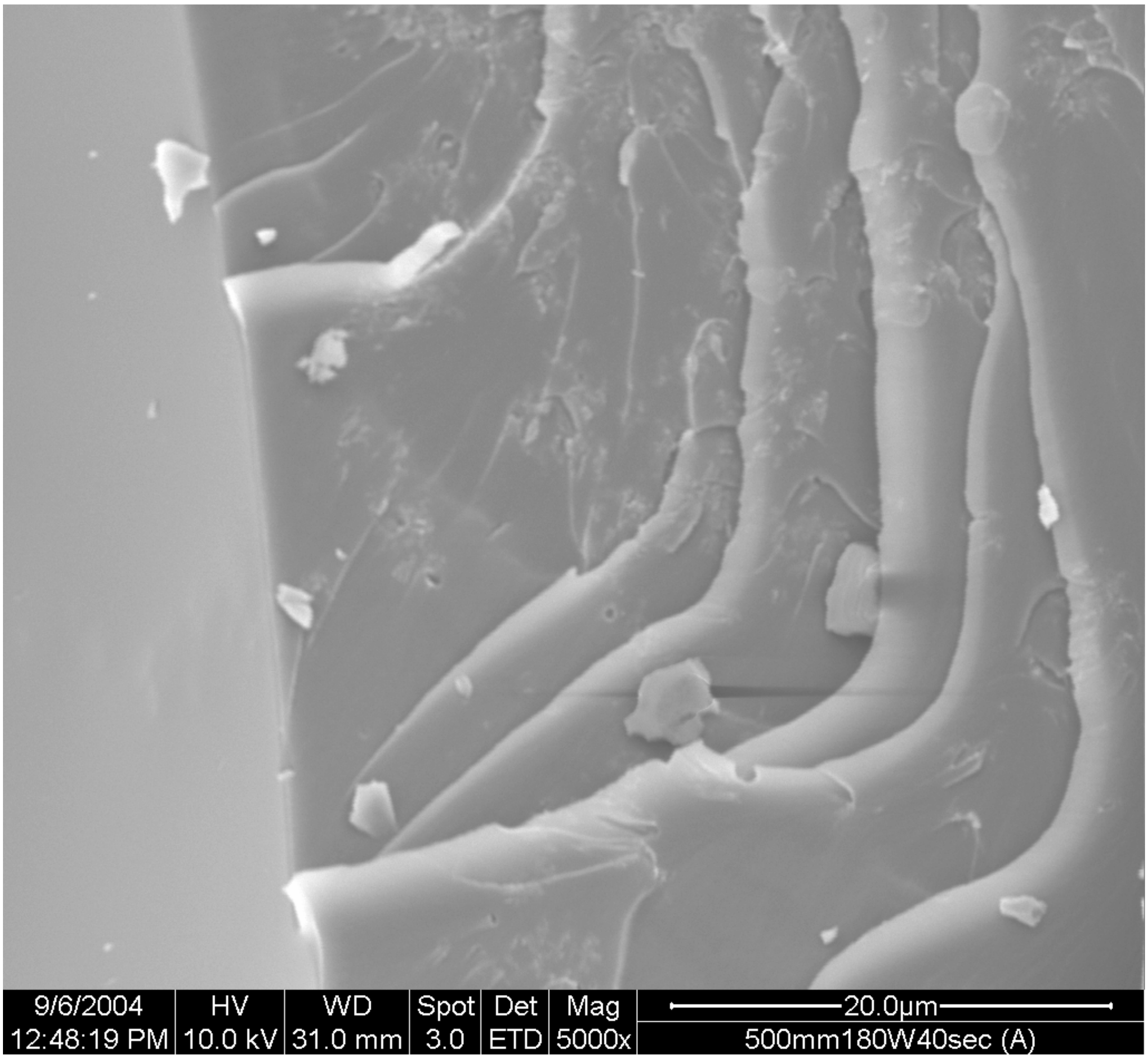


Figure 8.1: Micrograph showing the propagation of multiple cracks from the filler-matrix interface. The multiple cracks are possibly shear cleavage of the resin.

8.2.2 Quasi Cleavage

This term describes the fractures involving fine-scale mixtures of crystallographic cleavage and ductile tearing. This feature may be shown in Figure 8.2.

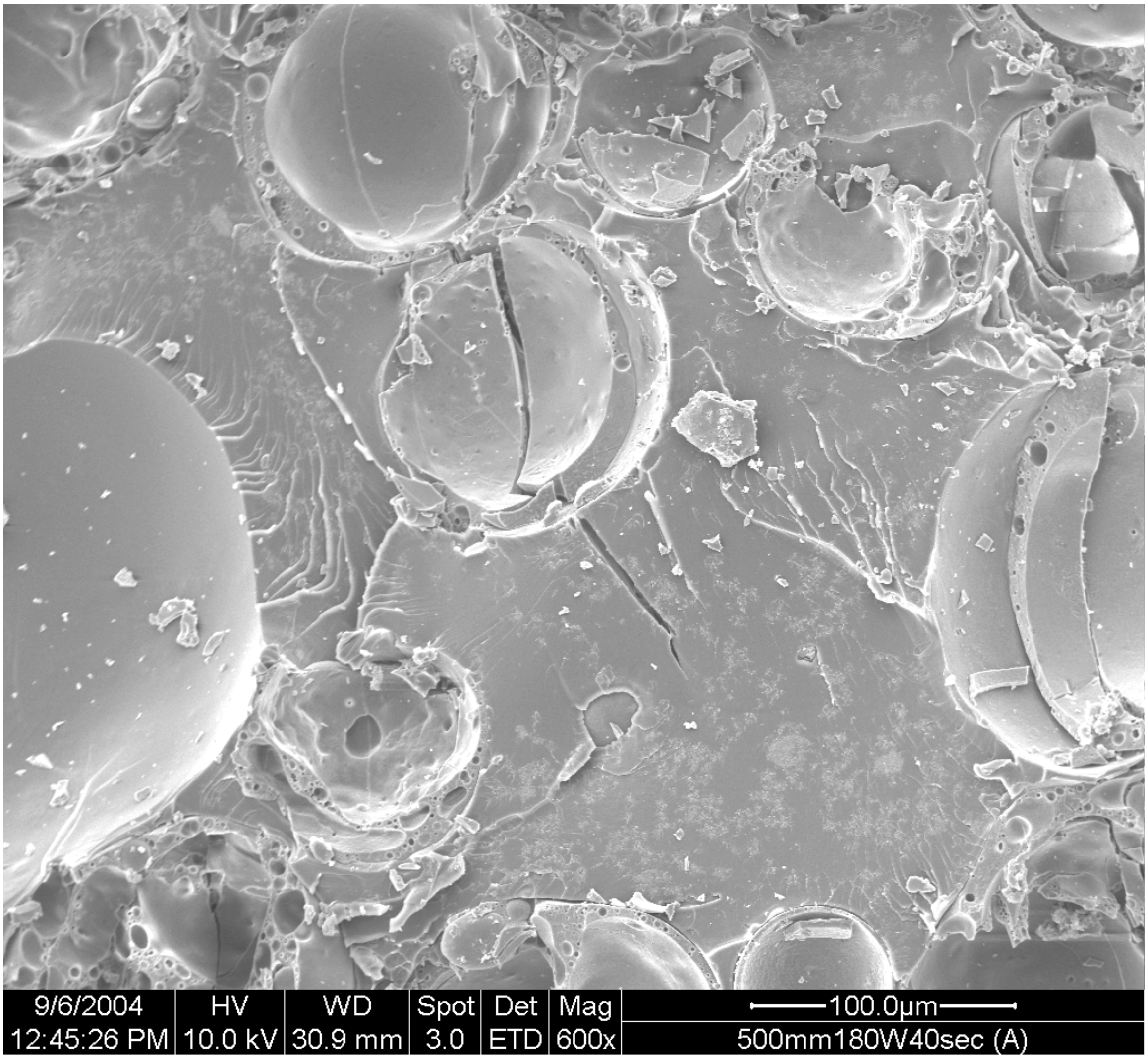


Figure 8.2: Micrograph showing non-uniform filler size, multiple crack paths emanating from the filler-matrix interface, fracture through the filler and filler de-bonding from the matrix.

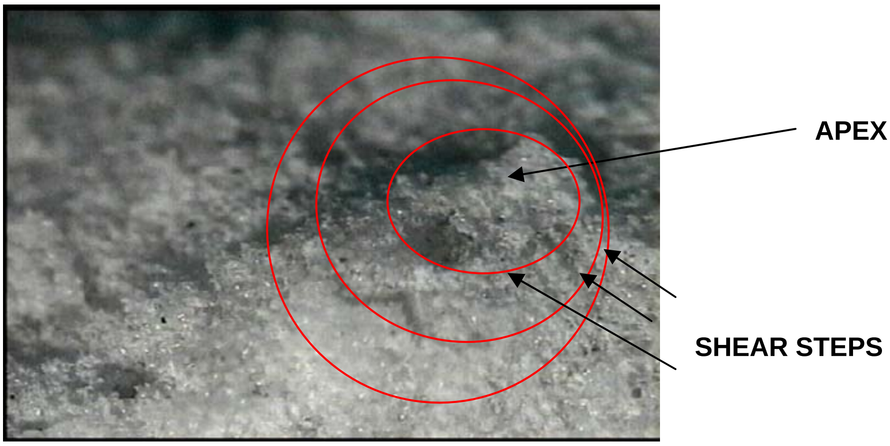


Figure 8.3: Still image captured from a stereomicroscope showing the apex of the shear cone and shear steps radiating out from apex.

Figure 8.4: Photograph of shear cone piece, typical of all fractured impact specimens showing cleavage steps radiating around the surface of the cone. The cones are roughly 45 degrees and are a result of shear stress concentration along some diagonal plane with the composite.

8.2.3 Shear Steps / Shear Cleavage

This can be illustrated macroscopically in Figure 8.5. As discussed in section 8.2.1, these cleavage facets are evident microscopically. The mode of loading causing these features may be mixed mode I and mode III and requires confirmation.

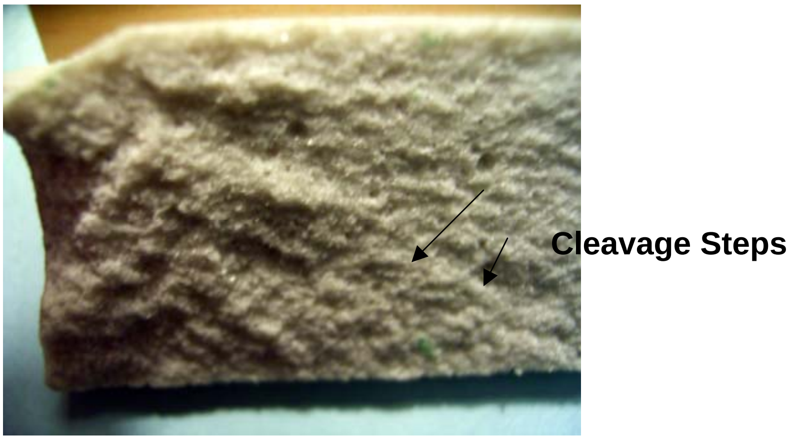


Figure 8.5: Photograph of fractured sample showing cleavage steps.

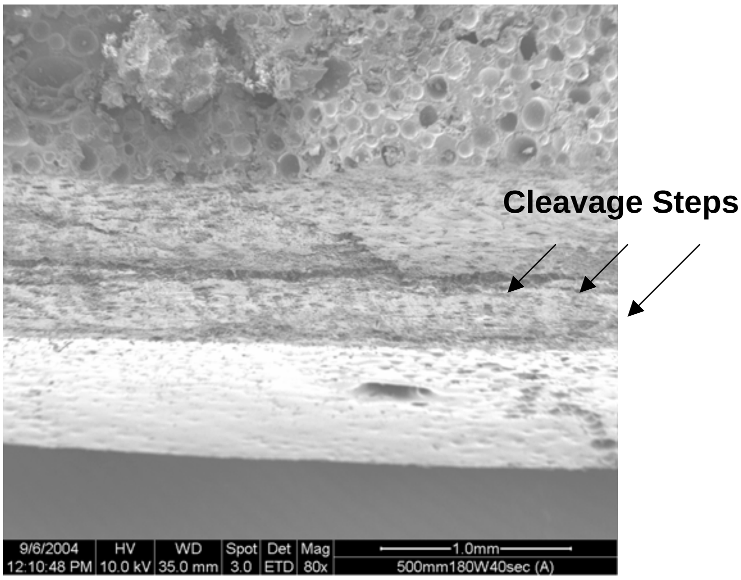


Figure 8.6: Micrograph showing cleavage steps near the surface of impact.

8.2.4 River Line Patterns

River line patterns are classically exhibited in crystalline materials. It has been observed in the VE/FLYSH (33%) composite and thus lends great support to ones suspicions that the matrix resin is indeed crystalline.

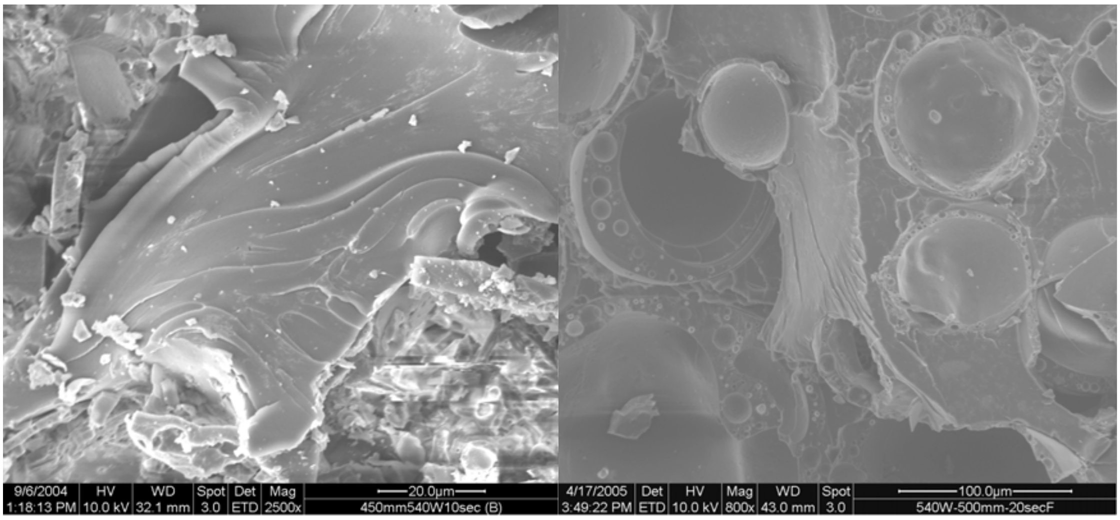


Figure 8.7: Micrograph of composite with multiple intergranular crack paths possibly following some crystallinity in the matrix.

8.2.5 Crack Growth through Composites

Crack growth through the composite appeared to progress through the matrix and through the some of the envirospheres. This was evident in both the impact and short rod tests. As illustrated before, a extensive quasi-cleavage and cleavage fracture has occurred in these composites. In the case of the impact test, this is more pronounced than in the short rod specimens. The short rod specimens exhibit more inter-granular or matrix crack propagation with cracks also passing through the particulate than the impact test; possibly due to micro-void coalescence (ductile fracture- hole joining hole). An interesting feature of the fracture specimens of the short rod test is the extensive de-bonding of the particulate from the matrix as we move away from the origin of the crack. This may be due to the state of stress or strain in this region or it could be that some canola oil has mixed with the envirospheres and thus prevented adhesion of the matrix with particulate. The general scheme of crack growth in the composite may be schematically represented in Figure 8.8. The branching and diversion of the tiny little cracks may be thought of as a toughening mechanism. The crack has to travel a greater distance as it is obstructed by the particulate in the composite.

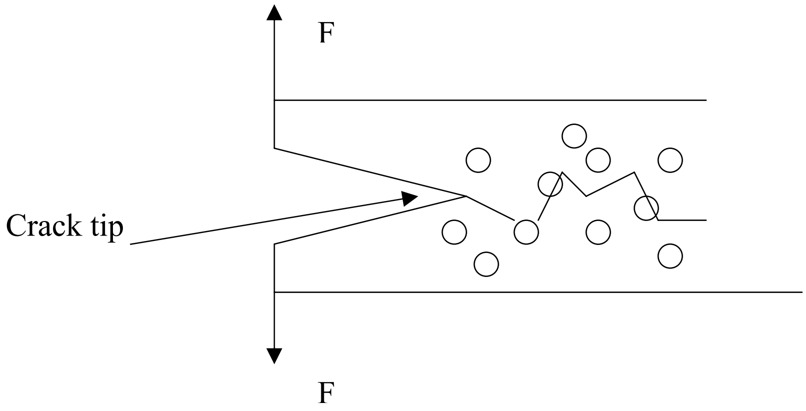


Figure 8.8: Crack path within VE/FLYASH (33%). Particulates are proposed to improve the toughness of the composite.

8.2.6 Porosity and Varying Particle Size

It has been observed that a number of voids are present in the fractured samples. These voids may have been introduced in the manufacturing process. Air may have been entrained during mixing. Another possibility is that styrene gas bubbles may have been trapped in the specimens due to the rapid curing of the composite by microwaves. The voids are particularly large and numerous in the short rod fracture test samples and could be a consequence of the larger volume of composite required to make the test specimens (Figure 8.9). Particulate size was not uniform and some were not hollow. The spheres also exhibited a degree of porosity within their shell walls and some were not hollow but had some grainy inclusions inside of them.

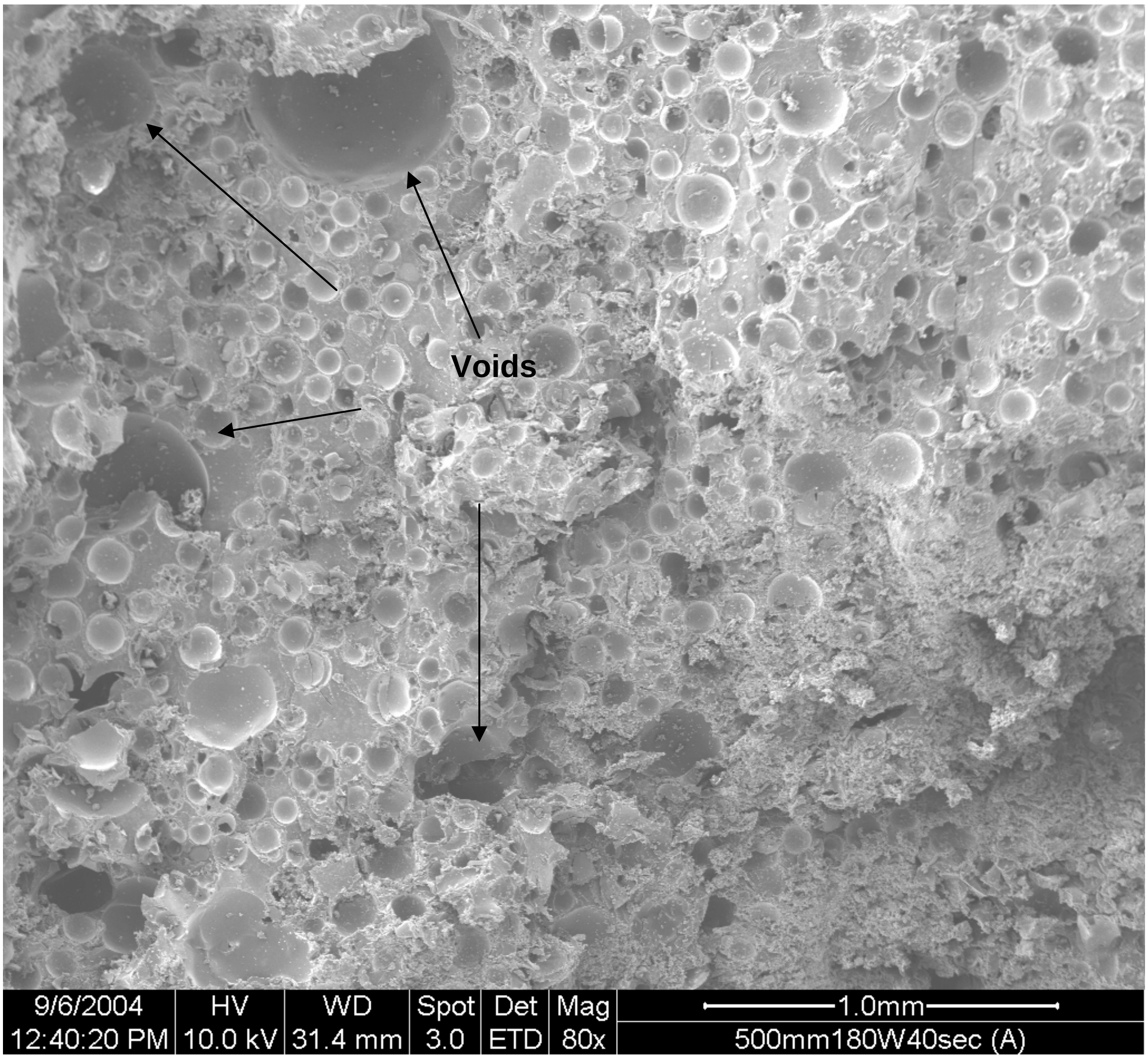


Figure 8.9: Micrograph showing several voids imparted in the material in the production process. The material inherently has flaws associated with the production process. Note the spheres are not uniform in shape.

8.3 Method of investigation

The method of investigation adopted will be described. A general micrograph of the sample was taken at a low magnification, typically 20X. From this image, five points of interest along the fracture surface were located and subsequently zoomed in on for greater detail. The aim of this was to take into account the variation in surface topography as one travels from the point of loading to the end of the fractured specimen. Any other interesting points were subsequently examined. Please refer to Appendix B i.e. Table 8.1 for further information.

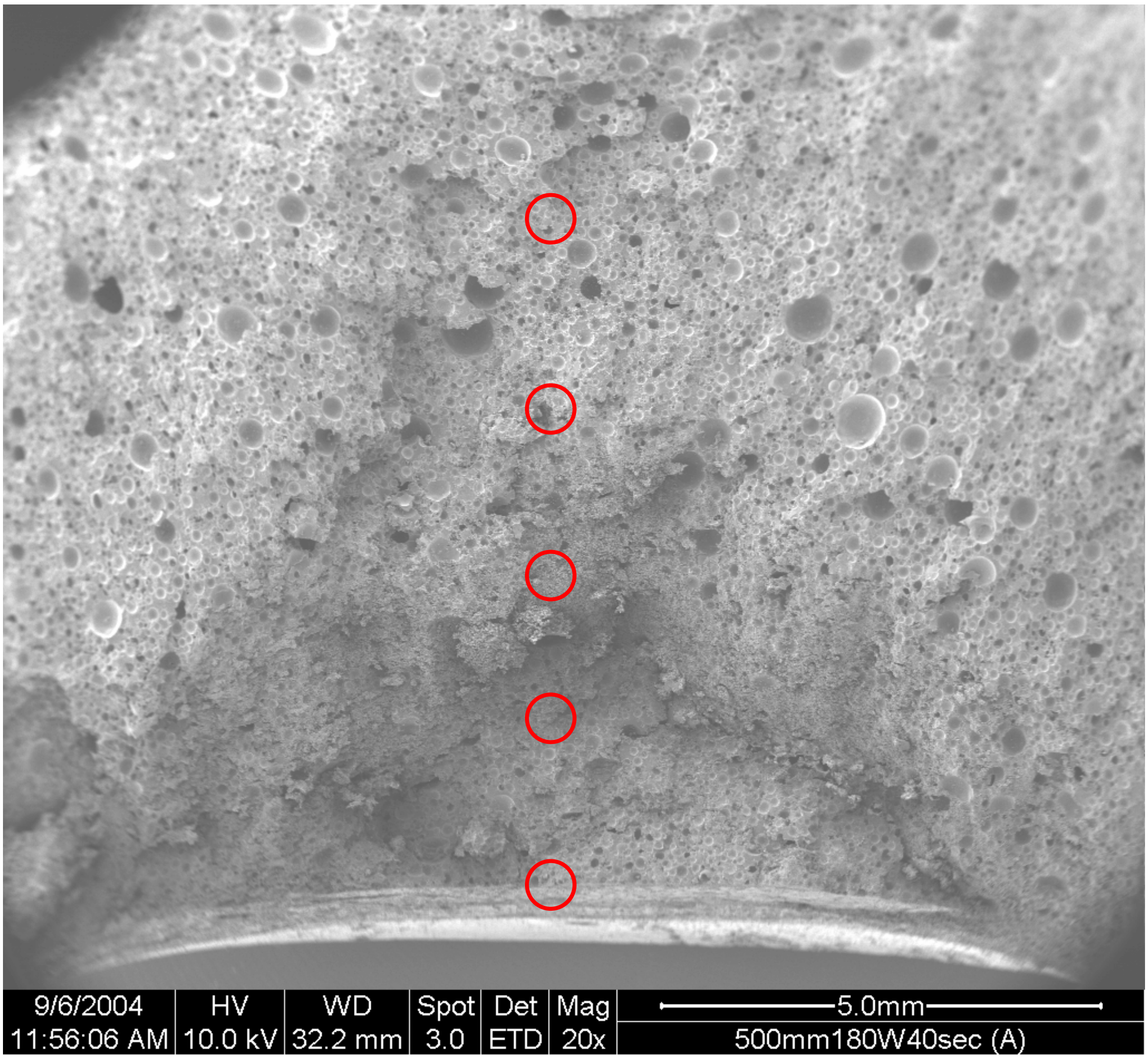


Figure 8.10: A micrograph of a sample that was cured at 180W for a duration of 40 sec and fractured at 500mm. The Image was captured at 20X mag.

Chapter 9

Results

The result of this project was the documentation of observed features of microstructure of the composite tested in both impact loading and tensile mode I loading conditions.

The most important points that have been revealed by a study of the fracture surfaces of the VE/FLYASH (33%) composite are:

1. All short rod test samples exhibited large voids produced in the manufacturing process and as a consequence of the entrapment of gaseous styrene.

2. Impact specimens had smaller voids

3. There seems to be a relationship between the volume and configuration of the specimen and resultant voids.

4. The spherical inclusions or envirospheres were not actually spherical in shape. Some were not hollow and the sizes of these spheres were not uniform. Hence some degree of packing of the filler was observed. It could not be confirmed if this packing had any bearing on the toughness or strength of the material. If segregation occurs, the distribution of the particle would certainly affect the material properties.

5. Impact test specimens cured at high power and long duration had large voids in their fracture surface. The same was observed for specimens cured at low power and long duration and very high power and short duration.

6. Paper fibres were found in test samples produced using paper

7. The use of polypropylene as a construction material was successful. Polypropylene does not adhere to vinyl ester and is removed easily. This was especially useful in the construction of the chevron notch for the short bar test.

8. Both the impact and the short rod test specimens failed in a brittle manner. However ductile (shear) features are present in the fractured samples

9. It is not sufficient to investigate micrographs and con to some conclusion about the material behaviour of the material. Micrographs form part of the whole analysis spectrum which encompasses testing, mathematical modeling and empirical equations.

Chapter 10

Conclusions and Further Work

10.1 Introduction

The results obtained in this research project were only a portion of the work that one originally wished to carry out. This was due to number of constraints, namely time and the difficulty experienced in producing good quality specimens, the need to work in with within the schedules of other students and some unforeseen problems. The results, problems and conclusions arising from this project can be used as a basis for those who follow up this work. By studying the results and problems encountered in this project, the follow up should be made easier with better results in a short period of time. In this chapter, the achievements made over the course of this research project will be summarized. Recommendations will also be provided to aid those interested in following up work related to the study of the micrographs of VE/FLYASH composites.

10.2 Achievements

10.2.1 Mould Implementation

Mould used in this research project had been implemented. The appropriate dimensions and how these moulds should be manufactured had been discussed.

10.2.2 Specimen production

The manufacture of specimens had been carried out successfully. The specimens produced were VE/FLYASH (33%) for both impact and short rod tests and cured under microwave conditions.

10.2.3 Testing

Testing of the short bar specimens was carried out successfully, specimens of approximately uniform shape and size were produced and yielded similar results. No fibrous inclusions from paper was left and a clean smooth chevron notch was left , all specimens failed. The use of a wooden tongue to form the grip groove produced smooth uniform surfaces that required little or no sample preparation before testing. Slip of the grippers was substantially reduced.

10.2.4 Fracture Analysis

Fracture Analysis had been carried out with the use of the SEM. The analysis had shown that the mechanics of fracture and the topographic features were similar for both types of tests. The SEM also revealed the porosity of some samples and the non-uniform size distribution of the filler material. Cracks generally went straight through the fillers and matrix in the impact samples whereas in the short rod test, the crack path deviated somewhat and traversed around the filler material.

10.3 Recommendations for Further Work

10.3.1 Specimen Production

Specimen production is very important in any experimental exercise. The problems encountered in the production of specimens in this research project were with the short bar test specimens:

- Time lapse between pour and microwave curing should be kept to a minimum.
- Mould construction time
- Some irregular specimens could not be used due to gross dimensional error as a result of poor design of internal walls.

In essence all specimens should be produced in the same way and under the same conditions. One is wary of the effect on specimen characteristics of placing three specimens in the oven for curing and placing six specimens, or using different construction materials for different specimens.

It is therefore suggested that instead of using the short bar method, that the short rod method be adopted. By adopting the short rod one could save an appreciable amount of time since the specimen could be constructed using a PVC pipe for the cylinder, a sheet of polypropylene for the chevron and a piece of wood for the tongue in the groove section. The bottom of the cylinder could be sealed with tape. This would make construction easy and fast and the moulds could be reused again. The mass of construction material would be approximately the same for all specimen production and hence the elimination of microwave absorption variances.

10.3.2 Number of Fractured Specimens

Only a limited number of fractured specimens were obtained, and statistical analysis could not be performed. For any meaningful statistical analysis to be carried out, at least forty-nine fractured specimens are required i.e a 7 X 7 matrix using the Latin Square.

10.3.3 Mathematical Modeling

One would suggest that there may be some merit in comparing a mathematical model of the crack growth associated with the loading situation within a test, with that obtained from the micrographs of fractured specimens.

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APPENDIX A

Project Specification

University of Southern Queensland
Faculty of Engineering and Surveying

ENG 4111/2 Research Project
PROJECT SPECIFICATION

FOR:	Richard Lee
TOPIC:	**Micrographs of the Fracture of Vinyl Ester Composites Cured by Microwaves**
SUPERVISOR:	Dr. Harry Ku
Co-SUPERVISOR:	Mr. Doug Baddeley

PROJECT AIM: This project is to investigate the fracture behavior and mechanics of particulate reinforced vinyl ester resins cured under microwave conditions, using a scanning electron microscope (SEM). The percentage by weight of the fly ash (reinforcement) will be 33%. The data collected may be useful in supporting the development of FCDD group in future.

PROGRAMME: 19th July 2004

1. Familiarization of equipment and literature reviews

   Begin : 19th July 2004
   Completion : 1st August 2004
   Approx. Hours : 80 hours

2. Produce and obtain drop weight impact and short bar fracture test samples for viewing under a scanning electron microscope.

   Begin : 26th July 2004
   Completion : 26th August 2004
   Approx. Hours : 40 hours

3. Analysis of the fractured pieces using SEM in QUT, Brisbane

   Begin : 6th September 2004
   Completion : 6th January2005
   Approx. Hours : 110 hours

4. Draw up conclusions.

   Begin : 6th January 2005
   Completion : 20th January 2005
   Approx. Hours : 40 hours

5. Discussion for the Thesis Outline with supervisor.

   Begin : 21st January 2005

Completion : 25th January 2005
Approx. Hours : 10 hours

6. Thesis initial drafting – each chapter in draft form is shown to supervisor so that the thesis can be finished reading by 20 April 2005.
   Begin : 25th January 2005
   Completion : 24th February 2005
   Approx. Hours : 60 hours

7. Final draft of thesis, to incorporate modifications suggested by supervisor.

   Begin : 24th February 2005
   Completion : 15th March 2005
   Approx. Hours : 40 hours

9. Complete the thesis in requested format

   Begin : 16th March 2005
   Completion : 20th April 2005
   Approx. Hours : 40 hours

AGREED: ______________ (student) ____________________

(Supervisor)

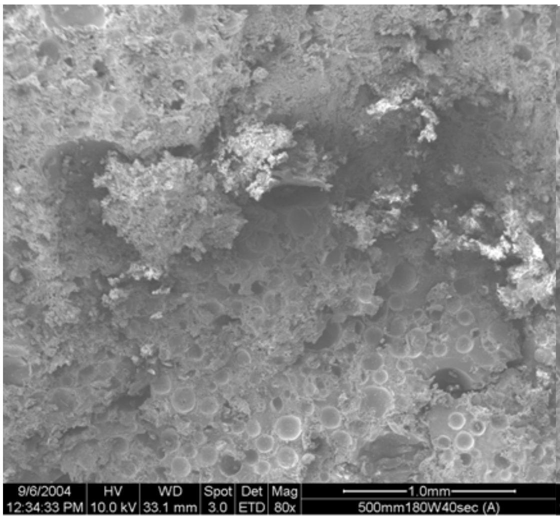
____

(Supervisor)

Date: _____________________________

APPENDIX B

SEM Images and Notes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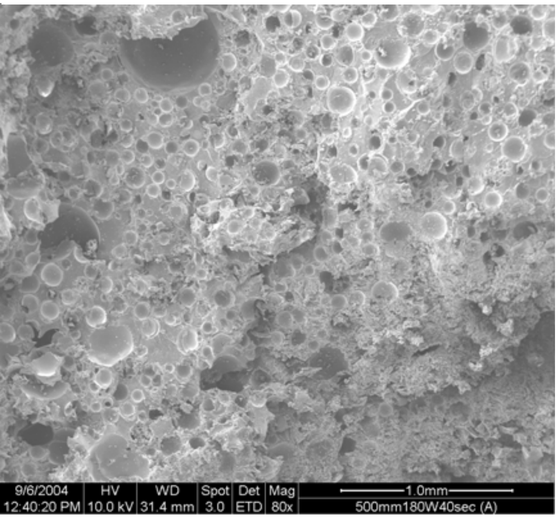
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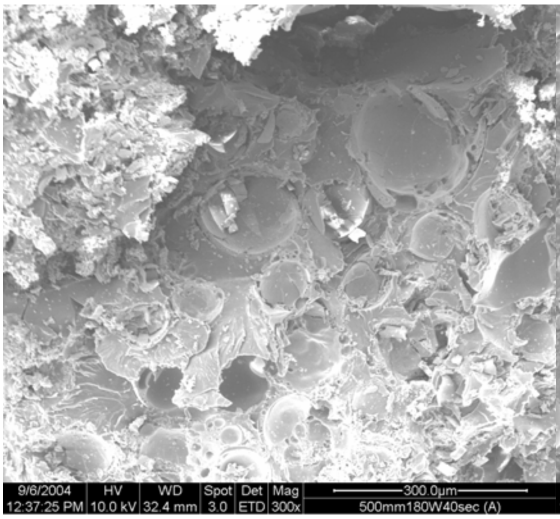
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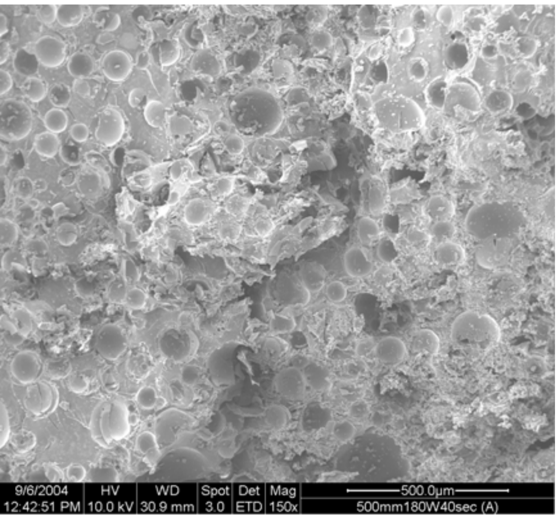
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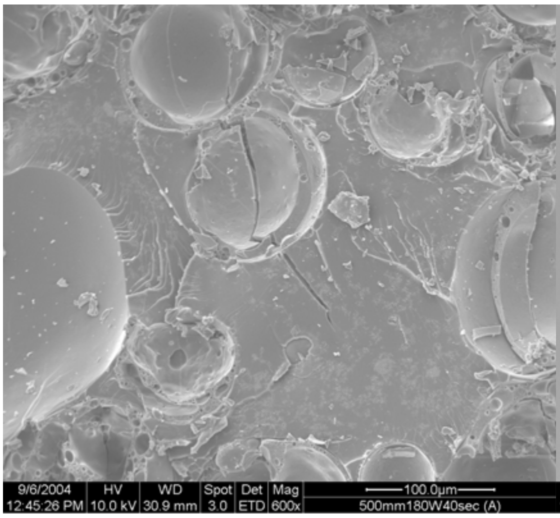
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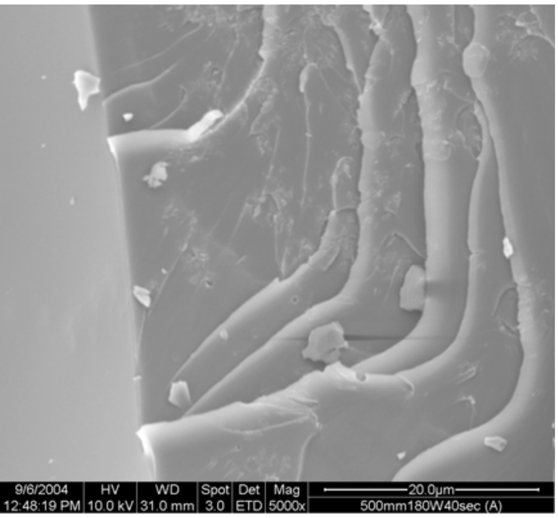
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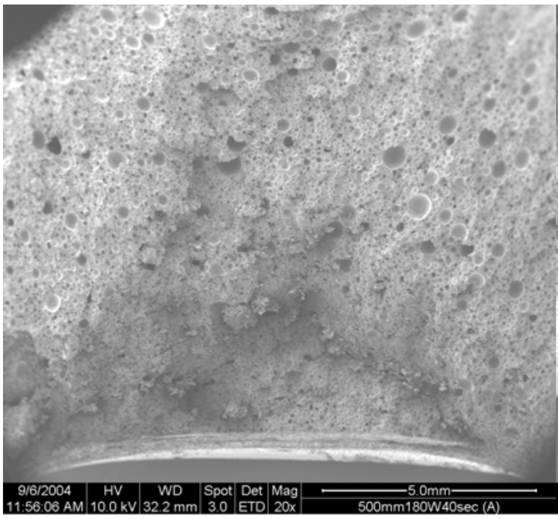
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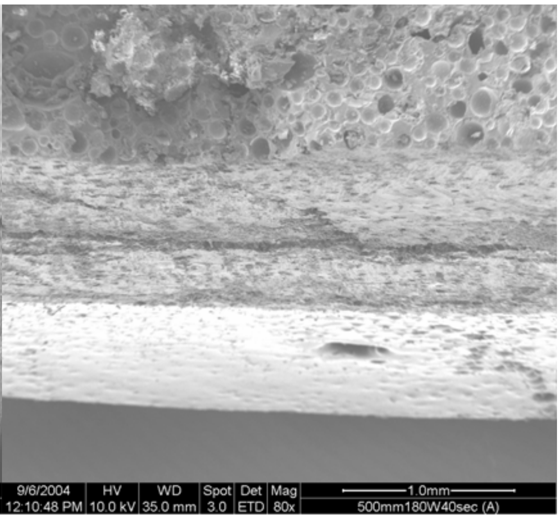
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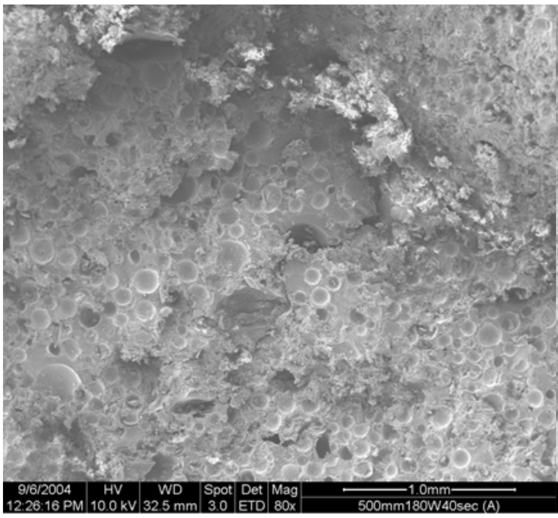
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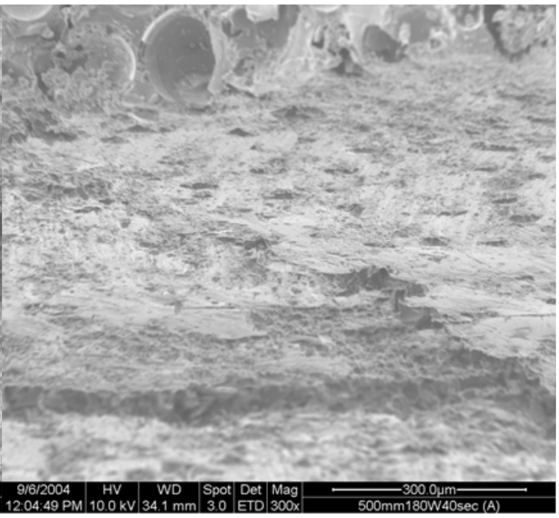
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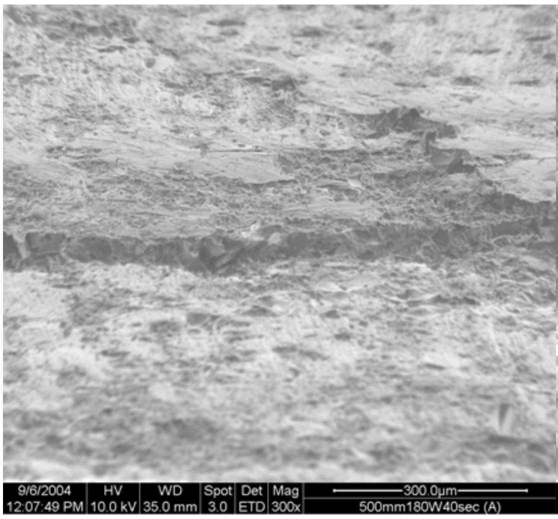
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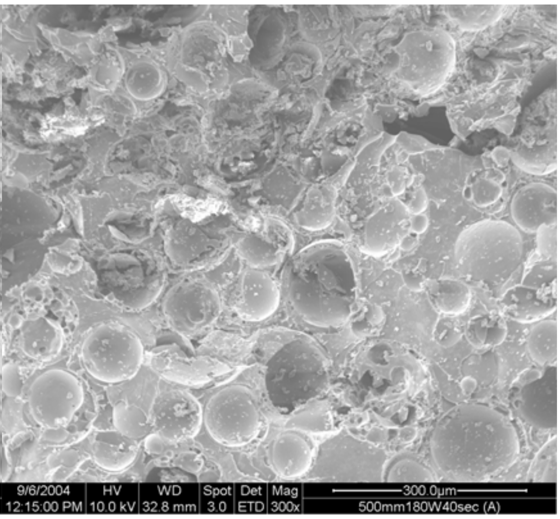
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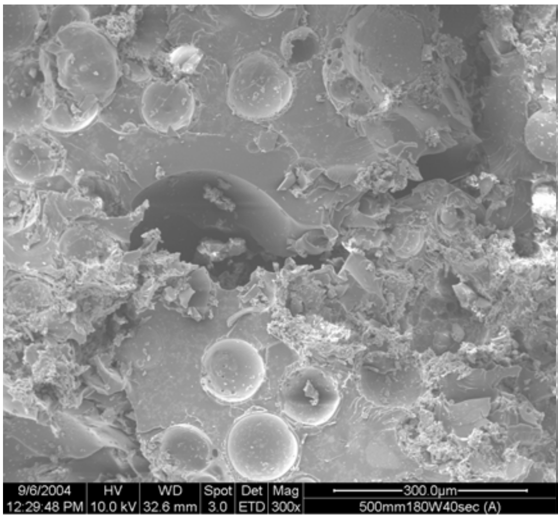
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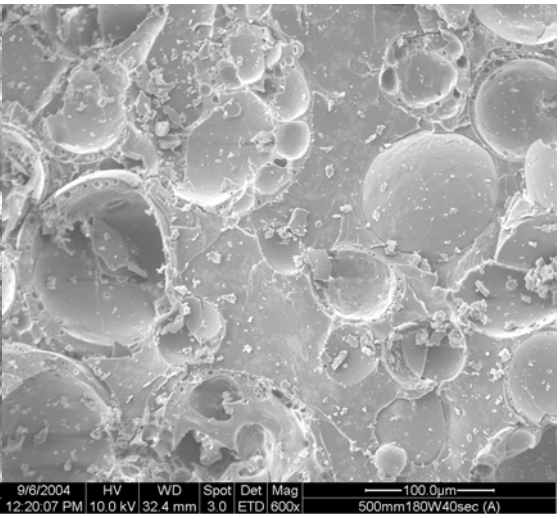
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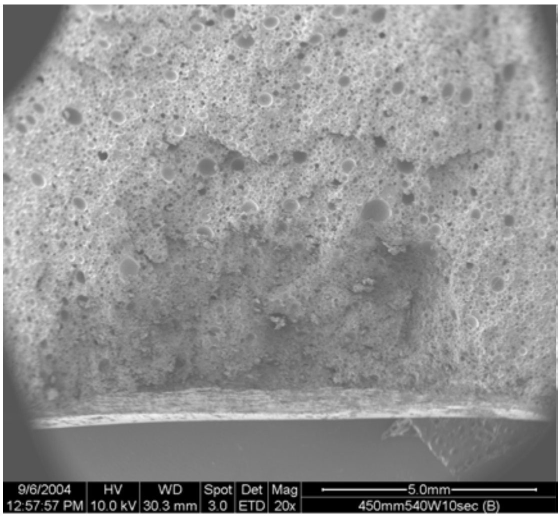
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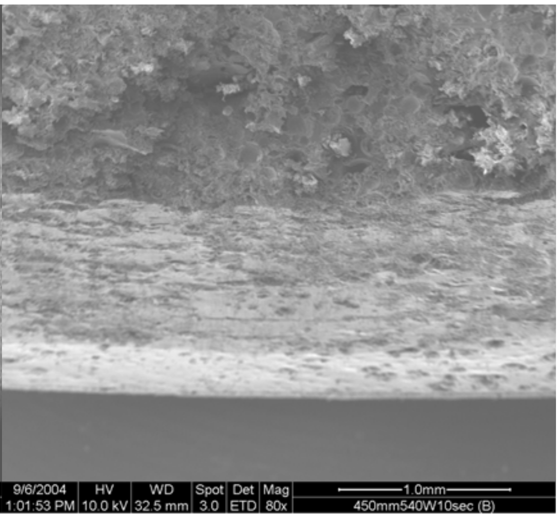
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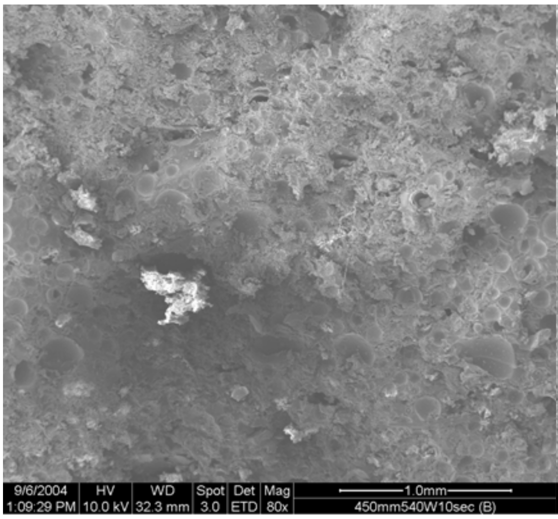
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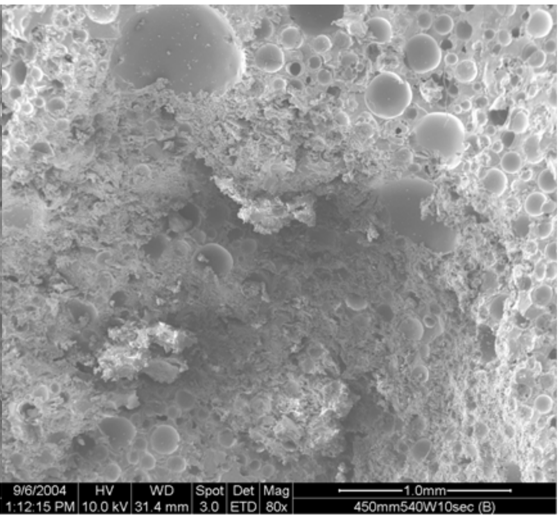
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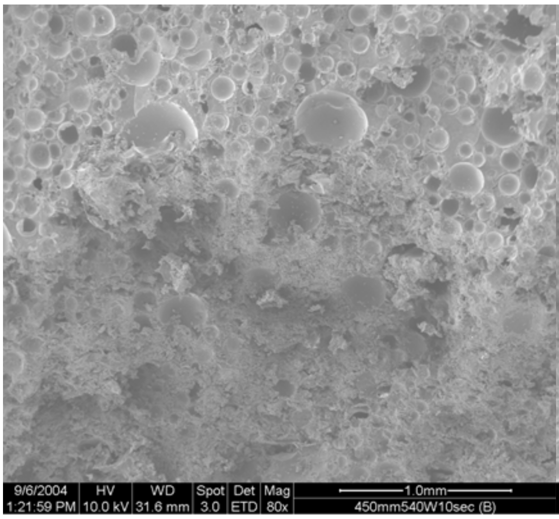
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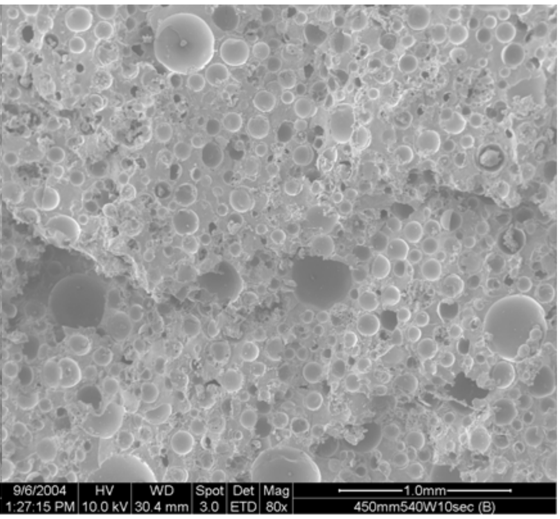
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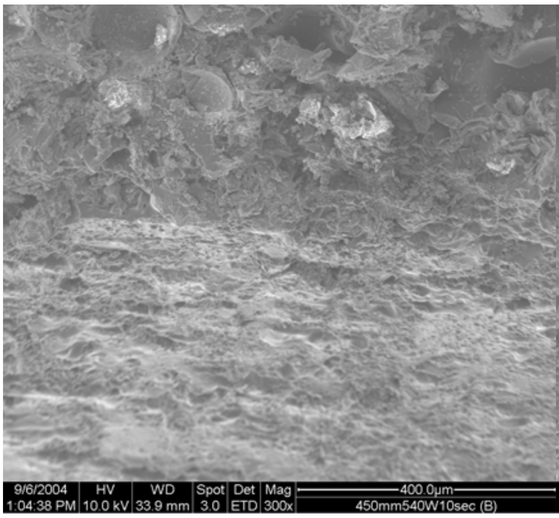
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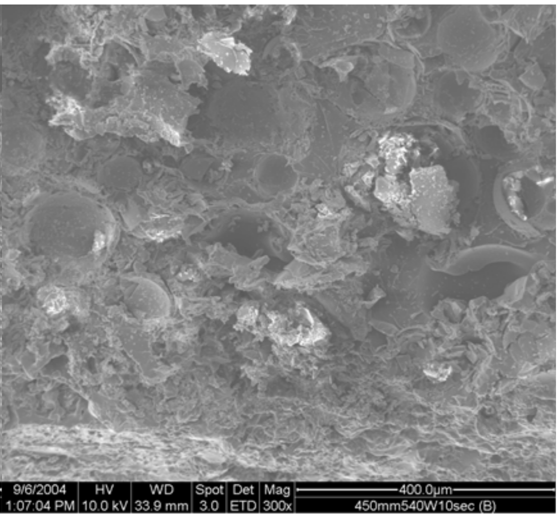
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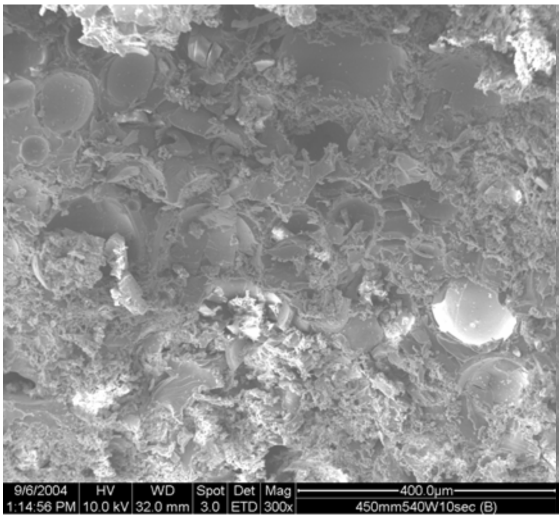
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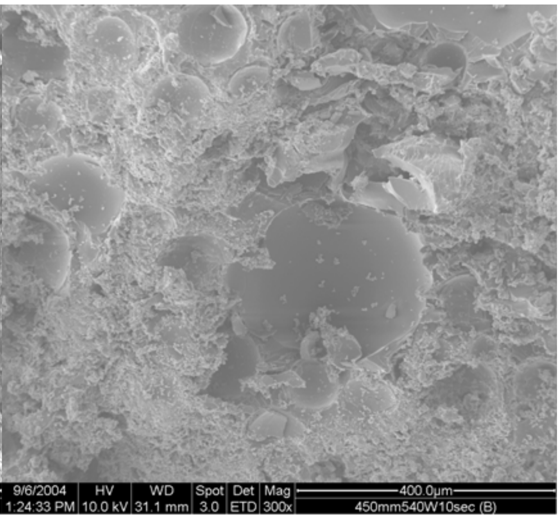
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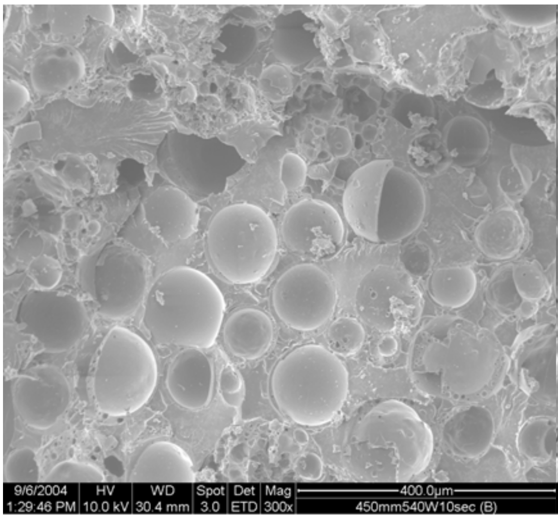
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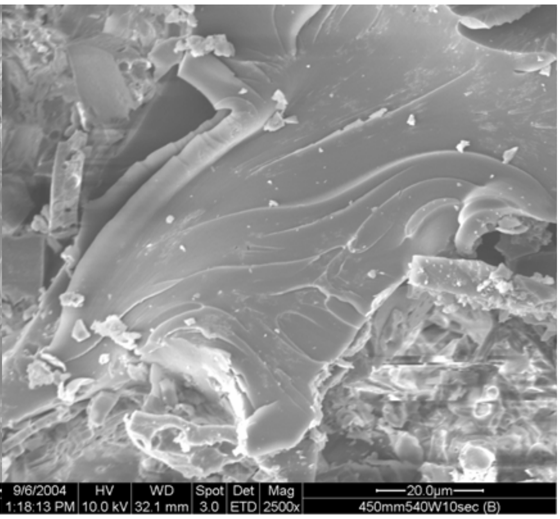
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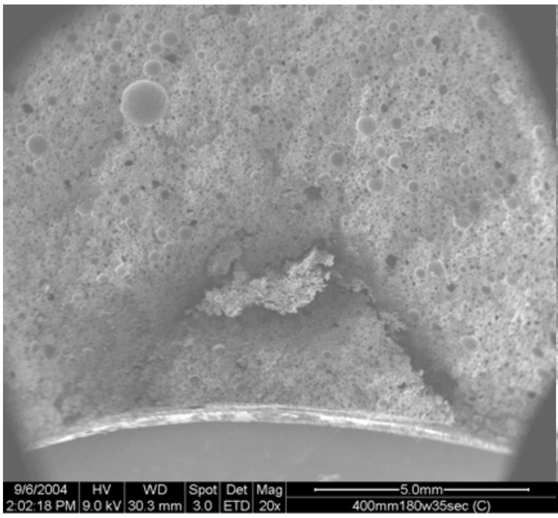
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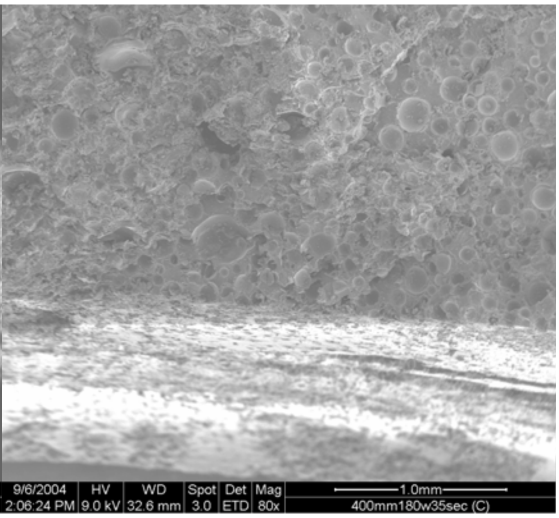
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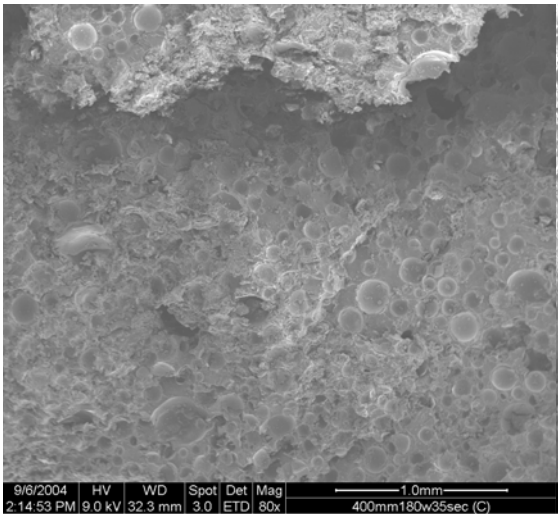
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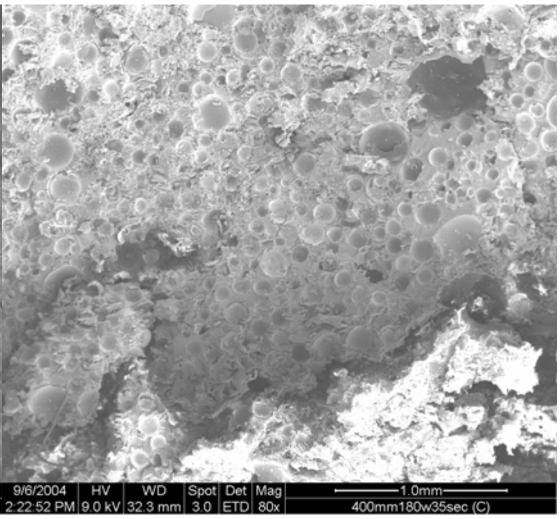
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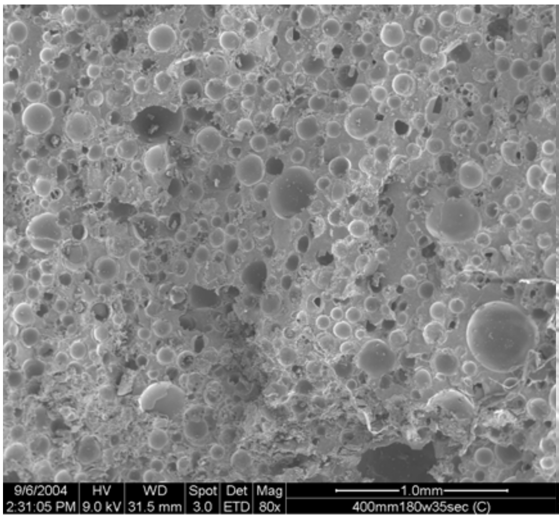
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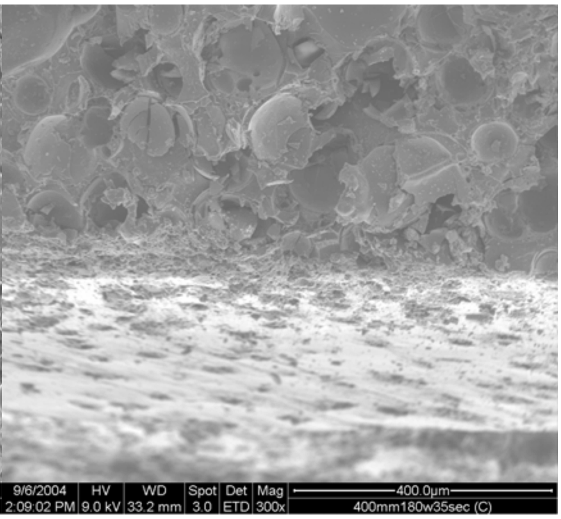
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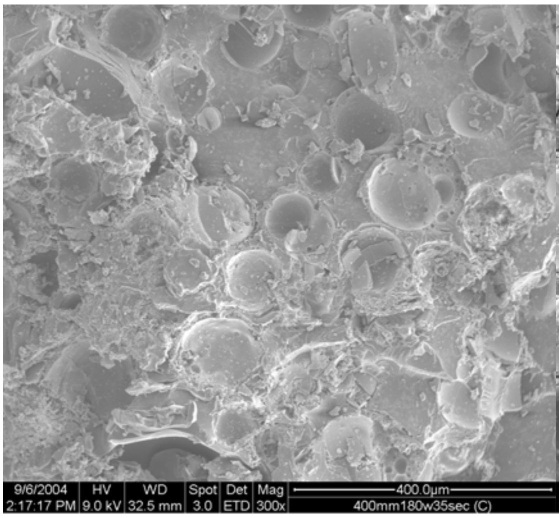
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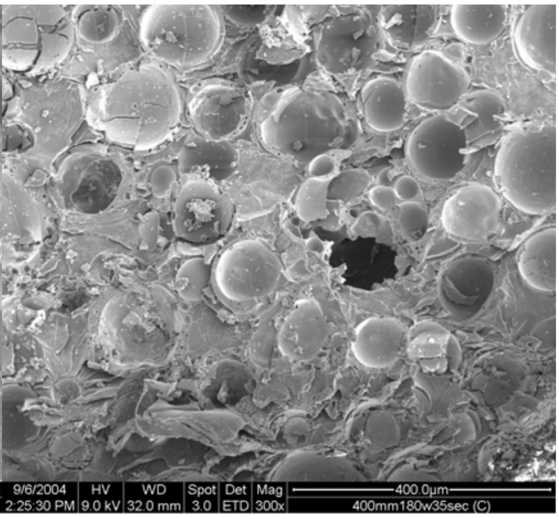
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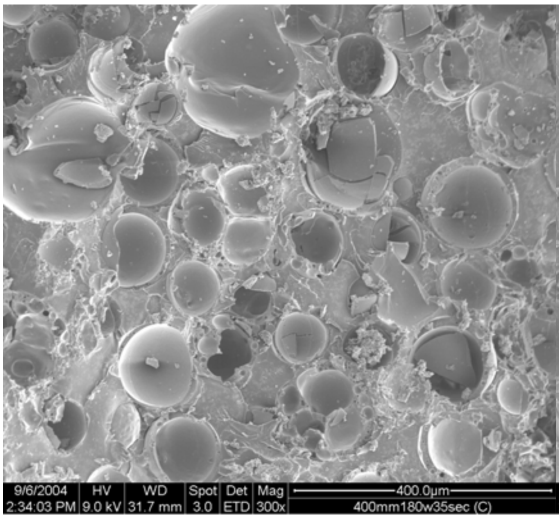
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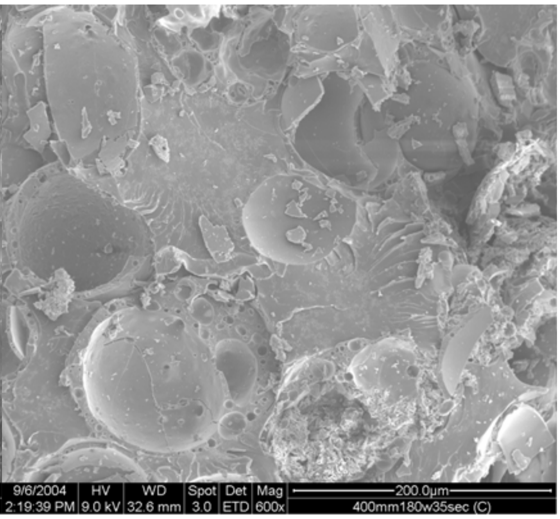
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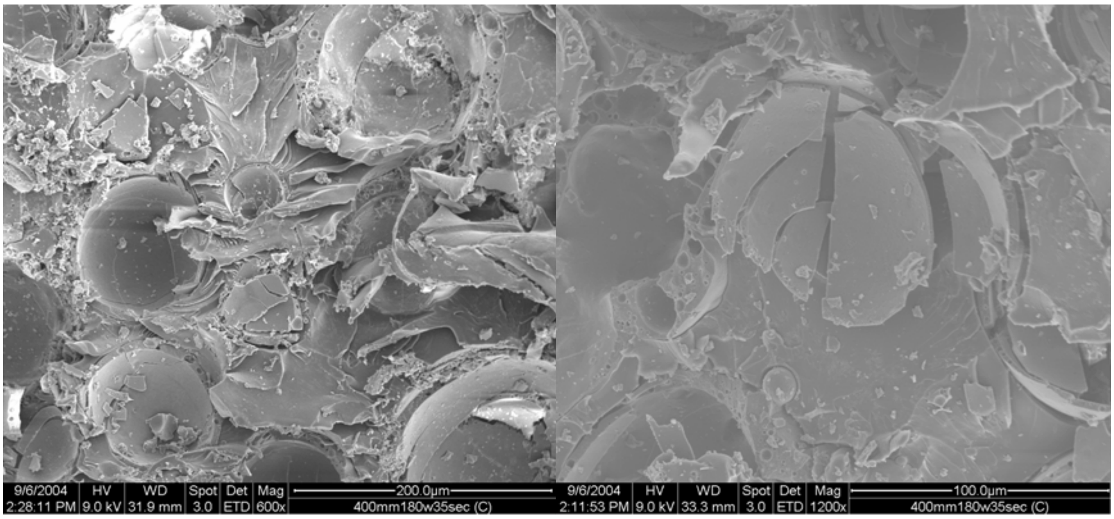
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Table 8.1: Viewing results from SEM, Impact Specimens (VE/FLYASH (33%))

Investigation Fracture Surface of Five Areas		
Area	Microwave Condition	
	Specimens A1 (180Watts;40seconds;500mm)	Specimen A2 (540Watts;10seconds;450mm)
1	A big crushed on the top surface (curving area) of the specimens was shown in Figure 6.9.	Most of the phenomenon was same with specimen A1 and nothing special was found in this area 1. .
2	Figure 6.10 showed the fracture surface started in this area 2. This area 2 showed a curving fractured surface. A small void was found when the magnification increase to 600X.	Same case with specimen A1 but the fracture surface was a little bit longer.
3	50% of crushed zone was found and 50% of fractured propagation zone was found. Besides that, a secondary cracking was found. The force was pulled to different directions from area 3.	70% of crushed zone was found and 30% of fractured propagation zone was found. Some small pieces of debris were found on the cracked surface when the zooming was increased to 2500X.
4	Another secondary crack was in this area 4. 90% of fractured propagation zone was found and 10% of crushed zone was found.	Less debris appeared as compared with specimen A1. Brittle fracture was also found in this area. Crack was also found propagating through fly ash particle. Particle de-bonding present.
5	Figure 6.9 showed some small pieces of debris were on the crack surface. A secondary crack was found in 600X zooming and a direction of crack growth to left hand side.	Figure 6.11 showed much of brittle fracture area appeared in the crack propagation zone. There was a lot of small bubble in fractured propagation zone.

Table 8.2: Viewing results from SEM, Impact Specimens (VE/FLYASH (33%))

Investigation Fracture Surface of Five Areas		
Area	Microwave Condition	
	Specimen B (540Watts;10seconds;450mm)	Specimen C (180W,30seconds,400mm)
1	This is a low magnification micrograph, taken at 20X. Shows area of crushed zone, typical cup and cone x-section. Crushed zone in lower half. Large no. of voids present in upper level	General 20X micrograph, same as for specimen B. Voids present, much less debris
2	Magnification 80. close up of lower section, lot of debris, pointy surface texture. Hollow spheres present, not uniform in diameter and not spherical, particle de-bonding and cracked particles.	Little debris, much the same as for B, noticeably clean topography80X, at mag 300X..cleavage can be seen cracks run around particles, de-bonding and partial particle cracking
3	This is the top part of the cup section. Beginning of clear section. Less debris at top of image. Many cracks, matrix cracking and secondary cracking present. Image at 80X	Onset of cleavage apparent, multiple crack paths, ductile features not noticeable – may be some but cannot see due to material??? 80X 300X..cleavage can be seen cracks run around particles, de-bonding and partial particle cracking
4	Large void in top left Many voids, crack propagation through spheres, micro cracking, and micro-void coalescence. Still a lot of debris at bottom of image. 80X	Relatively clean fracture through particles, porosity present. Fracture through matrix looks clean and smooth at this low mag.80X 300X..cleavage can be seen cracks run around particles, de-bonding and partial particle cracking
5	Good packing of spheres, number of voids present. Overall clean with cracking of matrix and through spheres. 80X at 300x can see define shear cleavage occurring in steps emanating from around the particles. Particle de-bonding from matrix.	Very good depiction of cleavage an driver line patterns…..at 300X, 600X and 1200X, hollow spheres actually have porosity within them.

Table 8.3: Viewing results from SEM, Short Bar Fracture Test (VE/FLYASH (33%))

Investigation Fracture Surface of Five Areas		
Area	Microwave Condition	
	Specimen D (unknown)	Specimen E (unknown)
1	Mag. 22X. porosity and fibrous inclusions from cardboard present. At 100X, large voids present, fracture through matrix and particle.500X, debris and possibly river line pattern	General 20X micrograph, same as for specimen B. Voids present, much less debris, porosity, fibrous material -paper ,pronounced crack around particles
2	Much the same, multiple cracks, cleavage at 100X, 500X – river line patterns hollow sphere has inclusions inside it-not hollow?, cleavage, little cracks and de-bonding.	Fibrous material – paper, voids, crack through particles, pronounced crack around particles.
3	Porosity of particles, definite river line pattern	Crack and multiple cracking around particles with particles intact, cleavage, particles seem to want to de-bond from matrix
4	River line patterns, through the matrix. Crack through particles.	Definite de-bond behaviour associated with multiple crack propagation in matrix. Most cracks have past straight through particles-clean cut at 500X
5	Much the same as for impact, crack through particles, debris, river line patterns, debris in hollow shell of particle.	Same as above. There seems to be a slope on the crack surface. Some of these slopes meet each other at an angle.