OPTIMISATION AND FABRICATION OF RAW MATERIAL COMPONENT FOR POLYMER WALL

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering

Faculty of Engineering and Science
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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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ABSTRACT

An epoxide resin reacts with a polyamine hardening agent to form a thermosetting polymer called epoxy. Epoxy is therefore a copolymer, formed from two chemicals, which undergo a polymerization process called "curing". In this investigation, epoxy was cured with fibre-reinforcement using fibres extracted from 'Ananas Comosus' fruit, or more commonly pineapple fruit. The volume ratio between epoxide, hardening agent and pineapple fibres were varied to obtain a range of result material. The resulting chemical & mechanical properties were investigated. SEM was carried out to show the facture points surface. EDX analysis showed no contaminants that would affect test results. The chemical resistance to corrosion of the resulting pineapple fibre-reinforced epoxy was investigated using an immersion test. The mechanical properties were investigated using the Tensile test and Hardness test.

Results showed an increase in hardness, a good resistance to corrosion and decreased tensile strength, which was properly explained in the report. An increase of 35% in hardness was observed in the reinforced material. No significant surface corrosion was observed when exposed to concentrated acids. The tensile strength of the optimised reinforced epoxy achieved was 31.73 MPa, which is above the generally accepted range of epoxy tensile strength (12-30 MPa). The surface structure and composition was analysed by SEM and EDAX, and a possible cause for the decrease in tensile strength was proposed.

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LIST OF SYMBOLS / ABBREVIATIONS

HR	Rockwell Hardness Number
E	Indenter Constant
e	Permanent increase in penetration depth
P	Applied load, kg
L	Average length of diagonals, mm
θ	Angle between opposite faces of diamond = 136°.

SEM	Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy
TETA	Triethylenetetramine
GRP	Glass-reinforced plastic
BSE	Back-scattered electrons
DOE	Design of Experiment

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CHAPTER 1

INTRODUCTION

1.1   Background

Epoxide resins mixed together with a polyamine hardener form a hard material called epoxy. The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fibre and fibreglass reinforcements. These can often be found in industries involving aerospace, wind energy, marine, electrical systems, and industrial tooling.

The favourable properties that epoxy materials show are; high hardness, good tensile strength, and high chemical resistance to corrosion. When used as a matrix material, epoxy can be reinforced with fibres, to increase these favourable properties. There has been extensive research on the effects of different fibre materials used, and the resulting consequence on the mechanical properties. This gives ground to consider less common fibre, organic pineapple fibre, while extending previous experimental literature by investigating chemical properties, and fibre structure at a microscopic level.

1.2 **Aims and Objectives**

The aim of this study is to investigate the chemical and mechanical properties of fibre-reinforced epoxy, internally reinforced with pineapple fibres.

1.3 **Research Objectives**

➢ To study the surface structure of the fibres using SEM
➢ To study the chemical characterisation of the fibres using EDX analysis
➢ To investigate chemical corrosion resistance of the reinforced epoxy using Immersion test.
➢ To investigate the tensile strength of the reinforced epoxy
➢ To investigate the hardness of the reinforced epoxy

CHAPTER 2

LITERATURE REVIEW

2.1   Epoxy

Epoxy or polyepoxide is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fibre-reinforced plastic materials and general purpose adhesives. (Green, 2005)

As mentioned by Professor Joseph Greene (2005), "epoxy is a copolymer; that is, it is formed from two different chemicals. These are referred to as the "resin" and the "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end."

Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals. The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily cross-linked, and is thus rigid and strong. (Green, 2005)

Such cross-linking gives the epoxy material favourable properties such as high tensile strength and hardness. Thus making it ideal as a matrix material for our investigation as a potential reinforced material for polymer wall.

2.2   Epoxy Chemistry

Ebert and Teraoka (1991) studied the mechanism at which the epoxide would attach to the polyamine. The basic adhesive chemistry involves a diepoxide and a polyfunctional amine, leading to a crosslinked system. The diepoxide is almost always derived from Bisphenol A and epichlorohydrin. Control of the reaction conditions can produce either a simple diglycidyl derivative of Bisphenol A or oligomeric compounds with epoxide end groups.
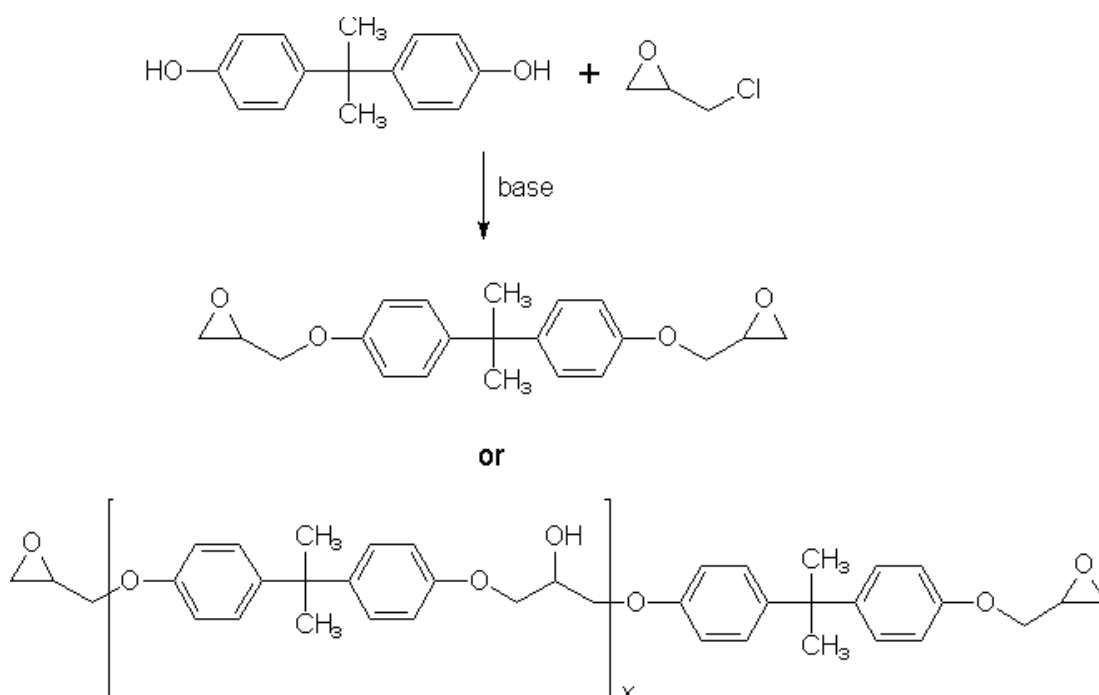
Figure 2.1: Epoxy polymerisation

Despite appearances, the initial attack of the phenolate nucleophile is not at the carbon bearing chlorine, but rather at the least substituted carbon of the epoxide. Internal ring closure reforms the epoxide ring. (Ebert, M. et al.)
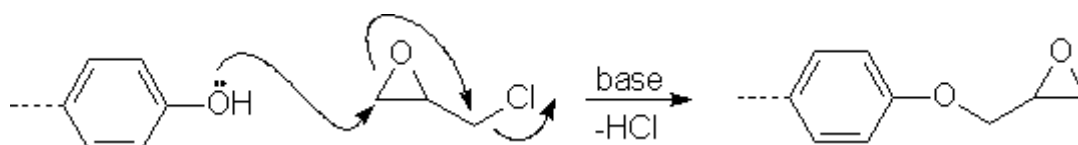
Figure 2.2: Phenolate Nucleophile attack mechanism

The polyfunctional amine can be a simple small molecule or an oligomeric compound with primary amine end groups. To use as an adhesive, the two components are simply mixed together and allowed to react. The rate of curing depends on the reactivity of the nucleophile and the temperature. (Ebert, M. et al.)

Room temperature was used for the initial curing of the reinforced experimental samples.
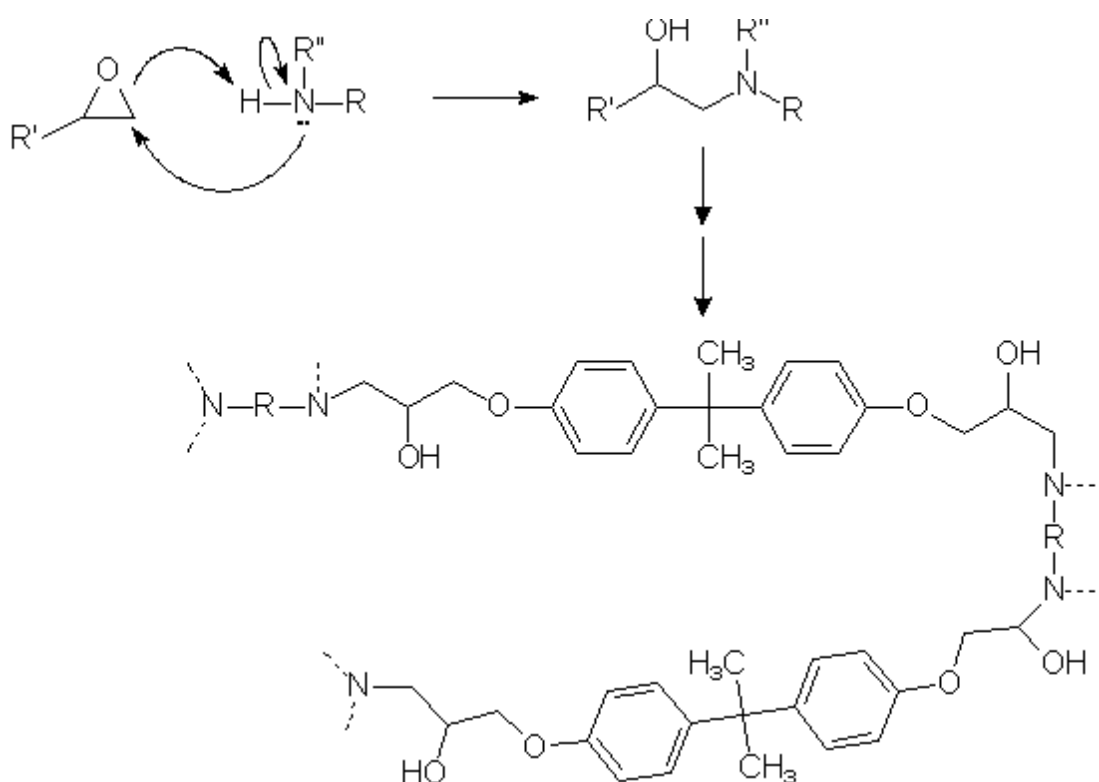
Figure 2.3: Crosslinking between monomer

The resulting network will not dissolve in any solvents, and resists all but the strongest chemical reagents. The plurality of OH groups provides hydrogen bonding, useful for adhesion to polar surfaces like glass, wood, etc. Epoxy polymers are often used to form composite structures filled with glass or carbon fibre. (Ebert, M. et al.)

The same mechanism will apply for the experiment in this report, utilising pineapple fibres.

2.3 Polyamine Hardeners

There are many different types of hardeners available and polyamine based hardeners are a common type. Polyamine hardeners are made up of an organic molecule containing two or more amine groups. Other types of hardeners include polyamide hardeners and anhydride hardeners, although these types react only with heat. Polyamine hardeners used by the composites industry are usually made up of more then one polyamine compound and other additives to give the required properties. (Composites Australia, 2004)

Polyamine hardeners are corrosive liquids and some are moderately toxic. They can cause irritation and chemical burns of the skin and eyes. If polyamine hardeners come in contact with the skin, sensitisation can occur. This can occur after short or long term exposure. Once a person has become sensitised, any future exposure results in an allergic response. Effects include dermatitis of the skin and redness and irritation of the skin and eyes, even with minimal exposure. (Composites Australia, 2004)

2.4 Matrix Material

The matrix material in fibre-reinforced plastics has three functions. The first is to support the fibres in place and transfer the stress to them. In this way, they can carry most of the load. The second function is to protect the fibres against physical damage. The third function is to reduce the propagation of cracks in the composite, by virtue of the greater ductility and toughness of the plastic matrix. (Kalpakjian & Schmid, 2002)

The matrix material usually consists of a thermoplastic or thermoset. These are commonly resins such as polyester, vinyl ester, phenolic, polyehersulfone, silicon or epoxy. In this report, epoxy is used as the matrix material.

2.5 Fibreglass

Fibreglass, also known as Glass-reinforced plastic (GRP), is a fibre reinforced polymer made of a plastic matrix reinforced by fine fibres made of glass. GRP is a lightweight, strong material with many uses, including boats, automobiles, water tanks, roofing, pipes, cladding and external door skins. The plastic matrix may be epoxy, a thermosetting plastic (most often polyester or vinylester) or thermoplastic. (Mayer, 1993)

As discussed by Nawy (2001), an individual structural glass fiber is both stiff and strong in tension and compression, that is, along its axis. The glass fiber is not stiff or strong in shear across its axis. Therefore if a collection of fibers can be arranged permanently in a preferred direction within a material, and if the fibers can be prevented from buckling in compression, then that material will become preferentially strong in that direction.

In this report, the fibres used are pineapple fibres. When encased in the matrix material, they will show similar mechanical strengths to that of fibreglass.

By laying multiple layers of fiber on top of one another, with each layer oriented in various preferred directions, the stiffness and strength properties of the overall material can be controlled in an efficient manner. In the case of glass-reinforced plastic, it is the plastic matrix which permanently constrains the structural glass fibers to directions chosen by the designer. With chopped strand mat, this directionality is essentially an entire two dimensional plane; with woven fabrics or unidirectional layers, directionality of stiffness and strength can be more precisely controlled within the plane. (Nawy, 2001)
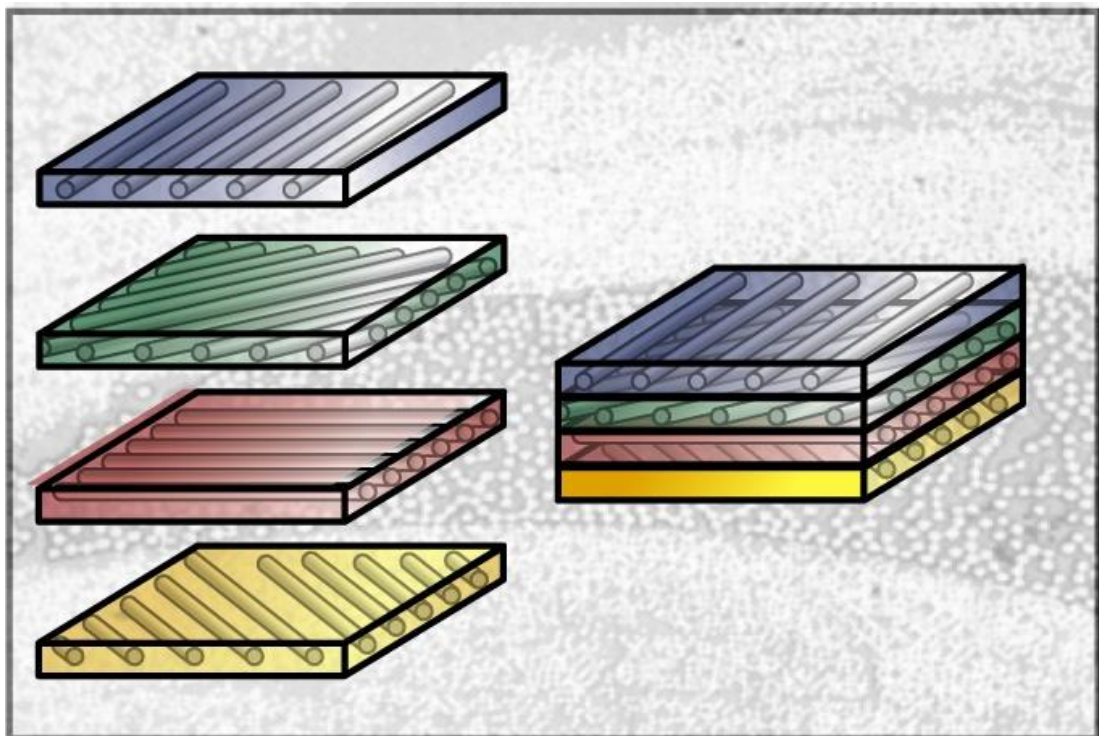

Figure 2.4:Layered fibre of differing orientation.

Epoxy resins are an important class of thermosetting polymers with many applications. Hence, much effort has been made so far in preparing fibre/epoxy composites using various methods including solution casting, ultrasonication, high shear mixing, chemical modification, and any combinations of these. (Qing-Ping et. al. 2010)

2.5.1 Organic Fibres - Pineapple

Fibre-reinforced polymeric composites have received widespread attention in the past four decades because of their high specific strength and modulus. Composites using high strength fibres such as graphite, Aramid and glass are commonly used in a broad range of applications from aerospace structure to automotive parts and from building materials to sporting goods. Lately, there has been a growing interest in the use of natural cellulosic fibres as the reinforcement for polymeric matrix. While these fibres may not be as strong as carbon and Aramid, their main advantages are low cost and biodegradability. (R.M.N. Arib 2006)

Pineapple fibre, which is rich in cellulose, relative inexpensive and abundantly available has the potential for polymer-reinforced composite. The present study investigates the tensile and hardness behaviours of pineapple fibre–epoxy composites as a function of volume fraction.

The cellular structures of the plant fibres also provide excellent insulation against heat and noise. Further, most cellulosic fibres are harvested yearly and the supply should be inexhaustible compared to the limited supply of the oil reserve from which many synthetic fibres are derived. (R.M.N. Arib 2006)

It is reported by George et al. (1995), that owing to the high price of composites, the user industries also demand a lower price for production of fibre components, at the same time with an improvement in quality. It was found that these could be achieved by the use of natural fibres.

As fibre-reinforced composite structures are taking the central stage in almost every sphere of material science, lingo-cellulosic natural fibres like pineapple fibres (PALF) come as viable and abundant substitutes for the expensive and non-renewable synthetic fibres. These with high specific strength improved the mechanical properties of the polymer matrix. In tropical countries, fibrous plants are available in abundance and at least some of them are agricultural crops. Pineapple is among them. PALF at present is a waste product of pineapple cultivation. Hence,

without any additional cost input, pineapple fibres can be obtained for industrial purposes. (L.U. Devi 1997)

Among various natural fibres, pineapple leaf fibres exhibit excellent mechanical properties. These fibres are multicellular and lignocellulosic. They are extracted from the leaves of the plant *Ananus cosomus* belonging to the Bromeliaceae family by retting. The main chemical constituents of pineapple fibres are cellulose (70–82%), lignin (5–12%) and ash (1.1%). The superior mechanical properties of pineapple leaf fibres are associated with their high cellulose content. (L.U. Devi 1997)

2.5.2   Fibre – Matrix interface

In reference to a similar project, published in the Materials & Design Journal, 22 July 2011, epoxy polymers were reinforced with carbon fibres, whereby Carbon Nano-tubes (CNTs) were uniformly grown onto the carbon fibres. (Feng, 2011)
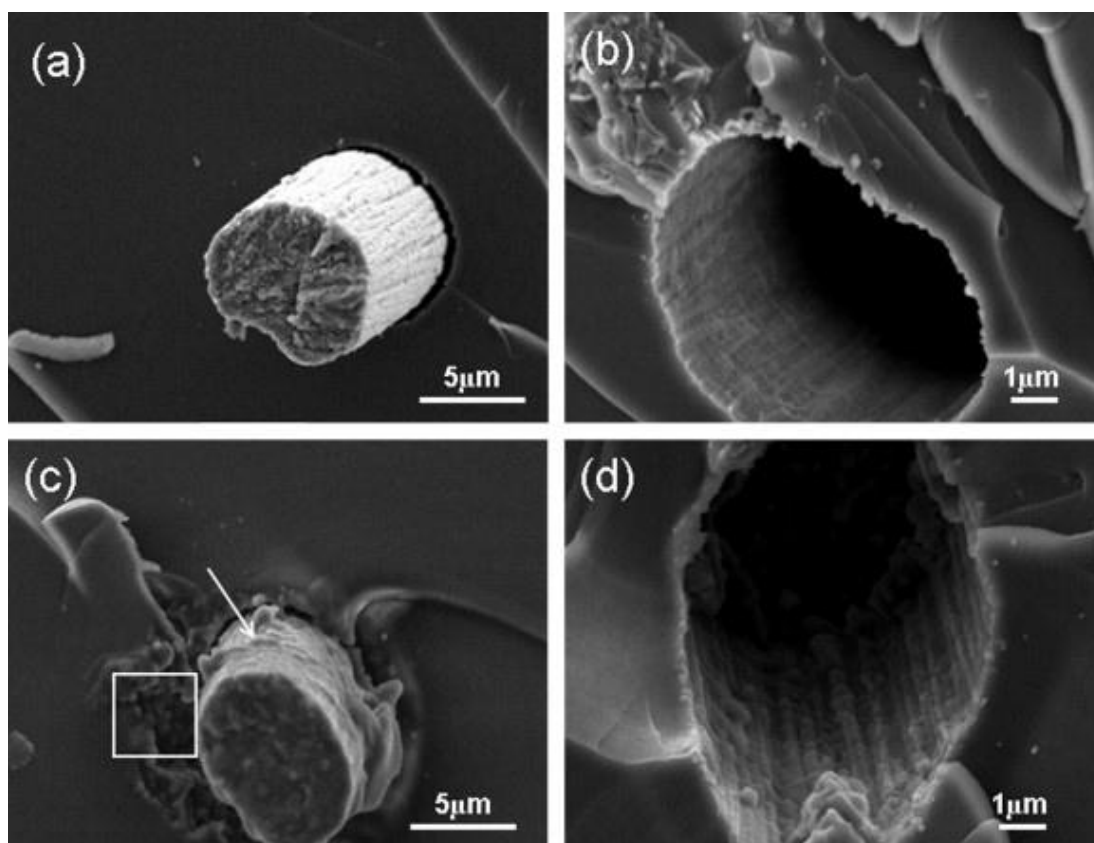

Figure 2.5: SEM Image of Carbon Fibre Reinforced Epoxy

The SEM images in figure 2.5 show the typical fractured surfaces of epoxy composite reinforced by a carbon fiber (Fig. 2.5a and b) and CNT-hybridized carbon fiber (Fig. 2.5c and d). Without CNTs grown onto carbon fiber, as shown in Fig. 2.5a, an obvious crack appears at the joint of matrix–fiber and indicates a **brittle** fracture. (Feng, 2011)

A small gap can be observed between the fibre and the surrounding polymer. Therefore, it is judged that the fracture planes initiated at the interface between matrix and fiber. From the enlarged SEM image of Fig. 2.2b, the internal surface of hole after pulling out a fiber is relatively smooth, indicating debonding along the fiber-matrix interface because of a poor adhesion. In contrast, due to the presence of CNTs, as shown in Fig. 2.2c, no crack can be observed. (Feng, 2011)

This debonding is unfavourable, as it reduces the shear and tensile forces transferred between the fibre and epoxy when the sample is pulled. In the case of pineapple reinforced epoxy, it is somewhat complex to grow carbon nanotubes onto the fibres, thus this method of increased bonding is emitted as it is not the focus of the project.

According to Feng (2011), when the fibre is pulled, the load can be transferred to the CNTs in the form of both shear and tensile forces. Then the stresses in the CNT transferred to the surrounding matrix through the CNT/matrix interface. Therefore, the presence of CNTs changes the interface behavior, which in turn leads to difference in fracture morphology of composite.

It therefore confirms that the grafting of CNTs on carbon fibre helped in creating locally interlocking between the fibers and the matrix. As illustrated in Fig. 2.2d, the CNT-carbon fibre pullout hole is fairly rough, and indicates the force of pulling out fiber from epoxy matrix increases a lot than pulling out an original fiber due to an improved frictional force resulting from the presence of Carbon nanotubes. (Feng, 2011)

As mentioned earlier, the pineapple fibres used will be unmodified after extraction from the fruit. The interface between fibre and epoxy will be shown in SEM results section of this report.

2.6   Mechanical Testing

The properties that can be obtained through mechanical testing are the stress, strain, elongation, yield point, yield strength, proportional limit, modulus of elasticity, ultimate strength, and many more. (Vishu, 1998)

The stress is the force applied to produce deformation in a unit area of a test specimen. Stress is a ratio of applied load to the original cross-sectional area. The strain is the ratio of the elongation to the guage length of the test specimen, or change in length per unit of the original length. The elongation is the increase in the length of a test specimen produced by a tensile load. (Vishu, 1998)

In this report, the mechanical properties investigated are the Tensile strength and Hardness.

2.6.1   Tensile Test

Tensile testing, also known as **tension testing**, is a fundamental materials science test in which a sample is subjected to uniaxial tension until failure. (Horst, 2006)

The results from the test are commonly used to select a material for an application, for quality control, and to predict how a material will react under other types of forces. Properties that are directly measured via a tensile test are ultimate tensile strength, maximum elongation and reduction in area. From these measurements the following properties can also be determined: Young's modulus, Poisson's ratio, yield strength, and strain-hardening characteristics. (Davis, 2004)

The most common testing machine used in tensile testing is the *universal testing machine*. This type of machine has two *crossheads*; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen. There are two types: hydraulic powered and electromagnetically powered machines. (Davis, 2004)

2.6.2   Hardness Test

The Vickers hardness test was developed in 1924 by Smith and Sandland at Vickers Ltd to measure the hardness of materials. The basic principle, as with all common measures of hardness, is to observe the questioned material's ability to resist plastic deformation from a standard source. The Vickers test can be used for all metals and has one of the widest scales among hardness tests. The unit of hardness given by the test is known as the Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH). The hardness number can be converted into units of pascals, but should not be confused with a pressure, which also has units of pascals. The hardness number is determined by the load over the surface area of the indentation and not the area normal to the force, and is therefore not a pressure. (Smith and Sandland, 1922)

The hardness number is not really a true property of the material and is an empirical value that should be seen in conjunction with the experimental methods and hardness scale used. (Smith and Sandland, 1922)

2.7   Energy-Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing

X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another. (Mukasyan, 2010)

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was.

An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. (Mukasyan, 2010)

2.8   Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. In a typical SEM, an electron beam is

thermionically emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter.

The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface.

Sputter coating in microscopy is a process of covering a specimen with a very thin layer of metal, generally a gold/palladium (Au/Pd) mixture. This coating increases the ability of a specimen to conduct electricity and emit secondary electrons when in a scanning electron microscope, acting as a "stain" for electron microscopy. Biological specimens, composed largely of carbon compounds, are usually poor emitters of secondary electrons due to the low atomic number of carbon. Rather than absorbing electrons from the electron source of the microscope and then emitting electrons for detection, carbon compounds tend to collect a charge. (Newbery, 1986)

In this project, a gold/palladium mixture was used to coat the SEM specimen prior to SEM imaging. The results are shown in the SEM results section of this report.

2.9 Immersion Test

Immersion Test can be used to investigate the resistance to corrosion of the specimen. Simple immersion tests basically involve small sections of the candidate material exposed to the test medium and the loss of weight of the material is measured for a period of time. Immersion testing remains the best method of screening and eliminating from further consideration those materials that should not be considered for specific applications. But while these tests are the quickest and most economical

means for providing a preliminary selection of best suited materials, there is no simple way to extrapolate the results obtained from these simple tests to the prediction of system lifetime. (Roberge, 2009)

This method can be used to compare the relative resistance of the specimens to typical chemical reagents. The temperature of the test, duration and concentration of the reagent are to be considered in this study.

CHAPTER 3

METHODOLOGY

3.1   Preparation of Specimens

During the curing process, it must noted that different ratios of epoxide resin to hardening agent will result in different mechanical and chemical properties of the final cured specimen. Therefore, a set of varying ratios are obtained.

Table 3.1: Ratio of Epoxy & Polyamine Hardening Components

Run No.	Epoxy Resin Component A:A (ml)	Hardening Component B:B (ml)
1	0.80	1.00
2	1.00	1.00
3	1.50	1.00
4	2.00	1.00
5	2.50	1.00
6	3.00	1.00

The Epoxy resin and Polyamine hardening agent will be added in the above ratios. The specimens are then cured using Hand Lay-up curing method in a pre-prepared mold. The impregnated fibre-epoxy was allowed to cure for 12 h at room temperature under normal pressure.

To investigate the effect of pineapple fibre reinforcement, the pineapple fibres will be added during the curing process with varying percentage of volume.

Table 3.2: Volume Percentage of Pineapple Fibre for Specimens

Specimen No.	Vol. % of Epoxy	Vol. % of Pineapple fibre
1	95	5
2	90	10
3	85	15
4	80	20
5	75	25
6	70	30

Figure 3.1: Fibre

The curing of all specimens take place at room temperature. From their respective moulds, two shape types are obtained, the dumbbell type, and square type. The Dumbbell shaped specimens are used for the tensile test, whereas the square type will be used for hardness and immersion test.

Dimensions for dumbbell type specimen:

Thickness = 9 mm, Width = 13 mm, Length = 23 cm

Dimensions for square type specimen:

Thickness = 7 mm, Width = 24 mm, Length = 24 mm
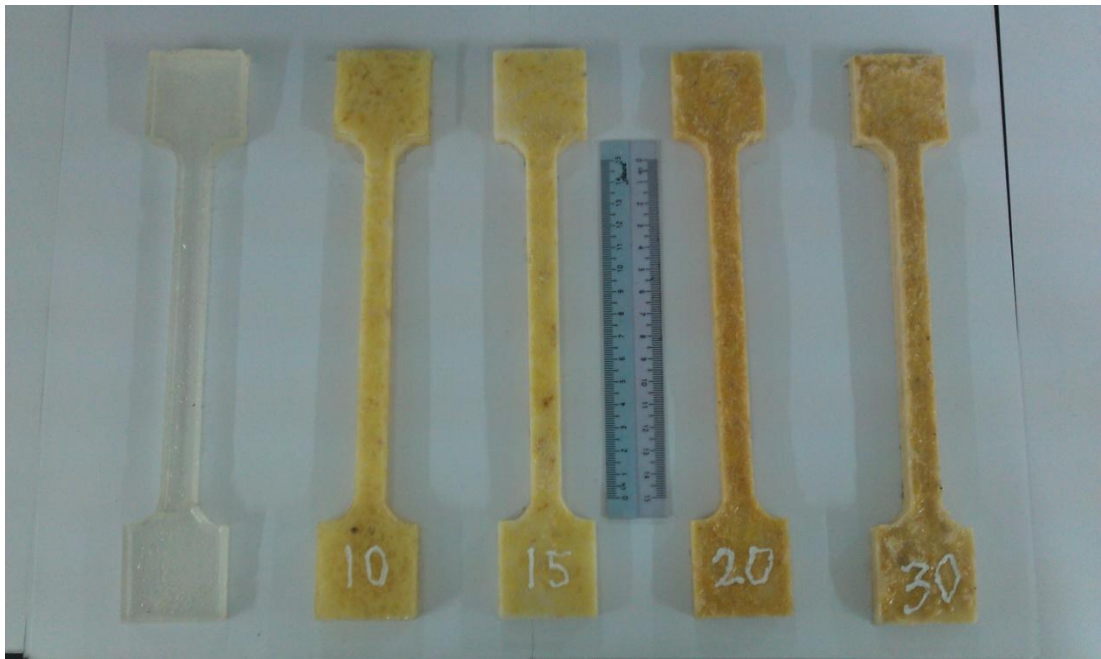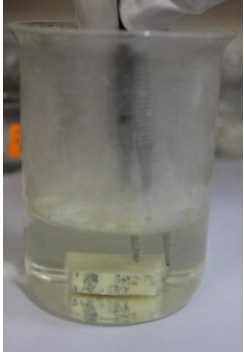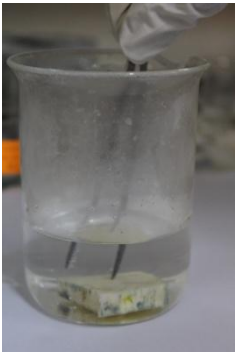
Figure 3.2: Samples
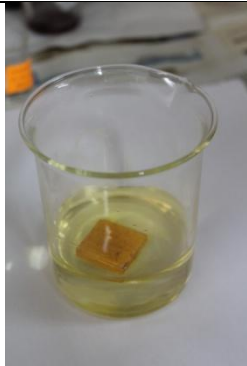
3.2   Immersion Test

Hydrochloric acid with a concentration of 36% and Sulphuric acid of 96% were prepared in beakers. Each square specimen is put into a beaker of 200ml of acid. The specimens will include the pineapple fibre reinforced epoxy and epoxy matrix

3.2.1   Immersion Test with 36% HCL

Specimen	With 36% Concentrated HCL	Specimen	With 36% Concentrated HCL
0% Volume Fibre		20% Volume Fibre	
5% Volume Fibre		25% Volume Fibre	
10% Volume Fibre		30% Volume Fibre	
15% Volume Fibre			

3.2.2   Immersion Test with 96^ Sulphuric Acid

Specimen	With 96% Concentrated Sulphuric Acid	Specimen	With 96% Concentrated Sulphuric Acid
0% Volume Fibre		20% Volume Fibre	
5% Volume Fibre		25% Volume Fibre	
10% Volume Fibre		30% Volume Fibre	
15% Volume Fibre			

3.3 Scanning Electron Microscopy

The pineapple fibres will undergo observation through SEM. These will be similar to the fibres used in the epoxy matrix, as they will be of the same source. SEM will allow detailed microscopic images to further describe the surface structure of these fibres.

A gold/palladium mixture was used to coat the SEM specimen via sputter coating prior to SEM imaging.

3.4 Energy-Dispersive X-ray spectroscopy

The pineapple fibres underwent observation through EDX. Similar to the SEM analysis, the fibres used were from the same source as those used in the epoxy matrix. This will give us a clearer picture of the chemical characterization of the fibres.

3.5 Tensile Test

For the tensile test, the equipment used is the INSTRON 5582. The dumbbell type specimens are placed in the grips of the machine at a specified grip separation and pulled until failure. For ISO 527, the test speed is typically 5mm/min or 50mm/min for measuring strength and elongation. For measuring modulus, 1mm/min is used. An extensometer is used to determine elongation and tensile modulus.

Figure 3.3: INSTRON 5582 – Tensile Test equipment

3.6 Hardness Test

The Hardness of the specimens are investigated using the INDENTEC 4150LK Rockwell Hardness Tester. The specimen is placed on the anvil of the apparatus a minor load is applied by lowering the steel ball tip onto the surface of the specimen. The minor load indents the specimen slightly and ensures contact between specimen and tip.

The indenter is pressed into the surface of the test piece using a two step application - a preliminary force P followed by an additional test force. The preliminary force should be applied and maintained for a duration that shall not exceed 3 s. The increase in force from the preliminary force condition to the total test force F should occur in between 1 and 8 s. This force is then maintained for a duration of 4 ± 2 s. The additional force is then removed and, while the preliminary force is maintained, the reading is made after a short stabilisation time. The result of the test is read directly from the machine as:

$$HR = E - e$$

where: E = indenter constant, and
        e = the permanent increase in penetration depth.

This allows us to determine the increase in hardness of the specimens when preparing the specimens with higher volume percentage of fibre.

Figure 3.4: INDENTEC Rockwell Hardness Tester

3.7   Micro Hardness Testing

Hardness measurements when carrying out the Micro Hardness Testing are generally measured using a Vickers hardness test. In this test a pyramidal diamond indenter is pressed into a polished surface under known loading conditions and the size of the indentation is related to the hardness of the material.

It should also be noted that the hardness value quoted for any material is a function of the type of test conducted and the loading conditions employed. Lighter loads typically provide higher hardness values.

Figure 3.5: Micro Hardness Tester
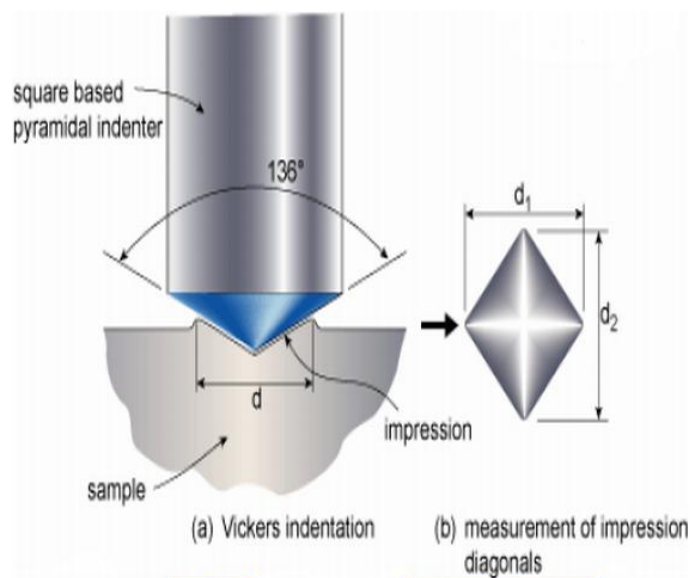
Figure 3.6: Vickers Test Indenter

The Vickers hardness test uses a square-base diamond pyramid as the indenter with the included angle between opposite faces of the pyramid of 136°. The test uses the loads ranging from 1-120 kgf, applied for between 10 and 15 seconds. For the test samples used in this experiment, only 10gf is used with a 10 second press time. A diamond pyramid indenter is used, which gives a perfect square when pressed onto epoxy. (Walkerm, 1999)
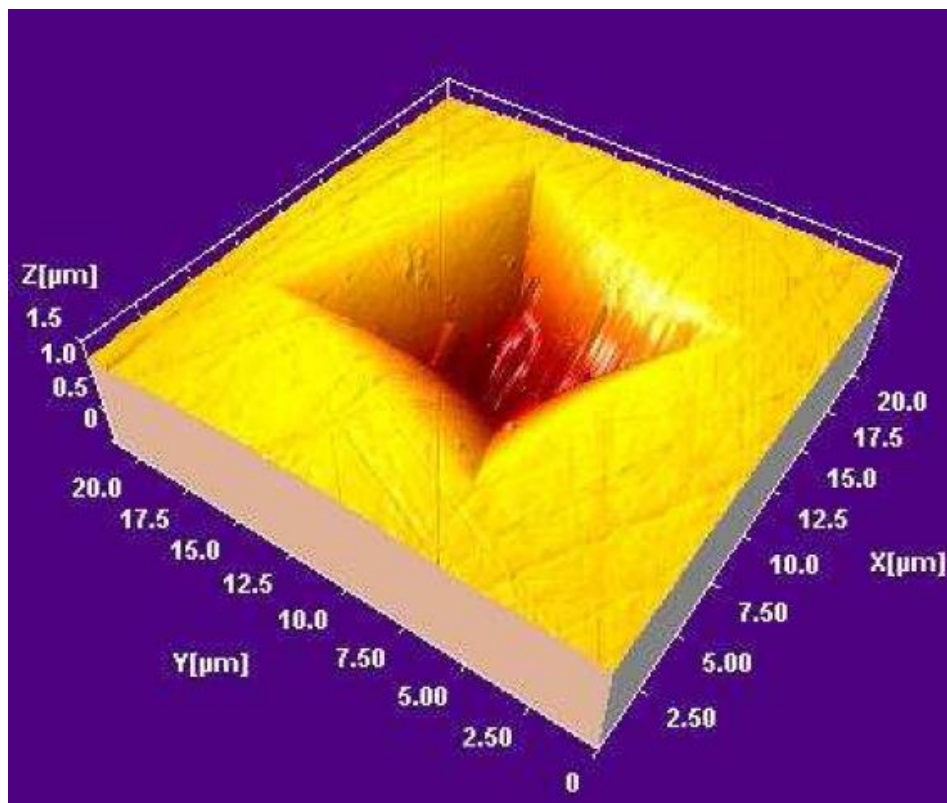
Figure 3.7: Vickers Test Indentation

$$VHN = \frac{2P\sin(\theta/2)}{L^2} = \frac{1.854P}{L^2}$$

P is the applied load, kg

L is the average length of diagonals, mm

θ is the angle between opposite faces of diamond = 136°.

The equation above is used to calculate the Vickers hardness number (VHN)

Defined as the load divided by the surface area of the indentation. (Walkerm, 1999)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1   Tensile Test Results

The fabricated samples of epoxy polymer underwent a tensile test. Determining the tensile characteristics of the material was the focus of the test. They are namely, Maximum Load, Tensile strain at Maximum Load, Tensile stress at Maximum Load, E-modulus.

4.1.1 Tensile Test Result Sample

Epoxy sample - 60% Resin, 40% Curing Agent

Dumbbell Shaped

Tensile Test - Sample pulled till failure.

Optimum Epoxy ratio confirmation

Epoxy 60% Curing Agent 40%
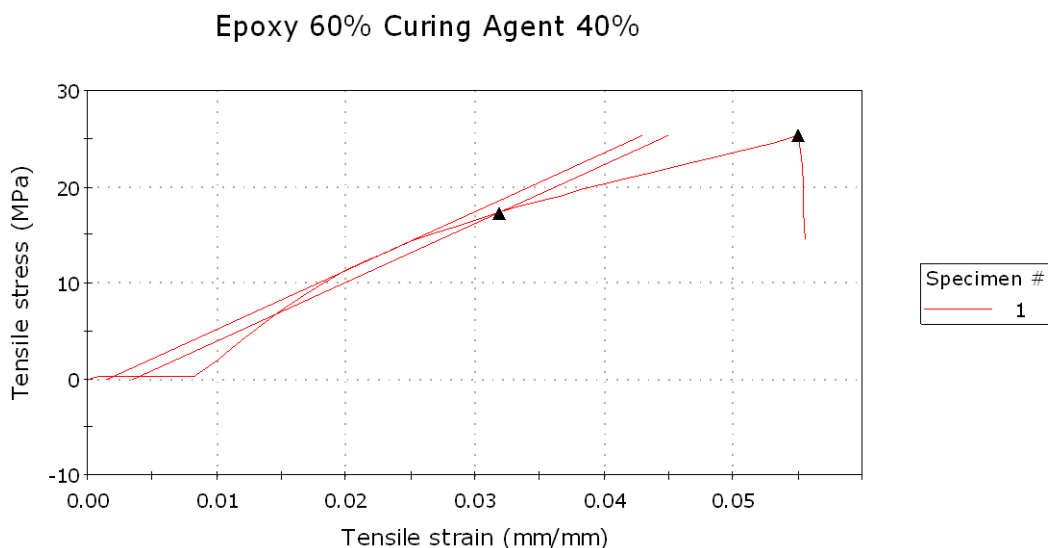
	Maximum Load (N)	Tensile strain at Maximum Load (mm/mm)	Tensile stress at Maximum Load (MPa)
1	2954.03	0.05500	25.25

	Modulus (E-modulus) (MPa)	Load at Yield (Offset 0.2%) (N)	Tensile strain at Yield (Offset 0.2%) (mm/mm)
1	608.38113	2022.88623	0.03192

	Extension at Break (Standard) (mm)	Tensile stress at Break (Standard) (MPa)	Tensile extension at Maximum Tensile stress (mm)
1	2.75002	25.24812	2.75002

This is a the tensile test result from the testing of an epoxy sample, cured at 60% volume of epoxy resin, and 40% volume of di-amine curing agent.

Pineapple Fibre Reinforced Epoxy 30% vol

Dumbbell Shaped

Tensile Test - Sample pulled till failure.

Pineapple Fibre Reinforced Epoxy 30% vol
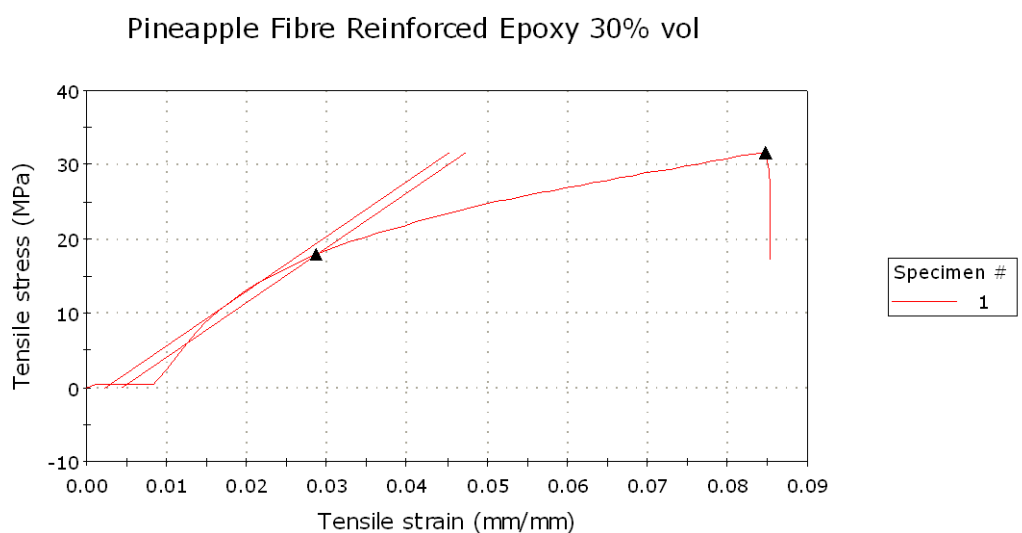
	Maximum Load (N)	Tensile strain at Maximum Load (mm/mm)	Tensile stress at Maximum Load (MPa)
1	3712.03	0.08477	31.73

	Modulus (E-modulus) (MPa)	Load at Yield (Offset 0.2%) (N)	Tensile strain at Yield (Offset 0.2%) (mm/mm)
1	736.10454	2105.13935	0.02876

	Extension at Break (Standard) (mm)	Tensile stress at Break (Standard) (MPa)	Tensile extension at Maximum Tensile stress (mm)
1	4.23830	31.72675	4.23830

This is a the tensile test result from the testing of a fibre reinforced epoxy sample, cured with 30% volume of fibre.

4.1.2 Epoxy Tensile Test Results

Table 4.1: Maximum Load & Tensile Stress for Epoxy Optimisation

Epoxy Resin to Curing Agent ratio	Maximum Load (N)		Tensile Stress (MPa)	
	Sample 1	Sample 2	Sample 1	Sample 2
0.8 : 1	950.12	980.37	10.46	10.73
1 : 1	3203.56	3501.24	27.36	27.42
1.5 : 1	6102.34	6352.84	52.47	52.68
2 : 1	5260.32	5060.32	44.93	44.51
2.5 : 1	4104.45	4604.72	35.05	35.45
3 : 1	1574.31	1344.31	12.09	12.69
3.5 : 1	80.21	110.21	0.62	0.62

Table 4.2: Tensile Strain & E-Modulus for Epoxy Optimisation

Epoxy Resin to Curing Agent ratio	Tensile Strain (mm/mm)		E-Modulus (MPa)	
	Sample 1	Sample 2	Sample 1	Sample 2
0.8 : 1	0.04235	0.02457	102.24	110.57
1 : 1	0.07671	0.07241	136.35	116.34
1.5 : 1	0.13001	0.13341	349.69	319.67
2 : 1	0.11833	0.10243	621.11	647.12
2.5 : 1	0.04932	0.04102	793.23	743.22
3 : 1	0.08275	0.08472	755.50	745.52
3.5 : 1	0.05753	0.04573	N/A	N/A

For the sample '3.5:1', E- modulus values were not able to be calculated as the stress vs strain curve for the test was not ideal.

4.1.3   Epoxy Tensile Test - Maximum Load

The maximum load of the epoxy samples were investigated, and the results were plotted to show,
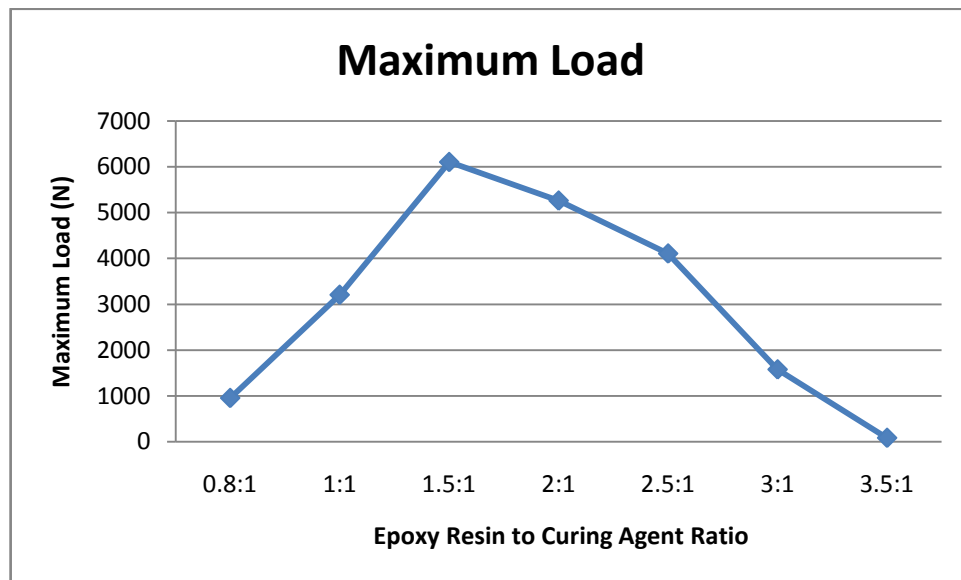
Figure 4.1: Maximum Load for Epoxy

The sample bearing the highest maximum load are those cured with 1.5:1 ratio. The highest value of maximum load being 6352.84 N. The relationship shows that an increase in epoxy to curing agent ratio increases the maximum load up to its peak at 1.5:1 ratio. After 1.5:1 ratio, the Maximum load decreases with increasing epoxy ratio.

4.1.4   Epoxy Tensile Test – Tensile Stress

The results for Tensile stress are plotted to show the following chart.
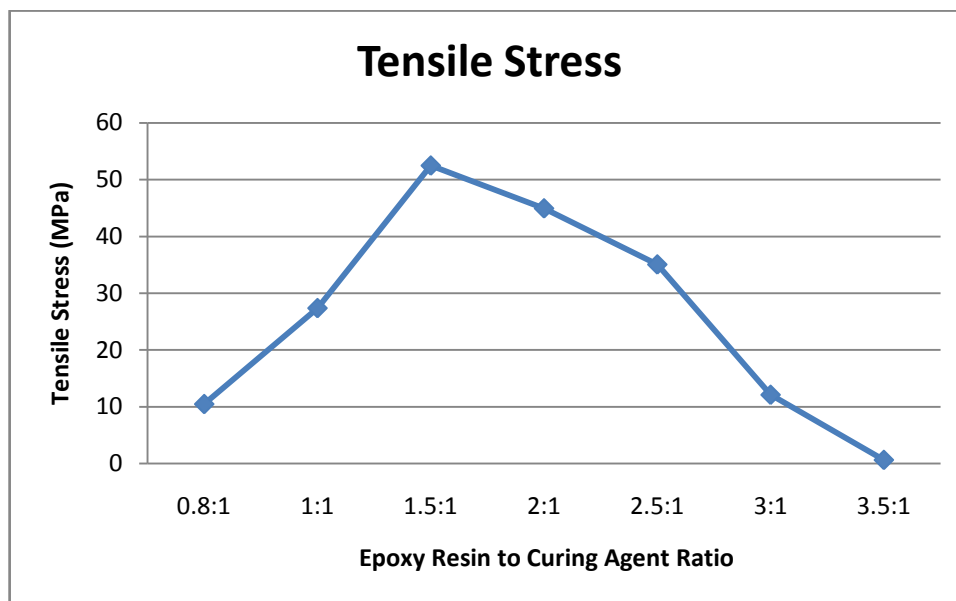
Tensile Stress
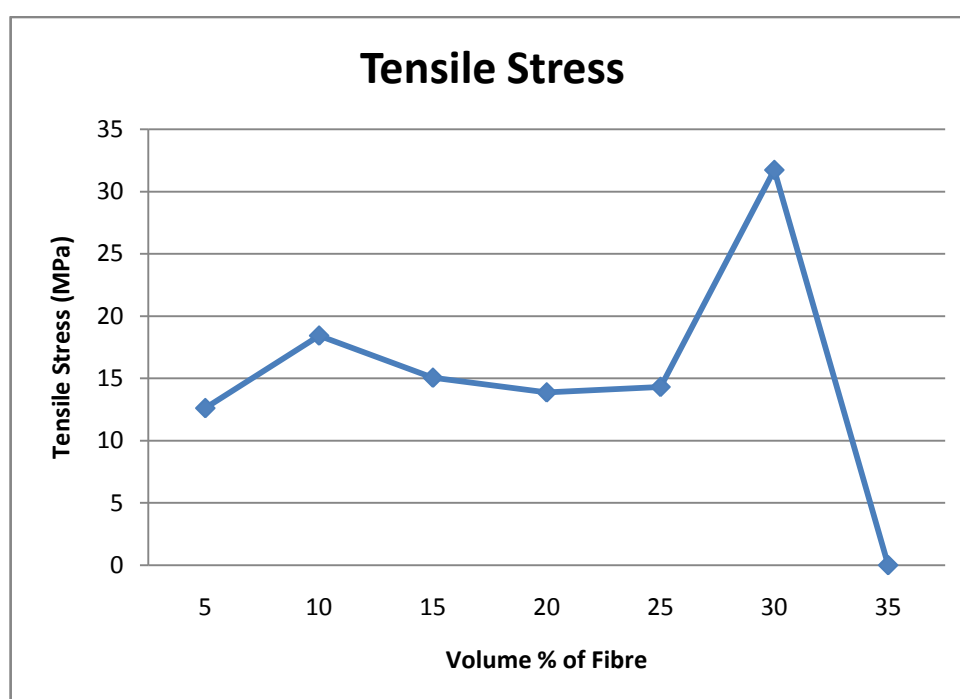

Figure 4.2: Tensile Stress for Epoxy

The relationship between Tensile stress and curing ratio is similar to that of the Maximum Load relationship. The samples bearing the highest Tensile stress are those cured with 1.5:1 ratio. The highest value of Tensile stress being 52.47 MPa. The relationship shows that an increase in epoxy to curing agent ratio increases the Tensile stress to its peak at 1.5:1 ratio. After 1.5:1 ratio, the Tensile stress decreases with increasing epoxy ratio.

4.1.5   Factors Affecting the Tensile Result

Specimen preparation and specimen size are the main factors that affect the tensile result. Molecular orientation has a significant effect on the tensile strength values. A load applied parallel to the direction of the molecular orientation may yield higher values than loads applied perpendicular to the orientation.

Achieving the optimum tensile strength is mostly a matter of obtaining the correct ratio of epoxy resin to curing agent. Each ratio will give a specific set of mechanical properties.

Temperature of curing also affects the strength of the specimens. The specimens used in this experiment were all cured at 26°C. Temperature was kept constant for all specimens. Therefore curing at a different temperature range may yield different strengths.

It is from the Maximum Load and Tensile stress results that the optimum epoxy ratio is chosen. The ratio "1.5:1" bears the highest values for both characteristics, therefore this ratio will be used in the subsequent preparation of samples for pineapple reinforced polymer.

4.1.6   Reinforced Epoxy Tensile Results

Table 4.3: Maximum Load & Tensile Stress for Fibre Reinforced Epoxy

Fibre reinforced Epoxy (% Volume of Fibre)	Maximum Load (N)		Tensile Stress (MPa)	
	Sample 1	Sample 2	Sample 1	Sample 2
5	1475.76	1413.15	12.61	12.34
10	2156.18	2203.48	18.43	19.05
15	1761.06	1842.03	15.05	16.02
20	1622.77	1602.23	13.87	13.43
25	1674.85	1642.16	14.31	13.46
30	3712.03	3675.26	31.73	30.64
35	0.00	0.00	0.00	0.00

Table 4.4: Tensile Strain for Fibre Reinforced Epoxy

Fibre reinforced Epoxy (% Volume of Fibre)	Tensile Strain (mm/mm)	
	Sample 1	Sample 2
5	0.59215	0.04863
10	0.01717	0.07241
15	0.56315	0.06486
20	0.01953	0.02346
25	0.05667	0.05486
30	0.08477	0.08135
35	0.00	0.00

4.1.7   Reinforced Epoxy Tensile Test – Maximum Load

The maximum load of the epoxy samples were investigated, and the results were plotted to show,
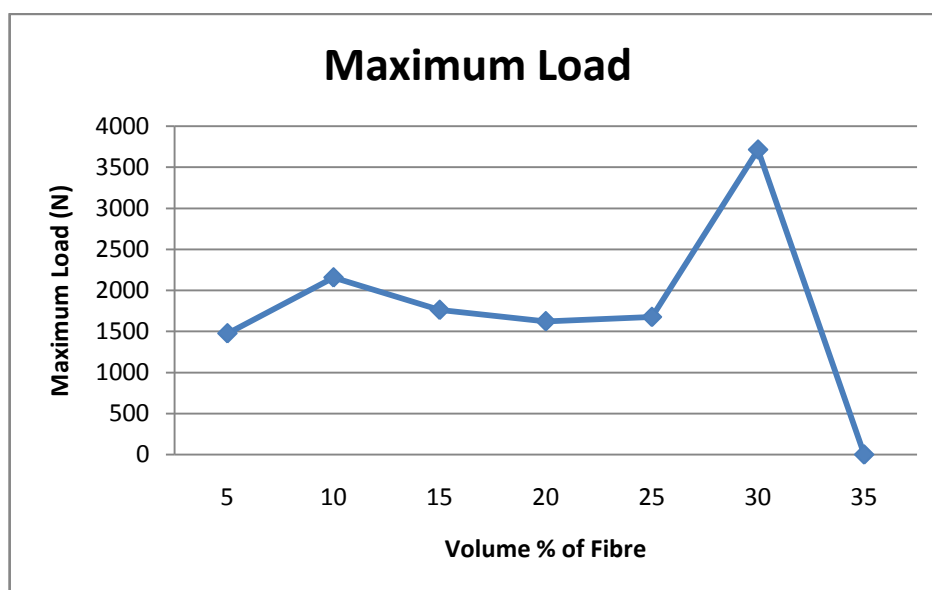
Figure 4.3: Maximum Load for Reinforced Epoxy

The highest value for Maximum load on the fibre reinforced epoxy is 3712.03 N. This value is given by the specimen cured with 30% volume of pineapple fibre.

This value is lower than that of the optimized epoxy, the reasoning for this is further explained in the SEM section of this report.

The sample reinforced with 35% was too brittle to withstand any load, and therefore resulted in zero value from testing.

4.1.8   Reinforced Epoxy Tensile Test – Tensile Stress

The results for Tensile stress are plotted to show the following chart.

Figure 4.4: Tensile Stress for Reinforced Epoxy

The relationship between Tensile stress and Vol % of fibre is similar to that of the Maximum Load relationship. The samples bearing the highest Tensile stress are those cured with 30% volume of fibre. The highest value of Tensile stress being 31.73 MPa. This value is lower than that of the optimized epoxy, and is explained in the SEM section of this report.

4.2   Hardness Testing Results

4.2.1   Rockwell Hardness Test

Table 4.5: Rockwell Hardness Test Results

Specimen		RC Measurement	
		60	150
Optimized Epoxy		0	0
Fibre Reinforced 5% Vol		0	0
Fibre Reinforced 10% Vol		0	0

Fibre Reinforced 15% Vol		0	0
Fibre Reinforced 20% Vol		0	0
Fibre Reinforced 25% Vol		0	0
Fibre Reinforced 30% Vol		0	0

The Rockwell Hardness test gives no results within range. This is because the specimens are too soft. Therefore a different method must be used. Micro hardness testing is then carried out.

It should be noted that there is **no decomposition** present on the test samples . Samples pictures may exhibit blue or black spots, this is due to the runoff from the hacksaw while cutting the sample to desired size.

4.2.2   Micro Hardness Testing

Table 4.6: Micro Hardness Test Results

Specimen		Vickers Hardness at 10gf (HV)	
		Specimen 1	Specimen 2
Optimized Epoxy		15.7	16.8
Fibre Reinforced 5% Vol		18.5	19.7
Fibre Reinforced 10% Vol		19.9	21.2

Fibre Reinforced 15% Vol		14.7	12.7
Fibre Reinforced 20% Vol		18.9	16.6
Fibre Reinforced 25% Vol		\17.5	16.6
Fibre Reinforced 30% Vol		18.5	18.5

It is seen that the hardness of the Epoxy is improved with the addition of pineapple fibres. The highest hardness value is 21.2 Hv, given by the specimen with 10% volume of fibre.

Samples pictures may exhibit blue or black spots, this is due to the runoff from the hacksaw while cutting the sample to desired size. White spots are residual 'Liquid-paper' from labelling, that do not affect testing.

4.2.3   Factors Affecting Hardness test

Factors that need to be taken into account when interpreting hardness data for Epoxy materials are the amount of porosity in the surface, the grain size of the microstructure and the effects of grain boundary phases.

Temperature of curing and curing times also affect hardness. The specimens used in this experiment have a curing time of 3 to 4 days. While this is sufficient time for subsequent testing, actual industrial materials have a curing time of 5-6 days for a complete and permanent cure.
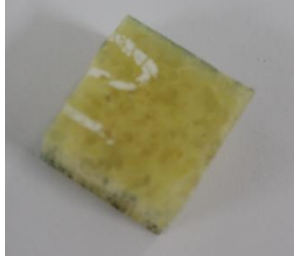
It can be seen from the results that addition of fibre increases the hardness of the specimens. The highest hardness achieved is 21.2 Hv, giving a 35% increase in hardness over that of the optimized epoxy.

4.3   Immersion Test Results

The specimen was immersed in 36% HCL & 96% Sulphuric Acid.

4.3.1   Immersion Testing with 36% HCL

Table 4.7: Immersion Test Specimens for Hydrochloric Acid.

Specimen with 36% HCL	Optimized Epoxy	Fibre Reinforced 5%	Fibre Reinforced 10%
Before			
After			

It should be noted that there is **no decomposition** present on the test samples . Samples pictures may exhibit blue or black spots, this is due to the runoff from the hacksaw while cutting the sample to desired size. White spots are residual 'Liquid-paper' from labelling, that do not affect testing.

Table 4.8: Immersion Test Specimens for Hydrochloric Acid.
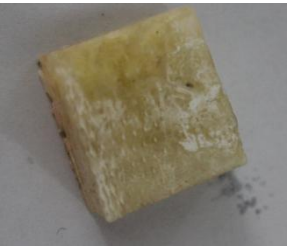
Specimen with 36% HCL	Fibre Reinforced 15%	Fibre Reinforced 20%	Fibre Reinforced 25%
Before			
After			

Table 4.9: Immersion Test Specimens for Hydrochloric Acid.

Specimen with 36% HCL	Fibre Reinforced 30%
Before	
After	

Table 4.10: Immersion Test Specimens for Hydrochloric Acid.

	Optimized Epoxy	Fibre Reinforced 5%	Fibre Reinforced 10%
Specimen			
Weight (gram)	6.457	5.784	6.253
Length (mm)	25.5	24.5	25.0
Width (mm)	25.2	23.7	24.5
Thickness (mm)	8.6	8.4	8.7

Table 4.11: Immersion Test Specimens for Hydrochloric Acid.
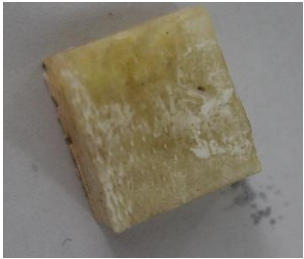
	Fibre Reinforced 15%	Fibre Reinforced 20%	Fibre Reinforced 25%
Specimen			
Weight (gram)	5.234	4.216	6.143
Length (mm)	25.0	24.5	25.6
Width (mm)	25.5	24.8	26.0
Thickness (mm)	7.5	7.2	7.9

Table 4.12: Immersion Test Specimens for Hydrochloric Acid.

	Fibre Reinforced 30%
Specimen	
Weight (gram)	5.592
Length (mm)	26.0
Width (mm)	23.5
Thickness (mm)	7.6

4.3.2 Immersion Testing with 96% Sulphuric Acid

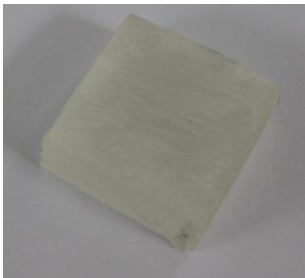**Table 4.13: Immersion Test Specimens for Sulphuric Acid.**

Specimen with 96% Sulphuric Acid	Optimized Epoxy	Fibre Reinforced 5%	Fibre Reinforced 10%
Before			
After			

Table 4.14: Immersion Test Specimens for Sulphuric Acid.

Specimen with 96% Sulphuric Acid	Fibre Reinforced 15%	Fibre Reinforced 20%	Fibre Reinforced 25%
Before			
After			

Table 4.15: Immersion Test Specimens for Sulphuric Acid.

Specimen with 96% Sulphuric Acid	Fibre Reinforced 30%
Before	
After	

Table 4.16: Immersion Test Specimens for Sulphuric Acid.

	Optimized Epoxy	Fibre Reinforced 5%	Fibre Reinforced 10%
Specimen			
Weight (gram)	4.861	5.684	6.414
Length (mm)	23.5	24.0	24.5
Width (mm)	26.0	23.9	23.7
Thickness (mm)	7.5	8.1	9.5

Table 4.17: Immersion Test Specimens for Sulphuric Acid.

	Fibre Reinforced 15%	Fibre Reinforced 20%	Fibre Reinforced 25%
Specimen			
Weight (gram)	4.997	4.473	5.031
Length (mm)	24.5	24.0	25.0
Width (mm)	20.0	23.0	25.3
Thickness (mm)	8.1	6.2	7.6

Table 4.18: Immersion Test Specimens for Sulphuric Acid.

	Fibre Reinforced 30%
Specimen	
Weight (gram)	3.601
Length (mm)	21.1
Width (mm)	24.0
Thickness (mm)	6.3

4.3.3   Immersion Test Interpretation

The immersion test results show an increase in weight for samples immersed in hydrochloric acid and sulphuric acid. The test duration was four weeks. No significant changes in length, width or thickness was observed. The weight increase could be contributed by absorption of the acid into the external pores of the sample structure.

The sample surfaces show little corrosion. A slight change in hue is observed, but no significant changes on the surface structure. This shows that the Epoxy samples are resistant to acids.

\

4.4   Scanning Electron Microscopy Results

SEM imaging was carried out on specimens of fibres, composite fracture point, and Epoxy surface. Each specimen was sputter coated with a Gold/Palladium mixture prior to testing.

15.0kV 6.6mm x150 SE   300um
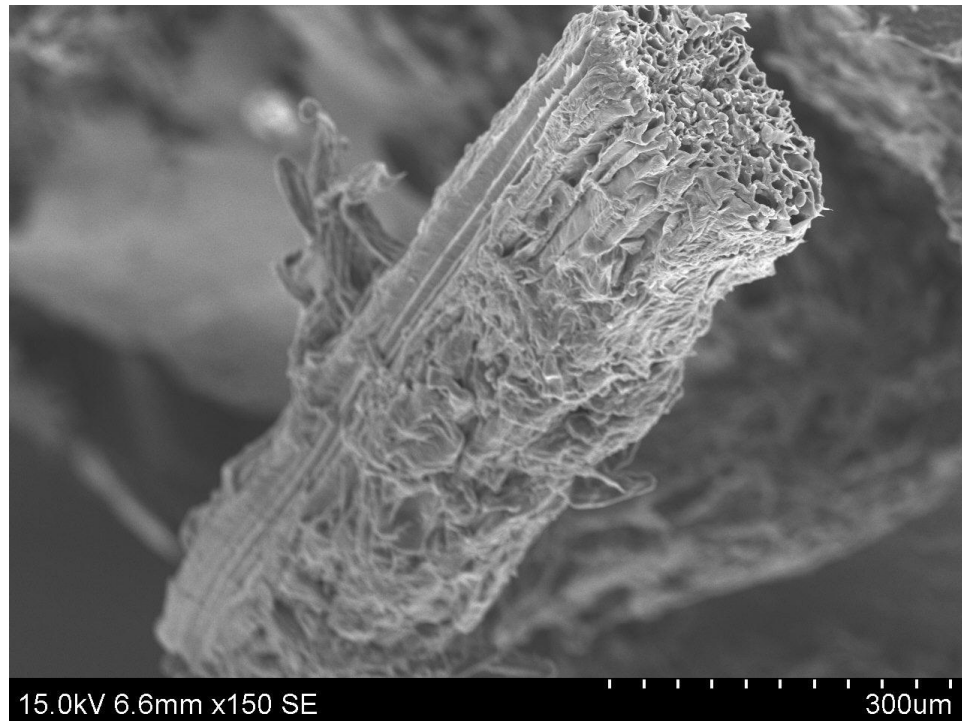
Figure 4.5: SEM image of Fibre

The figure above shows an enlarged SEM image of a pineapple fibre. The cylindrical cellulose structure can be clearly observed, with a porous cross-sectional area suggesting a fibrous interior structure.

The external surface of the pineapple fibre is rough, with protruding fibres on the side. This would, if in direct contact with the epoxy, increase the strength of the composite significantly due to fibre-matrix interface force transfer. However, this is not consistent with the tensile results obtained, therefore further SEM imaging may be needed to explain this phenomenon.
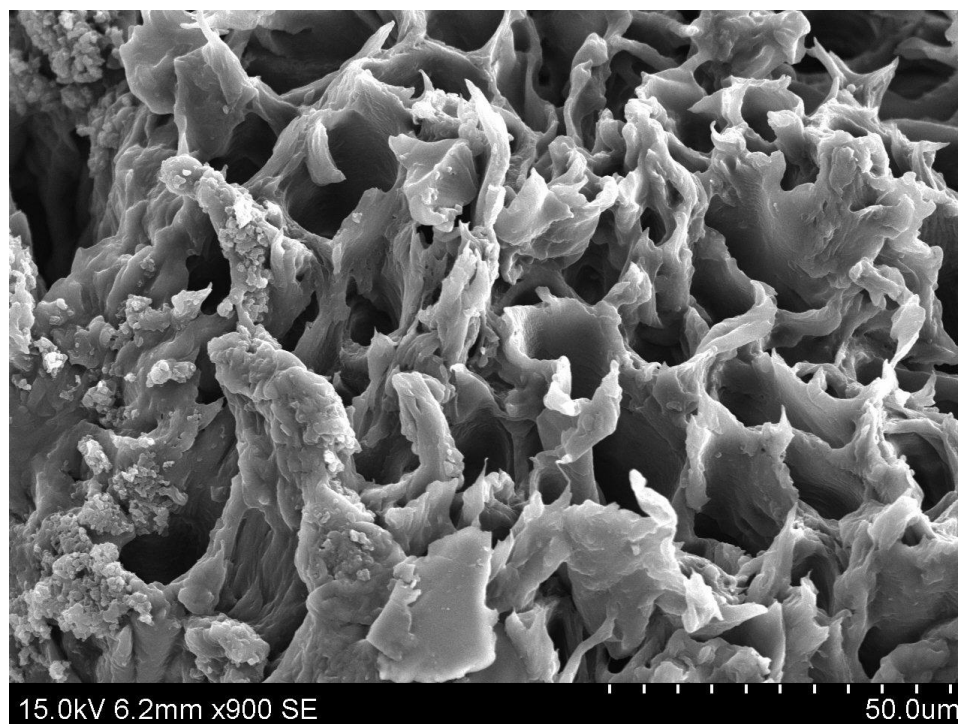
Figure 4.6: SEM image of Fibre Cross-section

The figure above shows an enlarged SEM image of the fibre cross-section. It shows hollow openings to internal fibrous structure. The fibre is then assumed to have a somewhat hollow interior. The long strands of cellulose fibre promote strength of the entire fibre. The hollow nature of the fibre suggest lightweight characteristics, favourable in producing a lighter, stronger material.

A fibre reinforced specimen with 30% volume of fibre was pulled in the tensile test until failure. The fracture point was analysed by SEM, to describe the point of failure.
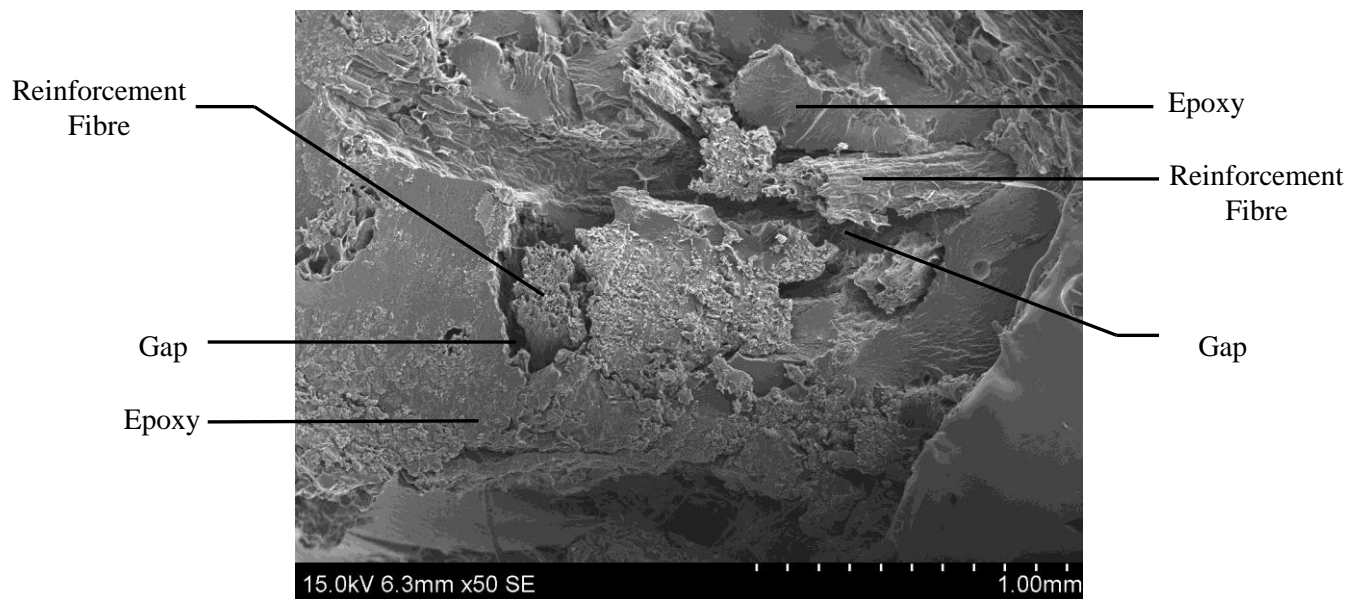
Figure 4.7: SEM image Fracture Surface

The image above shows the point of fracture. The fibres can be clearly seen in the epoxy matrix. Due to the nature of the curing method, the fibres are well distributed throughout the epoxy matrix.
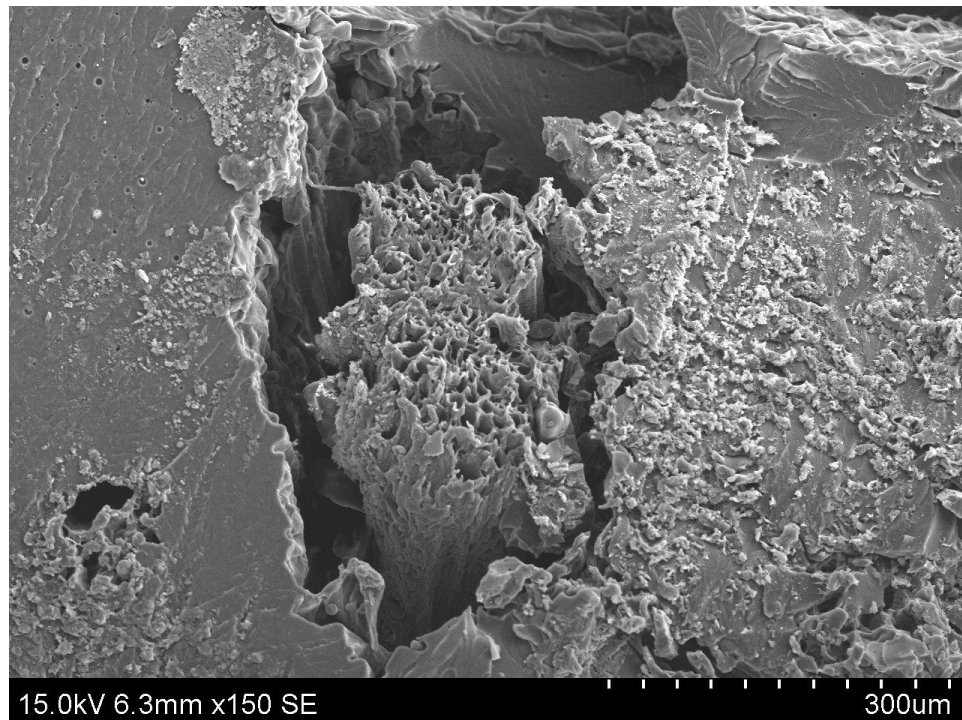
Figure 4.8: SEM image of Fibre-Matrix Interface

The image above, Figure 4.8, shows an increased magnification of the fibre-matrix interface from the previous image. It can be clearly seen that the fibre is embedded deep into the epoxy matrix.

It should be highlighted that the fibre is not in direct contact with the epoxy material, as a gap can be seen between epoxy and the fibre. These gaps are highlighted in the red box in Figure 4.9.

This gap reduces the shear and tensile forces that can be transferred between the fibre and epoxy matrix during pulling. Thus rendering the fibre unable to efficiently increase the tensile properties of the material.

"When a conventional fibre is pulled from a composite, the tensile force is transferred to the matrix through the shear stress on the fibre surface."

– Feng An (2011)

The gap also weakens the epoxy composite as it increases the internal porosity. This causes a drop in the materials tensile strength, as crack propagation will occur along the gap and the epoxy matrix.
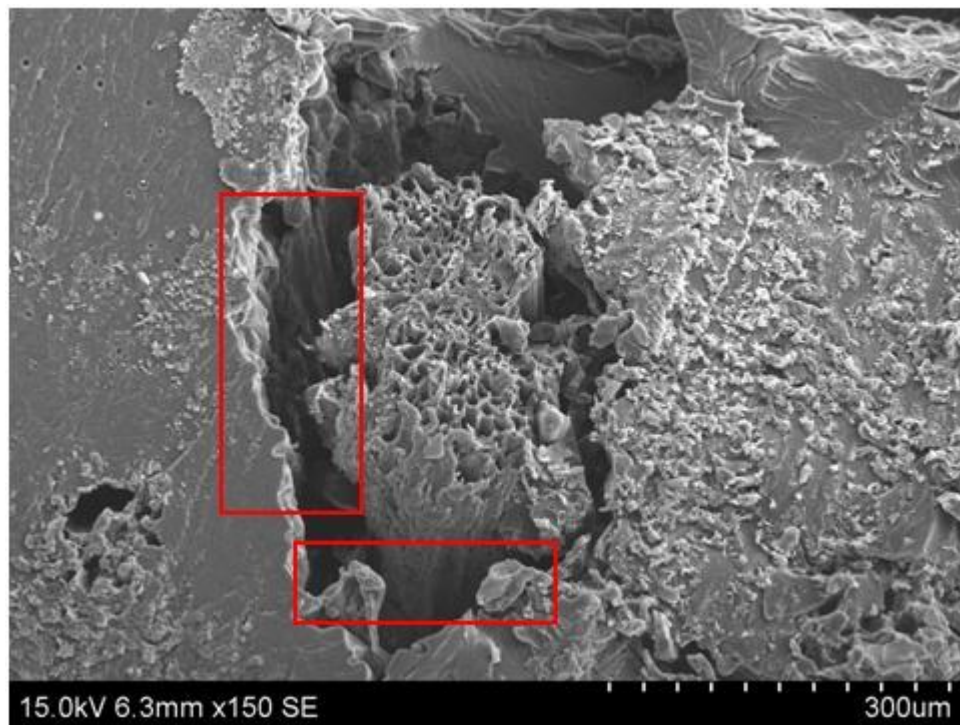
Figure 4.9: SEM image of Gaps Between Fibre and Epoxy
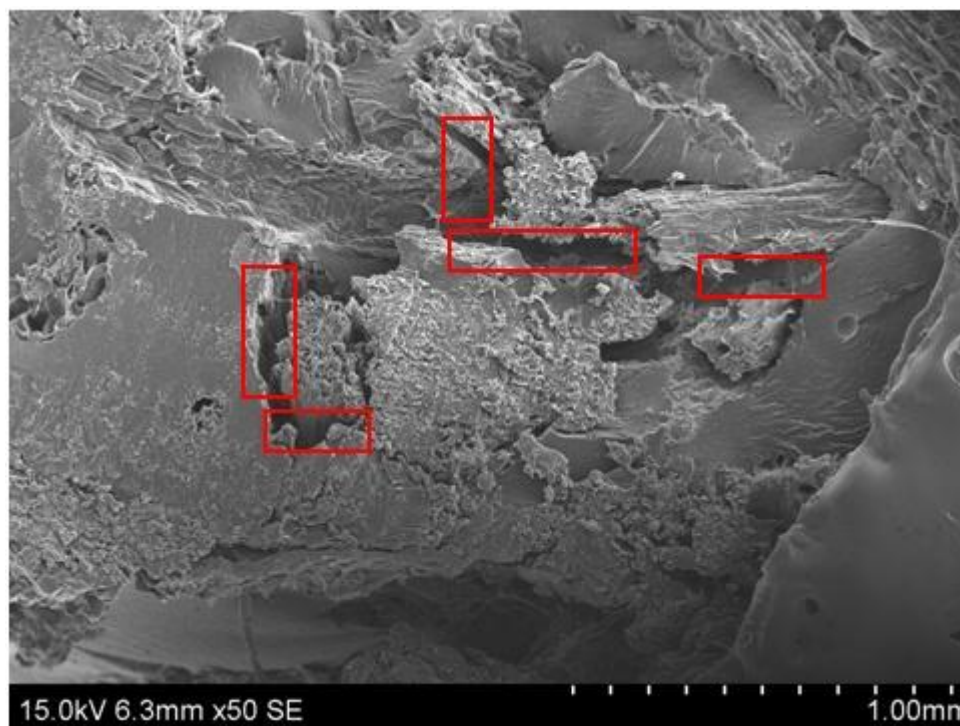
Figure 4.10: SEM image of Gaps Between Fibre and Epoxy

The gaps appear to be present at the locations of the fibre. One of the possible causes for these gaps is the water vapour released from the organic pineapple fibres.

"When working with organic material, it is always important to consider the numerous problems that may arise from the organic nature of such materials, such as decomposition, and other factors." – Dr. Lee Tin Sin (2011)

Since all organic material contains a certain amount of water, it is possible that due to the exothermic reaction of the curing, the heat released caused the internal water from the fibre's internal structure to evaporate and be released. This water vapour thus causes a gap to exist between the fibre and epoxy.

This is just one possibility from many, and further studies are required to determine the actual cause for gaps between the fibres and epoxy.

The fibres used in this project were blow dried with hot air prior to curing. The drying was continued until no changes of mass occurred within the same minute. This process does not however eliminate all the water content of the fibres, as water is retained inside the fibres at a cellular level. This drying was chosen as opposed to heating in an oven, because the cellulose fibres require water to retain rigidity and integrity of the fibre. Drying the fibres to crisp would cripple the mechanical and tensile properties of the fibre.

In reference to Feng An et. al.'s paper on "*Preparation and characterization of carbon nanotube-hybridized carbon fiber to reinforce epoxy composite",* Figure 4.11b), it is favourable to obtain a minimal gap between the fibre and epoxy, although the gap can be minimised (through grafting for example), it is unlikely that the gap can be eliminated altogether.
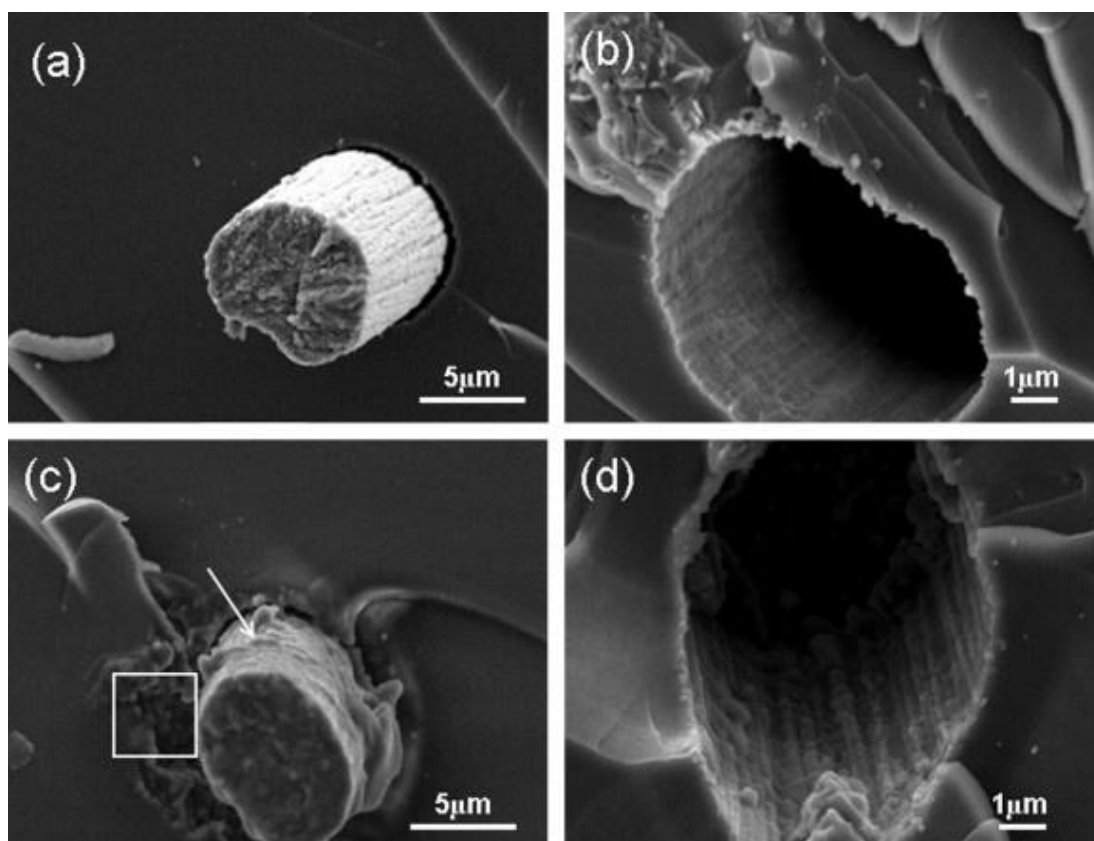
Figure 4.11: SEM image Carbon fibre in Epoxy by Feng An et. al. (2011)

15.0kV 6.2mm x150 SE   300um
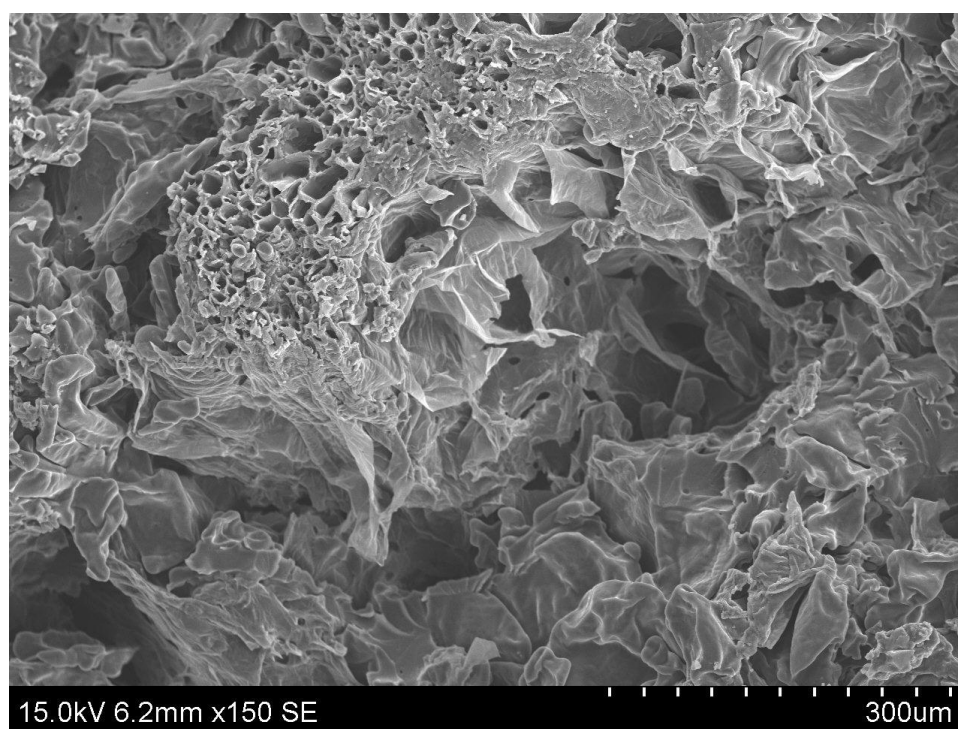
Figure 4.12: SEM image of Fibres Surface
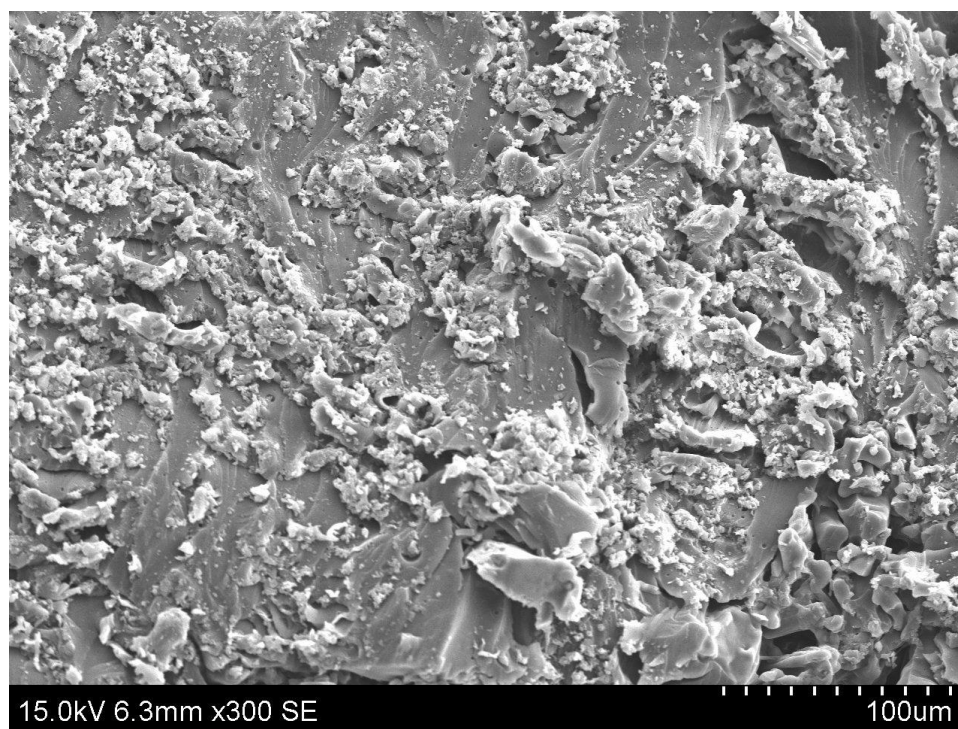
Figure 4.13: SEM image of Epoxy Surface
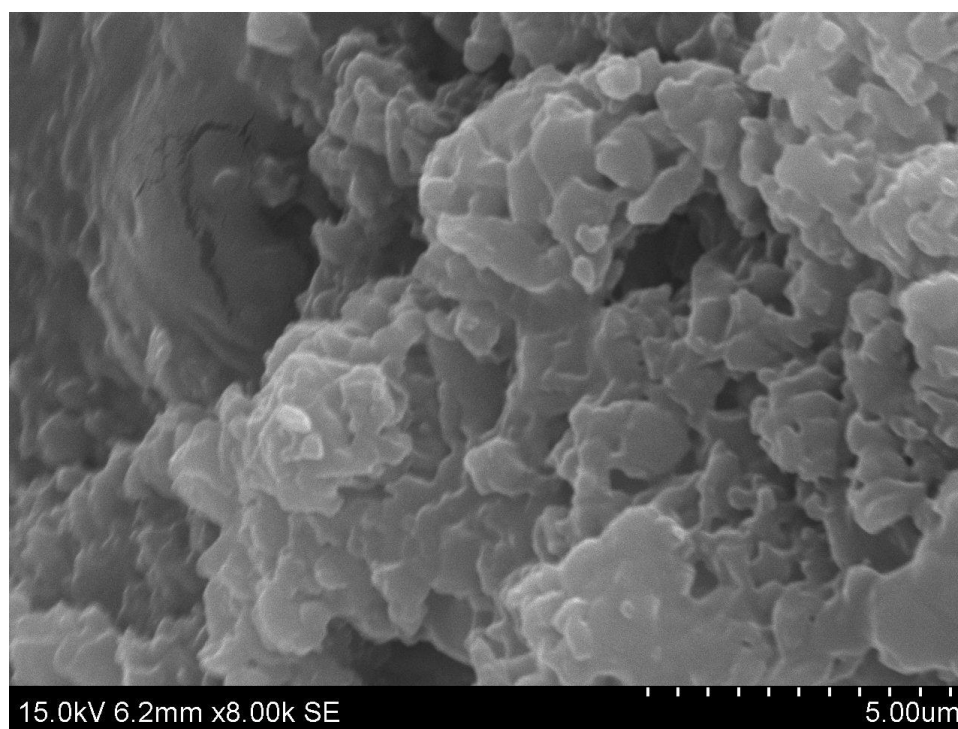
Figure 4.14: SEM image of Epoxy Surface at High Magnification

4.5   EDAX Results

EDAX analysis carried out on Fibre is shown below:

Prepared for: ***UTAR***

Prepared by: ***Winston H. Cho***   ***24/8/2011***

C:\Users\Administrator\Desktop\DrTioh\24082011\EPOX(1).spc 24-Aug-2011 14:56:12
LSecs : 57
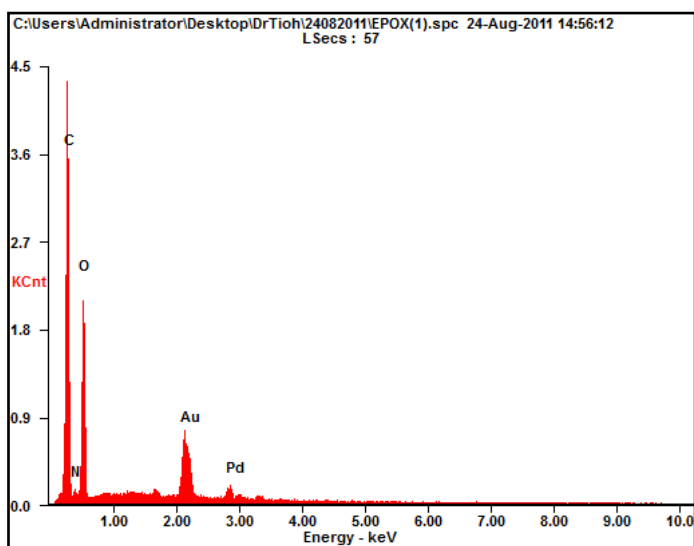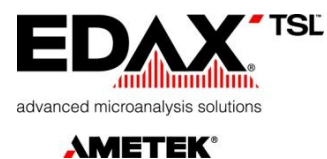
Element	Wt%	At%
CK	34.74	57.92
NK	02.45	03.50
OK	27.46	34.37
AuM	28.19	02.87
PdL	07.17	01.35
Matrix	Correction	ZAF
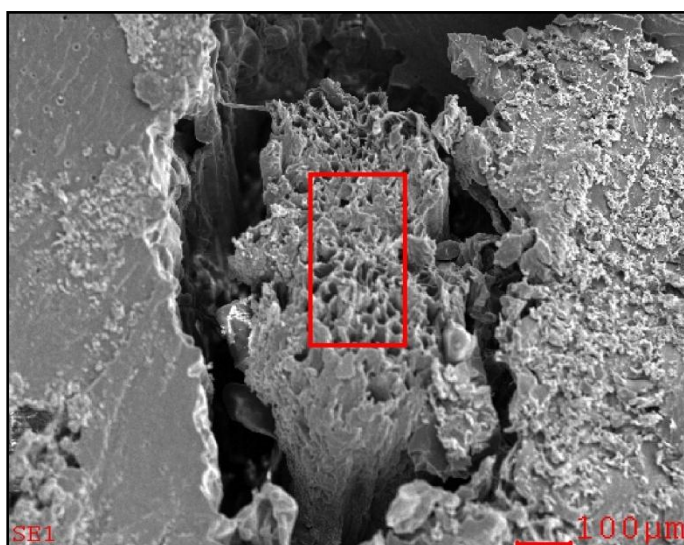
EDAX analysis carried out on Epoxy surface is shown below:

Prepared for: **UTAR**

Prepared by: **Winston H. Cho** *24/8/2011*
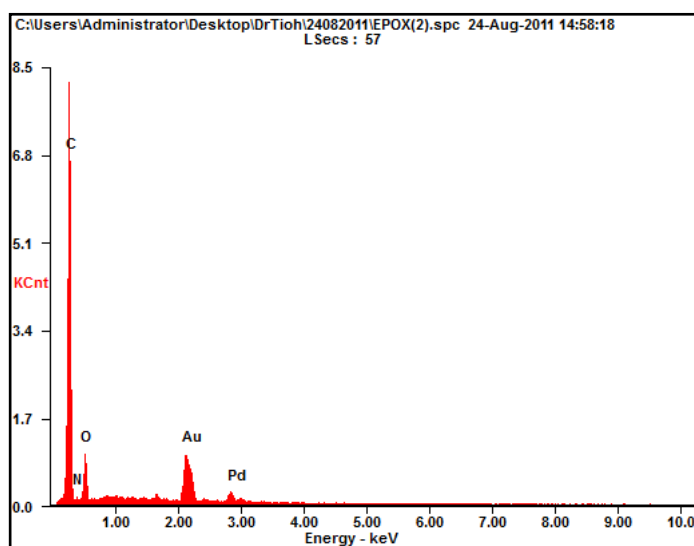
Element	Wt%	At%
CK	49.43	80.80
NK	01.61	02.26
OK	10.08	12.37
AuM	30.65	03.05
PdL	08.23	01.52
Matrix	Correction	ZAF
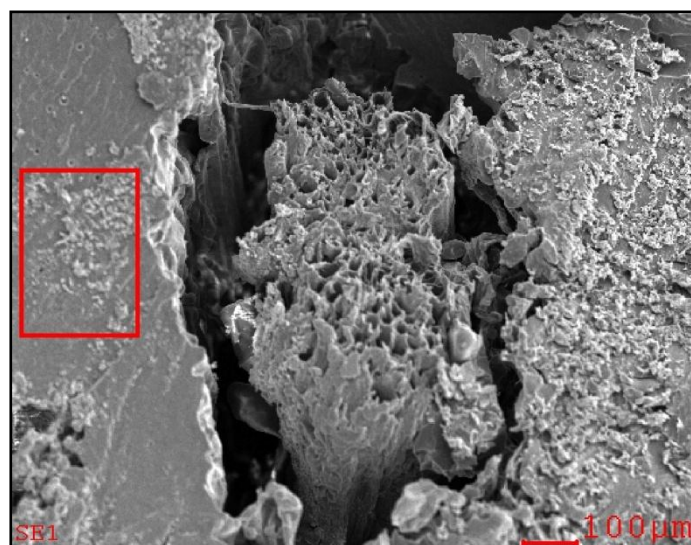
4.5.1   EDAX Analysis

From the EDAX results obtained from the analysis on the fibre surface, it is shown that Carbon and Oxygen are the main constituents of the test, at 34.74 Wt% and 27.46 Wt% respectively. A small amount of nitrogen is present, naturally occurring from the organic nitrogenous nature of plant fibre. The gold and palladium readings show the sputter coating. Little other elements are detected , therefore it can be assumed that the fibre surface is clean of any contaminants that may have affected the test results.

From the EDAX results obtained from the analysis on the Epoxy surface, it is shown that Carbon and Oxygen are the main constituents of the test, at 49.43 Wt% and 10.08 Wt% respectively. A small amount of nitrogen is present, occurring from the Di-amine group from the curing agent. The gold and palladium readings show the sputter coating. Little other elements are detected , therefore it can be assumed that the epoxy surface is clean of any contaminants that may have affected the test results.

4.6   Decomposition Analysis

An additional test was carried out to observe the decomposition of the various pineapple parts, not limited to the fibres used in the epoxy. Analysis included pineapple leaves, pineapple leaves cut into fibres, fruit fibre, external skin strips.

Figure 4.15: Decomposition Analysis

"When working with organic material, it is always important to consider the numerous problems that may arise from the organic nature of such materials, such as decomposition, and other factors." – Dr. Lee Tin Sin (2011)

The organic materials were divided into two sets, one which was left in the laboratory at constant temperature of 25°C, and another set left outdoors to be exposed to all climate conditions except for rain. The decomposition was observed for the duration of the project, or 7 months.

No bacterial or fungal growth was observed on both sets. The specimens lost water content over the first week, and the physical structures remained so for the next few months.

It should be noted that there is **no decomposition** present on the test samples . Samples pictures may exhibit blue or black spots, this is due to the runoff from the hacksaw while cutting the sample to desired size.

CONCLUSION AND RECOMMENDATIONS

An optimised epoxy composite was fabricated through conventional hand-layup curing technique. The ratios of the epoxy resin and curing agent were varied to obtain a range of specimens, each with unique mechanical properties. The mechanical properties of the specimens were tested, and an optimised ratio was chosen. This ratio was used in the fabrication of a fibre reinforced epoxy with pineapple fibres. The resulting reinforced epoxy were then tested for tensile strength, hardness, resistance to corrosion, and underwent SEM and EDAX analysis. Results showed an increase in hardness, a good resistance to corrosion and decreased tensile strength, which was properly explained in the report. An increase of 35% in hardness was observed in the reinforced material. No significant surface corrosion was observed when exposed to concentrated acids. The tensile strength of the optimised reinforced epoxy achieved was 31.73 MPa, which is above the generally accepted range of epoxy tensile strength (12-30 MPa). The surface structure and composition was analysed by SEM and EDAX, and a possible cause for the decrease in tensile strength was proposed.

For future studies on pineapple fibre reinforced epoxy, it is suggested to experiment with completely dried fibres, with no water content. This may greatly reduce fibre strength but also reduce the fibre-matrix gap. Also, experimentation on the occurrence of gaps in the fibre-matrix interface can be sufficient as a research in itself. Different species of pineapple fruits may be used, which may bear better mechanical property results. A different extraction method of the pineapple fibres, such as pressing, may allow for longer fibres to be obtained and tested.

For pineapple reinforced polymer studies, different types of polymer can be used, such as Poly-vinyl Chloride (PVC), Chlorinated Poly-vinyl Chloride (CPVC) or poly-propylene (PP). Epoxy can be used as well, with a different diamine hardening agent, which will give different casting times and mechanical properties.

For fibre reinforced epoxy studies, stronger fibres may be used, such as coconut husk fibres or banana tree stem fibres.

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