Interlaminar Fracture Toughness Behaviour of Flax/Basalt Reinforced Vinyl Ester Hybrid Composites

A Doctoral Thesis by

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Abstract

Natural fibre reinforced composites have been extensively used in non-structural components, mainly in automotive industry. For these composites to be used in structural applications, an understanding of fracture toughness behaviour is important. In this study, the influence of water absorption and hybridisation of flax and flax/basalt hybrid laminates are presented with the aim to investigating the Mode I and Mode II interlaminar fracture toughness characteristics. Four types of composite laminates namely, neat vinyl ester (neat VE), flax fibre reinforced vinyl ester (FVE), flax fibre hybridised basalt unstitched (FBVEu) and flax hybridised basalt stitched (FBVEs), were fabricated by vacuum assisted resin infusion technique. Double cantilever beam (DCB) and Three-point-end-notched flexure (3ENF) tests were performed to evaluate the critical strain energy release rates, G_{IC} and G_{IIC} (initiation and propagation) as well as the crack length (R-curve) in dry and wet conditions by using different data reduction methods. The morphology of delamination and the fracture shear failure of composite laminates were evaluated using scanning electron microscopy (SEM) and X-ray micro computed tomography (μCT).

From the experimental results, it was found that the Mode I fracture toughness initiation $G_{IIC\ init.}$ and propagation $G_{IIC\ prop.}$ of water immersed FVE composites were decreased by an average of 27% and 10% respectively, compared to the dry specimens, whereas the fracture toughness propagation of water immersed FBVEu and FBVEs composites were increased by approximately 15% and 17% compared to dry specimens. The results of Mode II fracture toughness obtained experimentally exhibited that the fracture energy of FBVEu composites, $G_{IIC\ init.}$ and $G_{IIC\ prop.}$ were improved by 58% and 21%, respectively compared to that of FVE dry specimens. Moisture absorption behaviour caused an increase in the ductility of matrix which resultantly improved the resistance to crack initiation. However, there was a reduction in the fibre/matrix interfacial strength of FBVEu wet composites and a deterioration in the delamination resistance to crack propagation. The critical strain energy release rate of neat VE increased about 52% with reinforcement of flax fibre composites. The fracture mechanisms showed energy dissipation through matrix deformation, fibre pull-out, fibre debonding, and fibre breakage. The experimental results confirmed that basalt fibre hybridisation enhanced the durability and water repellence behaviour of flax fibre reinforced composites.

Finally, this thesis provides a unique manufacturing technique to improve the interlaminar fracture toughness of flax fibre and flax/basalt hybrid composite laminates to be used in load-

bearing applications as an alternative to E-glass fibre reinforced composites. The outcomes of this study will be beneficial to automotive, marine and construction industries. In addition, the findings of this study will be useful for academic and researchers who are involved in the research and development of sustainable composites for light-weight structural applications.

Keywords: Natural fibre reinforced composites (NFRCs), Flax fibres, Interlaminar fracture toughness, Delamination, Mode I (DCB), Mode II (3ENF)

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List of Publications

Several publications have emerged from the work described in this thesis and other collaborative work with the team of Advanced Polymer and Composites (APC) research group. The dissemination has been included of peer-reviewed journal papers, reviewing journal paper, conference papers and presentations. A critical review article which derived from the literature review in chapters 1 and 2, and original research articles, based on chapters 3, 4 and 5 have been published in peer-reviewed journals.

Peer-Reviewed Journal Papers

1. **Almansour, F. A.,** Dhakal, H. N., & Zhang, Z. Y. (2018). Investigation into Mode II interlaminar fracture toughness characteristics of flax/basalt reinforced vinyl ester hybrid composites. Composites Science and Technology, 154, 117-127.
2. **Almansour, F. A.,** Dhakal, H. N., & Zhang, Z. Y. (2017). Effect of water absorption on Mode I interlaminar fracture toughness of flax/basalt reinforced vinyl ester hybrid composites. Composite Structures, 168, 813-825.
3. **Almansour, F.A.,** Dhakal, H.N., Zhang, Z.Y. and Ghasemnejad, H. (2015). Effect of hybridization on the mode II fracture toughness properties of flax/vinyl ester composites. Polymer Composites, 38, 1732–1740.
4. **Almansour, F. A.,** Dhakal, H. N., & Zhang, Z. Y. (2018). A review of interlaminar fracture toughness of natural fibre reinforced polymer composites. "In-Progress''
5. Dhakal, H. N., Bourmaud, A, Berzin, F, **Almansour, F. A.,** Zhang Z. Y., Shah, D. U. Beaugrand, J. (2018). Mechanical properties of biodegradable waste leaf sheath date palm fibre reinforced polycaprolactone (PCL) biocomposites. Industrial Crops and Products, "Under Review''

Conferences (Presentation, Poster and Attendance)

1. 5th International Conference on Natural Fibre Composites, Rome 15-16 October 2015. (Oral presentation)
2. 8th Saudi Students Conference, Imperial College, London, UK, 31 January – 1 February, 2015. (Poster)
3. 7th Saudi Students Conference, Edinburgh University, UK, 1-2 February, 2014. (Poster)
4. 5th International Conference on Sustainable Materials, Polymers and Composites, Birmingham, UK, 3-4 July, 2013. (Attendance)

Abbreviations

NFRCs	Natural Fibre Reinforced Composites	AE	Acoustic Emission
LEFM	Linear Elastic Fracture Mechanics	MBT	Modified Beam Theory
EPFM	Elastic-Plastic Fracture Mechanics	CC	Compliance Calibration
FRP	Fibre Reinforced Polymer	MCC	Modified Compliance Calibration
DCB	Double Cantilever Beam	ELS	End-Loaded Split
3ENF	Three-point End Notched Flexure	SBT	Simple Beam Theory
ASTM	American Society for Testing and Materials	CCM	Corrected Calibration Method
SEM	Scanning Electron Microscopy	MMB	Mixed-Mode Bending
μCT	X-ray Computed Micro-Tomography	CLS	Crack Lap Shear
APC	Advanced Polymers and Composites	HBP	Hyperbranched Polymers
MMC	Metal-Matrix Composites	PLLA	Poly (L-Lactic Acid)
CMC	Ceramic-Matrix Composites	CT	Compact Tension
PMC	Polymer-Matrix Composites	SENB	Single Edge Notch Beam
VE	Vinyl-Ester	FCP	Flax Hybridised Carbon
EP	Epoxy	FUD	Flax Unidirectional
MAPP	Maleated Polypropylene	SEA	Specific Energy Absorption
MSO	Methacrylated Soybean Oil	VARTM	Vacuum Assisted Resin Transfer Moulding
HDPE	High Density Polyethylene	FVE	Flax fibre reinforced vinyl ester
VIS	Visual Observation	FBVEu	Flax fibre hybridised basalt reinforced vinyl ester unstitched
NL	Non-Linearity	FBVEs	Flax fibre hybridised basalt reinforced vinyl ester stitched
MLP	Maximum Load Point	neat VE	neat Vinyl Ester

Declaration

I hereby declare that this thesis is a presentation of my original research work and effort and that it has not been submitted anywhere for any award. Where other sources of information have been used, they have been acknowledged.

Signature: ……FAHAD…….

Date: ……30/01/2018……

1 Chapter 1: Introduction

1.1 Background and Research Motivation

In recent years, natural plant fibres were getting much attention as reinforcing materials in composites (Ahmad, Choi, and Park 2015; Pickering, Efendy, and Le 2016; Ramesh, Palanikumar, and Reddy 2017). Natural fibre reinforced composites (NFRCs) have become important materials due to their potential to replace synthetic materials such as glass and carbon fibre reinforced composites. By 2020, it is expected that fibres obtained from bio-based sources can reach up to 28% of the total market in the reinforcement materials (Shah 2013b). These attributes include, but are not limited to, high specific properties, low cost, low density and good biodegradability. These materials have inherent potential for use in many engineering applications (Faruk et al. 2012). Thus, NFRCs are promising and sustainable green materials for industries especially automotive. However, major issues with natural fibres are variation in properties and their susceptibility to moisture absorption because of their hydrophilic nature, which reduces the interfacial adhesion between fibre and matrix that effect on the mechanical properties (Summerscales et al. 2010). To tackle these problems, hybridisation of natural fibres with mineral or synthetic fibres has been used to have superior moisture resistance and thermal stability properties.

More recently, attention has focused on natural fibres hybridised with synthetic fibres, such as glass fibres (Sanjay, Arpitha, and Yogesha 2015) and mineral fibres, such as basalt fibres (Dhand et al. 2015; Fiore et al. 2015). The latter has lower amount of energy consumption compared to glass fibres (Fiore, Scalici, Badagliacco, et al. 2016). There are three possible ways to hybrid natural fibres into composites based on the type of materials, for example: natural–synthetic, natural-mineral and natural-natural fibres. The hybridisation of composite materials provide a better properties than single fibre reinforced composites such as strength, stiffness and ductility (Nunna et al. 2012).

Recent developments in NFRCs have led to renewed interest in semi-structural and structural applications especially in the automotive and construction sectors as an alternative material to synthetic fibre reinforced composites. The reasons for this shift to the use of natural fibre composites include increased global awareness and new environmental legislation requiring manufacturers to adapt sustainable materials (Hughes, Hill, and Hague 2002). Natural (bast) fibres have superior mechanical properties due to their chemical and structural composition

which contains high cellulose (about 74%) and aspect ratio with low micro-fibril angles. Thus, these fibres can be most appropriate to be used as reinforcements in the composite industries as these fibres provide the best potential integration of light weight and low cost, with high specific strength and modulus (Yan, Chouw, and Jayaraman 2014). However, NFRCs have low-durability and inherently absorb high moisture. These drawbacks can reduce their properties and thus affect the long-term performance of resulting composites. For example, increased moisture content into natural fibres causes swelling and alters their dimensions because of the poor adhesion/compatibility between the hydrophobic matrix and hydrophilic natural fibres (Dittenber and Gangarao 2012; Faruk et al. 2012). It is well accepted that the water absorption has significant influence on the properties of NFRCs, such as hemp (Dhakal, Zhang, and Richardson 2007), jute (Zamri et al. 2011) and flax (Anandjiwala et al. 2007). The inherent moisture presents in natural bast fibres is due to high cellulose and voids content. This behaviour can lead to inferior mechanical properties such as tensile and flexural strength of NFRCs.

Despite having many advantages, NFRCs have been mainly used in automotive interior components, hence have been restricted to non-structural applications (Faruk et al. 2014). Figure 1.1 depicts the applications of NFRCs in Mercedes E-class. One of the factors for this is due to not having enough test data on how these composites behave under different fracture toughness modes. Although, natural fibre composites have been slowly extended to structural applications, because of delamination and crack, as well as quest for high quality products. Detailed knowledge of crack resistance by improving fibre toughness is highly necessary. Natural fibre composites as far as their mechanical (tensile, flexural and impact), thermal and environmental behaviours are a concern and have been well investigated. However, there are very limited reported works investigating the fracture toughness behaviour of natural fibre reinforced composite materials.

Delamination is one of the most prevalent failure mechanisms in composite laminates; it usually occurs due to dynamic loadings, such as low-velocity impact when the structure is subjected to cyclic or static loading conditions (Zulki et al. 2002). Structural composites are essential to sustain external loads for long period of time. Thus, sufficient ability to absorb fracture energy is an important requirement for structure design, which is dependent on the fibre and matrix properties. Because of this, use of natural fibres, in the form of non-woven mats and short fibres, is limited in non-structural applications (Hughes, Carpenter, and Hill

2007). However, in order to obtain high performance composites in terms of stiffness and strength, it is important to use long continuous unidirectional fibres or woven non-crimp fabrics. It is well established that composite materials undergo different failure modes when different loading conditions are applied. These include delamination, matrix cracking and fibre breakage. However, in the case of natural fibre composites, there are further limitations in their application of structural or semi-structural applications as their delamination cracking and fracture toughness behaviour are not well investigated and understood. Therefore, understanding the fracture toughness and crack resistance behaviour under different modes of loading conditions are important and these are still at an early stage requiring more research for NFRCs to be used in load-bearing applications.

Figure 1.1 Applications of natural fibres reinforced composites in a Mercedes E-class, image adopted from (JEC Magazine, 2009).

1.2 Fracture Mechanics of Composite Materials

Fracture defined as a separation of the material into two pieces when subjected to stress, while toughness is the tendency of a material to withstand the crack propagation, and classified as brittle or ductile fractures. For example, brittle fracture behaviour results in rapid and unstable crack extension which absorbs low energy and has little plastic deformation like ceramics and glass fibres. Ductile fracture behaviour results in slow and stable crack extension which absorbs high energy and has large plastic deformation such as steel and aluminium (Zhu and Joyce 2012), as depicted in Figure 1.2. Fracture toughness is related to the amount of energy required to create fracture surfaces that describes the ability of the material to resist the crack when

applied to stress action (D.R. Moore, J.G. Williams 2001; Prasad, Venkatesha, and Jayaraju 2011). Griffith (A. A. Griffith 1920) has proposed the first theory of the essential energy for brittle materials such as composites, where the resistance was supposed to come only from the surface energy of the material. However, in the metallic materials, elastic deformation created at the crack tip absorbs more applied energy than the surface energy. Therefore, Griffith's energy theory underestimates the fracture strength of metals (Zhu and Joyce 2012). Irwin (G. R. Irwin 1956) modified this theory by using the strain energy release rate G, as the measure of the energy available of crack propagation. Irwin stated that when the strain energy release rate, G prevails upon the critical value G_c, as known fracture toughness, catastrophic propagation of the crack will occurred (G. R. Irwin 1957).

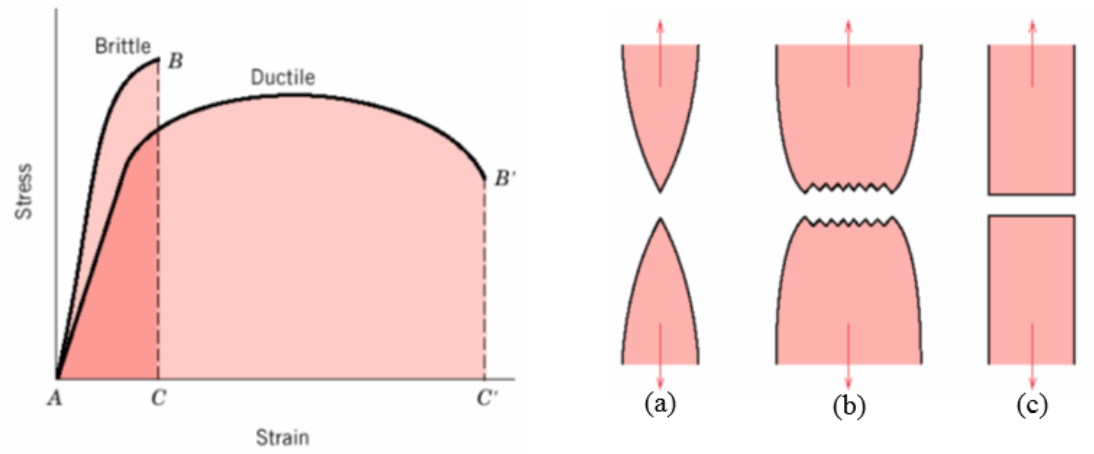


Figure 1.2 Brittle and ductile toughness, (a) very ductile, soft metals. (b) moderately ductile fracture (c) brittle fracture (Rocha-Rangel 2011).

The fracture toughness behaviour in composites can be characterised by using Linear Elastic Fracture Mechanics (LEFM) and Elastic-Plastic Fracture Mechanics (EPFM). These conditions depend on the attendance of all basic ideal conditions analysed in LEFM in which every material is elastic except at a point near the crack tips. In the study of the fracture toughness, one has to consider two important factors: the critical stress intensity factor (K_c) and the critical strain energy release rate (G_c). The former is a local parameter or a function of stress, strain and displacement near the crack tip and the latter describes a measure of energy necessary for crack initiation (T. L. Anderson 2005). The K_{Ic} which characterizes at a critical stress state can be calculated as it depends on the crack length [1.1]. Therefore, it is important to determine the fracture toughness of materials as cracks grow under stresses at the crack tip with catastrophic consequences.

$$K_{IC} = \sigma_f \sqrt{\pi \alpha} \qquad [1.1]$$

Where α is crack length at the outset and σ_f is an applied stress.

There are several tests that have been carried out in order to measure the interlaminar strain energy release rate of Fibre Reinforced Polymer (FRP) composite materials for different modes: mode I (tensile/opening), mode II (shear), mode III (tearing shear), and mixed Mode I/II, as illustrated in Figure 1.3 (Hull and Clyne 1996; Knott 1973). Mode I has been intensively studied using the Double Cantilever Beam (DCB) test and is universally accepted, but there are fewer tests that have been done or proposed to validate results in mode II. However, there are three fundamental tests used in mode II to measure the strain energy release rate, G_{IIc}. The most common test is Three-point End Notched Flexure (3ENF), but it is not yet approved by American Society for Testing and Materials (ASTM). It was developed for wood fracture characterization (Barrett and Foschi 1977; Panthapulakkal and Sain 2007). For plain strain fracture toughness in mode I/II, the strain energy can be related to the stress intensity factor as found in [1.2]:

$$G_{IC} = K_I^{\,2} \left(\frac{1-v^2}{E}\right) \qquad [1.2]$$

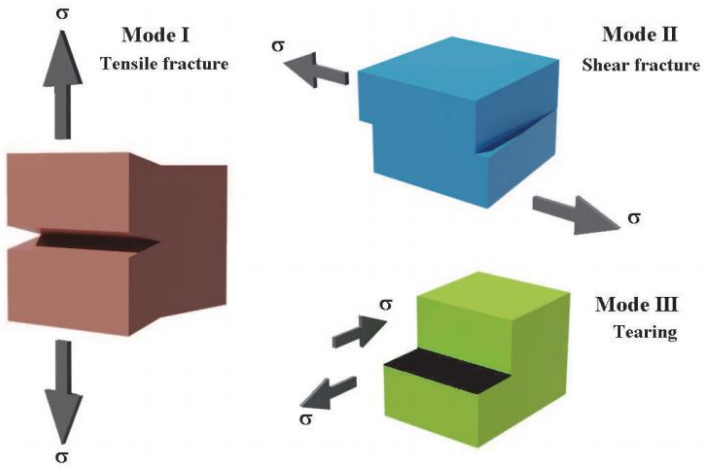


Figure 1.3 Fracture toughness modes (Rocha-Rangel 2011).

1.3 Research Aims and Objectives

The main aim of this PhD research was to achieve improvement in the interlaminar fracture toughness behaviour of natural fibre reinforced composites (NFRCs) by employing hybridisation and stitching techniques through thickness reinforcement. Most of the reported works on natural fibre composites have focused on the investigation of mechanical properties

such as impact, tensile and flexural behaviours. However, the applications of NFRCs composites have been limited to non-structural components due to lack of enough data and knowledge of delamination cracking and fracture toughness behaviour of these composites. Therefore, understanding the fracture toughness and crack resistance behaviour under different modes of loading conditions are important and these are still at an early stage, requiring more research on NFRCs to be used in load-bearing applications as an alternative to E-glass fibre reinforced composites.

In this study, bast fibres (flax, hemp, jute, ramie and kenaf) are chosen because of their attractive mechanical properties and easy availability as potential replacements for polymer-matrix composites towards the sustainability of green composites. In order to achieve high performance composites in terms of stiffness and strength, woven non-crimp fabrics as reinforcing materials embedded in a thermoset matrix have been employed. A vacuum infusion process was used for composite fabrication due to its versatility and cost effectiveness.

The main objectives of this PhD study are outlined as follows:

1- To achieve an in-depth understanding of natural (bast) fibre composites and their properties, especially the fracture toughness behaviour of composites and their damage characterisation.
2- To manufacture flax and flax/basalt fibre reinforced vinyl ester hybrid and stitched composite laminates.
3- To study the effect of hybridisation and stitching on Mode I and Mode II interlaminar fracture toughness of flax fibre and flax/basalt reinforced vinyl ester composites.
4- To investigate the influence of water absorption behaviour and its effects on the fracture toughness of hybrid and stitched composites.
5- To analyse the damage mechanisms of fractured surface and delamination of the composites using Scanning Electron Microscopy (SEM) and X-ray Computed Micro-Tomography (μCT).

1.4 Research Implications/Novelty

This PhD research is one of the first extensive work undertaken to study the fracture toughness behaviour of NFRCs. The outcomes of this research have been disseminated in the form of published papers in high impact factor journals such as Composites Science and Technology and Composite Structures, as highlighted in section 1.7.

This PhD research study has investigated the interlaminar fracture toughness behaviour of NFRCs by using novel techniques and has improved the delamination resistance of flax fibre reinforced vinyl ester composite materials for structural applications.

1.5 Timeline

This PhD research project started in February 2014 and ended in Jan 2018. A detailed plan and activities are presented in Appendix A.

1.6 Thesis Outlines

This thesis presents different aspects of the potential of plant (bast) fibres as reinforcements in structural or semi-structural polymer composites. The thesis consists of six chapters and three appendices. This chapter, *chapter 1*, describes a general introduction to the subject and briefly background of the fracture mechanics. In addition, explains the aims, objectives and outlines of the thesis. *Chapter 2*, contains a comprehensive review of natural (bast) fibres on their types, structures, characteristics, cultivation, harvesting, processing methods and applications. Other aspects related to the use of physical, chemical treatments, hybridisation and stitching to improve fibre-matrix adhesion and composites resulting in the enhancements of the mechanical properties and fracture toughness behaviour. In *chapter 3*, details the experimental procedures of the materials and fabrication of composite laminates. Evaluates interlaminar fracture toughness obtained from DCB and 3ENF tests, water absorption and characterisation testing. *Chapter 4 and 5* the effect of water absorption on Mode I and Mode II interlaminar fracture toughness of flax/basalt reinforced vinyl ester hybrid and stitched composites is investigated, with focus on the reduction methods of the experimental data. Furthermore, attention is paid for morphology study on the failure mechanisms of the fractured surfaces. Finally, *Chapter 6* presents the main conclusions and highlights points for the future work.

2 Chapter 2: Literature Review

Part I: Overview of Natural Fibre Reinforced Polymer Composites (NFRCs)

The previous chapter outlined the background and motivation of this research which address the importance of fracture toughness behaviour on natural fibre reinforced polymer composites. In order to understand this behaviour, it is important to review the main areas of natural fibres and composite materials in terms of structure, properties, growth and harvesting of bast fibres. In addition, it reviews the manufacturing process and composite materials characterisation using mechanical, fracture toughness and their morphological characterisation. It also reviewing and evaluation the previous studies of fracture toughness behaviour on natural fibre reinforced composites. In order to improve the interlaminar fracture toughness to be used in structural applications, the hybrid system and stitching through-thickness reinforcement will be covered. Furthermore, this chapter considers the current applications and future trend in automotive and construction industries.

2.1 Composite Materials

A composite material is made up of two or more materials, which collective form a new material. Figure 2.1 shows composition of composite materials between fibre and matrix. That new material has characteristics of both the materials, which enhance the performance and endurance of the new material. Composite materials are very light in weight, but they are very strong as compared to other materials existing naturally. Materials were selected on the basis of their unique characteristics that are required in the new material. Composite materials are very strong material because fibres and resin matrix are used to prepare that material. Fibre provides flexibility and endurance to the material, whereas resin matrix holds the fibres in place. Resin makes the material strong enough from outside to absorb any external impact, and it also protects the material from any damage (Matthews and Rawlings 1999).

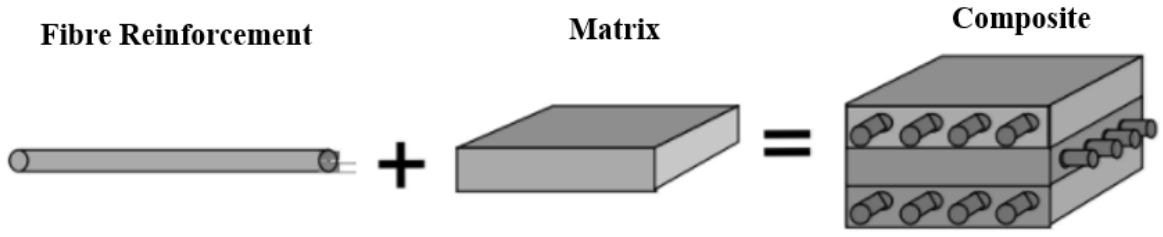


Figure 2.1 Composition of composite materials.

2.1.1 History of Composite Materials

Humans use composite materials from ancient times, but in 1930 its existence was recognised. Ancient Egyptian does not have any knowledge about composite materials, but houses found in ancient Egypt were made up of composite material. They use clay and straw from hay to make bricks for their homes. Use of these materials makes bricks stronger, but they did not know that these materials collectively form stronger brick as compared to regular brick built of clay. Another example of a composite material used in the past is bows used by Mongols. They made their bows using wood, cattle tendons, and silk and it is light, short, and strong. This short and strong bow provides them ease to use while riding the horse without losing its strength (Matthews and Rawlings 1999). In the World War I and II, composite materials were used to make aeroplanes, which helped to reduce the weight of the aircraft to increase its speed and performance. Later on, the composite material is used in automobile industry. Automobile industry uses this material in manufacturing frames and body of vehicles because this material is light and robust enough to replace aluminium (Chawla 1998).

2.1.2 Categories of Composite Materials

There are two types of composite materials: natural and artificial. For example, naturally occurring composite material is wood, and it is a composite of lignin and cellulose, which usually occur in the environment (Hoa 2009). The artificial composite materials are those materials which cannot occur in nature. Two or more materials are used to make an artificial composite material. Technology to produce better composite materials are improved in recent years, so it is used to manufacture a variety of materials like Metal-Matrix Composites (MMC), Ceramic-Matrix Composites (CMC) and Polymer-Matrix Composites (PMC) also increases. On the basis of reinforcement, it is further categorised into three types, namely particulate composites, fibre-reinforced composites, and structural composites (Yang et al. 2012), as shown in Figure 2.2.

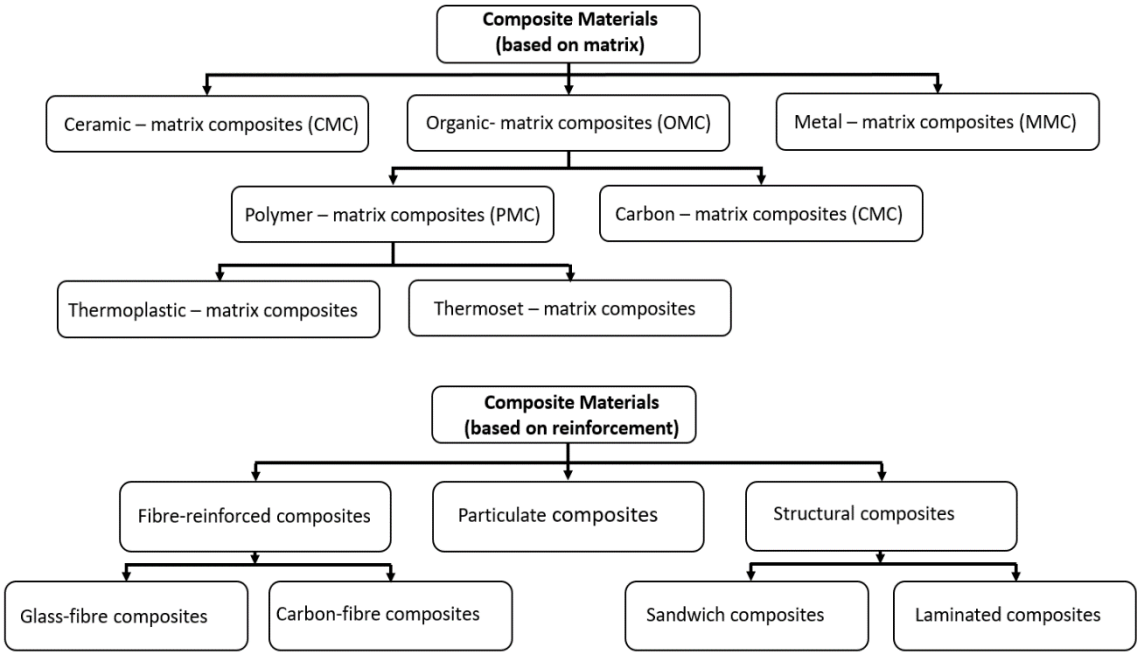


Figure 2.2 Classification of composite materials a) based on matrix and b) based on reinforcement.

2.1.3 Bio-composites

Biocomposites are made of reinforcing synthetic polymers or biopolymers with natural fibres to produce alternative material to replace glass fibre. Scientists are trying to create biocomposite materials using polymer matrices and fibres like grasses, sisal, hemp, flax, jute, wood, and banana (John and Thomas 2008).

Biocomposite materials have high demand in the world due to its vast use and petroleum crisis, which increases the need for this material in engineering and research sector. Composite material changed the global market by its verity of uses in different fields like automobile industry and aviation industry. It replaces the traditional polymer composites, which are made by mixing plastic and natural fillers. Traditional polymer does not show their properties after mixing (Faruk et al. 2012). Biocomposite material made by renewable resources is a futuristic technology helps to shape the future of engineering due to its vast application and properties (Amar K. Mohanty, Manjusri Misra 2005).

As petroleum resources are declining day-by-day and price of imported oil is increasing so it is necessary to find alternative of petroleum-based composites. Biocomposite is eco-friendly so that it provides the alternative solution to reduce the dependency on petroleum, which also helps to reduce carbon emission. Nowadays, industries prefer more green composites to enhance their growth, competitiveness, and sustainability (Mohanty, Misra, and Drzal 2002).

2.2 Polymer Matrices

Polymer composites have improved strength as compared to its essential components, and they are lightweight as compared to metals, so they are used in structural applications. Composites are good alternative for material due to its various properties like corrosion resistance, damage resistance and good toughness but associated cost of raw materials and difficult manufacturing process is the main issue in its production (Astrom 1997). The polymer matrix is of two types thermoplastic and thermosets. Composite materials are made by using polymeric matrix. Polymeric matrix plastic is made of a long chain of polymer molecule held by the covalent bond having similar chemical structure (F. L. Matthews 1999). Comparison between them as presented in Table 2-1.

Table 2-1 Comparison between thermoplastic and thermoset polymers (Matthews and Rawlings 1999; Stevens 1999).

Feature/Type	Thermoplastic polymer	Thermoset polymer
Structure	Linear	3-D network molecules
Material state	Solid	Liquid
Strength	High impact strength	Low impact strength
Viscosity	High	Low
Processing Pressure	High	Low
Processing Temperature	High	Low
Processing Time	Short	Long
Chemical reaction	No	Yes
Consolidation	By cooling	By chemical reaction
Reversibility	Can be reshaped	Cannot be reshaped
Recyclable	Can be recycled	Cannot be recycled
Reinforcements	Optional	Necessary
Fibre Concentration	Low	High
Manufacture	Injection and Extrusion	Hand lay-up, Vacuum bagging, Compression Moulding

2.2.1 Thermosets

Matrix is used to hold the fibre of the composite material, which is very important to manufacture the composite material. Both thermoplastic and thermosets can be used as the

matrix material to bind the natural fibre. A large number of components like catalyst, base resin, curing agent, and hardener are used to manufacture thermoset composites. This composite is heat resistant to some extent due to its cross-linked structure and resin becomes hard. The process of hardening of resin material when heat is applied is called vitrification (Chawla 1998). Its thermal stability is due to cross-linking structure, which increases the use of this composite in numbers of fields like the development of nano-composites. Thermosets turn into cross-linked structure due to undergoing molecular change in structure in which it turns from liquid to rigid cross-linked structure; this process is called curing. By controlling composition of thermoset and cure process, the composite can be turned into useful material (Lionetto and Maffezzoli 2013). It was reportedly that thermoset-based natural fibre reinforced composites (NFRCs) have better mechanical properties than thermoplastic-based NFRCs (Shah 2013a). Some examples of thermoset polymers are epoxy, vinyl esters, phenol formaldehyde, urethane and unsaturated polyesters. These resins are initially relatively low viscosity liquids, which cure to form a three-dimensional cross-linked polymer of essentially infinite molecular weight. Thermosets are more useful than thermoplastic due to their three-dimensional cross-linked polymer structure, for example, better dimensional stability and less flow under stress (Hull and Clyne 1996). The following is a brief description of thermosetting polymer matrix, which has been used in this study.

Vinyl Ester

Vinyl Ester (VE) resin is very rigid material, which is also chemical and moisture resistant in nature. It has excellent properties and it also provide hydrolytic stability as compared to other polymer resins (Guo et al. 2008; Sultania et al. 2010). Polymer resins other than VE do not offer control over cure process and favourable condition for reaction. VE resins are considered to have the best properties of epoxies and unsaturated polyesters (Holbery, J., & Houston 2006). There is a large number of areas where VE can be used, like in manufacturing of sports goods, electrical components, parts of automobile, adhesives, laminations, and coatings in the chemical industry. VE can also be used as thermoset in the field of infrastructure and transportation industry. VE gains its popularity in making of pipes, tanks, and reinforced structures due to its remarkable properties (Guo et al. 2008; Ku, H., Chan, W. L., Trada, M., & Baddeley 2007).

The chemistry of vinyl esters is complex reaction between epoxy and unsaturated carboxylic acid forms vinyl esters. It is more flexible due to cross-linking that occurs only at the end of

the molecule of VE in comparison to other cured polyester resins, as shown in Figure 2.3 and 2.4.

In polymerisation process, cross-linking is formed and it can also dissolve in styrene monomer due to its low viscosity (P.K. Mallick 2007). Its maintenance cost is very low as compared to other polymer resin in the long term (Ku, H., Chan, W. L., Trada, M., & Baddeley 2007). It is the new thermosetting polymer, but it has remarkable properties like high chemical resistance and high flexibility in design as compared to other polymer resins. Flexibility and moisture resistance of this material is enhanced by curing at room temperature so that it is used in automobile industry. Its chemical, thermal, and mechanical properties increase its use in different sectors like making deck, hull of ship, and energy absorption capability makes it more stringent and providing heat resistance to withstand up to 200°C (Marsh 2007). Furthermore, "the location of reactive sites at the ends of molecular chains on the vinyl ester resins means that these chains can absorb energy resulting in a polymer which is overall tougher than the alternatives" (Holbery, J., & Houston 2006).

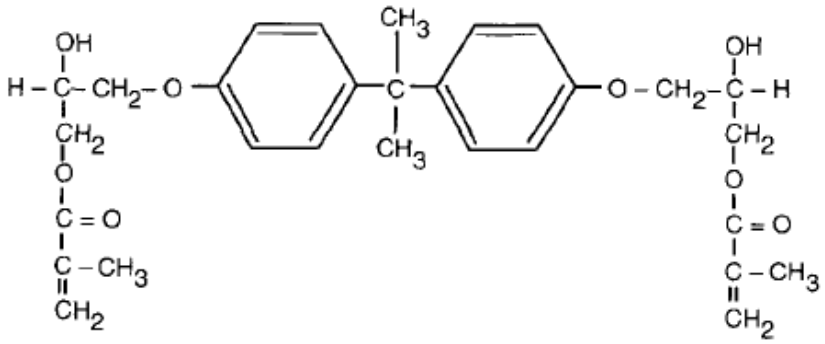


Figure 2.3 Vinyl ester chemical structure (S.T. Peters 2013).

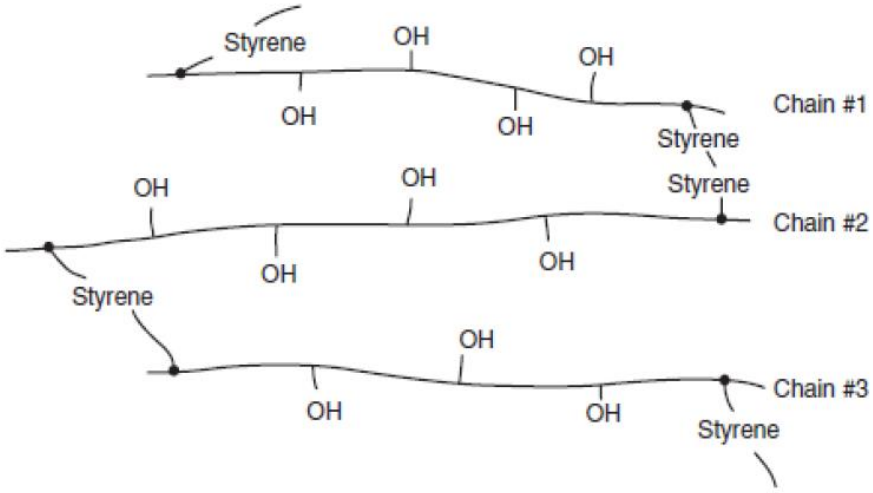


Figure 2.4 Schematic representation of a cross-linked vinyl ester resin (P.K. Mallick 2007).

Epoxy

Epoxy (EP) is traditional thermoset, which has excellent chemical resistance and it also has remarkably high mechanical properties as well as good heat resistance. Epoxy is used as the binding agent to hold the fibre in composite materials, which have the common epoxied group. These epoxied groups provide better functionality to conventional epoxy. Price of epoxy alone increases, as the use of epoxy with carbon fibre helps to reduce the production cost of the product made up of carbon fibre. Carbon fibre is used in military and aerospace industry to build military planes, vehicles, and space shuttles (May 1987).

2.2.2 Thermoplastic

Thermoplastic is a polymer, which has properties like plastic that can be melted or reshaped by applying heat and refreeze its shape after removal of heat. Its properties are different compared to thermosetting material, which cannot be reshaped after heating. Thermosets and thermoplastics are more useful within polymer industry because it is very easy to manufacture and it also has wide variety of applications. It cannot be used in places where the temperature is very high which causes melting of the polymer and losing its shape (Donald R. Askeland 2015). There is two common thermoplastic extracted from petroleum, PP and PE which is used in natural fibre reinforced composites (Faruk et al. 2014).

2.2.3 Bio-based polymers

Bio-degradable and bio-based polymers are different from each other. Bio-based polymers are manufactured by using a naturally occurring material and bio-degradable polymers are those

that can degrade automatically in nature without causing harm to the environment. For example, natural fibre reinforced composite is made up of natural fibre binds with any polymeric matrix to hold fibres in the place, whereas bio-composites or completely biodegradable composites are made up of natural fibres, which can completely degrade in the environment (Dittenber and Gangarao 2012).

Natural fibres and synthetic matrix are combined to form semi-disposable composites because the production of biopolymers is costly and they are not readily available in the market. Nowadays, popularity of bio-based polymers is increasing, and researches are conducted to replace the conventional plastic with bio-based polymers. Bio-degradable polymers have lower carbon footprint as compared to conventional polymers. Traditional plastic harms the environment because of lack of its biodegradable properties (Markarian 2008). Scientists are researching to introduce more eco-friendly technologies, which have less impact on the environment as compared to present technologies. Industrial ecology, eco-efficiency, and green engineering shape the future of technology by introducing biopolymers, bio-based, and biodegradable materials. These materials are becoming more popular in next generation, which spreads awareness toward eco-friendly materials to save our environment. These materials also help to improve the quality of life of people living all over the globe (Nair and Laurencin 2007). By 2020, it has been predicted that use of bio-based plastics across the world are going to increase by 3.45 million metric ton. PHA, PLA and starch-based plastic products are going to be used widely in the future (Faruk et al. 2012).

Material scientists are researching to find more applications of these materials to save our environment and to make this world a better place for living. Bio-based material is mainly of two types, which are biopolymers and bio-derived polymers. Bio-polymers are synthesis biologically by micro-organism, plants, and animals inside their biological system, whereas bio-derived polymers are chemically synthesised, which is made up of monomers, derived from amino acids, sugars, natural fats, or oils (Figure 2.5). Biopolymers have no impact on the environment as compared to bio-derived polymers because of their bio-degradable nature (Shakoor 2013).

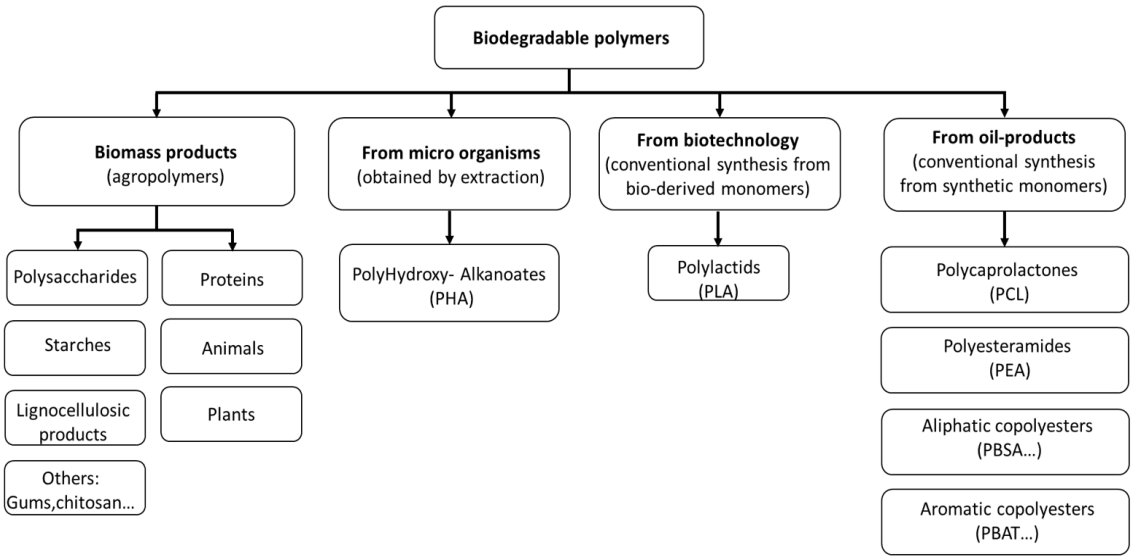


Figure 2.5 Classification of biodegradable polymers.

2.3 Natural Fibres

These fibres are naturally occurring fibres, which have no human intervention in its existence. These are obtained from plants and animals, some examples of natural fibres obtained from plants are hemp, jute, cotton, silk, and flax (Stevens and Müssig 2010). Natural fibre is readily available in nature, so they are used in reinforcement by humans in the past. Naturally occurring fibres are of two types, which are protein based and cellulosic fibre. Natural fibres are also obtained from vegetables, plants, and seeds. Cotton and sisal are the fibres obtained from seeds and leaves of plants. Natural fibres can be extracted from fruits and stems of plants; for example, the outer covering of coconut gives coir. The natural fibre obtained from coconut stems of plants is beneficial to make ropes because of their high tensile strength. Animal fibres are protein based fibres, and plant fibres are cellulose base fibre. Animal fibre like mohair, wool, and silk are obtained from sheep and worm or spiders, and feathers of birds give avian fibre. The natural fibre that is produced by the spider is used to form their web, which is very strong naturally occurring fibre (Saheb and Jog 1999).

2.3.1 History of Natural Fibres

Natural fibres play a significant role in the survival of ancient man in any situation and weather. Ancient man used plant and animal fibres to build their homes, make clothes out of animal skin, and ropes from the intestine of animals. Ancient Egyptians use natural fibres with mud to strengthen the brick from which they build their houses. In Denmark, archaeologists have found clothes of ancient humans, which are made up of animal skin and nettle. India and Europe are

using cotton as natural fibres for very long time; some of them like leaves used for making clothes are discontinued in modern days. Synthetic fibres are extracted from petroleum product, so it becomes more costly to produce as compared to natural fibre (Frederick T. Wallenberger 2003). At the time of World War I and II, synthetic fibre gains popularity over natural fibre, but as the price of crude oil increases, so the popularity of synthetic fibre is decreased as compared to natural fibre. Synthetic fibres are not eco-friendly and it is not bio-degradable in nature as compared to natural fibre. Nowadays, people are more concern about the environment; people prefer eco-friendly products as compared to conventional products, so they gravitate towards natural fibre. Natural fibres are bio-degradable in nature, which means they have no carbon footprint so that new generation prefers these over synthetic materials (Mallick 1993).

2.3.2 Advantages and Disadvantages of Natural Fibres

Many benefits are associated with the use natural fibre in place of synthetic fibres. The very first benefit of natural fibre is that they are environment-friendly and hence biodegradable. Biodegradability of any product is related to the time they take for disintegration. The natural fibres take lesser time than the synthetic fibres such as carbon and glass. Moreover, the amount of energy required for producing these products is also low when compared with carbon fibre and glass (Alhuthali, Low, and Dong 2012; Osorio et al. 2011). Secondly, the density of natural fibre is as low as 1.25-1.5 g/cm^3 while the density of synthetic fibre varies with the product. For example, the density of carbon fibre is 1.8-2.1 g/cm^3, and the density of E-glass is 2.54 g/cm^3. Therefore, the product fabricated with natural fibre is lighter compared to the one produced with synthetic fibres (Sgriccia, Hawley, and Misra 2008). The third benefit linked to natural fibres is the modulus-weight ratio of these fibres is matchless which makes the stiffness-critical design successful (P.K. Mallick 2007). Lastly, the acoustic dumping property of these fibres makes them preferable to noise attenuation in interior parts and products of automobile. (Alhuthali et al. 2012; P.K. Mallick 2007).

However, with benefits, there are some disadvantages of natural fibres, more specifically as reinforcement in polymer composites. The natural fibres may not be compatible with polymer matrices, may form aggregates during processing, have variation in price and quality, have lower durability, moisture resistance capability is also poor, and it is difficult to use an established process of manufacturing (Araújo, Waldman, and De Paoli 2008; Dittenber and Gangarao 2012). The interface strength of these fibres is lower than glass and carbon fibres

composites due to incompatibility with polymer matrices. The presence of polar groups such as hydroxyl makes the fibre hydrophobic in nature which in-turn leads to incompatibility with hydrophobic polymer matrix (Chen, Miao, and Ding 2009; Dittenber and Gangarao 2012; Xie et al. 2010). Natural fibres have weak adhesion to hydrophobic matrices due to the hydrophilicity, which is high moisture absorption and retention property. This property of natural fibres can cause the produced composites to fail if the conditions are wet as the product tends to swell or delaminate (Araújo et al. 2008; Dittenber and Gangarao 2012).

2.3.3 Types of Natural Fibres

Natural fibres are the oldest fibres to be used in reinforcement due to their easy availability. Natural fibres especially those from vegetables have further been categorised according to their source. There are three types of natural fibres. The natural fibres based on the sources that are used in day-to-day activities include animal fibre, plant fibre and insect fibre. The animal fibres are obtained from an animal such as wool, plant fibres such as cotton, are derived from plants, and lastly, mineral fibres like basalt is obtained from volcanic rock (Hull and Clyne 1996). The plant fibres can be obtained through leaves, steam, and fruits (Figure 2.6). The following section 2.4 will be focused more on the bast (stem) fibres.

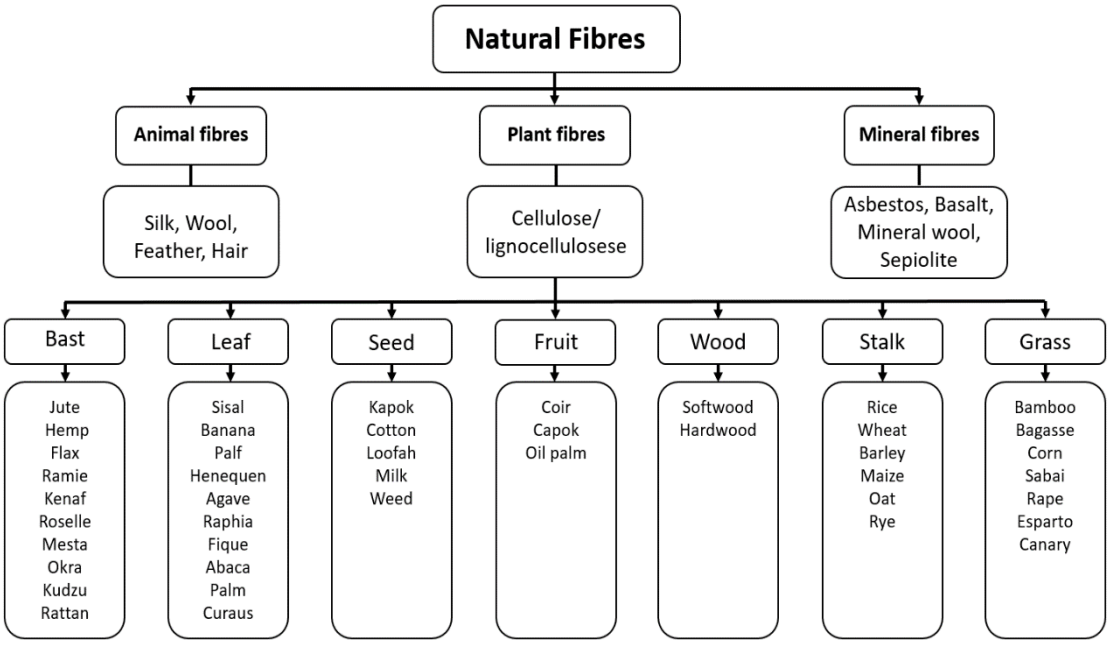


Figure 2.6 Classification of natural fibres (Mohanty et al. 2002).

2.4 Bast Fibres

One of the natural fibres most used as reinforcement for polymeric materials are bast fibres that are obtained from the outer layer of different plants' stems. Natural fibres from the family of bast plants (flax, hemp, jute, kenaf and ramie) are potential replacements for synthetic or manmade materials (Summerscales et al. 2010). Natural bast fibres have been around for many years and used as reinforcement before synthetic fibres were made or discovered (Frederick T. Wallenberger 2003). Recently, bast fibres are actually being used as reinforcements in several industries (automotive, construction and building) because of increasing environmental awareness (Faruk et al. 2014). In addition, they offer many advantages of these fibres are low density (lightweight), low cost (cost effective one third or less than glass fibre), excellent mechanical properties with good specific properties, recycling (towards for green products), biodegradability and renewable resources (the desire for green environment) (Faruk et al. 2012, 2014). However, there are some disadvantages which limit their application use in industrial sector such as incompatibility of hydrophilic fibres with hydrophobic polymer matrices, high moisture absorption (causes swelling fibres), lower strength properties and variable quality during different stages of production (from plant growth to supply stage) (Biagiotti, Puglia, and Kenny 2008; Faruk et al. 2014; Saheb and Jog 1999).

2.4.1 Flax

Flax, of botanical name *Linium usitatissimum*, is located in the stalks of a dicotyledenous plant (Singleton et al. 2003). There are 180 species around the world. In the UK they are mainly sown in March-May and can reach up to a metre in height (Lewington 2003). Figure 2.7 shows three types of flax in forms of (a) plant, (b) fibre and (c) fabric. Flax fibre has a capability to absorb water up to 12% of its own weight, and when wet its strength increase by 20% (Tahir et al. 2011). India and North America are the main producing for flax seeds but flax is really grown in Russia, China and Western Europe for the production of fibres. Oil is extracted from its seeds and it is being used in other industries, for example in cosmetics, feedstock, medicines and paints (Morvan et al. 2003). Its applications in composites is widely accepted over glass fibres because of the environmental impact (Baley 2002). The flax fibres that were good value assets in the textile industries are now widely making their way into the composite sectors, (Faruk et al. 2012), and are amongst the natural fibres used in thermoplastic matrix composite

panels found inside car door panels, car roofs, boot linings and shelves (Bledzki and Gassan 1999; Brahim and Cheikh 2007; Summerscales et al. 2010).

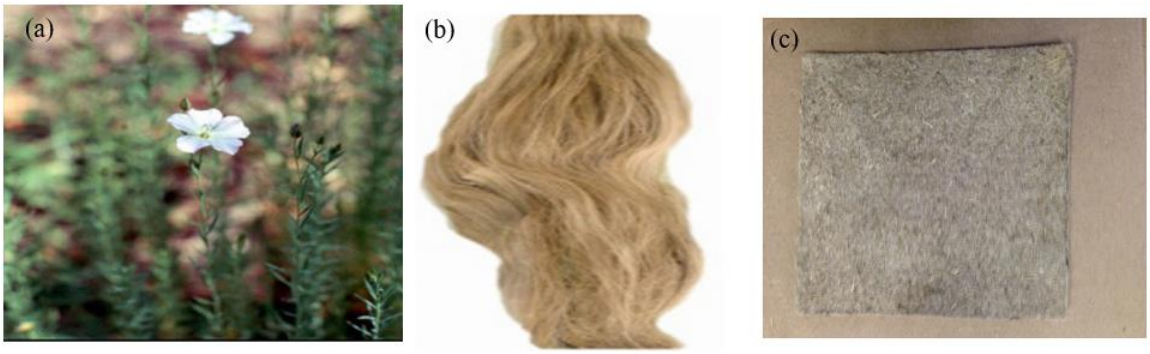


Figure 2.7 (a) Flax plant (Ramesh et al. 2017), (b) flax fibre (Satyanarayana et al. 2009), (c) non-woven flax fabric mat.

2.4.2 Hemp

Hemp is another plant used in composite materials and belongs to the family of *Cannabis sativa L.* It is grown in moderate climates (Faruk et al. 2012). The range length of hemp fibre from 1.0–2.5 m (Summerscales et al. 2010). Figure 2.8 depicts three kinds of hemp in form of (a) plant, (b) fibre and (c) fabric. Beside other natural fibres used in polymer composites, hemp is well blended with these composites. Among the all producers of hemp, China is considered to be the biggest (Niu et al. 2010). The strength of the plant is due to the structures of the fibres within the stem that provide the stiffness and rigidity that makes hemp a useful material to be used in reinforcing composite materials (Shahzad 2011) . In the European Union (EU), hemp is important for the pulp, automotive and paper industries (Karus and Vogt 2004). Hemp fibres have been used in different application for a long time. It is used in making cords, clothing and medicines, but more recently it has found its way into car manufacturing for non-structural components due to its remarkable strength and it is less expensive than conventional materials used in reinforcements (Dhakal et al. 2007; Karus and Kaup 2002).

Figure 2.8 (a) Hemp plant (Ramesh et al. 2017), (b) hemp fibre (Satyanarayana, Arizaga, and Wypych 2009), (c) non-woven hemp fabric mat.

2.4.3 Jute

Jute, another potentially suitable fibre, is extracted from the stem of plants, is generally widely available in Europe, imported from Asia (Menachem Lewin 2010). Jute comes from the genus *Corchorus* and the most common are the *Corchorus capsularis* that has a globular shaped pod and the *Corchorus olitorius* which is cylindrical in shape. Figure 2.9 illustrates three kinds of jute in form of (a) plant, (b) fibre and (c) fabric. Besides cotton, it is the second most common natural plant cultivated in the world for its fibres (A. K. Mohantya & M. Misraa 1995), and it is one of the cheapest natural fibres which are produced in large quantity (about 100 species) (Faruk et al. 2012). Either in hot or humid environments the plant can reach 2.5 to 3 metres in just 4 to 6 months (Mwaikambo 2006). Jute has been spun into coarse, strong threads, for the making of fabrics and now it is used in the composite industries for the making of panels, profiles, frames, doors and roofing (Singh and Gupta 2005). More reasonably, it can be used in the automotive industries.

Figure 2.9 (a) Jute plant (Tahir et al. 2011), (b) jute fibre (Source: *www.commons.wikimedia.org*), (c) non-woven jute fabric mat.

2.4.4 Kenaf

Its scientific name is *Hibiscus cannabinus, L*. Kenaf is a member of the *Malvacea* family. The fibres of Kenaf have been used in composites and in automotive industries (Karnani, Krishnan, and Narayan 1997). The cultivation of Kenaf can be found in the United States, Asia (India, Bangladesh and Thailand), in the South-east of Europe, South Africa and Brazil. In the latter, it is cultivated throughout the year (Amel et al. 2013; Shi et al. 2011). Figure 2.10 shows three types of kenaf in forms of (a) plant, (b) fibre and (c) fabric. Kenaf is known to be adaptive to a wider range of climates and soil than any other fibre plants. Its cultivation in the United States is of commercial aspect and has been a source of textile fibres for such products as ropes, canvas and other fibre products (Zampaloni et al. 2007). As a cellulose rich plant, it has great advantage both ecologically and economically. Under suitable conditions, the plant can grow to a height of 2.7 to 3.6 metres with a base diameter of 3 to 5 cm (Abdul Khalil et al. 2010; Akil et al. 2011). Kenaf has a combination of bast fibres (outer bark) and inner core fibres. The

bast fibres make up 30-40% and 60% of the stem on a dry weight basis (Lee and Eiteman 2001). Kenaf is also suitable for reinforcement in composite materials but it needs to be treated

Figure 2.10 Kenaf plant (Ramesh et al. 2017), (b) kenaf fibre (Satyanarayana et al. 2009), (c) non-woven kenaf fabric mat (Sharba et al. 2016).

2.4.5 Ramie

Ramie (*Boehmeria nivea chinensis* or *Boehmeria nivea indica)* belongs to the nettle family *Urticacea* and there are about 100 species. It is a bast fibre and the part that is being used is the bark of the stem or stalk. Figure 2.11 describes three kinds of hemp in form of (a) plant, (b) fibre and (c) fabric. Ramie did not join the same popularity as other bast fibres for textile uses because the extraction and treatment are expensive (Faruk et al. 2012). Ramie can reach a height of 1 to 2.5 metres and it can be harvested 3 to 6 times a year (Mwaikambo 2006; Zhang and Yan 2013). It is one of the oldest fabrics that recently regained popularity. It grows mainly in China, Taiwan, Korea, the Philippines and Brazil. The two species referred to in this section share similar properties and have been found to be widely used in the paper and textile industries (Paiva Júnior et al. 2004). Ramie can be found in many commercial products such as clothing, tablecloths, napkins, handkerchiefs and often in combination with cotton and other fibres for its strength. It is also used in fish nets and fire hoses (Robert R. Franck 2005).

Figure 2.11 Ramie plant (Ramie 2009), ramie fibre (Source: *www. Etsy.com*), (c) ramie-cotton fabric mat (Satyanarayana et al. 2009).

2.5 Structure of Bast Fibres

Natural bast fibres are strong, cellulosic fibres obtained from the phloem or the outer bark of plants like jute, kenaf, flax, ramie and hemp. The fibre is around the outside of the plant and comprises one-third of the weight. The centre (core) has many uses, including animal bedding and oil absorbents. Unlike synthetic fibres, bast fibres are made up of bundles of fibres. These bundles are broken down mechanically or chemically to obtain the best quality for their specific uses in different industrial products which include cars and planes. Flax, jute and hemp have been shown to be the best in improving the physical behaviours, such as tensile, bending strength and the modulus in composites (Biagiotti, Puglia, and Kenny 2004).

Natural bast plants (hemp, flax, jute, ramie and kenaf) have similar properties. For example, the macrostructure of flax fibres that produced from the stem is contained in epidermis, bark, phloem, bundle, xylem, marrow and hollow (Figure 2.12). The microstructure of flax fibres is actual complex because of its hierarchical structure through different size scale; their classified as primary and secondary cell walls encircling a central cavity known as lumen, which results to water uptake (Baley 2002; Fiore, Scalici, Calabrese, et al. 2016). The primary cell wall which is the first layer at the beginning of cell growth surround the outer of secondary wall and constitute only 0.2 µm of thickness (Baley 2002; Yan et al. 2014). The secondary cell wall divided into three parts as called S1 (0.5-2 µm), S2 (5-10 µm) and S3 (0.5-1 µm). In the middle of cell wall S2 layer has a thick size that determine the physical and mechanical properties of the entire fibre, as depicted in Figure 2.13 (Fiore, Scalici, Calabrese, et al. 2016). Flax fibre has a high cellulouse around 65% with form of crystalline fibrils spirally in a matrix of amorphos hemicellulose about 16% and liginin of 3% (Baley 2002; Bismarck et al. 2002).

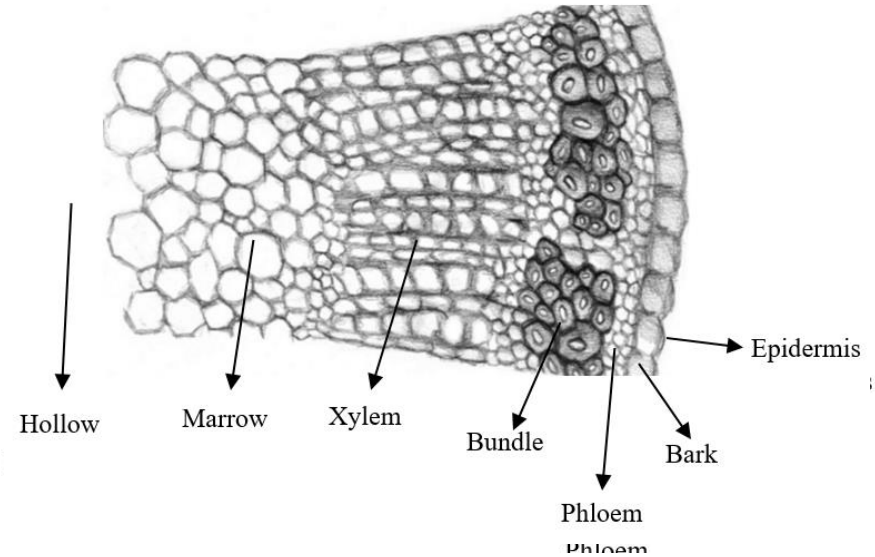


Figure 2.12 Structure of flax fibre from the stem at the macro level.

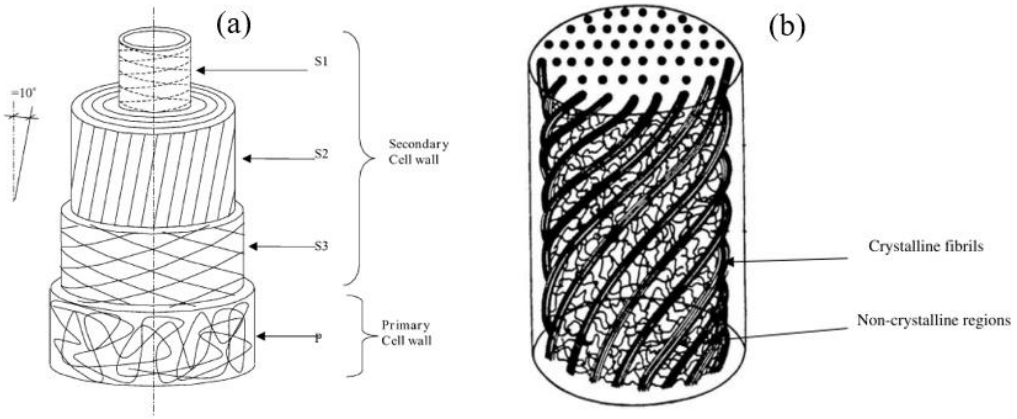


Figure 2.13 (a) Elementary structure of flax fibre cell (Baley 2002; Stamboulis et al. 2001), (b) Standard of flax fibre structure at the micro level, represent spirally layout of fibrils in cellulose fibre (Baley 2002).

2.6 Chemical Composition

Natural plants from bast have a woody core that is enclosed by a stem. Inside the latter there are a number of bundles, which contains individual cells or filaments. The filaments are mainly cellulose, hemicellulose, lignin and pectin (Biagiotti et al. 2008; Morvan et al. 2003; Shahzad 2011; Yan et al. 2014). The stem is divided into an outer cell wall or primary cell wall and an inner secondary cell wall. Each layer is composed of cellulose, hemicellulose pectin and lignin in varying proportion among the bast family. A brief study of each of these components (cellulose, hemicellulose, pectin and lignin) is described in this section 2.6.

2.6.1 Cellulose

Cellulose is essential to plants. It is an organic compound, which consists of carbon, hydrogen and oxygen (Baley et al. 2006; Bledzki and Gassan 1999; Wang, Sain, and Oksman 2007). It has a linear structure and the general chemical formula is written as $(C_6\ H_{10}\ O_5)_n$, where n stands for the number of glucose, $C_6\ H_{10}\ O_5$, molecules joined together to form a chain like structure, as revealed in Figure 2.14 (Summerscales et al. 2010). The nature of bonding between the glucose molecules in the cellulose structure provides the strength of the fibres and contribute to the stability of the bast plants under different environmental conditions (Biagiotti et al. 2004). According to (Akil et al. 2011; Biagiotti et al. 2004), the bonding is caused by hydrogen bonds between adjacent molecules of glucose that form the cellulose fibres. For example, the fibres that are produced in the stems of flax bast plant are a cellulose polymer, their structure is more crystalline, which makes their stronger. The plant can grow up in length

up to 90 cm and it possesses strong fibres all along its stem. The average diameter of the fibres is between 12 and16 μm (Yan et al. 2014). The outer cell wall also referred as the primary cell wall surrounds the secondary cell wall which is responsible for the strength of the fibres. The secondary cell wall which is mainly crystalline cellulose micros-fibrils, which are embedded in the matrix. It is made up of pectin and hemicellulose (Baley et al. 2006; Shahzad 2011; Wang et al. 2007; Yan et al. 2014).

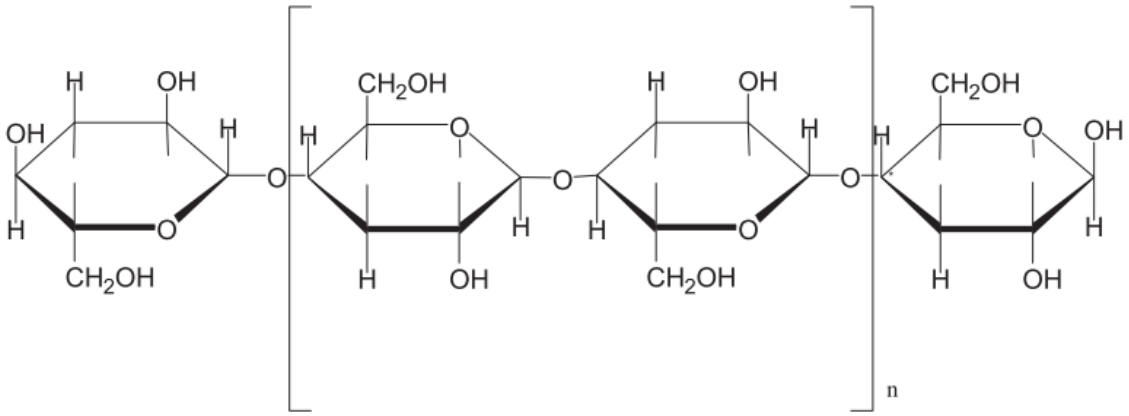


Figure 2.14 The structure of cellulose (Akil et al. 2011)

2.6.2 Hemicellulose

Hemicellulose contains many different sugar monomers (See Figure 2.15). In contrast, cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose is xylose, which is present in large amount. It is a branched polymer and consists of short chains of sugar, whereas cellulose is linear and made of long chains of sugar. While cellulose has finite structure, hemicellulose has irregular shape due to presence of branches in its structure (Biagiotti et al. 2004). Hemicelluloses are embedded in the cell walls of plants. They are bound to cellulose by pectin to form a network of cross-linked fibres. Hemicellulose is partly soluble in water and hygroscopic because of its open structure and containing many hydroxyl and acetyl group. Lignin and pectin act mainly as bonding agents.

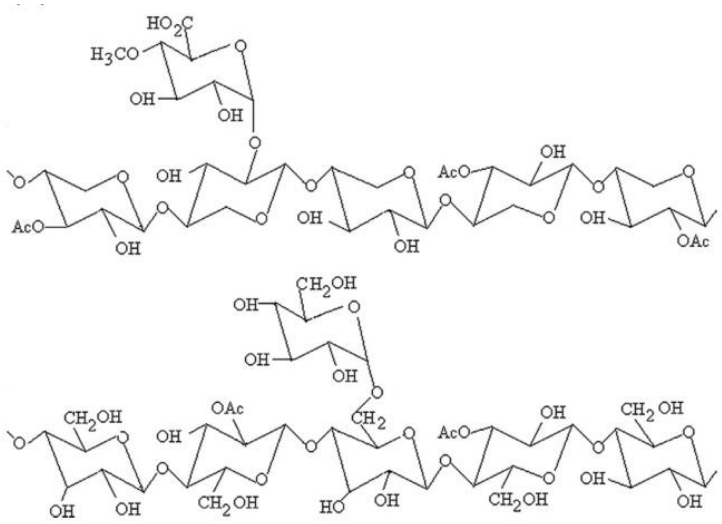


Figure 2.15 Chemical structure of hemicellulose (Thakur and Thakur 2014).

2.6.3 Pectin

Pectin is a complex set of polysaccharides contained in the primary cell walls of bast plants . In the middle lamella, pectin helps to bind cell together. It is also present in primary cell walls. Over time in a plant, the chemical and structural compositions of pectin may differ from the root to the top of the plant and from one plant to another in the same field. The presence of pectin important cell wall because it allows primary cell wall extension and plant growth (Biagiotti et al. 2004; Yan et al. 2014).

2.6.4 Lignin

Lignin is an aromatic organic compound. It is most commonly derived from wood, and is an integral part of the secondary cell walls of plants. It may play some role in holding the bundles together in the cell walls (Morvan et al. 2003). The composition of lignin varies from species to species. It may vary between 0.9% and 13% (Morvan et al. 2003; Shahzad 2011).

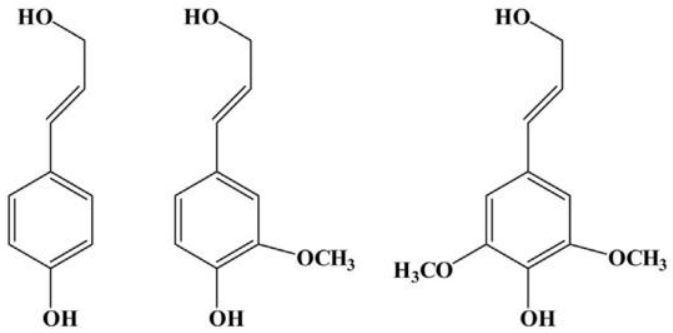


Figure 2.16 Structure of lignin (Vijay Kumar Thakur 2013).

The following tables summarise the percentage composition of the four constituents described above for different bast fibres. Tables 2-2 and 2-3 present the difference in the constituents of flax and hemp fibres which is attributed to various species, the variety of plants, and the quality of the soils, weathering conditions and the process used to obtain the bast fibres (Shahzad 2011; Yan et al. 2014) and Table 2-4 illustrates five bast fibres considered in section 2.4 (Akil et al. 2011).

Table 2-2 The chemical composition of flax fibres (Baley et al. 2006; Yan et al. 2014).

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)
64.1	16.7	1.8	2.0
67.0	11	-	2.0
73.8	13.7	-	2.9
65.0	-	-	2.5
62.0 – 72.0	18.6 – 20.6	2.3	2 - 5
71.0 – 75.0	18.6 – 20.6	2.2	2.2

Table 2-3 The chemical composition of hemp fibres (Shahzad 2011).

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)
67.0	16.1	0.8	3.3
74.4	17.9	0.9	3.7
74.0	18.0	1.0	4.0
55.0	16.0	18.0	4.0
76.0	11.5	1.3	3.2
57 – 77			9.0 – 13.0
75.1	< 2		8.0
70.0 – 74.0	17.9 – 22.4	0.9	3.7 – 5.7
75.6	10.7		6.6
78.3			2.9
76.1	12.3	1.6	5.7

Table 2-4 The chemical composition of commonly used bast fibres (Akil et al. 2011).

Fibres	Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)
Flax	71	18.6 – 20.6	2.3	2.2
Hemp	70 – 74	17.9 – 22.4	0.9	3.7 – 5.7
Jute	61 – 71.5	13.6 – 20.4	0.2	12 – 13
Kenaf	45 – 57	21.5	3 – 5	8 – 13
Ramie	68.6 – 76.2	13.1 – 16.7	1.9	0.6 – 0.7

2.7 Processing of Production Bast Fibres

Different methods can be employed to extract fibres from bast plants. The production techniques of fibres depend on their application of industry. Several extraction methods of fibres are explained below:

2.7.1 Retting

The stems are allowed to decompose in the field for the extraction of fibres, and this complete process is referred as retting (Figure 2.17). The decomposition of Pectin, which acts as a binding agent for cellulose fibres and tissues, is made by micro-organisms (Baley et al. 2006). The different techniques in which retting is performed are Dew Retting, Water Retting and Chemical or enzymatic Retting.

Figure 2.17 Retting process for hemp fibre (Source: http://www.lohascouture.com).

The operation of dew, sun and fungi, which are dispersed on the ground after the removal of leaves and seeds from the bast plants, is incorporated in the process of dew retting. The duration of dew retting varies from 2 to 4 weeks (Baley et al. 2006; Tahir et al. 2011). The process of dew retting relies on the climatic conditions and fibres which are polluted with soil (Tahir et al. 2011). For instance, to generate a dark flax (grey in colour), the flax straws are kept open to the atmosphere for 3 to 4 weeks by spreading them on the ground or any open area. A mechanical separation of fibres for the plant residues is made with the scutching process (Baley et al. 2006)

Bast plants are immersed in the stagnant pools, rivers, ditches (dam retting), or in specially designed tanks in the process of water retting. To carry out the bacterial decomposition process of bast plant stem, by dam retting process, a duration of 3 to 4 week is required. A few days are needed in the process of tank retting through warm water for obtaining the bast fibres. However, a long duration of time is required in Stream retting for the removal of fibres from the stem. The fibres thus obtained are uniform in nature, and their quality is also superior (Bismarck et al. 2002; Tahir et al. 2011; Yan et al. 2014). Environmental pollution is caused by the process of ware retting (putrid odour and water contamination) (Tahir et al. 2011).

A reaction of dried plants is carried out with an aqueous solution of sodium hydroxide, sodium carbonate, soaps, or mineral acids, in the process of chemical retting. The protection of fibres from damage is an important concern, as this factor affects the quality and mechanical properties of the fibres. The quality of fibres produced is responsible for the process of chemical retting is not superior in comparison with the process of dew or water retting (Tahir et al. 2011). This process is beneficial as it takes lesser time than water or dew retting. Additionally, the waste products generated through this process is cheaper than the process of chemical retting.

A uniform quality of fibres is produced with the Enzymatic retting process, as this method is advantageous over other methods of retting. This process is expensive in comparison to the traditional methods of fibre generation process (dew or water retting) (Tahir et al. 2011).

2.7.2 Extraction

The process involved in the extraction of fibres contains highly negatively charged polymers. The polymers which exist in bast fibres are treated with an alkaline solution to extract the pure strands. The hemicellulose and pectin are also removed by the treatment of alkaline solution (Morvan et al. 2003).

Figure 2.18 Linen fabric is extracted from the stems of the flax plant. Source: (htt*ps://www.naturalfibersinfo.org*).

Other methods, for instance, boiling, high-temperature loosening method, and bleaching can be used to generate bast fibre of high quality such as hemp, ramie and flax. The fibre extraction process is carried out by two times bleaching process, two times boiling of alkali and the process of high-temperature loosening (Xu 2009). Chlorine and oxygen are used in the process of two times bleaching process. Sodium Hypochlorite (concentration of 3-8 g/L), at a temperature of 35 to 45^0C is used in the process of chlorine bleaching. In the same context, Hydrogen Peroxide (concentration of 4-6 g/L) is used at a temperature between 80 and 100^0C in the process of oxygen bleaching. The releasing of fibres is made in the presence of caustic soda which has a concentration of 100 to140 g/L (Xu 2009), and the process of releasing is done after two times boiling and bleaching by maintaining a temperature between 100 and 140^0C. Lignin, which is present in this process is removed, and production of fibres which are rich in cellulose is carried out efficiently (Wang et al. 2007).

2.7.3 Hackling

The quality of fibres can be enhanced with an extra process which is referred as a combing process. The dirt and short length fibres are separated from the sliver lap with the support of hackling process which incorporates following techniques.

- A thin lap of fibres is gripped between the specially designed jaws across the width of jaws.

- The needles which are placed closely, are made to pass through the protecting through jaws.

Figure 2.19 Combing the bundle of flax fibre on a hackling process. Source: (https://gatherandgrow.org).

The quality of sliver which is generated from the hackling machine is enhanced through the process of combing. The parallelisation of fibres is achieved through the process of combing, as it eliminates short fibres and straightens curls, and impurities. The purpose of this process is to obtain a superior quality of fibres, and the objectives of raw materials must be fulfilled to achieve raw materials which have physical and mechanical features above than the average level, that is used at the starting of spinning process (Goutianos et al. 2006; Miao and Finn 2008). The curls behave in a similar way as curls when they are combed properly in the process of parallelisation and hence they are removed if straightening is not done efficiently. It becomes necessary to reduce the number of curls before the stage of combing, as they generate a large amount of waste fibres. In the stage of combing preparation, some of the curls are straightened naturally, and hence it becomes necessary to pass the curls through hackling machine (James M. Dempsey 1975).

2.7.4 Spinning

The twisting process, used for both natural and synthetic fibre, can be used to generate yarn and filaments (Figure 2.20). Two techniques can be employed for spinning in the bast industry. These methods are referred as ‘wet spinning’ and ‘dry spinning’ (Summerscales et al. 2010). The polymers which are dissolved in a solvent employs the process of dry spinning. A current of hot air is used to evaporate the solution in the process of dry spinning, and this process helps

in obtaining filaments which are solid in nature, and the recovery is solvent is also made in the process. The solution is made to pass through spinnerets in a chemical bath, and a solid filament is formed after the removal of solvent (Parr 1976). Both scutching and hackling produce waste fibres known as tows which has been used in coarse count yarns (through the dry spinning method), and in industrial products like ropes and twines (Miao and Finn 2008).

Figure 2.20 Flax fibre spun into yarn or thread.
Source: (https://www.pinterest.com).

2.7.5 Steam Explosion

An alternative retting procedure is represented by the method of steam (Bismarck et al. 2002; Hepworth et al. 2000). High temperature and pressure are applied to the plants with an appropriate content of cellulose, in this process. The clean output is generated with a rough surface and enhanced crystalline index (Mwaikambo and Ansell 2002). For a duration of 1 to 10 minutes, the process of a steam explosion is carried out at 450 psi either/or 3.1MPa of the pressure value, and after this process, products are discharged at a specific value of atmospheric pressure (Biagiotti et al. 2008). Space which exists between fibres in the bundle of Bast fibres is covered by high-pressure steam and high-temperature application (flax for example) (Bledzki and Gassan 1999). Lignin is separated from celluloses because of this process (Biagiotti et al. 2004). The bonding between lignin and cellulose that material contains is modified with an explosion of continuous steam, in high pressure and controlled conditions of time and temperature. In context to this, a reduction can be seen in the use of chemicals and energy which are employed in the process of refining the fibres (Biagiotti et al. 2008). According to Biagiotti et al. (2008), the properties of resultant fibres of flax are enhanced, and their response is improved when they are treated with a solution of hydrogen peroxide. The fibres are washed and dried at room temperature. The fibres thus obtained after the process of

the steam explosion have comparatively high drainage rate and purity with the other method of fibre extracting.

2.8 Cultivation and Quality Issues

2.8.1 Cultivation

Several traditional and new age products use Bast fibres. A number of synthetic materials are replaced by natural fibres, which is due to increase in the requirement of recycling products (Thomas and Pothan 2009). In this section 2.8.1, briefly describes the condition for cultivating the common bast plants.

Hemp

The climatic conditions that are required for hemp are 625 to 750 mm of rainfall, humid and mild atmosphere. Along with these circumstances an appropriate soil moisture for germination of seeds is required (Tahir et al. 2011). The biggest producers of hemp are China, South Korea, and Russia, as they produce 70% of the total production of hemp fibres (Tahir et al. 2011). The organic process of growing hemp is a natural process, as herbicides, fungicides or pesticides are not required in the growth process of hemp (Summerscales et al. 2010).

Flax

Flax is one of the oldest fibres that has been known to mankind (Nguong, Lee, and Sujan 2013). A period of three months is required for the complete growth of flax with appropriate conditions of temperature and moisture (Tahir et al. 2011). Since 1994, Canada serves as the largest producer and generator of flax, about 1.035 million tonnes of flax, of which 60% is being exported to the EU, 30% to the US and 4% in Japan (Flax 2017a). The producers from France, Belgium and Netherlands also have 130000 acres of land which is used for growing and cultivating flax (Flax 2017b). The growth of flax is influenced by the climatic conditions and it is considered as a crucial cash crop with the increased demand for linen manufacturing (Yan et al. 2014). The growth cycle of flax is just 100 days which includes sowing in the month of March and harvesting in July in the Western European region (Libeco 2017)

Jute

The jute requires a dull kind of alluvial soil and standing condition of the water. The condition for temperature which is needed for successful cultivation of jute is between 20 to 40^0C and a relative humidity of 70 to 80% (Jute 2017). In context to the study made by Alves (Alves et al. 2010), no irrigation facility is required by jute when there exists an annual rainfall greater

than 2200mm. At the time of overflow of Amazon river, the prerequisite condition of nutrients and soil humus for jute are fulfilled automatically. The top producers of jute around the world includes India, Bangladesh and China (Tahir et al. 2011).

Kenaf

The growth of Kenaf can be made on different kind of soils, but its growth is shown at the best level in well-drained, sandy loam, moist climate, tropical or sub-tropical, without excess rains and a high presence of wind. The fibres of kenaf are about 0.9 meters long, and they are lustrous with a pale colour. The strength of kenaf is similar as that of jute. India, Bangladesh, Thailand and China are considered as the leading producers of kenaf (Tahir et al. 2011).

Ramie

The areas which have enough rainfall and warm climate support the growth and cultivation of Ramie (Robinson 1940). A fertile loamy or sandy soil is required for the growth of Ramie as it is a perennial plant which has a long life of several years (Niir Board Of Consultants & Engineers 2005). The decomposition of ramie is difficult to process at the time of retting. The harvesting for ramie can be made up to six times a year in the good quality of soils (Mwaikambo 2006). The leading producers of ramie are China, Brazil, Philippines, India, South Korea and Thailand (Mohanty, Misra, and Drzal 2001).

2.8.2 Quality Issues

In several parts of the world, the quality of extracted fibres from Bast plants depends on conditions of soil and weather where these plants are grown. Other factors such as retting, chemical or enzymatic treatments affect the quality of fibres along with the process of extraction of fibres.

By keeping a check on retting process, the quality of fibres can be maintained. This factor also ensures the separation of Bast fibres from the inner core of the fibre without any prior damage to them. Moisture in the climatic conditions is required for the process of retting. The significant weather conditions are responsible for quality of fibres which are obtained at the time of dew or filed retting. This process is accepted at a wide extent as it is inexpensive in comparison with mechanised process and also do not need water (Tahir et al. 2011).

Some disadvantages which are associated with the process of retting are described in (Biagiotti et al. 2008; Tahir et al. 2011) as follows:

1. The process of retting depends on the specific conditions of temperature and moisture and contamination of soil in the process of dew retting.
2. The process of water retting produces lower quality of fibres which are affected by the environmental pollution.
3. A less flexibility can be seen in the characteristics of the retting process.
4. The process of retting occupies the agricultural fields for several weeks.

2.9 Challenges for Bast Fibres as a Reinforcement in Polymer Composites

If bast fibres are to be used as a substitute for synthetic ones in composites, they have to show convincing mechanical and physical properties as single or in the matrix when combine with other polymers that they are intended to reinforce or replace. In the following sections, will focus on two possible aspects that might affect or favour bast fibres as a suitable substitute in novel products. These two characteristics are:

- Interphase
- Moisture absorption

2.9.1 Interphase

It has been shown that relative humidity and the length of fibres have an effect on the tensile strength of bast fibres. As the length of the fibres increases, the bonds between molecules weaken which introduce imperfection in the structure (Yan et al. 2014). In longer fibres, failure occurs because of the relatively pectin interphase that links the elementary fibres together. The pectin interphase lies mainly in the longitudinal direction of the fibres. Therefore, it breaks by shear failure, whereas in shorter fibres, failure does not occur through the pectin interphase, but through the cell wall of the elementary fibres which are rich in cellulose. To improve fibre/matrix interfacial bonding, chemical treatment needs to be considered (Yan et al. 2014).

Bast fibres are hydrophilic and contribute to polar matrices, whereas resins are hydrophobic. These two different characteristics will impact on the interfacial energy in composites. In order to make a fibre reinforced composite, a good adhesion is necessary between fibres and matrix, like a strong interfacial bonding. Therefore to use natural fibre as reinforcement in composite, the interfacial adhesion between fibres and resins needs to be improved. This can be achieved by chemical treatment of the fibres, which will remove impurities from the fibres' surfaces. This treatment will eventually reduce moisture absorption and at the same time creating a good interfacial adhesion between the cellulose fibres and the resins (Li, Tabil, and Panigrahi 2007;

Mwaikambo and Ansell 2002). The effect of a good interfacial adhesion will improve the mechanical properties between fibres and polymers in the composite (Joffe, Andersons, and Wallström 2003; Li et al. 2007; Mwaikambo and Ansell 2002).

2.9.2 Moisture Absorption

Natural fibre reinforced composites (NFRCs) absorb water when exposed to a humid environment. NFRCs have low-durability and inherently absorb high moisture which can reduce their properties and thus affect the long-term performance. For example, increased moisture content in natural fibres causes swelling and alters their dimensions because of the poor adhesion/compatibility between the hydrophobic matrix and hydrophilic natural fibres (Dittenber and Gangarao 2012; Faruk et al. 2012). Previous studies have reported the effect of water absorption on the properties of NFRCs, such as hemp (Dhakal et al. 2007), jute (Zamri et al. 2011) and flax (Anandjiwala et al. 2007). These reports have shown that increased moisture uptake of natural bast fibres is due to high cellulose and voids content, and the mechanical properties such as tensile and flexural strength would be significantly lowered as a consequence of weak interfacial adhesion between fibre and matrix.

The water present in the polymer can either be free water or bound water. The difference between these is that the molecules in free water can move independently through the voids while, in the bound water, the molecules are dispersed and bounded to polymer's polar group (Azwa et al. 2013). Figure 2.21 shows the conditions of moisture in a polymer matrix. The effect of absorption of water or moisture leads to the degradation of fibre-matrix interface region that reduces the mechanical and dimensional properties of the composites. Improvement in the mechanical properties of composites requires strong adhesion between the natural fibres and polymer matrix. The compatibility between composite components can be improved by using either physical or chemical modification of the polymer, filler or by using coupling agents (Joffe et al. 2003). As described by different authors, chemical treatment of bast fibres in particular flax fibres has improved their mechanical properties and reduces the water absorption which causes swelling that eventually cause fibres to rupture (Dhakal et al. 2013; Mwaikambo and Ansell 2002). Therefore, the main problem of natural fibre/polymer composites is the incompatibility between the hydrophilic natural fibres and the hydrophobic matrices (Yan et al. 2014).

In the case of flax fibres, the hydrophilic characteristics of the fibres can lead to a poor fibre/matrix adhesion due to the presence of hydroxyl and polar groups in composites (See

Figure 2.22). The outcome can be a high moisture uptake which can seriously lower the tensile properties of composites and thus lower their mechanical performance. To improve fibre/matrix interfacial bonding, chemical modifications need to be considered. Absorption of water causes the fibres in the composite to swell which in turn reduces the mechanical properties of the composite (fibre/polymer composite). Therefore, it is important to reduce the absorption of water by the flax fibres using treating with suitable coupling agents or by coating with suitable resin in order to produce materials with better mechanical properties and environmental performance (Yan et al. 2014).

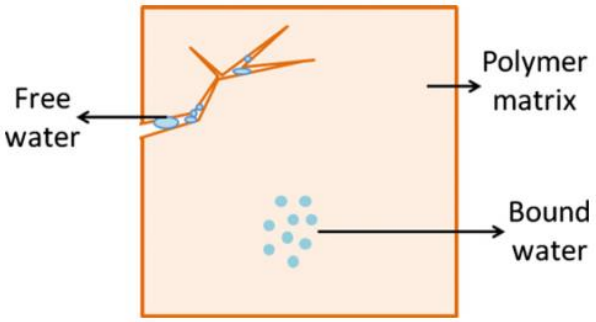


Figure 2.21 Free water and bound water in polymer matrix (Azwa et al. 2013).

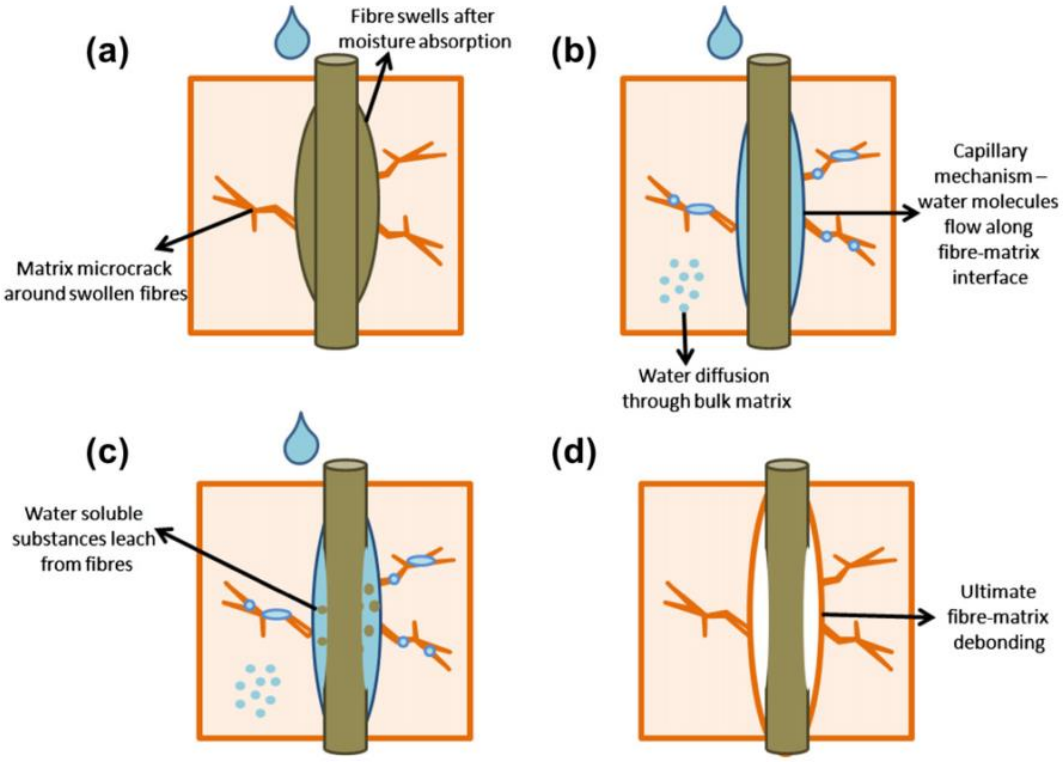


Figure 2.22 Effect of water on fibre-matrix interface (Azwa et al. 2013).

2.10 Chemical Modification of Natural Bast Fibres

As mentioned in section 2.8 chemical treatments affect the mechanical and physical properties. In this section is explained how different chemical treatments influence the properties of bast fibres.

Alkaline Treatment

The objective of the chemical treatments was to remove the starch, hemi-cellulose, lignin/ pectin surrounding cellulose. Sodium hydroxide (NaOH) is the most commonly used chemical for this purpose (Mwaikambo and Ansell 2002). This method is known as alkalization of fibres. The method is carried out by immersing the fibres in a solution of sodium hydroxide (NaOH) for a period of time (Akil et al. 2011; Aziz et al. 2005; Aziz and Ansell 2004; Mwaikambo and Ansell 2002; Sawpan, Pickering, and Fernyhough 2011; Yu et al. 2010). The effects of sodium hydroxide on the fibres are to remove hemicellulose, lignin, wax and oils covering the external surfaces of the cell walls. Thus, it has increased the surface roughness and has also increased the amount of cellulose on the surface. Alkaline treatment reduces the diameter of the fibres by doing so it increases the aspect ratio (length/diameter). In addition, the alkaline treatment has a lasting effect on the mechanical behaviour of bast fibres (Akil et al. 2011). Several studies have shown that there has been an increase in mechanical properties (strength and stiffness) in bast reinforced composites (Akil et al. 2011; Baley et al. 2006; Ehresmann, Huo, and Ulven 2012; Yu et al. 2010).

Silane Treatment

Silane is a chemical compound that has been describe as coupling agent which allow natural (bast) fibres to adhere to a polymer matrix (Aziz and Ansell 2004; Baley et al. 2006; Sawpan et al. 2011). In the presence of water, silane form a compound known as silanol which then reacts with the hydroxyl group of the fibres forming strong covalent bond with the cellulose molecules in their cell walls (Akil et al. 2011; Yu et al. 2010). This reaction takes place on the surface. The treatment with silane reduces the swelling of the fibres (Akil et al. 2011). It has been reported that the treatment with silane has a positive impact on the mechanical properties of bast fibres reinforced composites (Akil et al. 2011; Sawpan et al. 2011; Yan et al. 2014; Yu et al. 2010).

Acetylation of bast fibres

Acetylation is carried out by reacting the cell wall hydroxyl groups (OH) in bast plants with acetic or propionic anhydride at an elevated temperature (Akil et al. 2011; Dhakal et al. 2007).

The reagent attacks the OH groups of the lignin and hemicellulose, while the former has little or no reaction with the hydroxyl groups of the cellulose. In the process, acetic acid is formed as a by-product and it has to be removed before the fibres can be used (Akil et al. 2011; Li et al. 2007). It can be said that acetylation improves the interfacial adhesion between fibres and matrices in composites.

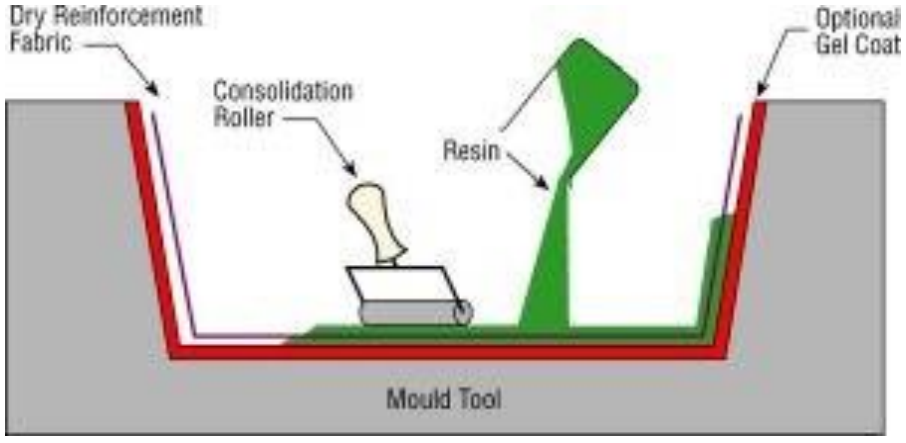
In all three cases, the chemical treatment performed on fibres as describes by some authors shows the modification of surfaces by creating great adhesion between fibres and matrices in composites due to less moisture absorption and therefore improves mechanical characteristics, like the tensile, flexural, compression and impact properties as well as resistance to wear (Akil et al. 2011; Aziz and Ansell 2004; Joffe et al. 2003; Yu et al. 2010).

2.11 Processing of Bast Fibre Reinforced Composites

A variety of manufacturing techniques has been developed to produce composites. Main techniques are described below:

2.11.1 Hand Lay-up

Hand lay-up or the wet lay-up process is the oldest method used for making composites. As shown in Figure 2.23, shapes of the composites are prepared with an open mould. This method follows some set instructions which show the information of the hand lay-up process; different size of moulds is required for the different size of composites. In this method, after mixing catalyst to the resin, it is applied to the reinforcement. Hand roller is then used to press the resin inside the layer after it has been applied to the reinforcement. The design requirement can be specified with the number of resin or the amount and the thickness. Finally, the risen is cured where can be done at room temperature then is removed the fibre reinforced polymer composite from the mould (George Lubin 2013).



· Figure 2.23 Hand lay-up diagram (Source: www. netcomposites.com).

2.11.2 Compression Moulding

Compression moulding technique is a combination of hot-press that requires high pressure and temperature for a required period of time as illustrated in Figure 2.24. This process of moulding is generally heated which follow some instruction to create a product that is in the beginning placed in opened heated mould bore; after that it closed with holding the upper part, then the pressure applied to force the material to stick into all mould areas, throughout the heat and the pressure kept the mould will cured, this process used resins in partly cured step. Compression moulding has high pressure and high volume which appropriate for moulding complex, high strength reinforcement fibreglass. One of the main benefit of compression moulding is its ability to mould complex, huge parts likewise it is the cheapest moulding process (Thompson 2007).

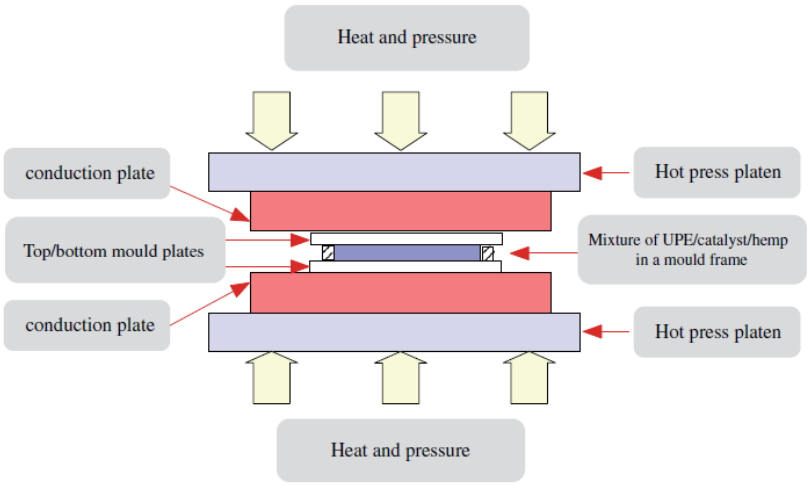


Figure 2.24 Schematic of the composite consolidation (Dhakal et al. 2007).

As reported by (Singleton et al. 2003), the use of compression moulding to fabricate composites consisting of flax fibres (mat) and high density polyethylene to test mechanical properties of the fabricated composites. The composite showed an increase tensile strength and tensile modulus when compared to recycled high density polyethylene.

Compression moulding fabrication technique with different fibre volume-fraction is used for kenaf reinforced polypropylene composites. These are then put to the test for measuring tensile and flexural strength along with comparing them with other composites. The results showed that kenaf composites showed to have higher tensile and flexural strength for a content 30% by weight is very similar to those of flax and hemp polypropylene that have content of 40% by weight. Furthermore, the kenaf composites with increasing fibre content had higher impact

strength (Akil et al. 2011). Another study carried out using different bast fibres (ramie) with varying volume fraction and orientation made by compression moulding. It was mentioned in the literature that the composites with 45% of ramie fibres showed an increase in tensile strength compared to polyester resin (Paiva Júnior et al. 2004).

2.11.3 Vacuum Bagging

Vacuum bagging utilizes atmospheric pressure as a clamp in order to hold laminate plies together. After that, use an airtight envelope to seal the laminate, it may be an airtight bag on one side and an airtight mould on the other. When it is successfully sealed to the mould, pressure on the inside and outside is similar to the atmospheric pressure. A vacuum pump is then used to suck the air from the envelope, thus the air pressure inside it is drastically reduced while outside it remains the same. Finally, the atmospheric pressure forces everything within the envelope and its sides together, as shown in Figure 2.25. Thus, equal pressure is obtained (Gougeon Brothers Inc. 2010). The difference in pressure amongst the outside and inside of envelope defines the amount of clamping force on the laminate. Ideally, a complete vacuum is needed to remove all air from within the envelope (Gougeon Brothers Inc. 2010).

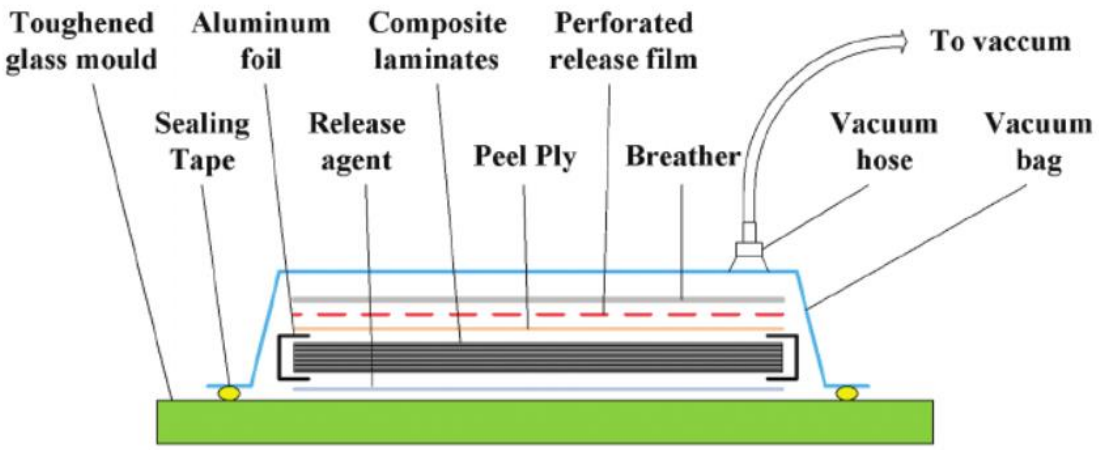


Figure 2.25 Typical components of vacuum bagging system for composite laminates (Hang et al. 2017).

2.11.4 Vacuum Infusion

To drive resin into a laminate, a vacuum infusion technique is needed to apply vacuum pressure. Before resin is brought forth, the vacuum is applied and the materials are laid dry into the mould. When a complete vacuum is attained, resin will be sucked into the laminate through a precisely placed tube, as depicted in Figure 2.26 (Yuhazri and Sihombing 2008). By using vacuum infusion, it is possible to produce composites with high volume fraction of fibres and

enables to reach a better strength to weight ratio (Yan, Chouw, and Yuan 2012). The fabrication of bast fibre/polyester composites by vacuum infusion process can improve the mechanical properties of the composite when compare to untreated bast fibres or composites made by hand lay-up process. The test described here is comparing the tensile properties of kenaf/polyester composite fabricated by vacuum infusion to that of hand lay-up. The former showed a higher tensile strength and Young's modulus than the hand lay-up process (Yuhazri and Sihombing 2008).

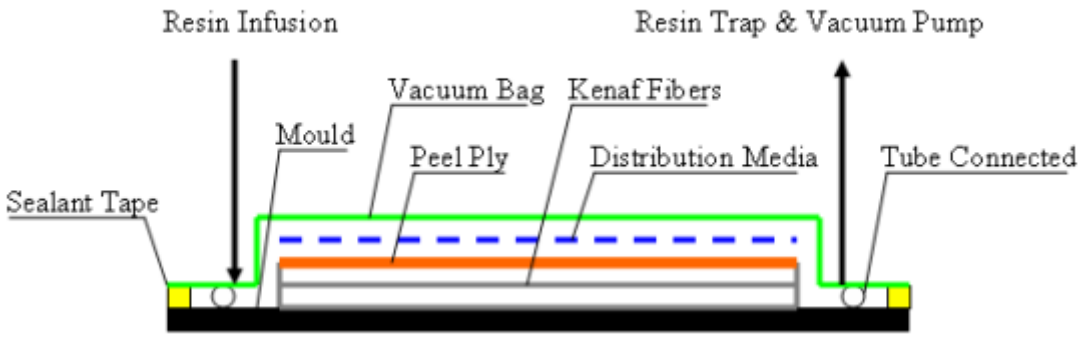


Figure 2.26 Configuration of vacuum infusion system (Yuhazri and Sihombing 2008).

2.12 Mechanical Properties

It is important to understand the mechanical properties of bast fibres in order to use as effectively as possible, mainly tensile, flexural and impact. In general, bast fibres are suitable to use as reinforcement in composites due to their relatively high specific strength, stiffness and low density as described in the previous section.

2.12.1 Tensile Properties

The tensile properties are among the most widely tested properties of natural bast fibre reinforced composites. Knowledge of the fibre strength can be an important factor when selecting fibres for particular application. A tensile test reflects the average dimensional property of the fibres. Tensile test is carried out in order to determine the amount of force needed to pull a material or specimen apart and to what extent it will stretch before rupture. The failure to exhibits identical tensile properties can be attributed to the condition under which fibres are left in the environment for retting (dew or water retting), damage caused by

processing fibres be hand or mechanised means, types of fibres (long or short fibres), adhesion between fibres in the bundles and fibre orientation (Yan et al. 2014).

Bast fibres are hydrophilic. They can easily absorb moisture/water from the surrounding environment. Therefore during mechanical testing it is important to maintain a constant conditions, like controlling the temperature and relative humidity of the working area, otherwise the fibres might absorb moisture and causing them to swell which will eventually affect the tensile properties (Saheb and Jog 1999; Stamboulis, Baillie, and Peijs 2001).

Fibres from different parts of the stem have different dimension and strength. Fibres from the stem are stronger and stiffer than those from the middle and close to the core of the plants. They also have different chemical compositions (less cellulose near the core of the plants). Therefore, fibres taken along the stem with suitable length and diameter will exhibit different tensile properties than those from the bottom and top of the stem, as presented in Table 2-5 (Charlet et al. 2009; Yan et al. 2014).

Table 2-5 Tensile properties of flax fibres based on their locations in the stem (Yan et al. 2014).

Location	Number of tested fibres	Diameter (μm)	Young's modulus (GPa)	Strength (MPa)	Ultimate strain (%)
Top[a]	36	19.0 ± 3.5	59.1 ± 17.5	1129 ± 390	1.9 ± 0.4
Middle[a]	37	19.6 ± 6.7	68.2 ± 35.8	1454 ± 835	2.3 ± 0.6
Bottom[a]	31	20.1 ± 4.1	46.9 ± 15.8	755 ± 384	1.6 ± 0.5
Top[b]	57	21.5 ± 5.3	51 ± 22	753 ± 353	1.8 ± 0.7
Middle[b]	45	21.3 ± 6.3	57 ± 29	865 ± 413	1.8 ± 0.7
Bottom[b]	59	21.3 ± 6.3	51 ± 26	783 ± 347	2.0 ± 0.9
-[a]	122	19.3 ± 5.5	63 ± 36	1250 ± 700	2.3 ± 1.1

The considered gauge length was10 mm.
[a] Fibres from Hermes variety.
[b] Fibres from Agatha variety.

The fibre length and the manufacturing method have a great influence on the tensile properties of the fibres. As mentioned earlier, a longer fibre has a lower tensile properties as compared to a shorter fibre (Barkoula, Garkhail, and Peijs 2010; Yan et al. 2014). For example, the tensile stress or strain of flax fibre is not consistent even though the fibres obtained from same region and grown under identical condition. The deformation of the fibres differed between the primary and secondary cell walls (Yan et al. 2014).

Flax fibres have been improved the tensile properties after modified by chemical treatments, as illustrated in Figure 2.27. It has been described in the previous literature that chemical treatments reduce water absorption and improving the adhesion between the fibres and matrix

which have a positive effect on the tensile properties of bast fibres (Baley et al. 2006; Joffe et al. 2003; Mwaikambo and Ansell 2002; Yu et al. 2010).

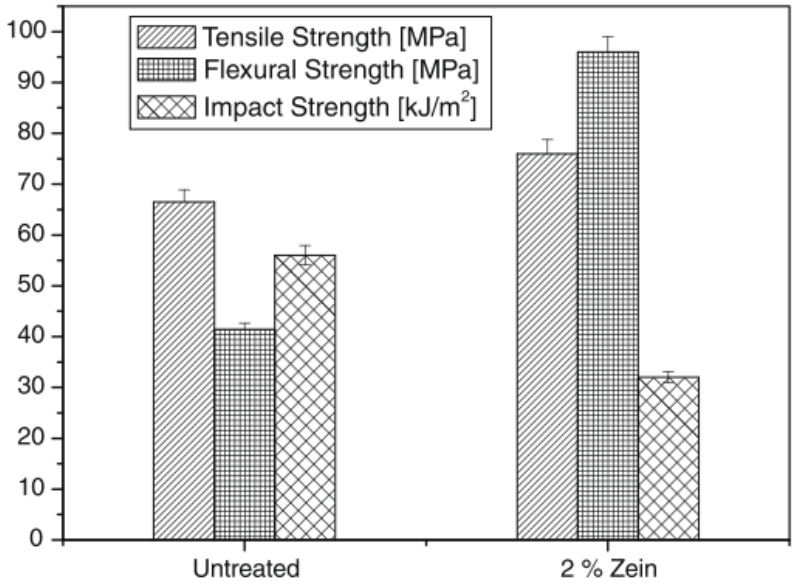


Figure 2.27 Effect of Zein modification on mechanical properties of flax reinforced polypropylene composite (30%) (John and Anandjiwala 2009).

Another factor that affect the tensile properties of bast fibres is the fibre volume fraction in composites. In different literature, the fibre volume fraction or fibre contents show an increase in tensile properties but in most cases, the amount of fibres in the composites reaches a maximum (Shahzad 2011). For example, the tensile strength of hemp fibre reinforced polyester composites increased linearly for a fibre volume above 11% and a maximum tensile strength was obtained with 35% of fibre volume fraction and the tensile modulus also have similar pattern (Rouison, Sain, and Couturier 2006). In addition, Pickering et al. (2007) studied the effect of Alkali treated fibres using Maleated Polypropylene (MAPP) coupling agent reinforced hemp composites. As the result shows, the interfacial bonding in the fibre composites can be improved by adding 3% by weight to a composite containing hemp up to 40% by weight. Further, an increase of 68% of tensile strength and 31% of Young's modulus can be recorded due to this. Assarar et al. (2011) have compared the tensile properties of flax and glass fabric reinforced epoxy composites. It was observed that the tensile strength of flax composite laminates was increased up to 380 MPa which showing it close to glass fabric reinforced epoxy composites. The tensile and physical properties of different natural fibres and glass fibres are highlighted in Table 2-6.

Table 2-6 Tensile and physical properties of natural fibres and glass fibres (Dittenber and Gangarao 2012; Yan et al. 2014).

Fibre type	Diameter (μm)	Relative density (g/cm^3)	Tensile strength (MPa)	Elastic modulus (GPa)	Specific modulus (GPa × cm^3/g)	Elongation at failure (%)
E-glass	<17	2.5–2.6	2000–3500	70–76	29	1.8–4.8
Abaca	–	1.5	400–980	6.2–20	9	1.0–10
Alfa	–	0.89	35	22	25	5.8
Bagasse	10–34	1.25	222–290	17–27.1	18	1.1
Bamboo	25–40	0.6–1.1	140–800	11–32	25	2.5–3.7
Banana	12–30	1.35	500	12	9	1.5–9
Coir	10–460	1.15–1.46	95–230	2.8–6	4	15–51.4
Cotton	10–45	1.5–1.6	287–800	5.5–12.6	6	3–10
Curaua	7–10	1.4	87–1150	11.8–96	39	1.3–4.9
Flax	**12–600**	**1.4–1.5**	**343–2000**	**27.6–103**	**45**	**1.2–3.3**
Hemp	25–600	1.4–1.5	270–900	23.5–90	40	1–3.5
Henequen	–	1.2	430–570	10.1–16.3	11	3.7–5.9
Isora	–	1.2–1.3	500–600	–	–	5–6
Jute	20–200	1.3–1.49	320–800	30	30	1–1.8
Kenaf	–	1.4	223–930	14.5–53	24	1.5–2.7
Nettle	–	–	650	38	–	1.7
Oil palm	–	0.7–1.55	150–500	80–248	0.5–3.2	17–25
Piassava	–	1.4	134–143	1.07–4.59	2	7.8–21.9
PALF	20–80	0.8–1.6	180–1627	1.44–82.5	35	1.6–14.5
Ramie	20–80	1.0–1.55	400–1000	24.5–128	60	1.2–4.0
Sisal	8–200	1.33–1.5	363–700	9.0–38	17	2.0–7.0

2.12.2 Flexural Properties

Flexural test is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. There are two methods that cover the determination of flexural properties of material: three-point and four point loading system. Flexural test is strongly influenced by the properties of the specimen nearest to the top and bottom surfaces. The stresses in a flexure test are maximum at the top and bottom surfaces and zero in the middle part of the specimen beam (Faruk et al. 2012).

John and Anandjiwala (2009) investigated the effect of chemical modification of flax non-woven mat/PP composites. Thy found that the flexural strength and modulus increased compared to untreated composites. This improvement in the flexural properties is due to better interfacial bonding between the fibre and polymer matrix. It was found that the flexural strength and modules of flax fibre reinforced vinyl ester with fibre volume fraction less than 30% were 81 MPa and 5.10 GPa, respectively. However, they are increased up to 130 MPa and 8.90 GPa, respectively at high fibre volume fraction of 35%. Thus, Flax fibre reinforced composites could be improve when increased the fibre volume fraction (Goutianos et al. 2006). Alavudeen et al. (2015) discussed the mechanical properties of banana/kenaf fibre reinforced hybrid unsaturated polyester composites. They reported that the mechanical properties (tensile, flexural and impact strength) of the hybrid composites of woven banana/kenaf fibres were superior to those without hybridisation, as depicted in Figure 2.28.

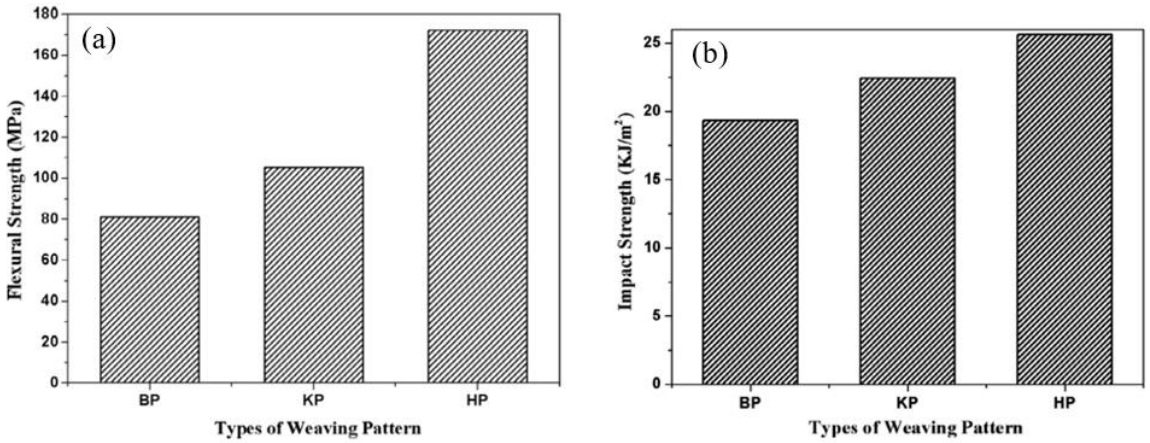


Figure 2.28 (a) Flexural strength and (b) impact strength of Banana-plain (BP), Kenaf-plain and Hybrid plain (Alavudeen et al. 2015).

2.12.3 Impact Properties

One of the most important factors of the behaviour of natural bast fibre reinforced polymeric composites is their response to the impact load and the dimensions of the composites to resist it through their service life. The Charpy impact test is used to determine a material toughness or impact strength in the presence of a flaw or notch. There are two types of impact tests are used by most researchers, high and low velocity impact test although many details of the actual test apparatus may differ (Agrawal, Singh, and Sarkar 2013).

Natural bast fibre reinforced composite materials have been found to be very susceptible to impact loading. Dhakal et al. (2014) investigated the effect of fibre orientation and thickness variation on the impact loading test of jute/methacrylated soybean oil (MSO). It is shown that the maximum load and the total absorbed energy increased linearly when increased the thickness. Additionally, the form, areal weight, and weave of fibre architecture can significantly influence the biocomposites. According to Singleton et al. (2003) an increase in toughness of flax fibre reinforced high density polyethylene (HDPE) composites over pure HDPE indicates that the fibre volume fraction of flax fibres improved the toughness of the composites under Charpy impact test. The impact strength of these composites increased with increasing fiber content. Furthermore, untreated hemp fibre reinforced unsaturated polyester composites exhibited the highest impact strength of 14.2 kJ/m^2 at fibre volume fraction of 35% (Shahzad 2011). Surface treatment of fibres (hemp) by alkalization (NaOH) shows an increase in mechanical properties except impact strength which showed a decrease due to the fibre and surface adhesion in the composites (Mehta et al. 2006).

Part II: Review of the Literature of Fracture Toughness on Natural Fibre Reinforced Polymer Composites (NFRCs)

2.13 Interlaminar Fracture Toughness of Composites

Delamination is one of the most prevalent failure mechanisms in composite laminates. It usually occurs due to dynamic loadings, such as low-velocity impact when the structure is subjected to cyclic or static loading conditions (Zulki et al. 2002). In general, the interlaminar fracture toughness of composite laminates is usually expressed in terms of the critical energy release rate, (G_c) rather than stress intensity factors, (K_c). Sufficient ability to absorb fracture energy is an important requirement for structure design, which is dependent on the fibre and matrix properties. Because of this, the use of natural fibres in the form of non-woven mats and short fibres is limited in non-structural applications (Hughes et al. 2007). However, in order to obtain high performance composites in terms of stiffness and strength, it is important to use long continuous unidirectional fibres or woven non-crimp fabrics (Goutianos et al. 2006).

When the crack propagates parallel to the piles, the beam specimens through the delamination of composite laminates can be used to measure the interlaminar fracture toughness. One of the main reasons of changing crack path is the variation of energy release rate. Moreover, the fibre volume fraction and fibre orientation have been influenced on the crack path (Keck and Fulland 2016). There are three fracture modes of interlaminar fracture: Mode I (open mode), Mode II (in-plane shear mode), and Mode-III (out-of-plane shear mode), as shown in Figure 2.29.

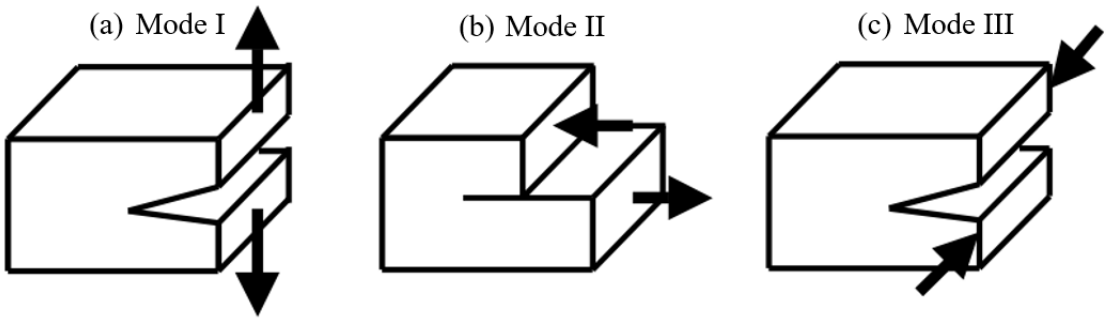


Figure 2.29 Types of fracture modes.

In the strain energy release rate, both values of $G_{init.}$ and $G_{prop.}$ are used in Mode I and Mode II tests as a toughness of the composites. The values of fracture energy increase with the delamination growth from the initial crack or at the beginning of crack tip. These behaviour are mainly influenced by fibre bridging which depends on the laminate thickness, ply orientation and manufacturing methods or parameters condition such as speed test and loading

rate (Compston et al. 2001; Zabala et al. 2014) .Thus, the initiation value of energy release rate, $G_{Ic\ inti.}$, is the most conservative criteria (Hojo, Kageyama, and Tanaka 1995). Evaluation of crack initiation in Mode I and Mode II is carried out using the following methods (de Morais and de Moura 2005):-

- **Visual Observation (VIS)**

The point at which crack onset is visually observed from the crack tip of the Teflon. This technique is known as the visual observation point and is only applicable to Mode I. The initial crack length is measured accurately by a microscope coupled with a video camera.

- **Non-Linearity (NL)**

By considering the graph of load against displacement in Figure 2.31, a non-linear critical point occurs first at a point of deviation from the linearity on the curve. This non-linearity is used by many factors which include nature/composition of materials, material yielding (at the crack tip) and local crack growth/propagation.

- **Maximum Load Point (MLP)**

Another method of evaluating the crack initiation in mode II is the maximum load point method. This point refers to the critical point at which maximum value of load is observed throughout the loading process.

- **5% Compliance Increase (5% offset Point)**

This is a point on the curve of load against displacement where there is 5% increase by compliance from its original value. This point is obtained by drawing a straight line with 5% decreased gradient (slope) of the original gradient for the curve of load against displacement (See Figure 2.30). The point of their intersection is referred to as the critical point. This method, applicable to mode II, has advantages of good and exact estimation of crack initiation and higher values when compared with the non-linearity method.

Other methods such as acoustic emission (AE) and strain gauges could also be used, but due to their relative complication and the requirement for additional sophisticated instruments, they are not be used in this study.

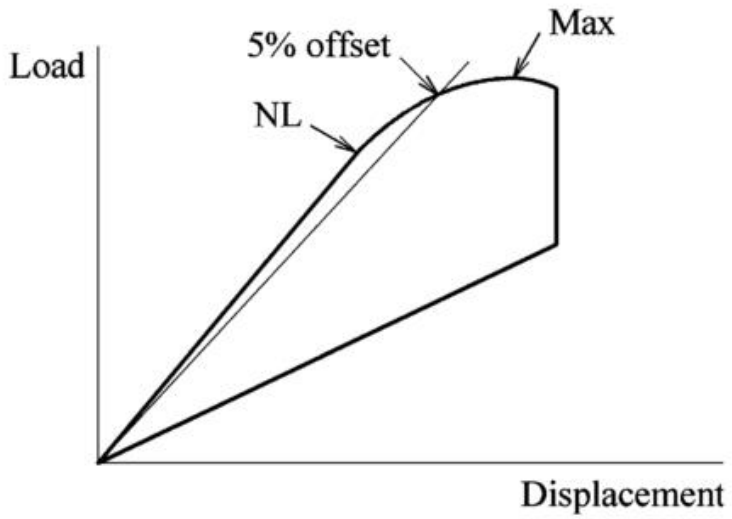


Figure 2.30 Crack initiation criteria.

2.13.1 Mode I Interlaminar Fracture Toughness Test

In order to obtain a mode I fracture energy of the adhesive bonds, a double cantilever beam (DCB) test is required. This is used to measure the fracture toughness of the adhesive in the presence of flaws. A Teflon film is then inserted by initiating a crack (See Figure 2.31). After pulling apart the two hinges or blocks at a certain rate a specimen is then loaded, this sudden increase in load will result in increased displacement of the specimen. Once it reached a certain critical load, the crack will start to grow, due to the increased compliance, resulting in a slight drop in the load. Once it reached this point, the displacement will be constant due to the beams being stopped from moving apart. The increasing crack length results in a drop in load and the crack length is cautiously followed. After the equilibration of the crack, the specimen is repeatedly unloaded then loaded. Preferably, if there is no more propagation of the crack throughout these two cycles, the compliance of the fixture ought to stay the same. This process is repeated many times in order to lead to a total cleavage in the specimen (Varun Ratta 1999). The collected data at various time interval encompasses of deflection, load, compliance, and crack length. This data can then be analysed using several different approaches based on the standard of American Society for Testing and Materials (ASTM) D5528 (ASTM D5528 2007). These are the modified beam theory (MBT), the compliance calibration (CC) method and the modified compliance calibration (MCC) method which are described below to determine the mode I critical strain energy release rate, $G_{Ic.}$

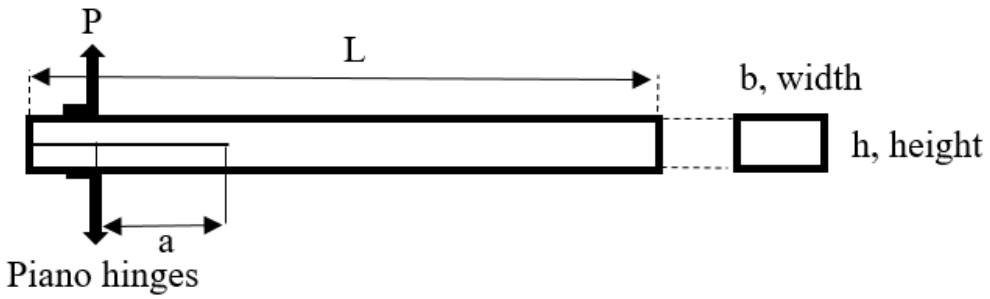


Figure 2.31 Shows a laminate with Teflon insert of length (a_0) at one end.

2.13.1.1 Modified Beam Theory (MBT) method

By using beam theory in terms of calculating the fracture energy of Mode I when the specimen is fully fixed at the front of delamination. However, some rotation might occur at the crack tip. Therefore, the modified data reduction method to determine the energy release rate was obtained from the pure Mode I as expressed by:

$$G_I = \frac{3P\delta}{2ba} \qquad [2.1]$$

and written as:

$$G_{Ic} = \frac{3P\delta}{2b(a+|\Delta|)} \qquad [2.2]$$

Where P is the applied load (N), δ the load point displacement (mm) and a the delamination length (mm), and b is the specimen width (mm). The crack length correction factor, Δ is obtained by plotting the cube root of compliance, $C^{1/3}$ as a function of delamination length a. The compliance, C is the ratio of the load point displacement to the applied load (δ/P) (ASTM D5528 2007; Mathews and Swanson 2007; Prasad et al. 2011)**.**

2.13.1.2Compliance Calibration (CC) method

The compliance calibration (CC) was the second method for DCB to measure the corrected energy release rate G_{IC}, as shown in the following equation:

$$G_{Ic} = \frac{nP\delta}{2ab} \qquad [2.3]$$

Where a is the delamination length and n is the linear slope of least- square fit of log (C) versus log (a) (ASTM D5528 2007; Mathews and Swanson 2007).

2.13.1.3Modified Compliance Calibration (MCC) method

In the modified compliance calibration method, the normalized value of the delamination length is used which is equal to a/h, where h is the thickness of the beam. The observed delamination value and the propagation values can be used to plot the graph of delamination length. The graph is normalised as the function of $C^{1/3}$ (compliance cube root). The slope of this line is *n*. The interlaminar fracture toughness for the MCC is calculated as follows:

$$G_I = \frac{3P^2C^{\frac{2}{3}}}{2\,nbh} \qquad [2.4]$$

Of the three methods, MBT method is recommended as it has yield the most repeated values of G_{IC} for 80% of specimen tested during ASTM round Robin testing (ASTM D5528 2007; Prasad et al. 2011).

2.13.2 Mode II Interlaminar Fracture Toughness Test

High performance composite materials are designed in order to exhibit high in-plane strength and stiffness. Weakness does exist between layers in composites which affects both shear and tensile stresses which in turn put the performance of these composites in risk. Reduction in strength is due to delamination between layers or plies. Failure in composites is a result of a combination of compressive and bending stresses caused by the delaminated plies as they buckle out of plane. The strength of composites is also affected by fibre breakage and cracks in matrix. The application of the mode II delamination test is used to study failure on composite materials (Prasad et al. 2011; Saidpour 2003).

End-notched flexure (ENF) test and end-loaded split (ELS) beam are used for characterising mode II fracture toughness (Blackman, Brunner, and Williams 2006). The former has two methods, simple beam theory (SBT) method and corrected calibration method (CCM) (Hadavinia and Ghasemnejad 2009). The specimens are tested in a displacement mode with a constant displacement rate (mm/min). The load and the displacement were recorded using data acquisition system to obtain the mode II critical strain energy release rate, $G_{IIc.}$ (Prasad et al. 2011).

2.13.2.1End-Notched Flexure (ENF) test

One of the most common methods to measure the interlaminar fracture toughness is End-notched flexure (ENF) test using in-plane shear deformation mode (called Mode II). Besides,

the fracture energy can be measured by subjecting a beam at the centre, using a load that is held on two support points at a distance L and applied to it at a constant rate, as shown in Figure 2.32. A crack can be created from the insert by presenting load by flexural forces. Then, the crack extended because of shear forces at the crack tip (Prasad et al. 2011). The critical energy release rate for Mode II interlaminar fracture toughness is calculated from the initial crack length and the load-deflection curve using the highest load and deflection level (Ogasawara, Yoshimura, and Ishikawa 2012). The equation to calculate G_{IIc} is written as:

$$G_{IIc} = \frac{9P\partial a^2}{2b\left(\frac{1}{4}L^2 + 3a^3\right)} \quad [2.5]$$

Where *P* is the load; δ is loading point displacement; *a* is a crack length measured from the outer pin; *L* is a half span of 3ENF specimen and *b* is a beam width.

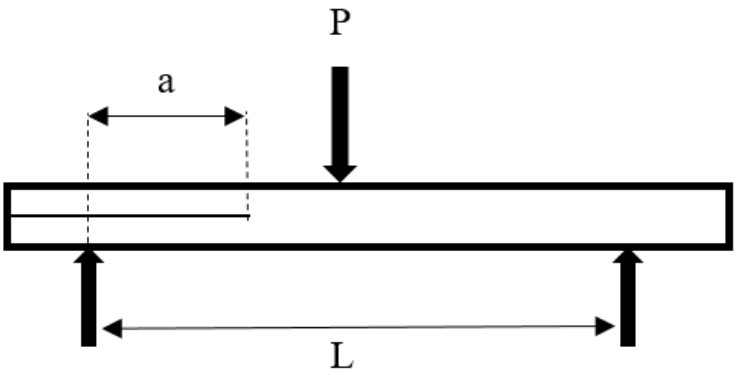


Figure 2.32 Three-point bend method or ENF under load.

2.13.2.1.1 Simple Beam Theory (SBT) method

In order to calculate the load-point compliance, the equation of G_{IIC} can be found by classical Simple Beam Theory (SBT) (Hadavinia and Ghasemnejad 2009; Russell, A.J. and Street 1982).

$$C = \frac{\delta}{P} \quad [2.6]$$

$$C = \frac{2l^3 + 3a^3}{8E_1 bh^3} \quad [2.7]$$

The compliance equation is given by

$$G = \frac{P^2}{2b}\frac{dC}{da} \quad [2.8]$$

The interlaminar fracture toughness can be obtained from [2.6 to 2.8]:

$$G_{IIc} = \frac{9P\delta\, a^2}{2b(3a^3+2L^3)} \quad [2.9]$$

Where P is load for stable crack propagation; δ is loading point displacement; a is a crack length measured from the outer pin; L is a half span of 3ENF specimen and b is a beam width.

2.13.2.1.2 Corrected Calibration Method (CCM)

In the Corrected Calibration Method (CCM) compliance is relies on the least square regression (D.R. Moore, J.G. Williams 2001; Hadavinia and Ghasemnejad 2009) as follows:

$$CN_1 = A + ma^3 \quad [2.10]$$

Where N_1 is a large displacement correction factor, A and m are data fitting constants. Hence,G_{IIc}, becomes

$$G_{IIc} = \frac{3mP^2a^2}{2b}\,\frac{F'}{N_1} \quad [2.11]$$

Where F' is an additional large displacements correction factor which was found negligible in 3ENF test.

2.13.2.2End-Loaded Split (ELS) test

The End Loaded Split (ELS) test has been used as mode II test and has a similar configuration to the ENF (Davies et al. 1990). It is rigidly clamped at one end and loaded at the other, as illustrated in Figure 2.33.

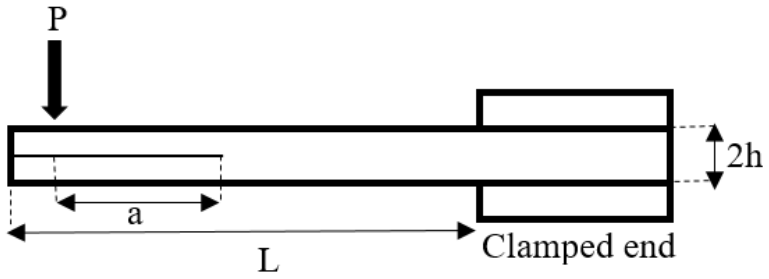


Figure 2.33 Shows a schematic for ELS Test.

Taking into account the strain energy in the body and the compliance of the beam, the expressions for the energy release rate for the ELS beam is given as:

$$G_{II} = \frac{9P^2(a+0.42\gamma h)^2}{4Eb^2h^3} \quad [2.12]$$

Where γ the correction factor for mode I and its expression is given in (Mathews and Swanson 2007).

2.13.3 Mixed Mode I/II Fracture Test

The tests required to study interlaminar fracture in mixed mode are based on mode I and mode II energy release rates. The criteria used in modes I and II are applied in developing the mixed mode analysis which are the beam equations and compliance measurements are still valid (Mathews and Swanson 2007).

To consider the energy release rate of a material, the Mixed-Mode Bending (MMB) test and the Crack Lap Shear (CLS) test are briefly discussed.

2.13.3.1Mixed Mode Bending (MMB) Test

The compliance of the structure and the strain energy in the body form the basis of beam analysis for MMB, the expressions for the energy release rates can be given as the following (Mathews and Swanson 2007):

$$G_I = \frac{12P_1^2(a+\gamma h)^2}{Eb^2h^3} \quad [2.13]$$

And

$$G_{II} = \frac{9P_2^2(a+0.42\gamma h)^2}{16Eb^2h^3} \quad [2.14]$$

P_1 and P_2 equations as described in (Mathews and Swanson 2007):

$$P_1 = P\left(\frac{3c-L}{4L}\right)$$

$$P_2 = P\left(\frac{c+L}{L}\right)$$

Where E is the Young modulus in the direction of the fibre.

Equations [2.13] and [2.14] present an insight about the interaction between mode I and mode II.

The ratio G_{II} to G_I is given by equation [2.15] after simplification:

$$\frac{G_{II}}{G_I} = \frac{3P_2^2}{64P_1^2}\left(\frac{a+0.42\gamma h}{a+\gamma h}\right)^2 \quad [2.15]$$

According to this equation [2.15] an increase in G_I will cause G_{II} increase as well, and vice versa, but according to the experiment described in (Mathews and Swanson 2007) as G_{II} increases the inverse effect is noted on, G_I that it is decreases.

Equation [2.15] presents a mathematical relationship between G_I and G_{II} but it does not take into account the interlaminar fracture taking place when the load in applied to the specimen under mixed mode bending test (see Figure 2.34).

From a fracture criteria point of view, a normalised criterion is being used to the expression of the critical energy release rate for pure Mode I and Mode II and the energy release rate corresponding to fracture under mixed mode (Mathews and Swanson 2007). The normalised equation is given by equation [2.16]:

$$\frac{G_I}{G_{Ic}} + \frac{G_{II}}{G_{IIc}} = 1 \qquad [2.16]$$

Other criteria have been suggested by taking into consideration of the total energy release rate G (Benzeggagh and Kenane 1996; Mathews and Swanson 2007).

$G = G_{Ic} + G_{IIc}$ as a ratio G_{IIc}/G

or

$$G = G_I + (G_{IIc} - G_{Ic})\,(GIIc/G)^{m} \qquad [2.17]$$

Where, m is the semi-empirical criterion exponent (Benzeggagh and Kenane 1996).

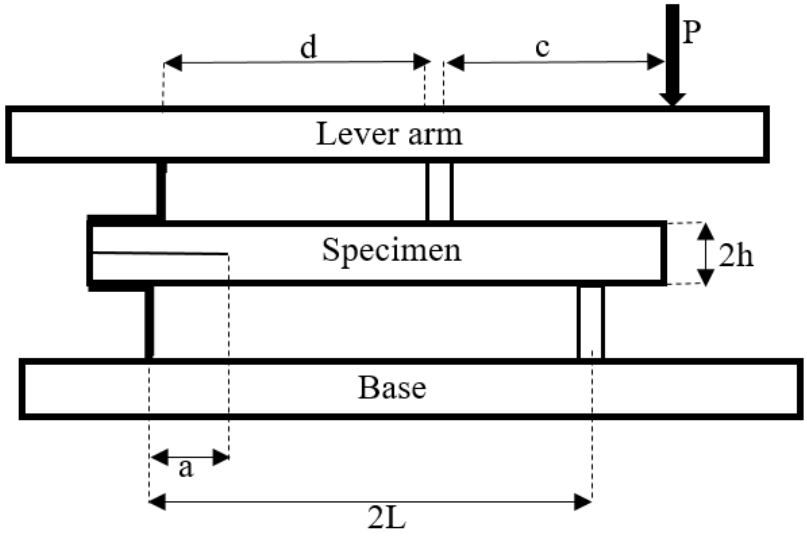


Figure 2.34 Mixed mode specimen (MMB).

2.13.3.2Cracked Lap Shear (CLS) test

The cracked lap shear is considered as a mixed mode due to the presence of both shear and stress (peel) in loaded adhesive joints (Tong and Luo 2008). This method can be used for investigating adhesive joint debonding and composite delamination (Brussat, Chiu, and Mostovoy 1977). The ASTM round robin is suggested to calculate the energy release rate for CLS specimen, as depicted in Figure 2.35. The specimen is subjected to tensile loading in four possible combinations for different support situations at both two ends which are (clamped-clamped, roller-clamped, roller-roller and free-fixed) (Johnson 1987).

Analysis of CLS specimen can be conducted to two steps (Tong and Luo 2008):

Step 1

By taking into account large deflection and the force components at the overlap are determined and then the energy release rates are calculated.

Step 2

The overlap forces and the adhesive energy release rates are determined simultaneously for failure prediction.

The energy release rates of G_I and G_{II} can be calculated using the following formulae:

$$G_I = t_a (\sigma_{max})^2 / (2 E_a) \quad [2.18]$$

and

$$G_{II} = t_a (\tau_{max})^2 / (2G_a) \quad [2.19]$$

Where t_a is the thickness of the adhesive; E_a and G_a are Young's and shear moduli of the adhesive; τ_{max} and σ_{max} are the adhesive shear and peel stresses (Tong and Luo 2008).

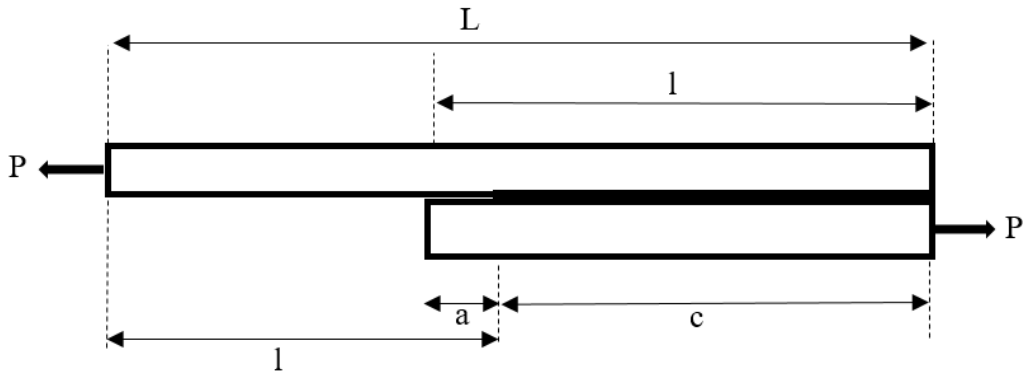


Figure 2.35 Crack lap shear specimen.

2.14 Relevant Studies of Fracture Toughness on Natural Fibre Reinforced Composites (NFRCs)

Recent developments in natural fibre reinforced composites (NFRCs) have led to renewed interest in semi-structural and structural applications especially in the automotive and construction sectors as an alternative material to synthetic fibre composites. The reasons for this shift to the use of natural fibre composites are due to increased global awareness and new environmental legislation requiring manufacturers to adapt sustainable materials (Hughes et al. 2002). Furthermore, due to increased consumer awareness and the need for lightweight components in order to reduce overall CO_2 emissions, the automotive industry is leading the way in using natural fibre composites and bio-composites. The hybrid composites developed by using flax and basalt fibres not only provide weight savings but also offer more environmentally friendly composites which can further be applied in the marine and construction industries (Dhakal et al. 2014).

In a recent extensive review relating to the use of natural plant fibres for structural applications, it has been highlighted that there have been several research works conducted focusing on the development of NFRCs for structural applications (Shah 2013b). The review concluded that natural (bast) fibres have superior mechanical properties due to their chemical and structural composition which contains high cellulose and aspect ratio with low micro-fibril angles. Thus, natural fibres can be most appropriate to be used as reinforcements in the composite industries as these natural fibres provide the best potential integration of light weight and low cost, with high specific strength and modulus (Yan et al. 2014). However, NFRCs have low-durability and inherently absorb high moisture which can reduce their properties and thus affect the long-term performance. For example, increased moisture content in natural fibres causes swelling and alters their dimensions because of the poor adhesion/compatibility between the hydrophobic matrix and hydrophilic natural fibres (Dittenber and Gangarao 2012; Faruk et al. 2012). Previous studies have reported the effect of water absorption on the properties of NFRCs, such as hemp (Dhakal et al. 2007), jute (Zamri et al. 2011) and flax (Anandjiwala et al. 2007). These reports have shown that increased moisture uptake of natural bast fibres is due to high cellulose and voids content, and the mechanical properties such as tensile and flexural strength would be significantly lowered as a consequence of weak interfacial adhesion between fibre and matrix.

Table 2-7 summarises the published data on Mode I fracture toughness of NFRCs. In addition, there are no reported works on the effect of water absorption on the fracture toughness of NFRCs. Also, very few studies have been undertaken to improve the fracture toughness of

NFRCs by chemical treatment (Li, Mai, and Ye 2005; Silva et al. 2006) and fibre or matrix hybridisation (Santhanam and Chandrasekaran 2014; Wong, Shanks, and Hodzic 2004). In addition, (Li et al. 2005) have conducted the interlaminar and intralaminar fracture toughness test to investigate the effects of fibre surface treatment of sisal fibre reinforced vinyl ester composites. They found that the permanganate and silane treated systems improved the interlaminar fracture toughness in comparison to the untreated systems with critical strain energy release rate (G_{IC}) of 1682.2 J/m^2 to 1488.3 J/m^2 and 1158.7 J/m^2, respectively, as shown in Figure 2.36. Moreover, these chemical treatments also improved the intralaminar fracture toughness compared to untreated composites with stress intensity factor (K_{IC}) of 6 MPa.m$^{0.5}$ to 5.5 MPa.m$^{0.5}$and 4.2 MPa.m$^{0.5}$, respectively. However, (Silva et al. 2006) reported that the alkaline treatment contributed to lower the fracture toughness of the sisal fibre reinforced polyurethane composites. This behaviour was attributed as a result of improved interfacial adhesion between fibre and matrix which affected debonding and fibre pull-out and then reduced the fracture energy absorption. Hence, the use of thermoplastic matrix material such as polypropylene and polyurethane leads to a decrease of mechanical properties caused by a weak bond to natural fibres, and they also have lower mechanical properties compared to thermosets (Goutianos et al. 2006).

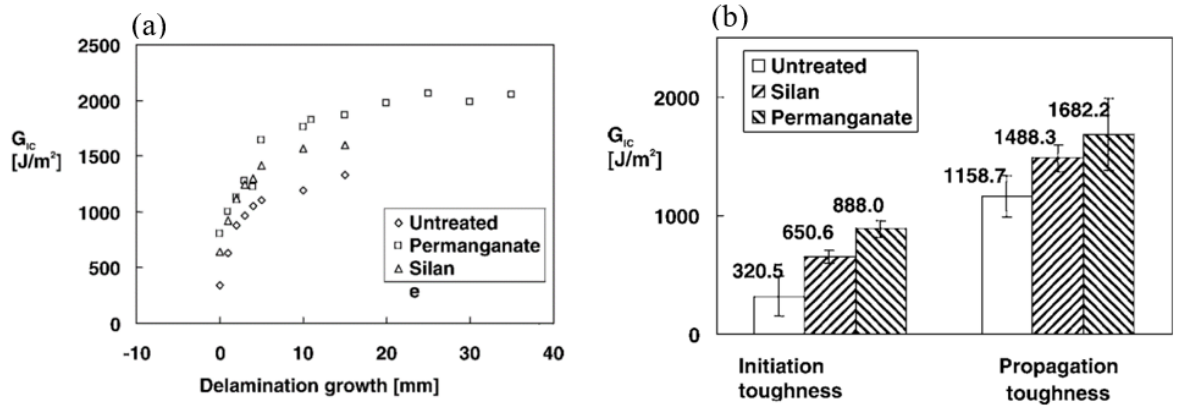


Figure 2.36 (a) R-curve and (b) Mode I interlaminar fracture toughness of sisal reinforced vinyl ester (Li et al. 2005).

It was noted that the interlaminar fracture toughness (G_{IC}) of flax fibre reinforced Hyperbranched Polymers (HBP) with Poly ($_L$-Lactic Acid) (PLLA) was significantly increased when modified and blended together. Moreover, the toughness properties were improved due to better wetting of the fibres by these matrices (Wong et al. 2004). Further work done by (Liu and Hughes 2008) reported that the "toughness is dominated by the fibre volume fraction,

rather than the reinforcement architecture", and also the addition of woven fabric in composite laminates results in all cases increasing the fracture toughness of composites. In another study carried out by (Zulkifli et al. 2008), increasing the number of silk plies so that increased the stiffness and interlaminar fracture toughness of composites. For example, the initiation and propagation of interlaminar fracture toughness of silk fibre/polyester composites for 10 layers are higher than that of 8 layers with percentage of 136% and 80%, respectively. Recently, (Bensadoun, Verpoest, and Van Vuure 2017) investigated the effect of fibre architectures on the interlaminar fracture toughness of flax fibre reinforced epoxy composites. The results showed that the interlaminar fracture toughness improved with woven textile compared to [0, 90] cross-ply lay-ups. All textile forms revealed that the type of architecture is effected on the value of fracture toughness (See Figure 2.37).

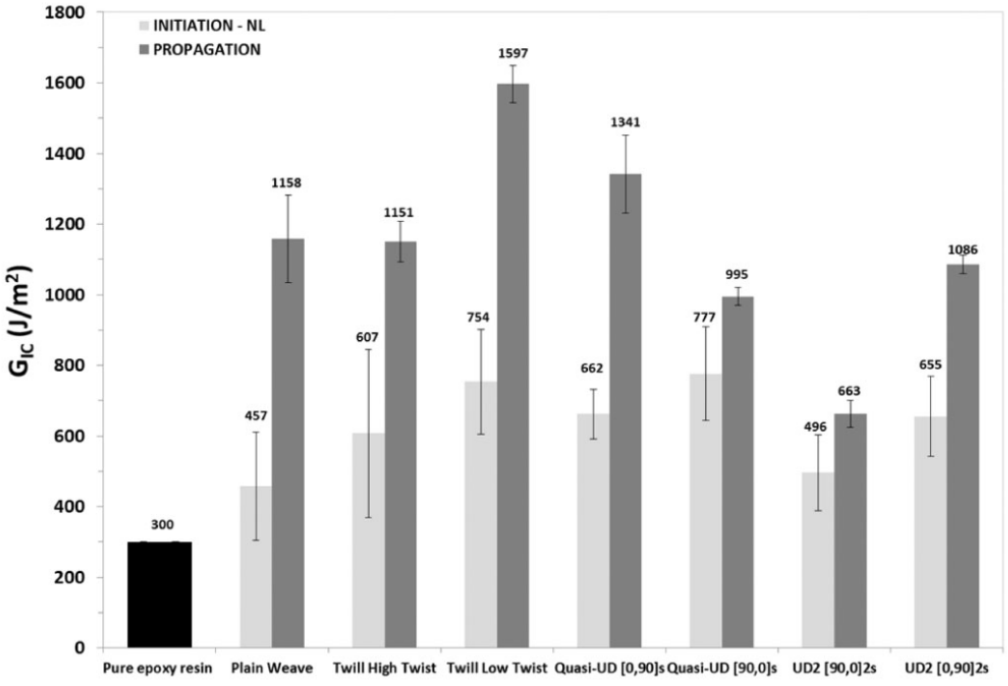


Figure 2.37 Effect of textile architecture on Mode I (DCB) of flax reinforced epoxy composites (Bensadoun et al. 2017).

It was observed that the intralaminar fracture toughness increased when increase the fibres length of banana/glass fibre hybrid composites using Compact Tension (CT) test (Santhanam and Chandrasekaran 2014). Jute and viscose fibres based homopolymer polypropylene composites using modified maleated polypropylene were studied in detail to investigate the effect of fibre content on the fracture toughness properties (Ranganathan et al. 2016). With only 10 wt% addition of viscose fibres to PP–J30 composites, the fracture toughness of K_{IC} and G_{IC} were significantly improved to 133% and 514%, respectively. However, adding 2 wt% of

MAPP in PP–J30–V10 composites were increased the fracture toughness and energy (from 9.1 to 10 MPa.m$^{0.5}$) and (from 28900 to 31200 J/m^2), respectively.

Table 2-7 Summary of published data on Mode I fracture toughness of natural fibre reinforced composites.

Composite materials	Composite fabrication	Method	Fracture toughness (Mode I)			References
			Critical stress intensity factor, K_{IC} (MPa.m$^{0.5}$)	Critical strain energy release rate, G_{IC} (J/m^2)		
Flax/Epoxy Epoxy neat	Vacuum infusion	CT	6.0 1.8	-		(Liu and Hughes 2008)
Bamboo /Polyester Polyester neat	Hand lay-up	CT	1.7 0.4 - 0.6	-		(Wong et al. 2010)
Glass+Banana/Epoxy (5mm) Fibre length (10mm) (15mm) (20mm)	Hand lay-up	CT	 1.5 1.9 2.5 2.6	-		(Santhanam and Chandrasekaran 2014)
Sisal short fibre/ Polyurethane Coconut short fibre/ Polyurethane	Compression moulding	CT	-	6300 (T), 6500 (UT) 7500 (T), 5600 (UT)		(Silva et al. 2006)
Silk/Polyester (8 Plies) (10 Plies) (12 Plies) (14 Plies)	Vacuum bagging	DCB	-	Initiation 436 1030 1244 1687	Propagation 847 1530 1638 1872	(Zulkifli et al. 2008)
Flax/Hyperbranched polyester(HBP) + poly(L-lactic acid) (PLLA)	Compression moulding	DCB	-	38.9 (0% v/v) 73.2 (10% v/v) 83.3 (30% v/v) 115.4 (50% v/v)		(Wong et al. 2004)
Sisal/Vinyl-ester (Untreated) (Silane) (Permanginate)	Compression moulding	CT, DCB	 4.2 5.5 6.0	Initiation 320.5 650.6 888	Propagation 1158.7 1488.3 1682.2	(Li et al. 2005)

Glass /NR+Polypropylene	Compression	DCB	-			(Zulki et al.
(5%NR)	moulding			1415		2002)
(10%NR)				1257		
(15%NR)				1170		
(20%NR)				1056		
Flax/epoxy	Resin Transfer	DCB	-	Initiation	Propagation	(Bensadoun et
(plain weave)	Moulding			457	1158	al. 2017)
(High twist twill)	(RTM)			607	1151	
(Low twist twill)				754	1597	
(Quasi-UD [0,90]s)				662	1341	
(Quasi-UD [90,0]s)				777	995	
(UD2 [90,0]2s)				496	663	
(UD2 [0,90]2s)				655	1086	
Epoxy neat				300	-	
polypropylene(PP)/Jute+	Twin screw	CT				(Ranganathan
viscose fibres and MAPP	extruder					et al. 2016)
(PP–J30)			3.9	4700		
(PP–J30–M2)			2.5	2000		
(PP–J30–V5)			5.8	11500		
(PP–J30–V10)			9.1	28900		
(PP–J30–V15)			7.9	21800		
(PP–J30–V10–M2)			10.0	31200		

A few works have been investigated on the Mode II fracture toughness behaviour of NFRCs, as presented in Table 2-8. Chemical modification on the fibre surface could improve the fracture toughness of NFRCs. It was reported that permanganate and silane treatment on the fibre surface could improve interfacial bonding properties between sisal fibre and vinyl ester matrix. Thus, the value of critical strain energy release rate G_{IIC} with treatment is higher than untreated composites (Li et al. 2005). Furthermore, (Almansour et al. 2015) highlighted that non-woven mat of flax/basalt hybridised laminates improved the fracture toughness compared to non-woven mat of flax composites without hybridisation using 3ENF testing. The results showed that the critical strain energy release rate G_{IIC}, and stress intensity factor K_{IIC}, were increased for flax/basalt laminates by 12% and 33%, respectively compared to flax composites without hybridisation. It was observed that the interlaminar fracture toughness increased when increase the fibres length of banana/glass fibre hybrid composites using ENF test (Santhanam and Chandrasekaran 2014). The results showed that the stress intensity factor K_{IC}, increased

from 0.24 (MPa.m$^{0.5}$) for (5mm length) to 0.98 for (20mm length). It can be seen that in Figure 2.38, longitudinal breakage of banana fibre, fibre pull-out and broken glass fibre from the matrix on Mode I (CT) test, whereas, banana fibre was broken on Mode II (3ENF) test. From a review of this literature, it can be concluded that of central importance in using natural fibre composites in structural applications is the measurement of their fracture toughness behaviour.

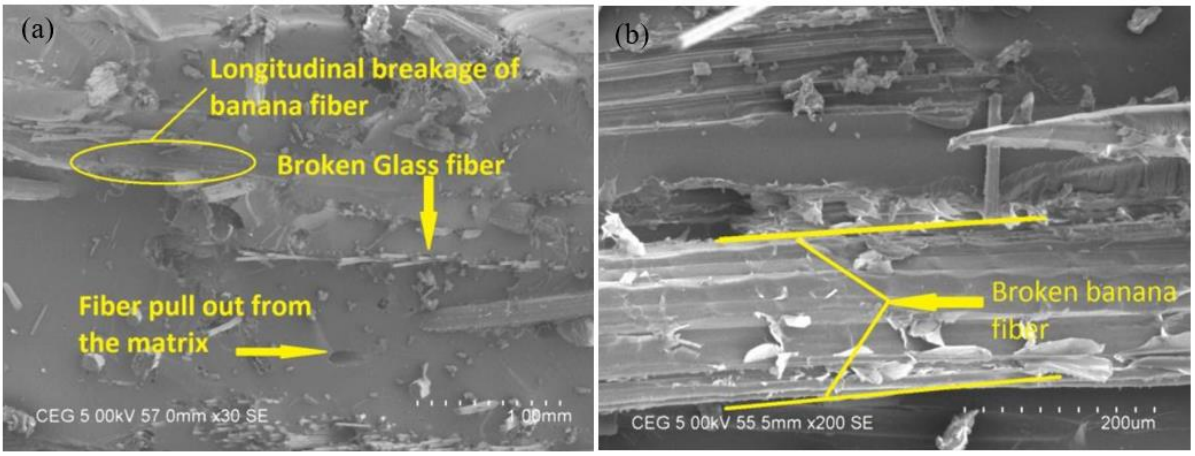


Figure 2.38 Morphology images by SEM for (a) Mode I (CT), and (b) Mode II (3ENF) of Banana/Glass hybrid composites (Santhanam and Chandrasekaran 2014).

Table 2-8 Summary of published data on Mode II fracture toughness of natural fibre reinforced composites.

Composite materials	Composite fabrication	Method	Fracture toughness (Mode II)		References
			Stress intensity factor, K_{IIC} (MPa.m$^{0.5}$)	strain energy release rate, G_{IIC} (KJ/m^2)	
Glass+Banana/Epoxy (5mm) Fibre length (10mm) (15mm) (20mm)	Hand lay-up	3ENF	 0.24 0.58 0.79 0.98	-	(Santhanam and Chandrasekaran 2014)
Sisal/Vinyl-ester (Untreated) (Silane) (Permanginate)	Compression moulding	3ENF	-	 2141 2242 2384.7	(Li et al. 2005)

Flax/Vinyl-ester Flax+Basalt/Vinyl-ester	Compression moulding	3ENF	0.13 0.18	1900 2200	(Almansour et al. 2015)
Flax/epoxy (plain weave) (High twist twill) (Low twist twill) (Quasi-UD [0,90]s) (Quasi-UD [90,0]s) (UD2 [90,0]2s) (UD2 [0,90]2s)	Resin Transfer Moulding (RTM)	3ENF	-	 1872 1588 1315 1570 1533 728 1006	(Bensadoun et al. 2017)

2.15 Evaluation of Factors Affecting the Fracture Toughness Behaviour

2.15.1 Fibre and Matrix Materials

It is important to determine the strength and stiffness properties of composite laminates in order to evaluate the fibre and matrix materials. The mechanical behaviour of the composite is defined not by the fibres alone, but also with the combined action between the fibres and the matrix (Friedrich and Almajid 2013). In general, laminated structures suffered from poor interlaminar fracture toughness and then lead to a delamination which subjected to interlaminar stress. It could be occurred from manufacturing defects, low velocity impact damage and poor adhesion between fibre and matrix. Most researchers have focused on the materials development in order to improve the fibre matrix interfaces and the mechanisms of the fracture toughness of the composites (Dransfield, Jainb, and Mai 1998; Jain, Dransfieldb, and Ma 1998). The bonding strength between the fibre and the matrix plays an important role in the strength of composites. The overall stress distribution is usually affected by the bonding properties. This change, in turn, can cause some variation in the fracture toughness of the material. The factors like modulus, the diameter of the fibre and matrix, and ductility affect the fracture behaviour. Furthermore, the selection of a matrix for a fibre is of significant consequence (Friedrich and Almajid 2013; Hull and Clyne 1996; Liu and Hughes 2008). In Figure 2.39, a strong evidence showing that improvement in the bonding between fibre and matrix by using modified fibre. Macroscopic failure observed that failure invariably happened through delamination and wide scale debonding between fibre and matrix. On the other hand, the mode of failure was noticed and change to brittle failure on both PrA and MeA modified flax fibre reinforced composites (Hughes et al. 2007). However, a strong interface commonly

affects in low toughness because the stress could not released through interfacial bonding. In order to have a high performance composite and show good interfacial bonding, it is important to consider that having a good balance of the interfacial properties to achieve high strength (Wong et al. 2004).

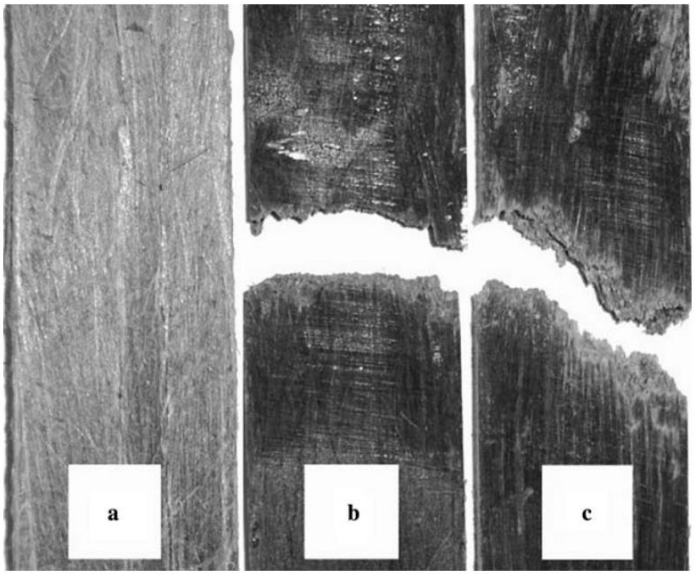


Figure 2.39 Fracture failure of modified flax fibre reinforced unsaturated polyester laminates at specimens: (a) unmodified, (b) methacrylic anhydride and (c) propionic anhydride (Hughes et al. 2007).

2.15.2 Through-Thickness Reinforcement

Amongst the several textile methods of inserting through-thickness fibre reinforcements, stitching, knitting and weaving are the methods used to improve the interlaminar fracture toughness. It is likely that the most common of these techniques is stitching because of its versatility and convenience (Beier et al. 2007; Tan, Watanabe, and Iwahori 2010; Velmurugan and Solaimurugan 2007). By using stitching through-thickness reinforcement, the fracture toughness of the composites has been improved as a result of providing a more integrated composite structure (Jain 1994; Sankar and Sharmab 1997). However, it has been observed in the previous studies that stitching can cause in-plain fibre damage and create resin-rich regions which can led to a reduction of the flexural, compressive and tensile properties (Khan and Mouritz 1996; Velmurugan et al. 2004). Indeed, it is difficult to predict the influence of stitching on the in-plane mechanical properties owing to many factors, such as the type of the composite laminates, fabrication techniques and also the important parameters of stitching (stitch density, pattern, span, yarn diameter, type of thread) (Mouritzas, Leongb, and Herszbergc 1997). More recent published work by (Ravandi et al. 2016) extensively examined the effects of stitching through-thickness reinforcement using natural fibres on Mode I

interlaminar fracture toughness of flax fibre/epoxy composites. It was found that the interlaminar fracture toughness of woven flax composites was significantly higher than glass fibre composites. In addition, it can be seen that large scale of fibre bridging in woven composites. Therefore, high amount of energy absorption during delamination through thickness reinforcement by fibre pull-out and fibre breakage mechanisms, as shown in Figure 2.40. Moreover, flax yarn stitches exhibited improved fracture toughness of the laminates compared to cotton thread stitches.

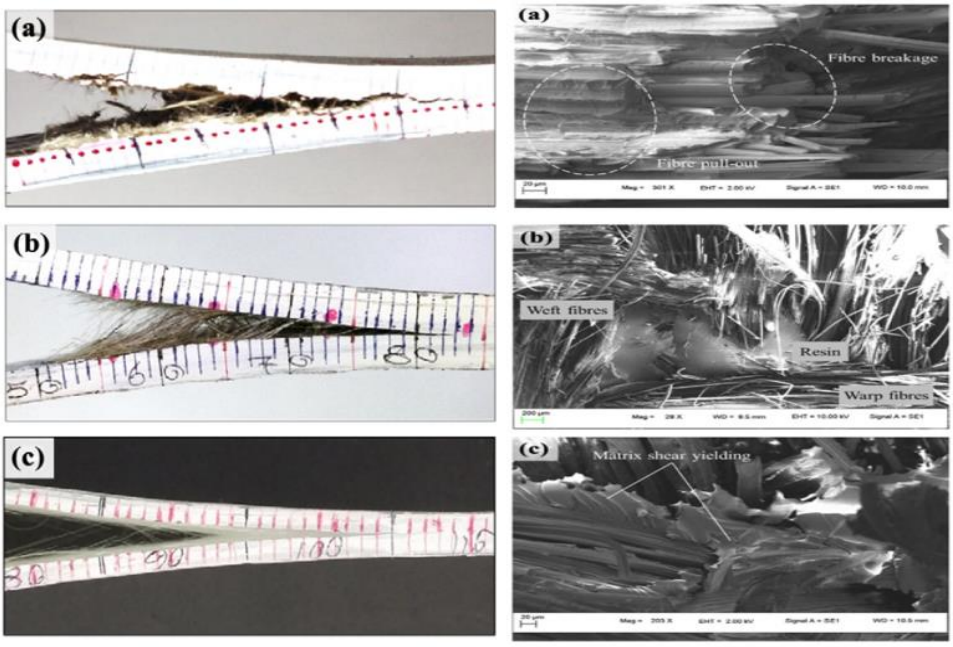


Figure 2.40 To the left images, Fibre bridging during delamination growth ; (a) woven flax fabric, (b) unidirectional flax, and (c) unidirectional glass fibre laminate composite. To the right images, SEM of a fractured surface of the flax woven fabric composite after DCB test; (a) fibre pull out and breakage, (b) a resin rich region between warp and weft fibres, (c) matrix shear yielding (Ravandi et al. 2016).

Previous studies investigated that the effects of stitching on the Mode II interlaminar fracture toughness of fibre reinforced polymer composites (Dransfield, Baillie, and Mai 1994; Jain et al. 1998; Sankar and Sharmab 1997) but on natural fibres composites still not yet reported. It was highlighted that the addition of stitching improved the mode II delamination resistance up to four times and observed stable crack propagation of carbon fibre reinforced epoxy composites, which depended on the parameters of stitch density, thread type and dimeter (Jain et al. 1998). The effect of stitches of through-thickness natural fibre on the epoxy compost laminates that are reinforced by woven flax has been investigated by low-velocity impact. A decrease of 16% in the woven flax intralaminar fracture toughness is observed in the stitching of flax yarn while a decrease of 5% is recorded in cotton yarn stitching (Ravandi et al. 2017).

2.15.3 Fibre Volume Fraction

The delamination and crack propagation of natural fibre reinforced polymer composites depends on the fibre volume fraction (Hughes et al. 2007; Liu and Hughes 2008; Wong et al. 2010). In this study (Wong et al. 2010), short bamboo fibre reinforced polyester composites and neat polyester were characterised using compact tension (CT) specimens with different fibre volume fractions from 0 to 60 vol.% at 4, 7 and 10 mm fibre lengths, respectively. The results showed that the highest fracture toughness for hybrid composite was achieved with improvement of 340% compared to neat polyester, whereas the fracture toughness decreased incrementally of 10, 7 and 4 mm at 50, 40 and 10 vol.% with critical stress intensity factors, K_{IC}, of 1.73, 1.62 and 1.50 MPa $m^{1/2}$, respectively, as illustrated in Figure 2.41. For this trend is ascribed to the enhancement of stress transfer from the matrix to the fibres through the interface.

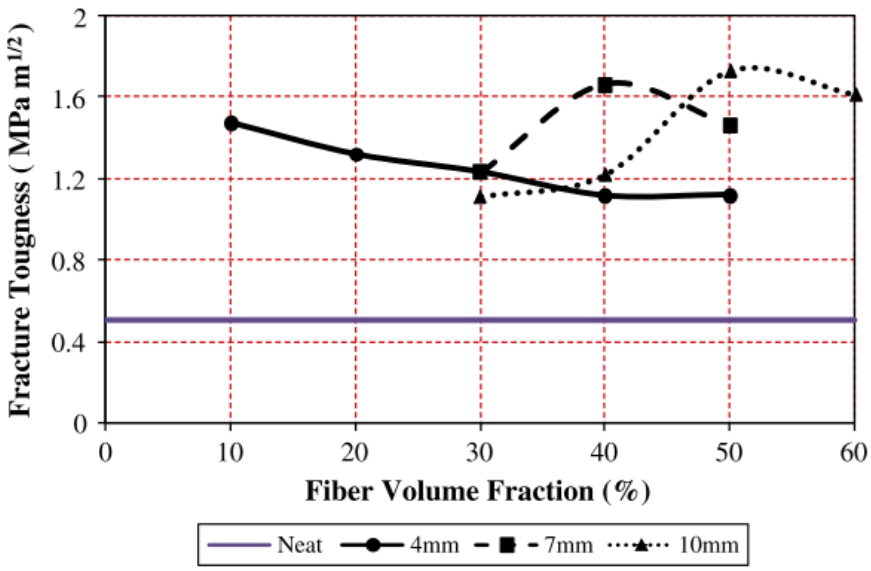


Figure 2.41 Effect of fibre volume fraction on fracture toughness of bamboo fibre reinforce polyester composites (Wong et al. 2010).

Another study by (Ranganathan et al. 2016) showed that hybrid biocomposites with the addition of 10 wt.% viscose fibres, 30 wt.% jute fibres, 58 wt.% polypropylene and 2 wt.% Maleic anhydride grafted polypropylene improved the fracture energy approximately by 563% compared with that of unmodified jute composites (PP-J30). The latter showed unstable crack growth resulting lower fracture energy but when added just 10 wt.% viscose fibre (PP-J30-V10) then the G_{IC} increased from 4.7 KJ/m^2 to 28.9 KJ/m^2 due to stable crack growth. In addition, polypropylene reinforced clay nanocomposites at different concentration from 1 to 5

wt.% was prepared using Single Edge Notch Beam (SENB) test. It was revealed from the study that the sample of 5 wt.% nanoclay improved 1.75 and 3 times than PP neat in K_{IC} and G_{IC}, respectively (Ramsaroop, Kanny, and Mohan 2010).

2.15.4 Fibre Orientation Angle

When composite materials are designed, the reinforcement are always oriented in the load direction. However, if the load direction is changed, that is it no longer parallel to the fibres, it is important to investigate the mechanical behaviour of the laminates (Brahim and Cheikh 2007). Some experimental results show that fibre orientation in the layers adjacent to crack plane affects the interlaminar fracture toughness. The effect of fibre orientation on the Mode I interlaminar fracture toughness of glass fibre reinforced epoxy composites was studied using DCB test in terms of different fibre orientation (0°, ±45°, ±60° and 90°), as dipicted in Figure 2.42. It was observed that the $G_{IC\ prop.}$ values are the lowest for 0° orientation while others are quite similar for ±45°and ±60°. However, the $G_{IC\ prop.}$ values of 90° orientation are the highest for all specimens, and are double than 0° orientation specimen (Shetty et al. 2000). It was noted that the fibre direction and fibre volume fraction are strongly influenced by the crack path which showed that more fibre content, the faster path of crack when growth with the fibre direction (Keck and Fulland 2016). Further, more investigation needs to be carried out with other pattern of composites to study the effect of fibre volume fraction and fibre orientation on the fracture toughness and also developing suitable testing and analysing procedures which studying delamination resistance of laminates with multidirectional orientation of fibres (Brunner, Blackman, and Davies 2008).

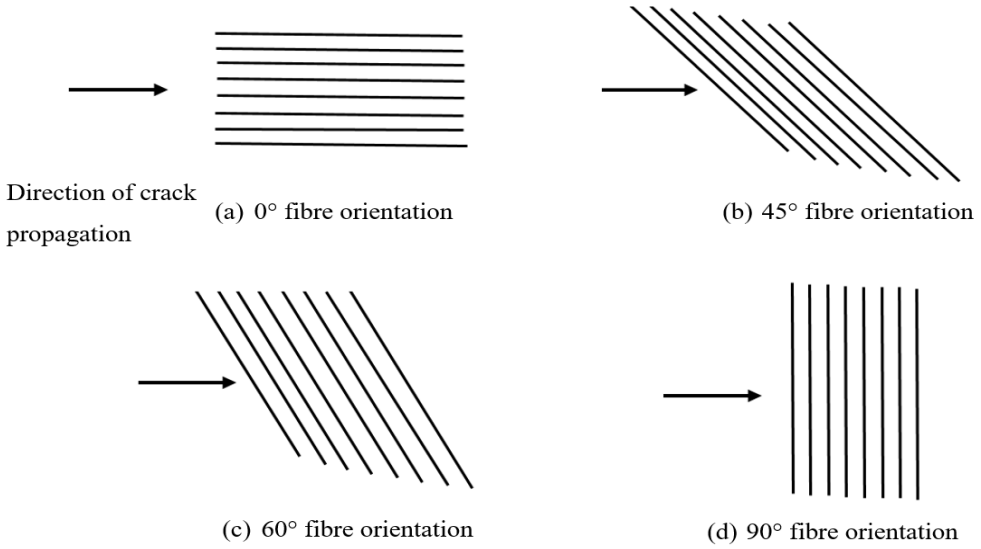


Figure 2.42 Schematic of different fibre orientation in a crack propagation (a) 0°, (b) 45°, (c) 60° and (d) 90°(Shetty et al. 2000).

2.16 Failure Modes and Mechanisms

Composite materials fail under different modes. It can be fail due to crack formation at any point in a composite upon loading. After further loading, the crack will grow causing delamination and finally rupture or failure occurs. In general, delamination corresponds to stable and unstable crack between the plies in composite applications ascribed to inherent defects from the materials or through process fabrication and damage incurred during the service life when composite undergoes to different loading and environmental conditions (Zhu, Bakis, and Adair 2012). In addition, composite materials have desirable properties; the presence defect of the materials is susceptibility to low-velocity impact damage. Therefore, the crack initiation and propagation for both interlaminar and intralaminar cracks is very important (Czabaj and Ratcliffe 2013). In Figure 2.43 (a), the models of interlaminar fracture or delamination process in the composite laminates that showed parallel fracture to fibres between two plies of a laminate. In Figure 2.42 (b), intralaminar fracture occurred through the entire laminate thickness into the vertical fibre direction (Kuwata 2010).

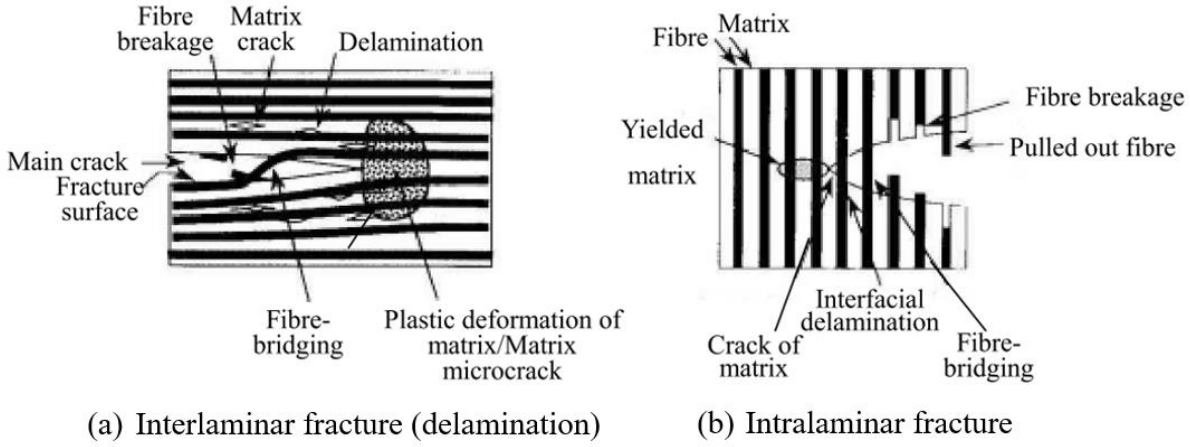


Figure 2.43 Schematic diagram of fracture composites (Kuwata 2010).

There ae several failure mechanisms modes such as delamination, matrix cracking, fibre breakage and fibre debonding. The failure mechanisms observed in carbon fibre composites is matrix cracking and the fibres fracture occurred in a brittle way. In the case of flax fibre hybridised carbon (FCP) samples and flax unidirectional (FUD), it was showed a considerable amount of matrix cracking and fibre bending. For FCP and FUD samples, there is an indication of matrix cracking and fibre pull-out (Dhakal et al. 2013). The effect of alkali treatment on the mechanical properties of flax fabric reinforced epoxy composites were prepared using a

vacuum bagging technique. It was found that the failure of fibre occurs along the load direction, debonding, fibre pull-out and brittle fracture of the matrix are the dominated failure mechanisms of flax fabric/epoxy composites (Yan et al. 2014). In the example considered, deformation and fracture behaviour of a flax fibre/recycled high density polyethylene (HDPE) composite laminates in being subjected to test and the failure mechanism is analysed. The Charpy impact tests were performed using single edge notched in 3-point bending. Delamination cracking at or in the front of crack tip between plies of fibre and matrix and at polymer and polymer interfaces. The initiation of tensile failure of flax fibre in flexural mode is by the formation of kink bands leading to final breakage (Singleton et al. 2003). The failure mode of composite box structure's progressive crushing is affected by the intralaminar crack growth of Mode I and Mode II. A significant contribution is made to Specific Energy Absorption (SEA) of the composite box by the failure modes such as brittle fracture, transverse shearing, lamina bending, and local buckling. The specific energy absorption of 0/45 box is highest. Additionally, the Mode I and Mode II toughness of interlaminar fracture of 0/0 is higher than the interface plane value of 0/45 and 45/45. When the total fracture energy increases beyond a threshold value, the mechanism such as bending, and friction increases (Hadavinia and Ghasemnejad 2009).

2.17 Morphological Characterisation Techniques

2.17.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopes (SEM) use a beam of electrons instead of light to provide an image of the specimen surface. It is an important tool in studying the morphological characteristic of pure specimen and composite materials. The microscope is used for radiation interaction with the sample and high voltage used to quicken it. Electromagnetic condenser lenses are used to reduce the beam in the scanning electron microscope which scans across the entire sample. A scintillate light pipe photo multiplier system is used to see the electrons which move away from the surface of the sample. The results are fed into a Cathode Ray Tube CRT after being amplified. This allows the creation of an enlarged image of the surface sample by scanning the surface at the time as the incident electron probe. The specimens are placed on the stubs for the specimen, and later they are enveloped with a minute layer of metal which has conductive properties, such as gold or platinum. Since the grounded specimen of the SEM is in contact with the aluminium specimen stub, it is conducted to the ground fact so that any charge is removed. This allows the prevention of the creation of high voltage charges for the

specimen. The role of secondary electors is played by the metal coatings, which help to conduct the heat away which can be damaging (Ludwig Reimer 1998).

The SEM micrographs of the fractured surfaces provide important information on how the specimens fail in relation to fibre-matrix adhesion and resulting failure mechanisms. SEM study showed in Figure 2.44 that the failure of fibre yarns with the load direction, fibre pull-out, debonding and brittle fracture of the matrix are the key factors of failure mechanisms of flax fabric reinforced epoxy composites (Yan et al. 2012). Micrograph of treated fibres can reveal the arrangement of fibres in untreated and treated flax specimen, existence of crank and kink in the structure of the fibres. The effect on the fibres after different chemical treatments. For example, a long exposure in NaOH can reveal the orientation of microfibrils and the nature in the presence of other chemical solutions, like formic acids and acetic anhydride plus sodium hydroxide (Baley et al. 2006). SEM results after chemical treatment that surface roughness of fibres was improved (Shahzad 2011). For untreated fibres the SEM analysis, the gummy polysaccharides of lignin, pectin and hemicellulose are located on the surface (Pickering et al. 2007). A study for determining the degree of resin fracture was conducted on the unidirectional carbon/epoxy composite's fractured surfaces by scanning electron microscopy. Hackles assessed the degree of microcracking that appears after fracture and the resin fracture (ductile vs brittle) both. The Mode II systems surface, as observed after SEM micrograph, have a rougher fracture and more hackles as compared to Mode I. Transverse cracks in resins were indicated by the rough hackles saw-toothed pattern of fracture. The ability of the material to absorb more energy is related to high G_{IIc} results (Saidpour 2003). SEM micrographs of the fracture surfaces with different fibre/matrix content can reveal the change in the composite specimen, like long fibres pull-out and presence of cavity between fibre and matrix, thus poor adhesion occurred between fibres and matrix (Niu et al. 2010).

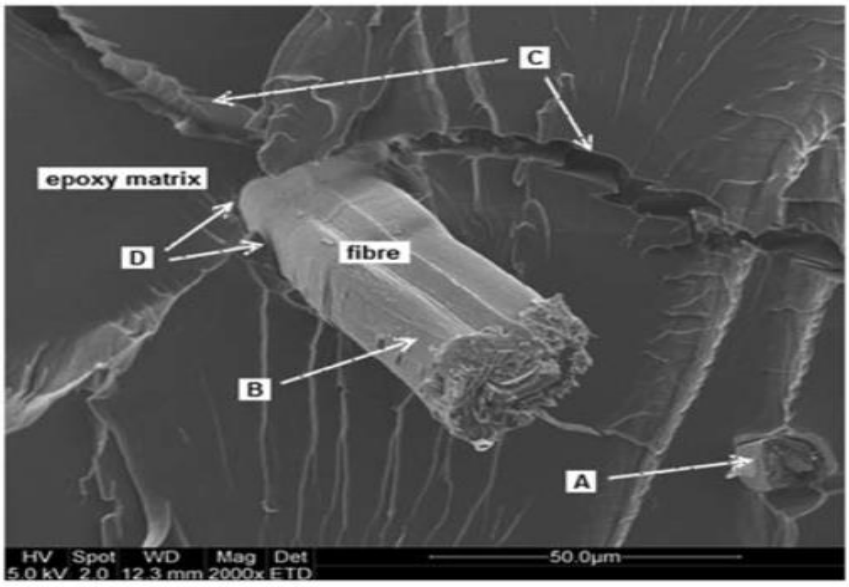


Figure 2.44 SEM images of failure modes of untreated flax fabric reinforced epoxy composites; A, failure of fibre; B, fibre pull-out; C, brittle fracture of epoxy matrix and D, fibre debonding (Yan et al. 2012).

2.17.2 X-ray Computed Micro-Tomography (µCT)

X-ray micro-computed tomography (µCT) is used to reconstruct the internal structure of a specimen as three-dimensional images. This test is known as non-destructive technique which is useful to analyse the defects of delamination and matrix cracking. It can also provide better images for the distribution of damages than optical microscopy (Symons 2000). The term of micro-tomography means that the results of spatial resolution found between 50-100 µm (Schilling et al. 2005). The sample is placed between the X-ray source and detector, then the magnification of the system will be set in order to obtain high resolution images by using X-ray µCT. Thus, the object stayed in the area of view of the detector for the entire rotation cycle. Usually, projection images are captured every 0.4 rotation step until 360 (Hamdi et al. 2015). It was resulted that X-ray µCT can help characterisation inside the geometry of flaws, including delamination and microcracking of fibre reinforced polymer composites (Schilling et al. 2005).

2.18 Hybrid and Stitch Composites

Hybrid composites are made from a combination of more than one type of fibre reinforced in the same matrix. At present, there is significant interest in enhancing the mechanical properties of natural fibre reinforced composites with the use of hybrid system. Hybridisation have many advantages such as reduce cost and weight as well as show an improvement to environmental effects, the hybrid systems can also have improved mechanical properties compared to glass FRP composites. Hybridisation of fibres or resins with natural materials can be used in high performance applications (Almansour, Dhakal, and Zhang 2017). However, natural FRP

composites are still limited in non-structural applications due to their higher moisture absorption, lower strength and stiffness properties (Faruk et al. 2012). To tackle this issue, a hybridisation of natural cellulosic fibres with mineral fibres that have superior ageing resistance and thermal resistance were investigated to improve the mechanical properties. At the present time, there is a significant interest for using basalt fibres as hybridising material into natural FRP composites due to their excellent properties such as mechanical, chemical, thermal and acoustic insulation (Dhakal et al. 2015; Fiore et al. 2017; Fiore, Scalici, Calabrese, et al. 2016). Fiore et al. (2016) investigated the effects of basalt fibre hybridisation as a double external layers on the impact and flexural properties of flax reinforced composites under different environmental conditions, as shown in Figure 2.45. They found that the impact, flexural strength and modulus of flax-basalt hybridised composites were higher than flax without hybridisation by 28%, 71% and 49%, respectively. Similar work carried out recently by Fiore et al. (2017) on jute-basalt fibre reinforced hybrid structures highlighted that all composite laminates performed lower in their mechanical properties with increasing ageing time but the sandwich structure of basalt hybrid performed best in terms of their mechanical performance compared to other generic composites. The properties enhancement realised can be related to source of basalt fibre. Basalt fibres are obtained from mineral through melting rocks, thus non-hazardous/toxic which can be considered as environmentally friendly compared to glass fibres (Fiore, Scalici, Badagliacco, et al. 2016; Sarasini et al. 2013). Therefore, basalt hybridisation into natural fibres can serve an effective means to enhance the mechanical properties and moisture resistance of composites by promoting improved fibre/matrix interface. From these benefits, the capability of the basalt fibres to be used as a hybridisation for a structural reinforcement material is extremely expected (Sim, Park, and Moon 2005).

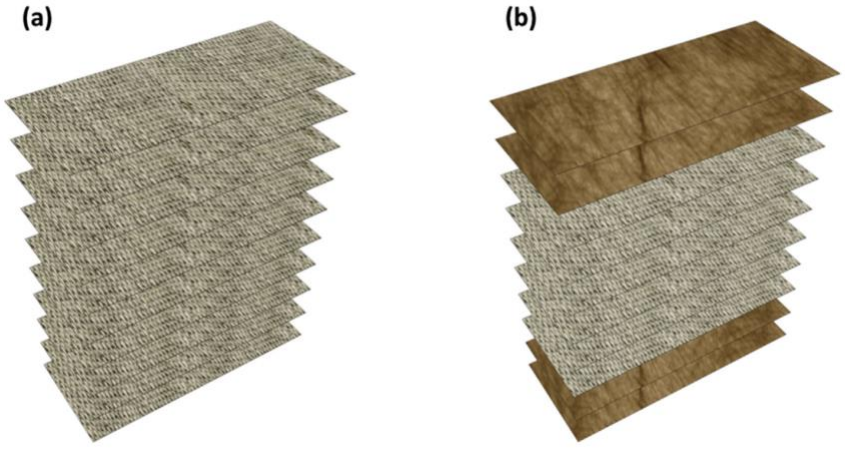


Figure 2.45 Schematic illustration of the stacking sequence of flax and flax/basalt hybrid laminates using a balanced layup (Fiore, Scalici, Calabrese, et al. 2016).

In general, delamination corresponds to stable and unstable crack between the plies in composite applications ascribed to inherent defects from the materials or through process fabrication and also damage incurred during the service life when composite undergoes to different loading and environmental conditions (Zhu and Joyce 2012). Therefore, there are some methods to reduce the interplay delamination by using toughened matrix, woven fabrics, through-thickness stitching and interleaving (Hosur et al. 2004). Amongst the several textile methods of inserting through-thickness fibre reinforcements, stitching, knitting and weaving are the methods used to improve the interlaminar fracture toughness. It is likely that the most common of these techniques is stitching because of its versatility and convenience (Beier et al. 2007; Tan et al. 2010; Velmurugan and Solaimurugan 2007). By using stitching through-thickness reinforcement, the fracture toughness of the composites has been improved as a result of providing a more integrated composite structure (Jain 1994; Sankar and Sharmab 1997). However, it has been observed in the previous studies that stitching can cause in-plain fibre damage and create resin-rich regions which can lead to degrade the flexural, compressive and tensile properties (Khan and Mouritz 1996; Velmurugan et al. 2004). In fact, it is difficult to predict the influence of stitching on the in-plane mechanical properties owing to many factors, such as the type of the composite laminates, fabrication techniques and also the important parameters of stitching (stitch density, pattern, span, yarn diameter, type of thread) (Mouritzas et al. 1997).

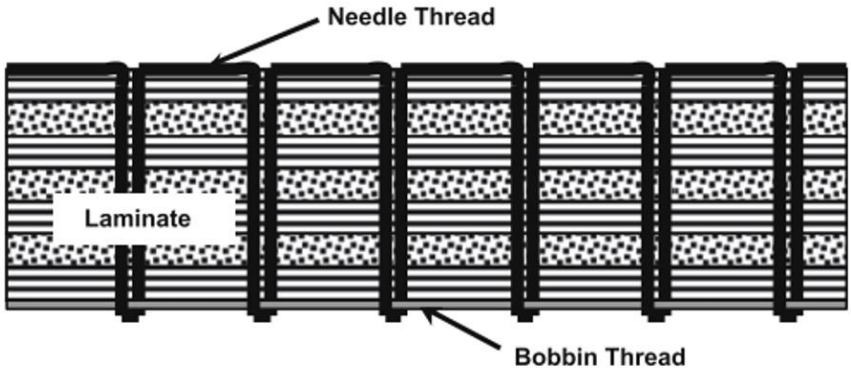


Figure 2.46 Illustration of a stitch pattern through a composite laminate (Mouritz and Cox 2010).

Previous studies investigated that the effects of stitching on the Mode II interlaminar fracture toughness of FRPs (Dransfield et al. 1994; Jain et al. 1998; Sankar and Sharmab 1997) but on natural fibres composites still not yet reported. It was reported that the addition of stitching improved the mode II delamination resistance up to four times and observed stable crack propagation of FRPs, which depended on the parameters of stitch density, thread type and dimeter (Jain et al. 1998). Ravandi et al. (Ravandi et al. 2017) have reported the effect of through-thickness natural fibre stitches on the low-velocity impact of woven flax reinforced epoxy composite laminates. Stitching of flax yarn led to decrease the intralaminar fracture toughness of woven flax composites about 16%, whereas the cotton yarn stitching was reduced by only 5 %. More recent published work by Ravandi *et al*. (Ravandi et al. 2016) examined the effects of stitching through-thickness reinforcement using natural fibres on Mode I interlaminar fracture toughness of flax fibre/epoxy composites. It was found that the interlaminar fracture toughness of woven flax composites was significantly higher than glass fibre composites. Moreover, flax yarn stitches exhibited improved fracture toughness of the laminates rather than cotton thread stitches, as illustrated in Figure 2.47.

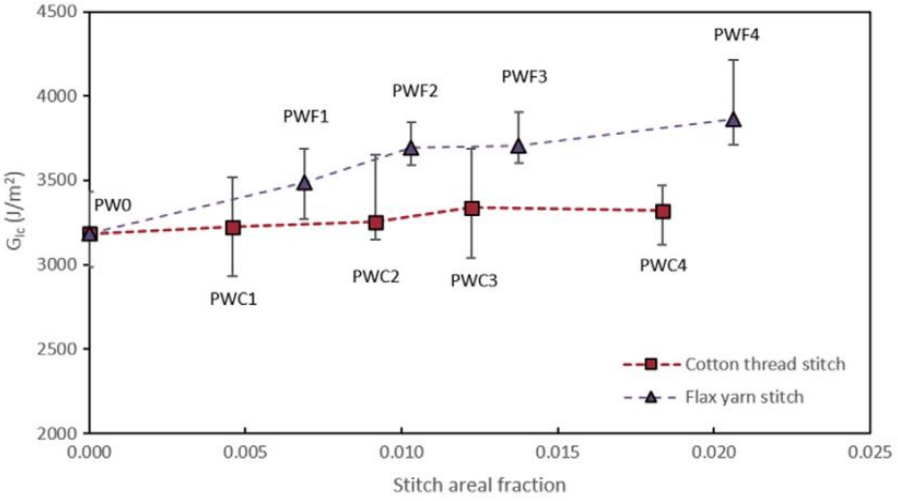


Figure 2.47 Effect of stitch material on the interlaminar fracture toughness G_{IC} (Ravandi et al. 2016).

2.19 Current Applications

Over the past few decades, many research studies conducted in the field of fibre reinforced polymer composites have focused on developing sustainable composites by replacing many of the conventional composite materials in various applications due to ecological issues related to climate change, the greenhouse effect and CO_2 emissions. Therefore, the development and use of sustainable composites not only deliver environmentally-friendly sustainable materials but

also provide composite materials with high-strength to weight ratio, biodegradability, lower energy requirements for processing and lower cost, compared to existing synthetic reinforcements such as glass and carbon fibres (See Figure 2.48) (Dhakal et al. 2007; Faruk et al. 2012; Goutianos et al. 2006; Saheb and Jog 1999). In the last few years, there has been a substantial increase in the use of natural fibres as reinforcement in composites, particularly in the automotive, marine, construction and aerospace industries. Some of the common natural bast fibres, which have been used in both thermoset and thermoplastic composites, are flax, jute, hemp, and kenaf. This is due to acceptable properties that include low density, low cost and renewability (Bledzki and Gassan 1999; Stevens and Müssig 2010).

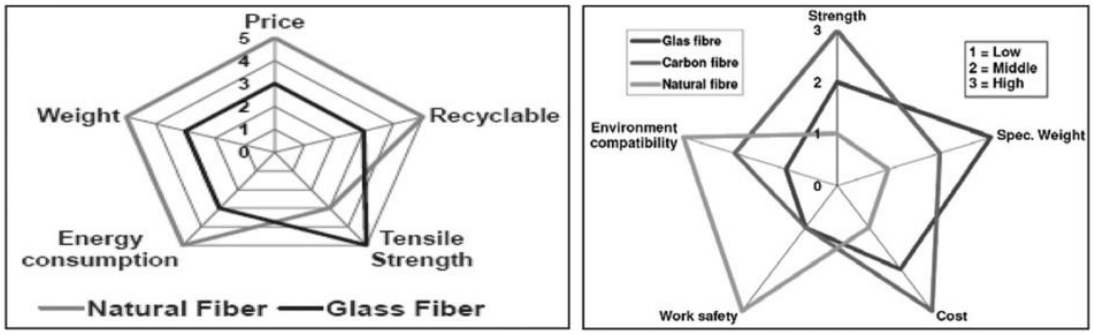


Figure 2.48 Comparison between natural fibre, glass fibre and carbon fibre (Faruk et al. 2014).

2.19.1 Automotive

Renewable materials of natural fibres are existed more in the markets that required low costs and high volume production with acceptable low performance. For example, automotive industry especially in the interior parts such as door panels, seat back, boot lining and parcel shelves, as shown in Figure 2.49 (Ashori 2008). Natural bast fibres have many advantages on their properties such as low density, high specific strength and low embodied energy, compared to synthetic fibres. Furthermore, automotive applications are forcing to shift the design from oil-derived polymers and synthesis fibres to natural materials focusing on the sustainability towards green products either biodegradable or recyclable (Alves et al. 2010). New environmental regulations besides sustainable concepts are requesting a crucial demand for new development materials that are environmentally friendly and independent of petroleum-based materials (Dittenber and Gangarao 2012). According to the United States (US) of Agriculture and Energy departments, they have set aims for using renewable materials derived from plant sources as a basic chemical into building blocks in 2020, increasing by 50% in 2050 (Amar K. Mohanty, Manjusri Misra 2005). In recent years, there has been resurgence for using bast fibres as reinforcement to composite materials with regard to replace glass fibres. In Europe and America, car manufacturers have already been used these fibres to achieve

Environmental Directives and in the US automotive companies are using bast fibres such as flax, jute, hemp and kenaf as reinforcement of thermosetting and thermoplastic polymers (Alves et al. 2010). For instance, natural fibre reinforced polypropylene has started in interior components such as dashboard and door-trim panels produced by Johnson Controls (Mohanty et al. 2002). Furthermore, composites are being used common form in the transportation. Some of the common parts used in automotive industry of natural fibres reinforcement are interior trim panels, boxes in family cars and storage systems in pickups, large panels on commercial buses and entire cabs for heavy trucks (Friedrich and Almajid 2013). For example, flax hybridised sisal reinforced polyurethane composites were used in door trim panels by Audi in 2000. In order to use natural fibres as an external application, Daimler Chrysler were improved their research and development in flax fibre reinforced polyester composites (Ashori 2008). It is expected that the energy consumption (gas) from vehicle about 75%, which is referred to several factors that connected with the weight of vehicles (Mohanty et al. 2002). Automotive companies are seeking more environmentally friendly materials with their products. Therefore, there is saving demand to produce lightweight vehicles in order to reduce cost effective and environmental problem. In addition, Natural fibres have an excellent acoustic and thermal insulation, and also, have better energy efficiency and vibration damping compared to glass fibres in their respective to composite structures (Miao and Finn 2008; P.K. Mallick 2007).

Figure 2.49 Interior parts of natural fibre reinforced composites. Source: Diamler,C-Class.

2.19.2 Building and Construction

Natural fibres are now more interested and noticed in structural and infrastructural applications in terms of offer its technical, economical and ecological benefits over synthetic reinforcement

fibres in polymer composites. They have been used to develop load-bearing components in composite industry as alternative materials for building and construction products such as roofing, frames, profiles, doors, pipes, tanks and multipurpose panels (See Figures 2.50 and 2.51) (Ticoalu, Aravinthan, and Cardona 2010). In automotive applications, natural fibres used with thermoplastic resins but most composites in infrastructural applications are reinforced with thermosetting resins. The challenge of NFRCs is still questionable because of high moisture absorption and their poor adhesion with the matrix. Over the past few years, natural fibres have undergone various treatment in order to make a suitable products in building and construction so that they can withstand environmental conditions (Singh and Gupta 2005).

One of the basic components used in building, bridges and other structures is the beam. Composite sandwich beam is used materials in top and bottom as skin layers and thick material between them as core which usually shows higher strength than core (Ticoalu et al. 2010). Dweib et al. (2004) studied those NFRCs for roof housing application and structural beam panels were manufactured using vacuum assisted resin transfer moulding (VARTM) method. The results showed that composite materials of natural fibres have good results for mechanical testing and with 20 to 25% by weight of fibres increases the flexural modulus compared to E-glass reinforced with the same resin and showed many advantages in both mechanically and physically. Another study (O'Donnell, Dweib, and Wool 2004) investigated the effect of mechanical properties of natural fibre reinforced soybean oil resin to be used in large-scale structure composites. They found that mechanical strength properties are suitable for some applications such as parts in furniture, housing construction materials and automotive applications as discussed in the previous section. Despite the recent noticeable interest in NFRCs for using in semi-structural applications, timidly few research studies overwhelmingly show the capability of natural fibre reinforced polymer composites over glass fibres reinforced composites for load-bearing applications (Shah, Schubel, and Clifford 2013).

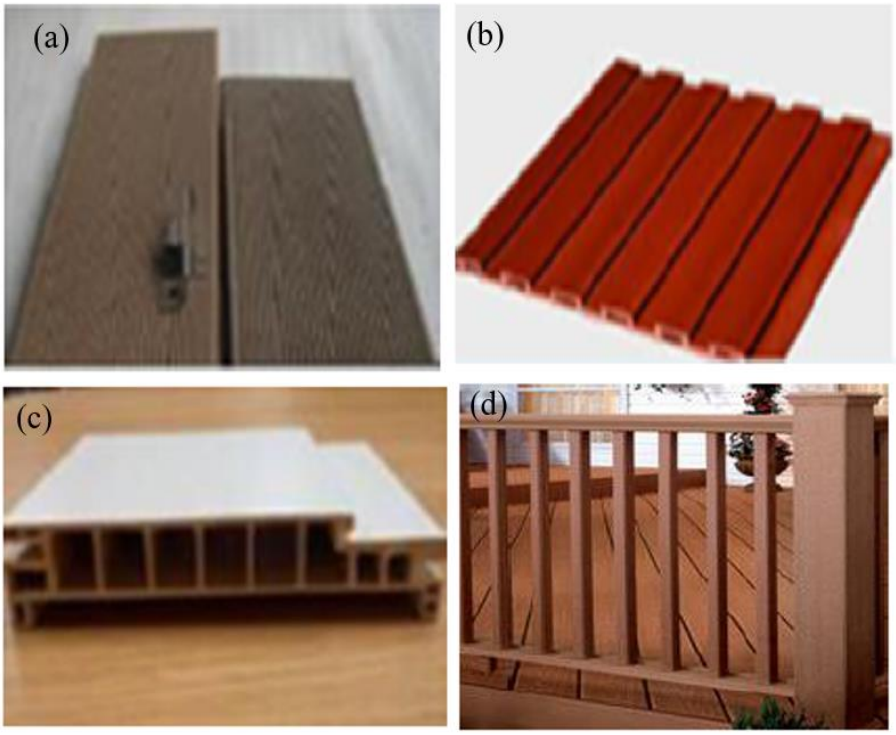


Figure 2.50 Construction products made from NFRCs; (a) decking, (b) panel, (c) window frame, (d) fencing (Renato Barboni 2015).

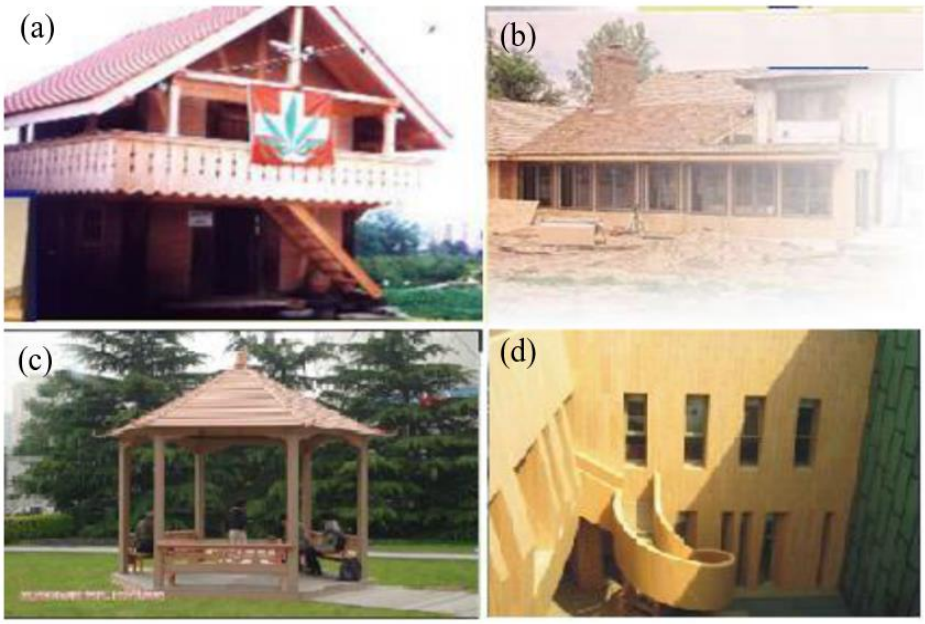


Figure 2.51 Building applications made from NFRCs; (a) traditional house, (b) roofing, (c) roof tiles, (d) exterior wall cladding (Renato Barboni 2015).

There is a strong potentially that natural bast fibre reinforced composites will more use in structural applications especially in automotive industries due to increasing demand in the

future for using sustainable materials such as biomaterials (fibres and polymers) and biocomposites (recyclable and biodegradable). However, there are some critical issues in terms of susceptible to absorb moisture and inadequate toughness as well as cost expensive if they are fully biodegradable. As the moisture resistance property of natural fibre is poor and due to lower durability, the applications of these fibres are limited to non-structural and interior applications only. However, these properties of natural fibres can be improved using innovative surface treatments, coating, additives, and resins. Nonetheless, there are many other challenges including manufacturing difficulties, fire resistance, fibre adhesion and variation in quality. For a structural application, the hybrid composites are a viable and acceptable alternative. Nevertheless, to explore the suitable applications for hybrid composite, more research is recommended. The hybrid composites such as synthetic-natural, synthetic-synthetic, and natural-natural can realise extensive application in the near future due to their excellent performance in high and low-velocity impact test and because of the requirement of the environment-friendly process, high structural performance, durability, and low-cost alternatives. In addition, the role of textile technology and design engineers will lead to sustainable development. The scientific literature is limited in this area and needs further investigation. These challenges provide the trend insights for future research and opening up a new area for materials scientists and technologists.

2.20 Research Gap

Natural fibre reinforced composites have many advantages but their use have been restricted in non-structural applications such as automotive interior components. One of the factors for this is due to not having enough test data on how these composites behave under different load bearing scenarios such as fracture toughness modes. Notwithstanding, natural fibre composites have been slowly extended to structural applications, as a result of problems encountered, include delamination and crack, towards manufacture of flaw-free products. Detailed knowledge of delamination and crack resistance of NFRCs are still not fully understood. There are many reported works on natural fibre composites as far as their mechanical (tensile, flexural and impact), thermal and environmental behaviours are concerned. However, there are very limited reported works relating to the investigation on fracture toughness behaviour of NFRCs.

In recent years, the uses of natural fibres as reinforcement in composites have increased significantly, particularly in the automotive, construction and packaging industries. Some of the common natural bast fibres, which have been used in both thermoset and thermoplastic

composites, are flax, jute, hemp, and kenaf because of their acceptable properties, such as high specific strength, low density and low cost. In addition, there are some key properties behind the growth of natural fibre composites, for example sustainability, biodegradability and environmental friendliness which increased their application when compared with synthetic fibres. Preferably, natural fibres are also used for acoustic and thermal insulators because of their good sound and heat energy resistance. Despite these benefits, as aforementioned, natural fibre composites are limited in non-structural applications so far. Investigating the fracture toughness behaviour of glass fibre and carbon fibre composites has been a mature area of study. However, understanding the effect of hybridisation and stitching on the fracture toughness of natural fibre composites is a new field of research and is a very important subject to be investigated to ascertain the capability of natural fibre composites. Apart from some very limited research work on the fracture toughness behaviour of natural fibre composites, the scientific literature is limited in this area and needs further investigation. This PhD study has provided some important information on how natural fibre composites behave under different modes of fracture toughness tests.

This PhD research study aims at is to investigating the interlaminar fracture toughness behaviour and use a novel technique to improve the delamination resistance of flax fibre reinforced vinyl ester composite materials for use in structural applications.

This PhD thesis intends to bridge the gap by:

1. Manufacturing flax and flax/basalt fibre reinforced vinyl ester hybrid and stitched composite laminates.

2. Studying the effect of hybridisation and stitching on Mode I and Mode II interlaminar fracture toughness of flax fibre and flax/basalt reinforced vinyl ester composites

3. Investigating the influence of water absorption behaviour and its effects on the fracture toughness of hybrid and stitched composites.

4. Analysing the damage mechanisms of fractured surface and delamination of the composite laminates.

Aiming to improve the performance especially covering fracture toughness behaviour, disseminate this information to automotive industry, academic and researchers who are involved in this field.

3 Chapter 3: Experimental Procedure

There are some key properties behind the growth of natural fibre composites, for example sustainability, biodegradability and environmental friendliness, which increased their application when compared to synthetic fibres. Despite these benefits, natural fibre reinforced composites are limited in non-structural applications so far and the scientific literature is also limited in this area and needs further study. Therefore, researchers have been encouraged to improve their outstanding applications, especially in structural components. Investigating the fracture toughness behaviour of natural fibre composites on different modes is a promising field of research. In this work our attention is focused on Mode I and Mode II tests.

In the present chapter, the first objective was to fabricate the composite laminates using approach of hybridisation and stitching to improve the toughness properties. The second objective was to examine the Mode I and Mode II interlaminar fracture toughness. The third objective was to investigate the water absorption behaviour in order to study the effect of moisture absorption on the fracture toughness. The final objective was to characterise the fracture morphology of the composites. The matrix and reinforcement fibres used in this study are presented in section 3.1. The fabrication process of the samples and cutting specimens are described in 3.2 and 3.3. The double cantilever beam (DCB) and three-point end notched flexure (3ENF) tests are presented in 3.5. Water absorption test are explained in sections 3.6. The failure mechanisms of the delamination toughness were examined using scanning electron microscopy (SEM) and x-ray computed micro-tomography (μCT) as described in section 3.7.

3.1 Materials

3.1.1 Matrix

The matrix material used in this study was based on commercially available vinyl ester, trade name: Scott-Bader Crystic® VE676-03, supplied by Scott-Bader. A thermosetting polymer, vinyl ester resins, are chemically similar to unsaturated polyesters and epoxy resins. It has great mechanical properties and better resistance to moisture and chemical attack than other polymer resins. Moreover, it offers excellent chemical resistance to acids, alkalis, hypochlorites, and other solvents. Vinyl esters have higher density in cross-linking sites which showing more heat resistant to polymer network. “Vinyl esters are unsaturated resins made from the reaction of unsaturated carboxylic acids (principally methacrylic acid) with an epoxy such as a bisphenol A epoxy resin” (S.T. Peters 2013). The typical structure of a vinyl ester resin is depicted in

Figure 3.1. Vinyl ester resin has low viscosity and widely used for marine composite fabrication by low cost manufacturing technique (Zhu et al. 2007). Typical physical and mechanical properties of vinyl ester resin are presented in Tables 3-1 and 3-2.

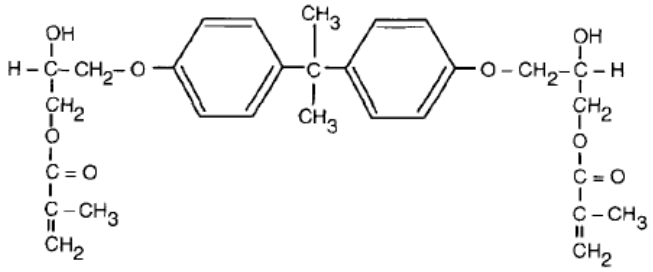


Figure 3.1 Vinyl ester chemical structure (S.T. Peters 2013).

Table 3-1 Physical properties of vinyl ester resin at liquid state (SCOTT BADER 2013).

Property	Liquid Resin	
Appearance	Yellow resin	
Viscosity at 25ºC Brookfield RVT	mPas	175 ± 25
Acid value	mgKOH/g	Max. 8.5
Volatile content	%	50 ± 2
Gardner colour	7 maximum	
Stability in the dark at 25ºC	months	6
Geltime at 25ºC using 2% Acc G, 2% Trigonox 239	minutes	29

Table 3-2 Mechanical properties of vinyl ester resin at fully cured state (SCOTT BADER 2013).

Property	Fully Cured* Resin	
Barcol hardness (Model GYZJ 934-1)	45	
Deflection temperature under load † (1.80 MPa)	ºC	98
Water absorption 7 days at 23 ºC	Mg	40
Tensile strength	MPa	75
Tensile modulus	GPa	3400
Elongation at break	%	4.0
Flexural strength	mg	120

* Curing Schedule - 24 hrs at 20°C, 3 hrs at 80°C.

3.1.2 Reinforcement Fibres

Woven flax and woven basalt fibres were used as the reinforcement (+/- 45 °) biaxial stitched non-crimp fabrics of 600 g/m^2 in weight, supplied by Net Composites Ltd and BASALTEX® respectively. Figure 3.2 shows woven flax and woven basalt mat fabrics. Chemical and structural composition of flax fibre and basalt fibre are presented in Table 3-3 and 3-4. Polytetrafluoroethylene (PTFE) layer of 20 μm thick was used to simulate a crack in the middle of reinforced panels. The physical and mechanical properties of flax and basalt fibres are presented Table 3-5.

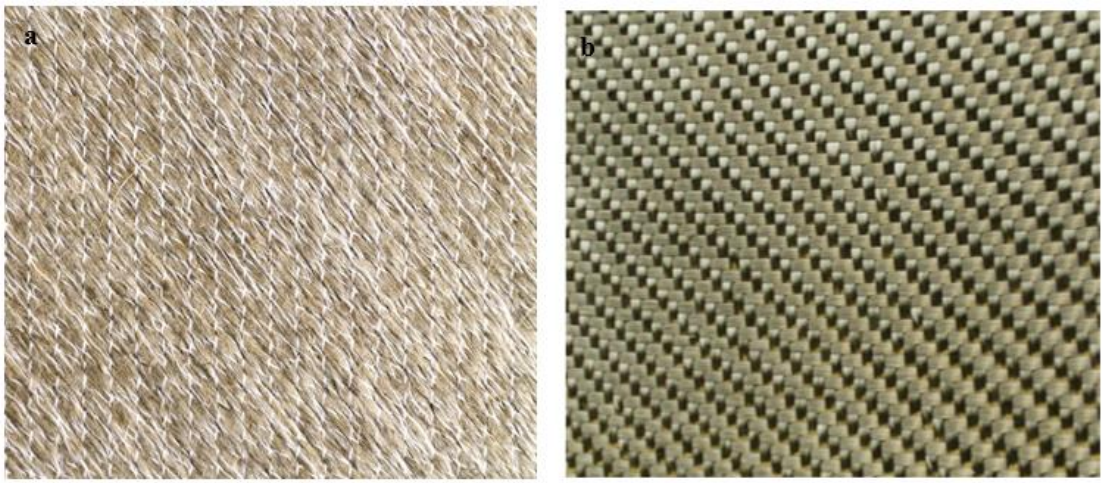


Figure 3.2 Reinforcement fibers a) Biotex flax ±45 biaxial fabric 600 g/m^2 b) Basalt multiaxial fabric BAS BI 600 g/m^2 (BASALTEX 2016; Composites Evolution 2012).

Table 3-3 Chemical and structural composition of flax fibre.

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Source
71	18.6 – 20.6	2.3	2.2	(Yan et al. 2014)
Cellulose crystallinity (%)	Cellulose content (wt.%)	Aspect ratio (l/d)	Micro-fibril angel (^{0})	Source
50-90	64-71	1750	5-10	(Placet et al. 2012)

Table 3-4 Chemical composition of basalt fibre (wt.%) (Wei, Cao, and Song 2010).

Composition	SiO_2	$Al2O_3$	CaO	MgO	K_2O	Na_2O	Fe_xO_y	TiO_2	B_2O_3
Basalt fibre	48.39	14.7	7.7	4.7	1.6	3.0	15.3	3.8	-

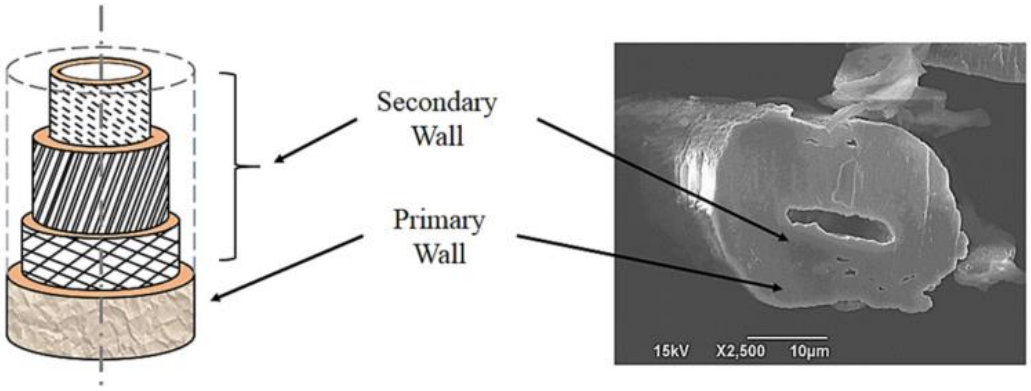


Figure 3.3 The structure of flax fibre cell (Amiri, Ulven, and Huo 2015).

Table 3-5 Comparative values of physical and mechanical properties of flax and basalt fibres.

Fibre type	Density (g/cm^3)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Specific modulus (GPa)	Source
Flax	1.5	30	345-1035	2.7-3.2	50	(Faruk et al. 2012; Saheb and Jog 1999)
Basalt	2.65	93-110	4150-4800	3.1	35-41	(Li and Xu 2009)
E-glass*	2.50	70	2000-3500	2.5	28	(Zhang et al. 2013)

* For comparison purpose.

3.2 Fabrication Methods of Composite Laminates

3.2.1 Vacuum Infusion Process

The composite laminates (250x250 mm^2, 5-6 mm thick) were fabricated by the vacuum infusion technique which used a vacuum pressure to drive resin into a laminate. Materials are laid dry into the mould and the vacuum is applied before resin is introduced. Once a complete vacuum is achieved, resin is literally sucked into the laminate through carefully placed tubing (Yuhazri and Sihombing 2008). By using vacuum infusion, it is possible to produce composites with high volume fraction of fibres and it enables a better strength-to-weight ratio with less

void content (Yan et al. 2014). The resin-infused laminates were made using a balanced layup, with the reinforcement of flax and basalt fibres as presented in Figure 3.4 and Table 3-6.

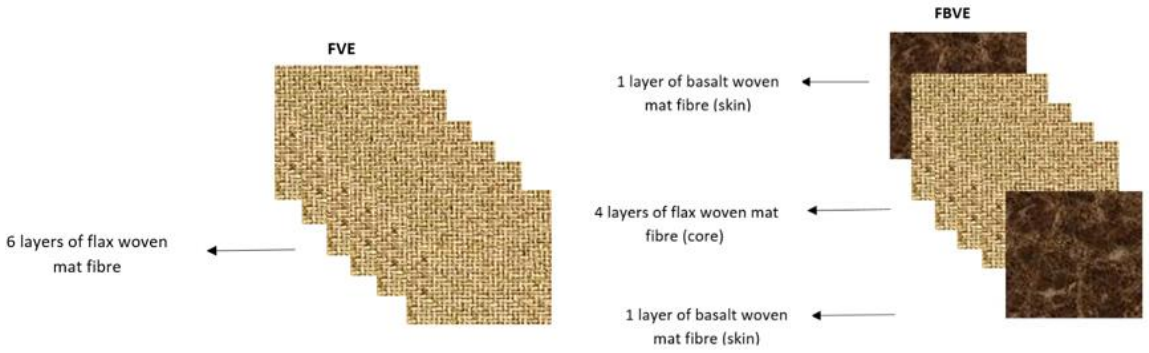


Figure 3.4 Schematic illustration of the stacking sequence of flax and flax/basalt hybrid laminates using a balanced layup.

Table 3-6 Reinforcement of composite laminates.

Reinforcement	No. of Layers / Thickness	Layup	Stitching Required?
None	6 mm	n/a	No
Flax	6 layers	Balanced	No
Flax + Basalt	4 x flax layers 2 x basalt layers	Balanced, basalt as outer layers	No
Flax + Basalt	4 x flax layers 2 x basalt layers	Balanced, basalt as outer layers	Yes

Firstly, the process started with the dry pack of layers which was then placed on top of a glass plate which had previously been treated with a release agent (Multishield) (See Figure 3.5). Secondly, the pack was covered with a layer of nylon peel ply release and a diffusion mesh was added to the top of the peel ply to help shorten the infusion time. In addition, a border of tacky-tape was then stuck in a rectangle around the prepared pack and resin inlet and also, outlet pipes placed on top of the tape and onto the edges of the layup (as clearly seen in Figure 3.6 a). The tape rectangle was then covered with a vacuum bag as shown in Figure 3.6 b, the inlet pipe capped off and a vacuum of -29” Hg applied. Once the resin had been mixed with accelerator and catalyst, the inlet pipe was submerged in a container of resin and the pipe was uncapped, allowing the resin to be infused into the layup. Finally, the infusion time was

approximately 10 minutes for the samples. Once set, the composite laminates were left to cure for 24 hours at ambient temperature followed by demoulding and post curing in an oven at 80°C for 3 hours.

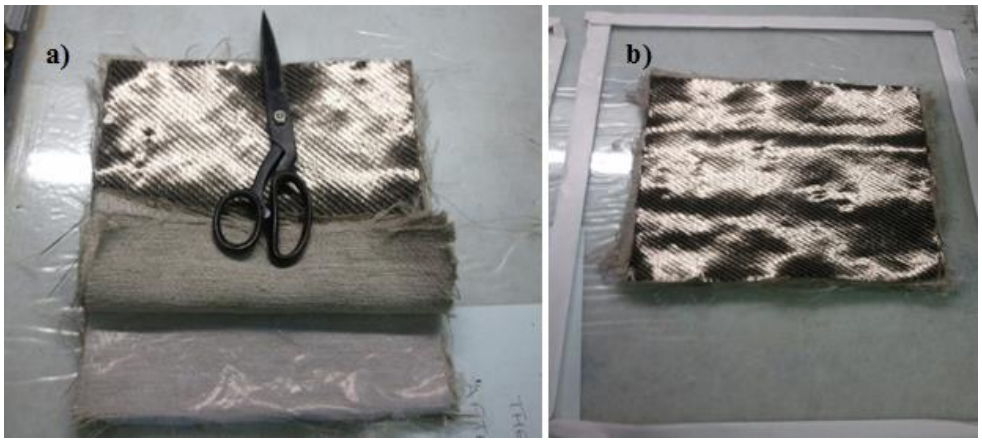


Figure 3.5 Woven Biaxial Fabrics: a) four layers of flax balanced, with one layer of PTFE μm in the middle; b) Six dry layers of flax on a glass plate.

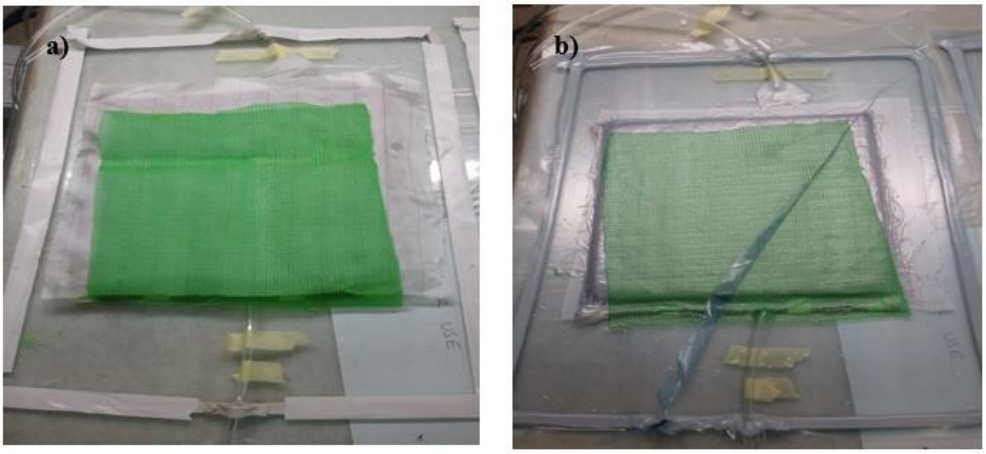


Figure 3.6 Vacuum infusion process: a) layer of nylon peel ply release in the top. b) Tape rectangle covered by vacuum bag.

Three types of composite laminates were prepared namely, flax fibre reinforced vinyl ester (FVE), flax fibre hybridised basalt reinforced vinyl ester unstitched (FBVEu) and flax fibre hybridised basalt reinforced vinyl ester stitched (FBVEs) as depicted in Figure 3.7. FBVEs panels were to have three straight lines at 2mm intervals using machine stitching by cotton thread across their widths, starting at a distance of approximately 5mm from the crack tip of the Teflon layer (see Figure 3.8). The latter was inserted along the central axis of each panel in order to simulate a starter crack of the delamination and reduce friction between the top and bottom of cantilever beam.

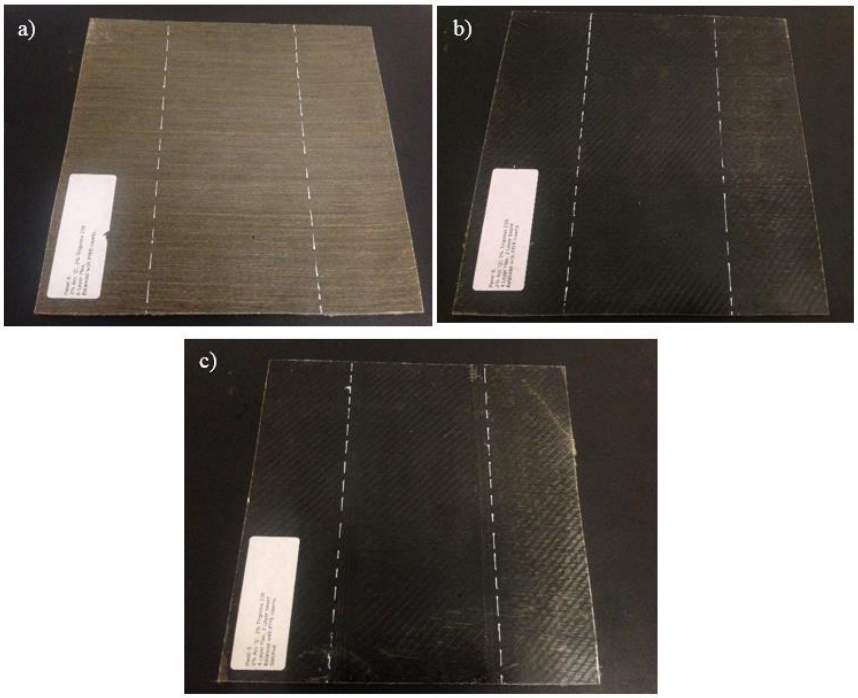


Figure 3.7 Final composite laminates a) FVE b) FBVEu c) FBVEs samples.

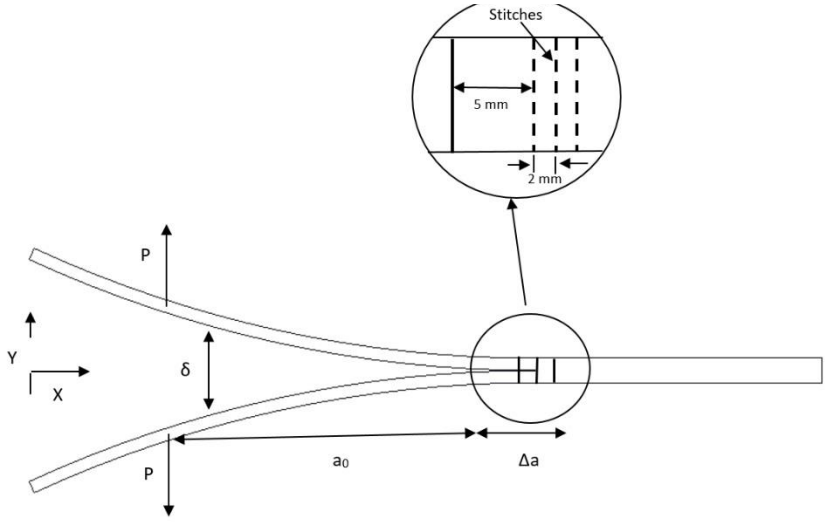


Figure 3.8 Schematic representation of the stitching pattern through-thickness reinforcement for DCB used in this study.

3.2.2 Vertical Cast Panels

The process of vertical cast was used to produce neat Vinyl Ester (neat VE) composite samples. Accelerator 'G' was added at 2% by weight along with Triganox 239 at 2% by weight as the catalyst. A PTFE layer of 20μm thick was inserted to simulate a crack in the reinforced panels but this thickness was found to be unstable for casting resin only panels due to problems

occurring trying to suspend the very thin layer of PTFE between the mould walls. Thus, it was necessary to substitute the layer of 20µm to 125µm for a glass/PTFE thickness. These panels were produced by suspending 125µm PTFE layers between two sheets of glass. Each glass sheet had been fitted with a silicone rubber seal on three sides. The silicone seals were each half the thickness of the desired panel width allowing the PTFE layer to be clamped in position between the two seals. This assembly was clamped securely using four 'G' clamps as shown in Figure 3.9. The resin\accelerator\catalyst mix was then poured into the gap between the rubber seals and the assembly and then gently agitated to remove any bubbles introduced during the pouring process. After curing for 24 hours at ambient temperature, the panels were de-moulded and post-cured in an oven for 3 hours at 80° C. The final composite of neat VE after post cured shown in Figure 3.10.

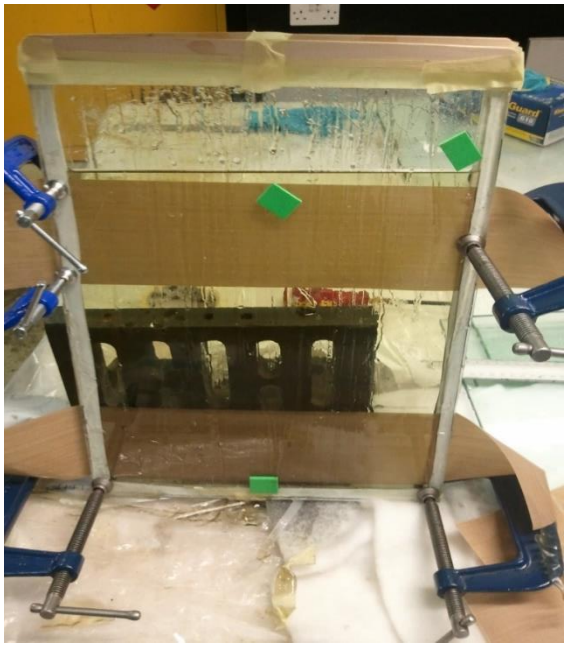


Figure 3.9 Vertical casting process of neat VE.

Figure 3.10 The panel of neat Vinyl ester (neat VE).

3.3 Specimen Preparation

All specimens of composite materials were cut according to the requirements of each test, based on geometry and dimension. The water jet method was used for cutting the specimens from the panels as clearly seen in Figure 3.11. After that, the specimens were dried at 50°C for 24 hours to remove any surface moisture absorbed. At least five identical specimens were created for each composite laminates in order to minimise any errors which might be happened during tests (See Figure 3.12). In mode I, each specimen has two piano hinges with 25 mm of steel bonded on both sides (top and bottom) of the specimen end with mixed epoxy and hardener resins glue of 50%. Before bonding the hinges, surfaces of both sides were cleaned with acetone and sanded with sand paper. When the surfaces were dry the hinges were bonded by using a C-clamp to attach them in place for 48 hours as shown in Figure 3.13.

Figure 3.11 The water jet cutting process of FVE panels.

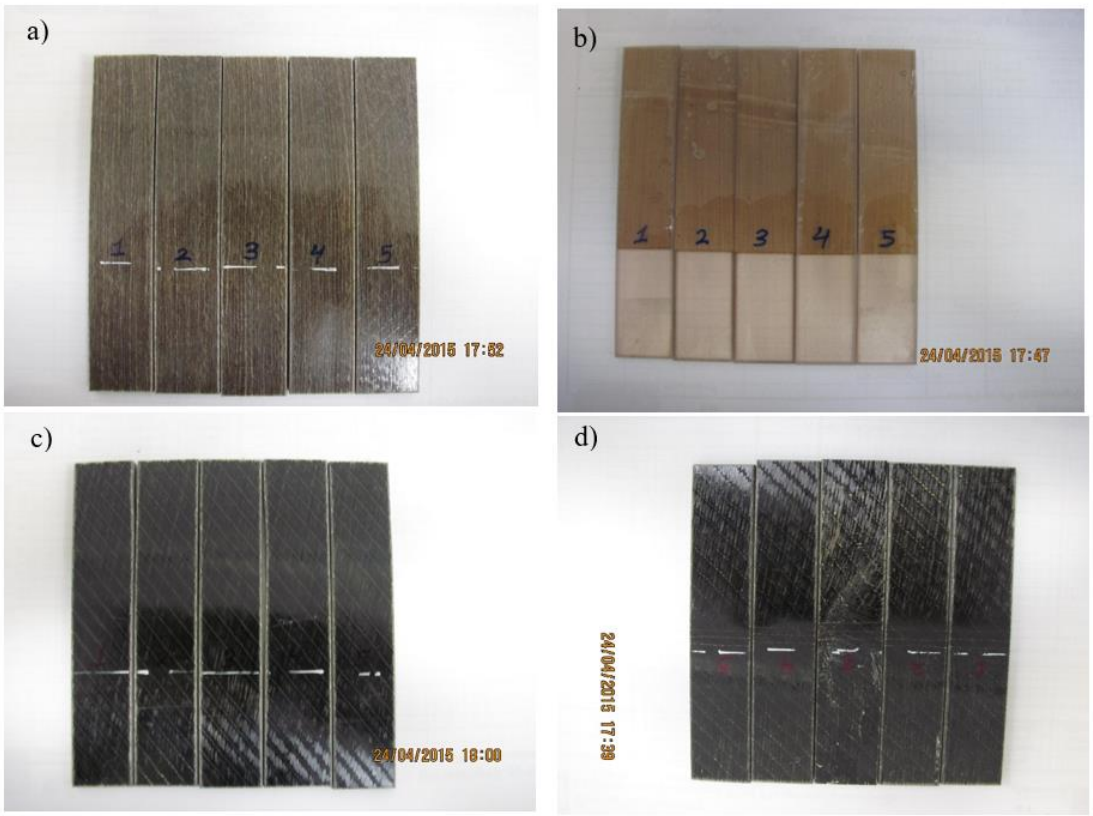


Figure 3.12 Five specimens after cutting of a) FVE. b) neat VE. c) FBVEu. d) FBVEs composites.

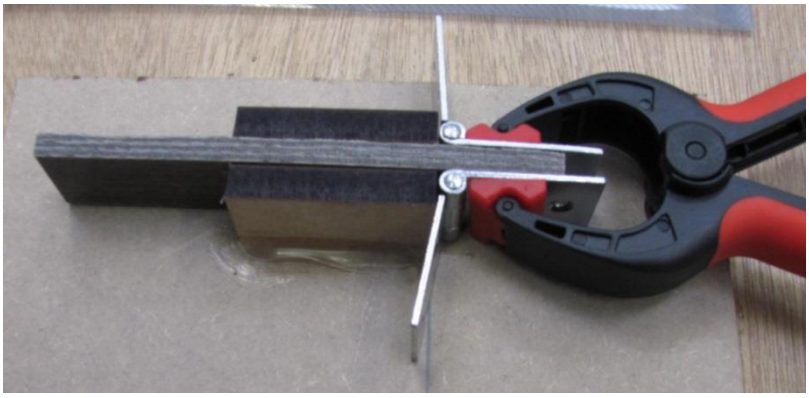


Figure 3.13 Using C-clamp to attach the hinges for DCB specimens.

3.4 Physical Properties

The physical properties of fibres and matrix have been presented in the previous Tables 3-1 and 3-5. The fibre volume fraction v_f and the matrix volume fraction v_m were calculated using equation 3.1.

$$v_f = \frac{\rho_c}{\rho_f} w_f \; ; v_m = \frac{\rho_c}{\rho_m} (1 - w_f) \qquad [3.1]$$

Where w and ρ are weight fraction and density, respectively while in that order of the subscripts *m, f and c* represents matrix, fibres and composite. The void contents v_v were determined using equation 3.2 according to ASTM D2734.

$$v_v = 1 - \rho_c \left\{\frac{w_f}{\rho_f} + \frac{w_m}{\rho_m}\right\} \quad [3.2]$$

3.5 Mechanical Testing

3.5.1 Mode I Interlaminar Fracture Toughness (DCB)

The fracture toughness tests were conducted on a Zwick/Roell Z250 universal testing machine fitted with 5kN capacity load cell as per ASTM D5528 (ASTM D5528 2007), as a specific standard for calculating G_{IC} in woven fabric composites does not yet exist (Hamer et al. 2014). Mode I interlaminar fracture toughness (G_{IC}) was measured using the double cantilever beam (DCB) method; specimen geometry and dimensions are shown in Figure 3.14. One side edge of each specimen was painted with white lacquer to assist optical crack length measurement. The crack initiation and growth was monitored using a digital camera with 3x magnifying lens. The load and displacement were recorded from the machine by testXpert software. The tests were carried out at a constant crosshead speed of 5mm/min in order to produce a stable crack growth. The test set up and the tool used to monitor the images during the test is shown in Figure 3.15. For each composite type, five specimens were tested to determine the average values of the initiation ($G_{IC\ init.}$) and propagation toughness ($G_{IC\ prop.}$).

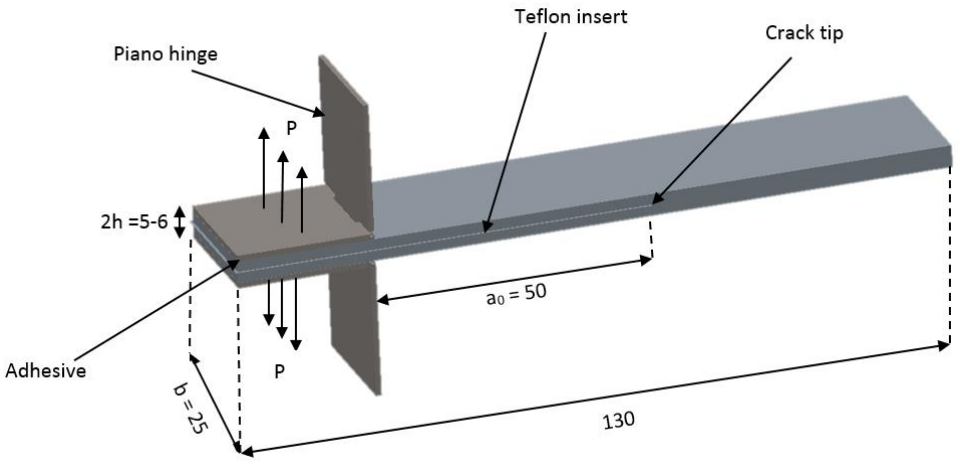


Figure 3.14 The geometry of the double cantilever beam (DCB) specimen for mode I (G_{IC}) testing (all dimensions in mm).

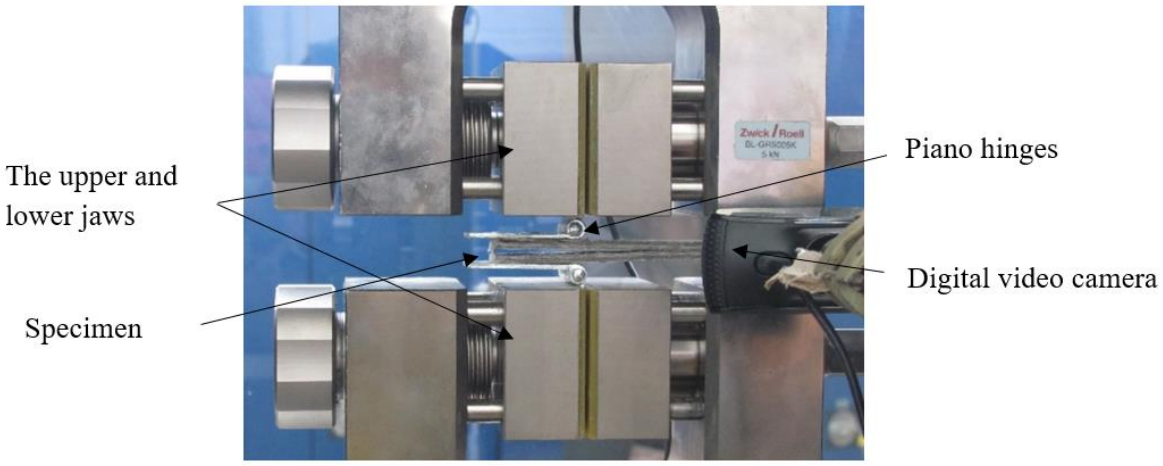


Figure 3.15 Mode I double cantilever beam (DCB) test set up.

In Mode I, the DCB test was used to obtain the critical energy release rate, G_{IC}, based on the theory of linear elastic fracture mechanics (LEFM) by using three data reduction methods (Prasad et al. 2011). In the modified beam theory (MBT), rotation may occur at the crack tip because the beam is not perfectly fixed. Thus, the strain energy release rate G_{IC} is calculated as follows:

$$G_{Ic} = \frac{3P\delta}{2b(a+|\Delta|)} \qquad [3.3]$$

where P is the applied load (N), δ the load point displacement (mm) and a the delamination length (mm), and b is the specimen width (mm). The crack length correction factor, Δ is obtained by plotting the cube root of compliance, $C^{1/3}$ as a function of delamination length a. (see Figure 3.16).

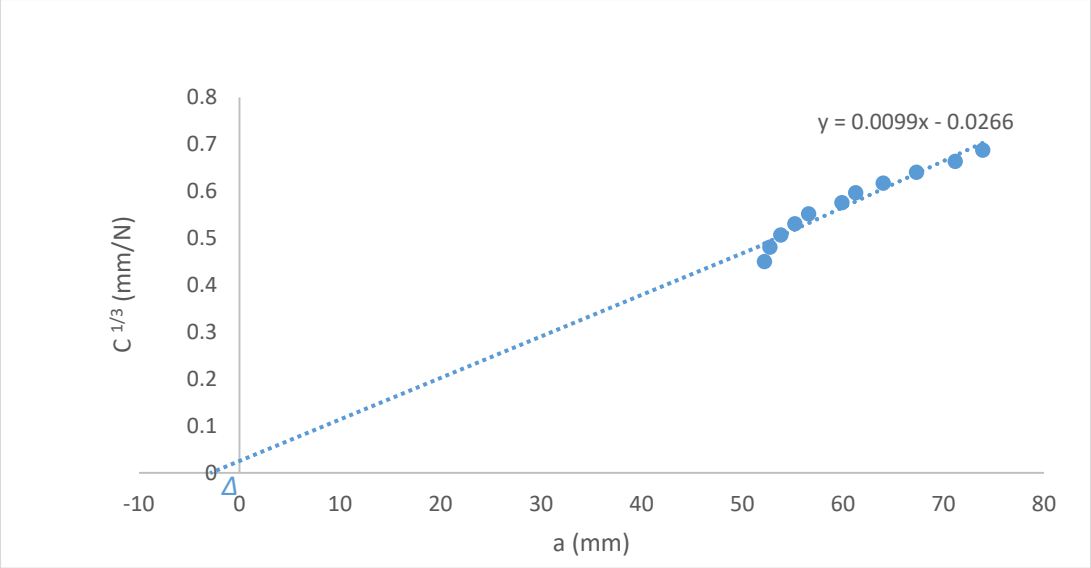


Figure 3.16 Representative $C^{1/3}$ versus crack length plots to determine crack offset Δ, for MBT method.

The compliance, *C* is the ratio of the load point displacement to the applied load (δ /*P*). In addition, the compliance calibration (CC) was the second method for DCB to measure the corrected energy release rate G_{IC} as shown:

$$G_{Ic} = \frac{nP\delta}{2ba} \qquad [3.4]$$

where *a* is the delamination length and *n* is the linear slope of least-square fit of log (*C*) versus log (*a*) as shown in Figure 3.17.

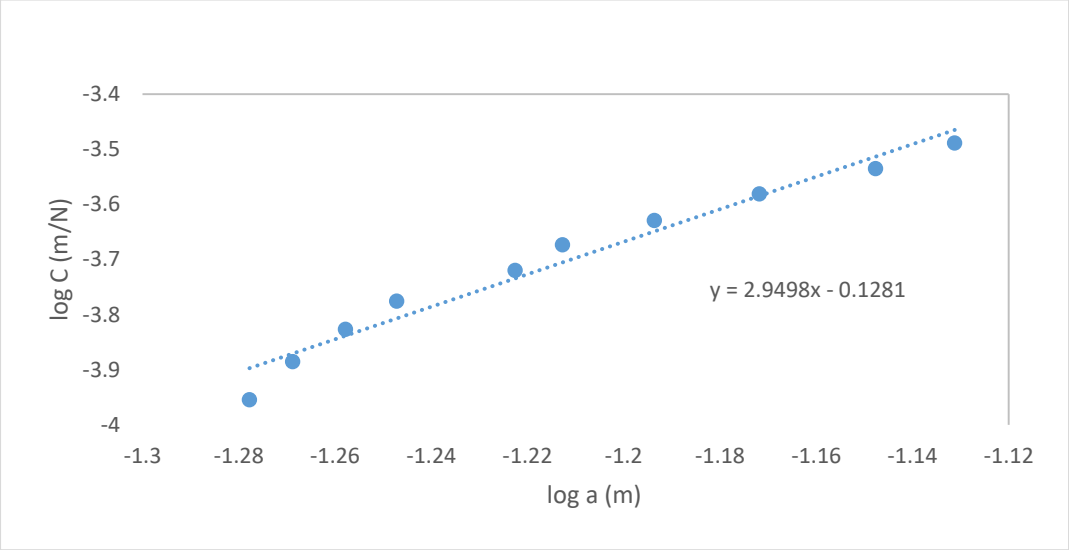


Figure 3.17 Representative log C versus log a plots to obtain the slope n, for CC method.

With the modified compliance calibration (MCC) method, the normalised value of the delamination length is used which is equal to *a*/*h*, where *h* is the thickness of the beam. The

graph of the delamination length normalised as a function of the cube root of compliance, $C^{1/3}$, is plotted using visually observed delamination of the initiation values and all the propagation values. The slope of this line is *n*. The interlaminar fracture toughness for the MCC is calculated using the equation below:

$$G_{Ic} = \frac{3P^2C^{2/3}}{2nbh} \qquad [3.5]$$

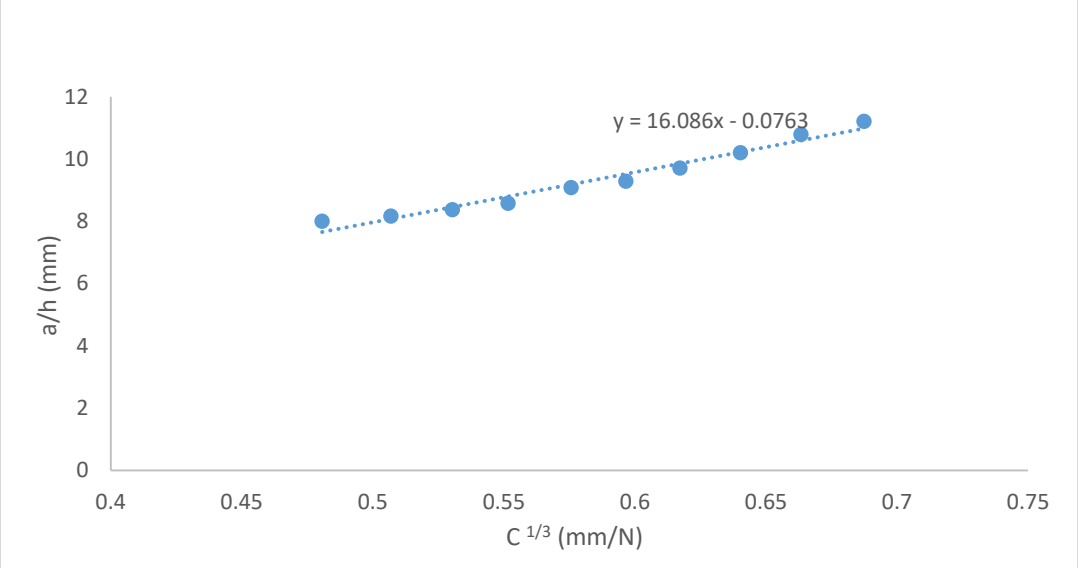


Figure 3.18 Representative a/h versus $C^{1/3}$ plots to find the slope, n, for MCC method.

3.5.2 Mode II Interlaminar Fracture Toughness (ENF)

The Mode II Interlaminar fracture toughness tests were conducted on a Zwick/Roell Z250 universal testing machine to determine the critical energy release rate (G_{IIC}) under in-plane shear deformation using three-point-end-notched flexure (3ENF) test based on the ESIS protocol (Davies P 1993). Specimens for 3ENF tests, of 25mm in width (b), 5-6mm in thickness (2h) and 130mm in length (L). The delamination length of 55mm from the start edge until the crack tip using a Teflon film and the spans were 80mm, as shown in Figure 3.19. The loading was carried out at a constant crosshead displacement rate of 2mm/min. Because of the difficulties to define the exact point of the crack initiation in Mode II tests, the non-linearity (NL) method was used to determine the crack onset. During the experiment of 3ENF tests, there is no any clear mouth opening of crack propagation. Thus, the initiation toughness ($G_{IIC\ init.}$) is more relevant than the propagation ($G_{IIC\ prop.}$). For each composite laminates, five specimens were tested to find the fracture toughness (initiation and propagation) except VE neat composites just four specimens.

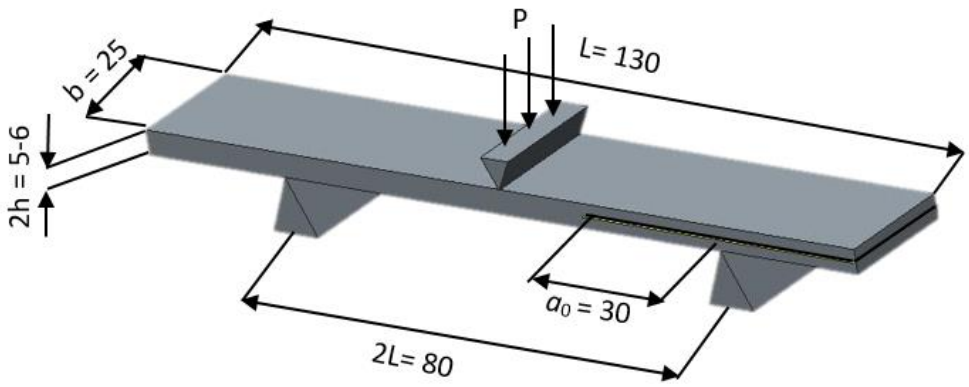


Figure 3.19 The schematic illustration of three-point-end-notched flexure (3ENF) specimen for mode II testing (all dimensions in mm).

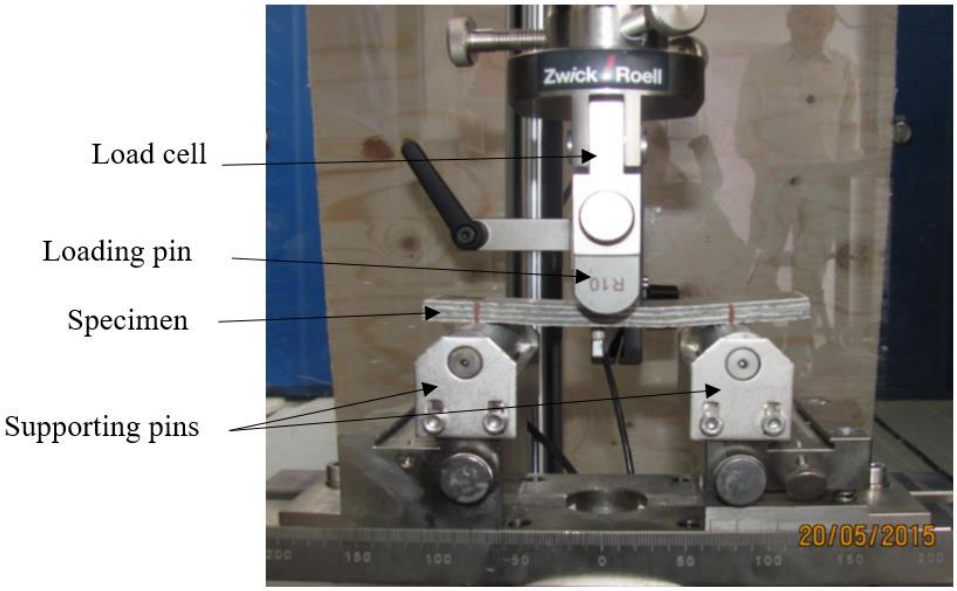


Figure 3.20 Mode II three-point-end-notched flexure (3ENF) test set up.

In Mode II, the 3ENF test was used to obtain the critical energy release rate, G_{IIC}, based on the theory of linear elastic fracture mechanics (LEFM) by using two data reduction methods. In order to calculate the load-point compliance, the equation of G_{IIC} can be found by classical simple beam theory (SBT) (Hadavinia and Ghasemnejad 2009; Russell, A.J. and Street 1982).

$$C = \frac{\delta}{P} \qquad [3.6]$$

$$C = \frac{2l^3+3a^3}{8E_1bh^3} \qquad [3.7]$$

The compliance equation is given by

$$G = \frac{P^2}{2b}\frac{dC}{da} \quad [3.8]$$

The interlaminar fracture toughness can be obtained from [3.6 to 3.8]:

$$G_{IIc} = \frac{9P\delta\, a^2}{2b(3a^3+2L^3)} \quad [3.9]$$

P: maximum load for stable crack propagation

δ: loading point displacement

a: crack length measured from the outer pin

L: half span of 3ENF specimen

b: beam width

In the Corrected Calibration Method (CCM) compliance is relies on the least square regression (D.R. Moore, J.G. Williams 2001; Hadavinia and Ghasemnejad 2009) as follows:

$$CN_1 = A + ma^3 \quad [3.10]$$

Where N_1 is a large displacement correction factor, A and m are data fitting constants. Hence,G_{IIc}, becomes

$$G_{IIc} = \frac{3mP^2a^2}{2b}\frac{F'}{N_1} \quad [3.11]$$

Where F' is an additional large displacements correction factor which was found negligible in 3ENF tests (D.R. Moore, J.G. Williams 2001; Hadavinia and Ghasemnejad 2009).

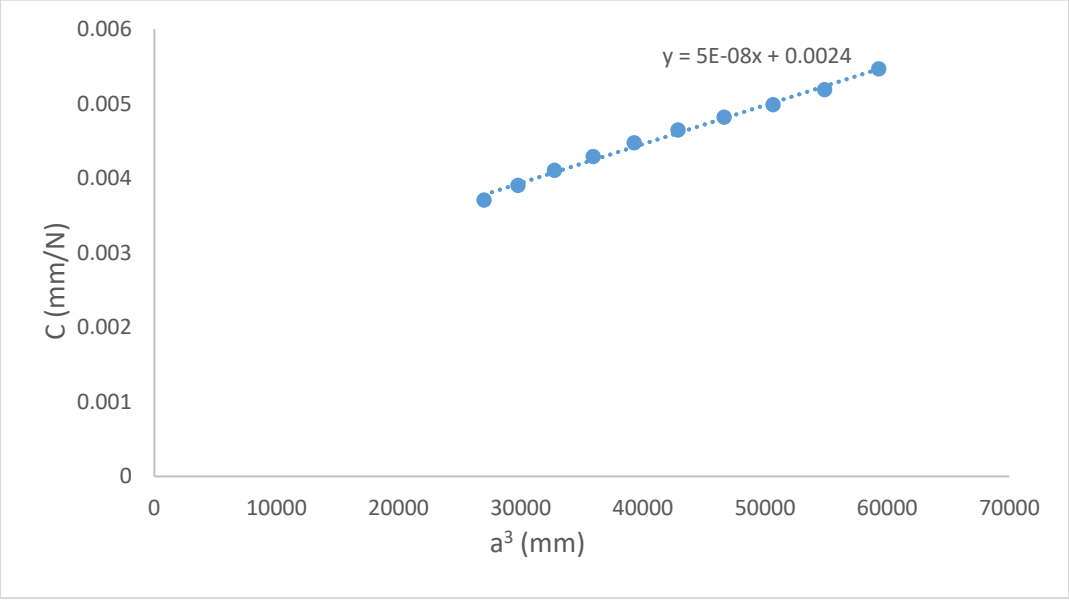


Figure 3.21 Representative C versus a^3 plots to find the slope, m, for CMM method.

3.6 Environmental Testing

3.6.1 Water Absorption Behaviour

This experiment test to assess the water uptake behaviour of natural fibre reinforced composites. The effect of water absorption on Mode I and Mode II interlaminar fracture toughness of FVE, FBVEu, FBVEs and neat VE were investigated in accordance with BS EN ISO: 1999 to calculate the moisture uptake percentage and the diffusion coefficient of different composites. Five specimens of each sample type were placed in a desiccator for 48 hours and then weighed to the nearest 0.1 mg. This process was repeated until a constant mass was reached. The specimens were immersed in a container of distilled water at room temperature of 23±1 °C for different time durations. After 24 hours from immersion, the specimens were taken out from the container of distilled water. Then the surface was dried with absorbent paper, re-measured and then put it back into the container immediately. The immersion time was continued for 42 days to ensure that it was enough to reach the equilibrium moisture content. The specimens were weighed at intervals of 24 hours up to 1008 hours exposure. Figure 3.22 shows process of water absorption test.

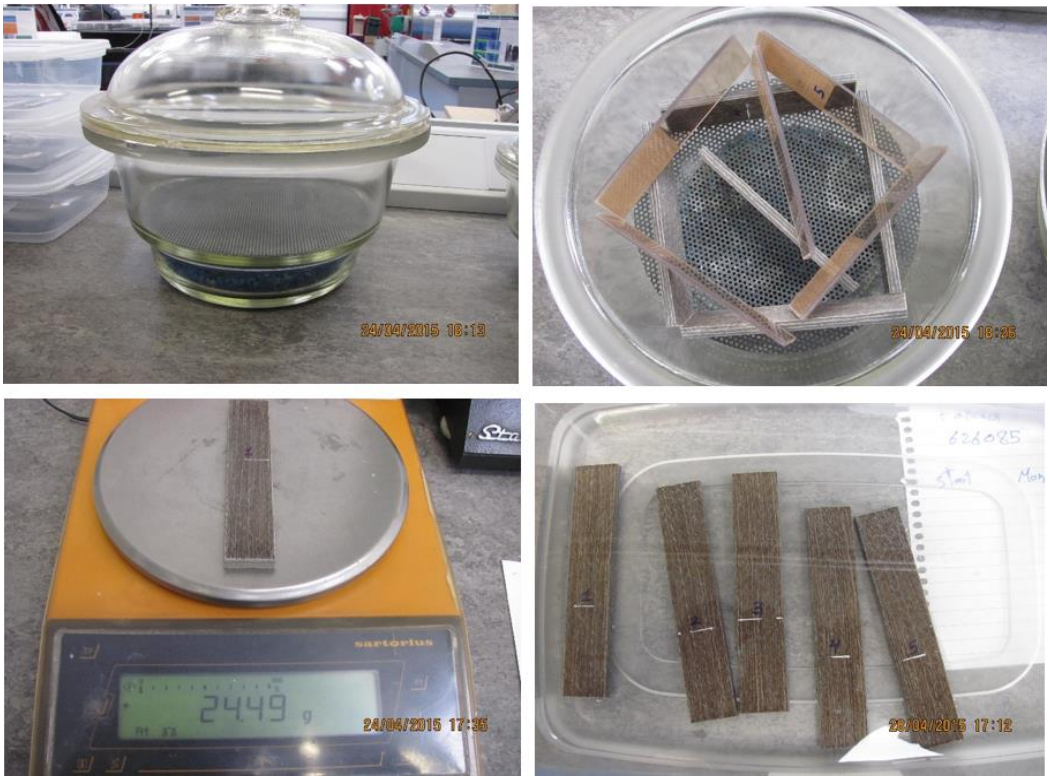


Figure 3.22 Process of water absorption test showing desiccator and weighing stages.

Water absorption percentage was calculated according to the following formula:

$$M_{(\%)} = \frac{M_t - M_0}{M_0} \times 100 \quad [3.12]$$

Where $M_{(\%)}$, is the moisture uptake in percentage; M_t is the weight of the water immersed specimens at a given time; M_0 is the initial weight of the sample at dry condition.

The diffusion coefficient (D) was calculated using the following equation:

$$D = \frac{d^2}{\pi^2 \times t_{70}} \quad [3.13]$$

where d is sample thickness (mm) and t_{70} is time taken to reach 70% of saturation (s).

The diffusion coefficient (D) is defined as the slope of the normalised mass uptake against square root of time $\sqrt{t}$ and has the form:

$$D = \pi \left(\frac{kh}{4M_m} \right)^2 \quad [3.14]$$

where, k is the initial slope of a plot of M(t) versus $t^{1/2}$, M_m is the maximum weight gain and h is the thickness of the composite (Crank 1975; Espert, Vilaplana, and Karlsson 2004).

3.7 Morphological Characterisation

3.7.1 Scanning Electron Microscopy (SEM)

The micrographs of the delamination provide important information on how the specimens fail in relation to fibre-matrix adhesion and resulting failure mechanisms. The fractured surfaces of the dry and wet samples after the fracture toughness tests were examined in order to study the effect of moisture absorption in delamination behaviour of the composite specimens using a Scanning Electron Microscopy (SEM) JEOL JSM 6100 at room temperature, as shown in Figure 3.23 (a). After adhering to SEM stubs, a thin layer of gold/palladium is applied to the specimens prior to SEM examination, as revealed in Figure 3.23 (b).

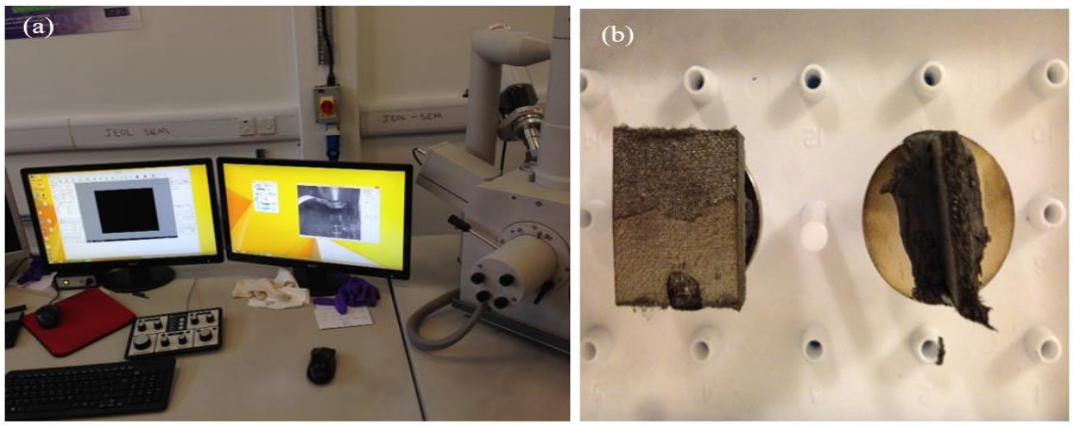


Figure 3.23 (a) image of SEM JEOL JSM 6100. (b) Specimens on the stubs with a thin layer of gold/palladium.

3.7.2 X-ray Computed Micro-Tomography (µCT)

The nature of the damage evolution in a composite structure is a complex phenomenon that includes delamination, matrix cracking, fibre pull-out and breakage. To effectively analyse these defects, high quality instruments are required (Růžek, Lohonka, and Jironč 2006; Schilling et al. 2005). X-ray computed micro-tomography (µCT) measurements were performed using a Nikon (Xtec) XT H 225 to obtain fracture damage characterisation through the thickness of the laminates. µCT methods were used to reconstruct the three-dimensional structure of the samples from a large number of X-ray projection images. VGStudio MAX was used to extract images and the X-ray source powered at 110 kV – 110 uA.

Figure 3.24 image of µCT machine of Nikon (Xtec) XT H 225.

4 Chapter 4: Results and Discussion of Mode I (DCB)

One of the key damage mechanisms in laminates is the initiation and propagation of a failure or a crack between individual layers; this is known as delamination and it must be considered in the design of a laminated structure. Delamination can be caused by imperfections during the manufacturing process or due to static and dynamic loads. Chapter 4 and 5 will be analysed and discussed in details the important parameters that affect the delamination of laminated structures. The value of strain energy release rate G_C, and the resistance curve (R-curve) assessed by experimental measurements on Mode I and Mode II tests. In addition, morphology study on the failure mechanisms of the fractured surfaces under dry and wet conditions.

In this chapter, the experimental results obtained from Mode I (DCB) tests are divided into five parts. The first part evaluates the sorption behaviour and the diffusion coefficient of flax and basalt fibres hybrid composites along with stitched composite specimens. The second part study the effect of hybridisation and stitching on the load and displacement curves under two different conditions. The third and fourth parts investigate the influence of water absorption behaviour and its effects on the Mode I interlaminar fracture toughness of hybrid and stitched composites. In the last part, the fracture damage mechanisms at the surface and delamination of these composite specimens are examined using SEM and micro CT scan.

4.1 Effect of Moisture Absorption on Mode I Interlaminar Fracture Toughness

4.1.1 Sorption Behaviour

Figure 4.1 shows the moisture absorption curves of three different composites (FVE, FBVEu and FBVEs), where each data point represents the mean value of each specimen type. The percentage of weight gain as a function of square root of time immersed in distilled water at room temperature of 23±1 °C for 1008 hrs (42 days) as shown in Figure 4.1 exhibit the results that for all the composite specimens, the moisture uptake at the beginning is linear and rapidly increases then slows down for a prolonged time until saturation reaches a plateau around 900 hrs (5 weeks). The moisture uptake results show Fickian behaviour at the room temperature.

The maximum weight gain of FVE, FBVEs and FBVEu composite specimens were 5.38%, 3.70% and 3.57%, respectively. Both types of FBVEu and FBVEs samples showed similar water absorption behaviours due to same balanced layup technique used, except for the small amount of stitched fibre. It is noted that stitching of natural fibres through-thickness

reinforcement would cause an increase of a small percentage of water absorption which might affect the stitching performance and mechanical properties. The saturation moisture uptake of FVE composites without hybridisation were much more than FBVEu composites by approximately 50%. This indicates that flax fibre absorbed moisture quickly which caused swelling of the fibre due to high cellulose of a hydrophilic nature (Bismarck et al. 2002). As a result, fibre swelling can cause micro-cracking in the brittle thermosetting polymer matrix composites. It is well established that the mechanical properties of water immersed natural fibre reinforced composites are reduced with increasing ageing time due to weak fibre-matrix interface created by the water ingress process. This can further promote the swelling of fibres as well as plasticisation of matrices which in turn results in the reduction of strength and stiffness for water immersed specimens compared to dry specimens. Moreover, moisture penetration occurred into the composite interface because of the diffusion of water molecules inside the micro gaps between polymer chains (Dhakal et al. 2007). For basalt hybridisation of FBVEu composites, the basalt fibre has helped to prevent water penetrating into the fibre-matrix interface as it has better water repellence behaviour compare to FVE specimens (Fiore, Scalici, Calabrese, et al. 2016).

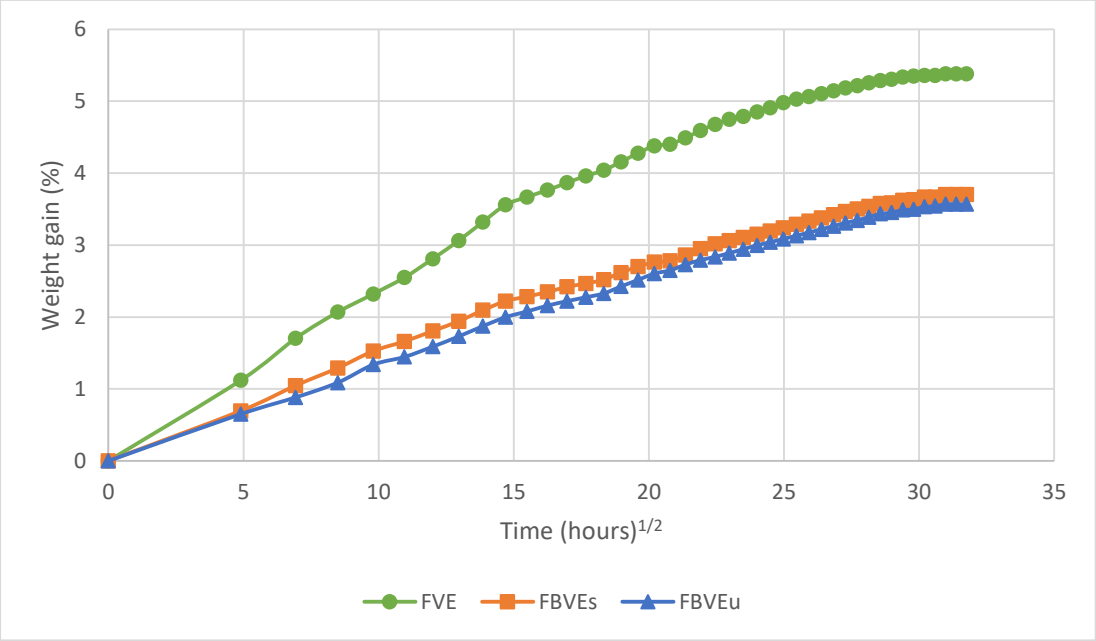


Figure 4.1 Water absorption as a function of time for DCB specimens of FVE, FBVEu and FBVEs composite laminates exposed to distilled water at room temperature.

The diffusion coefficient is a kinetic parameter which describes the capability of solvent molecules to move through the polymer segments. Table 4-1 illustrates the diffusion coefficients of FVE, FBVEs and FBVEu composites immersed in distilled water. It is observed

that the maximum moisture content and the diffusion coefficient values decrease with hybridised FBVE composites compared to non-hybridisation composites of FVE by 50% and 44%, respectively. This is attributed to the external basalt layers in FBVE composite specimens which protect the internal layers from degradation during ageing environmental exposure. On the other hand, FVE composites shrink, expand and debond between the fibre and matrix which creates voids acting as water reservoirs and thus raising the saturation level. Similar observations have been recently reported for flax (10 layers) and flax/basalt (6 flax layers in the middle, 4 basalt layers as external skins, 2 each side) laminates (Fiore, Scalici, Badagliacco, et al. 2016). Their results highlighted that the percentage of water uptake for flax fibre composite is higher than flax/basalt composite, and both reached saturation level after 4 weeks of ageing as similarly reported (Fiore, Scalici, Calabrese, et al. 2016).

Table 4-1 Moisture uptake of FVE, FBVEu and FBVEs composite laminates immersed in distilled water at room temperature.

Type of sample	Saturation moisture uptake M_m (%)	Initial slope of plot (*k*) *M(t)* versus $t^{1/2}$	Diffusion coefficient, D, $x10^{-3}(m^2/s)$
FVE	5.38	0.23	1.50776E-06
FBVEs	3.70	0.14	1.04705E-06
FBVEu	3.57	0.13	1.04705E-06

4.1.2 Load and Displacement Curve

Crosshead-load and displacement curves $(P-\delta)$ for both dry and water-aged samples of FVE, FBVEu and FBVEs composite specimens were obtained from the DCB test. The plotted curves for different specimens can be classified into three stages as shown in Figure 4.2. Firstly, the linearity of the load to the displacement of all samples occurred when the load was 128 N. For FVE and FBVEu specimens linearity stopped at load 175 N and 141 N respectively, after recorded displacement of 2 mm showing much resistance to deformation before the initiation of crack. In this elastic deformation stage (I), there is no visual damage or any crack initiation as depicted in Figure 4.3 (I). Secondly, the curves showed an increased nonlinear behaviour in load with increased displacement. The crack initiation for FVE, FBVEu and FBVEs dry composites were visually observed at load 211.97 N, 187.24 N and 171.37 N respectively. When the crack first visibly initiated from the white lacquer of the crack tip zone, the load and displacement were recorded after crack initiation, as shown in Figure 4.3 (II). The load required to initiate crack is lower for the water immersed specimens compared to their dry counterparts.

For example, the load required to initiate crack of FVE wet specimens was 30% lower than that of dry FVE specimens. For flax basalt hybrid specimens, the load required for water immersed specimens was 15% lower than that of dry specimens. The lower load for crack initiation for wet specimens is attributed to weak fibre- matrix interface due to moisture ingress (Dhakal et al. 2007). It is worth noting that the load required to initiate crack for flax basalt hybrid specimens was much higher than that of flax alone without basalt hybrid specimens. This improvement is attributed to higher stiffness and better dimensional stability at wet conditions of basalt fibre as well as their water repellence behaviour. It can be seen that aged samples show less resistance to crack initiation that unaged samples. Thirdly, a maximum load plateau occurs before complete failure and the crack propagates as shown ductile behaviour materials. All sample types exhibited that a stable crack propagation occurred with constant crosshead rate except stitched composites.

It was observed that extensive fibre bridging occurred during the crack propagation with a slight deviation in the path of the crack, as clearly illustrated in Figure 4.3 (III). This implies that imitations of these cracks created load reduction and then lead to delamination failure and fibre breakage. In the case of stitched, both dry and wet composites have the lowest displacement. The crack propagation is unstable beyond the peak load. This is because the existence of stitch threads create voids when needle inserts the through-thickness reinforcement, and then decreases the stiffness of the composite due to damage caused to woven fibres (Velmurugan and Solaimurugan 2007).

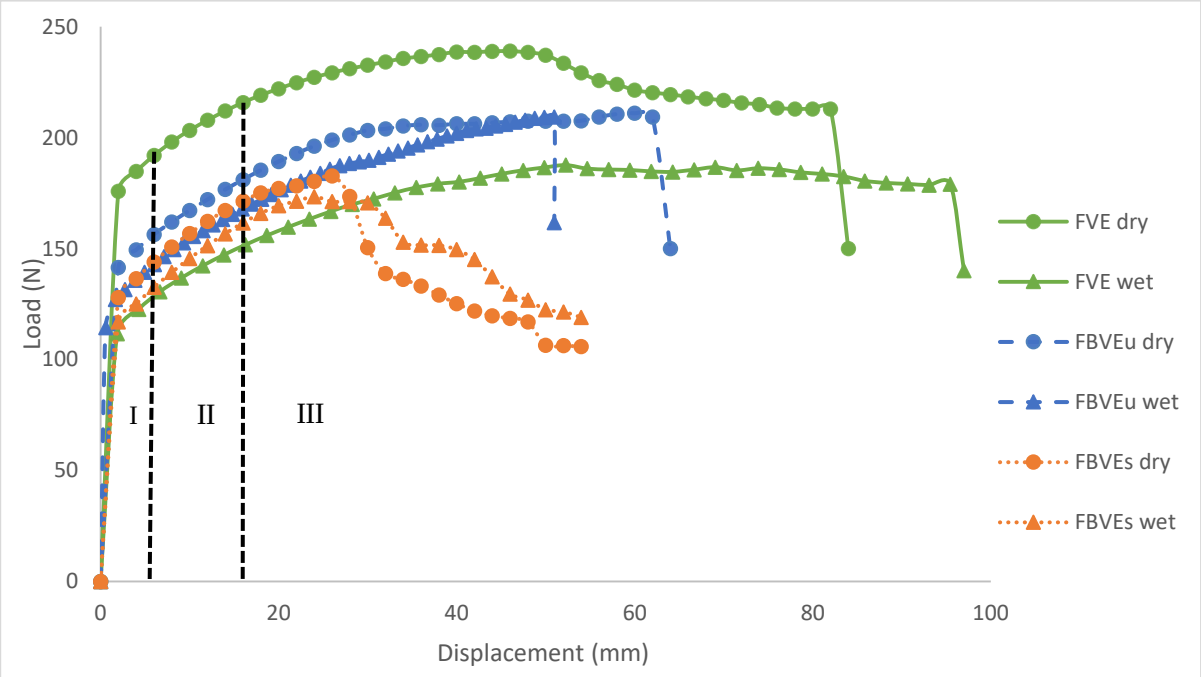


Figure 4.2 Load vs. displacement curves of Mode I dry and wet samples for FVE, FBVEu and FBVEs specimens.

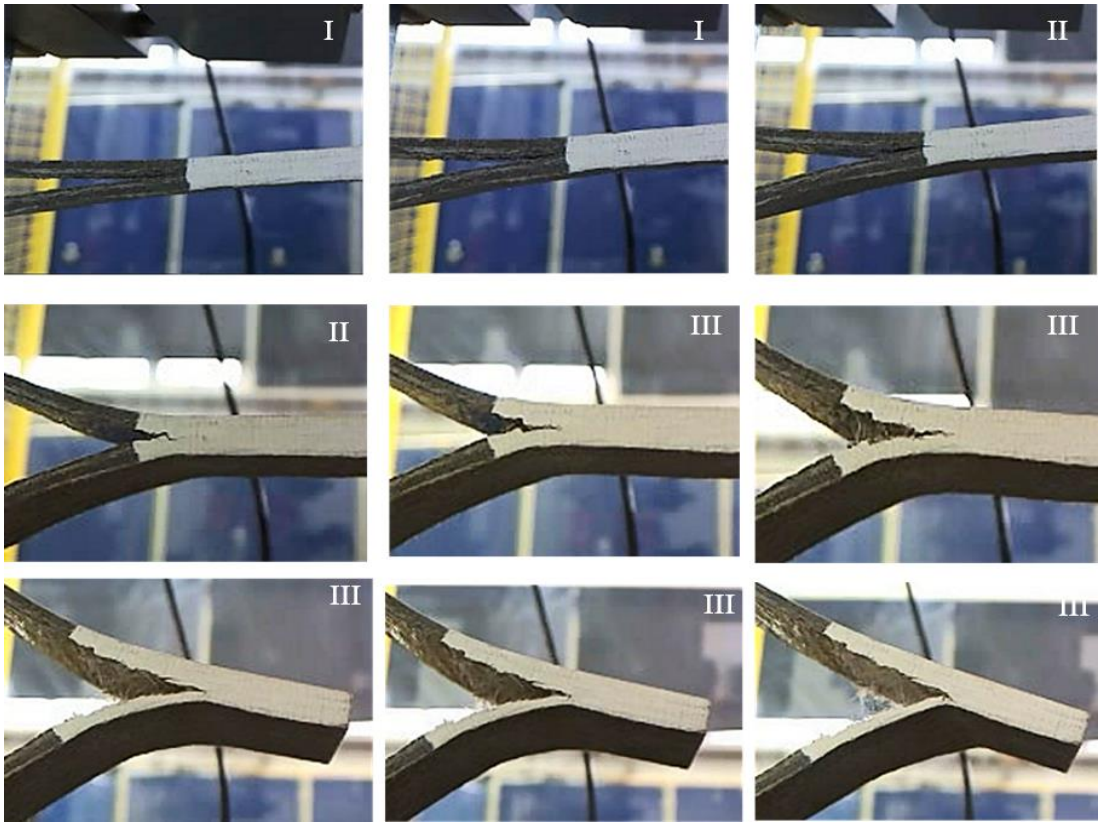


Figure 4.3 Series stages of FVE dry composites at mid-plane interface of DCB test a) Elastic deformation I, b) Crack initiation II, c) Crack propagation III.

4.1.3 Delamination Crack Growth Resistance Curve

The experimental resistance curves (R-curve) which presents the relationship between the Mode I strain energy release rate (G_{IC}) and the delamination length (a), were obtained to determine the initiation and propagation of a crack length in both dry and wet specimens. Referring to the results of other research works carried out on Mode I (DCB) tests, three different data reduction methods of MBT, CC and MCC were employed based on the standard to determine the interlaminar fracture toughness. Each of the samples exhibited similar properties using different methods where this validates the reliability of the data obtained from the experimental results in this study. Figures 4.4 to 4.6 show the crack growth resistance curves for three groups of samples: FVE, FBVEu and FBVEs, respectively.

Considering the FVE samples as shown in Figure 4.4, an increase of G_{IC} can be seen in the crack zone between 52 mm to 62 mm and then it changes to less steep with steady-state between 62 mm to 74 mm. All three methods are very close to each other and some points for CC and MCC coincide. The crack length grew up to 24 mm and 20 mm of FVE dry and wet

respectively, with reasonable constant speed in stable state. In wet conditions, the fracture toughness decreased with crack propagation up to 70 mm. It can be noted that less resistance to crack propagation was shown by FVE wet composites compared with the dry ones. This is because of the high percentage of cellulose and hemicellulose consisting of flax fibres that are susceptible to absorbing more water into their hydrophilic properties, which causes weak fibre matrix interface bonding (Biagiotti et al. 2004). For these FBVEu specimens in Figure 4.5, the G_{IC} values for the dry composites increased almost in a linear form of crack length from 50 mm to 62 mm. However, there are different behaviours for those water-aged samples, especially in the region between 52 mm and 54 mm: curves are steeper and then decrease after 54 mm. The data reduction methods CC and MCC are equal together in dry composites between 53 mm and 62 mm, while those of the MBT run parallel to them. The crack lengths of FBVEu dry composites were higher than wet laminates with approximately 12 mm and 9 mm respectively. However, the characteristic behaviour for the interlaminar fracture toughness G_{IC} values are different due to more water ingress into the flax fibres in the middle of the starter crack before the crack tip zone that could affect the fracture toughness initiation for their properties rather than the propagation. The results presented demonstrate that hygrothermal conditioning has a significant effect on the delamination and crack growth.

In the case of stitched composites of FBVEs as shown in Figure 4.6, these results imply that the stitched composites have the lowest crack length with only 5mm because of the barrier against further crack propagation of stitched yarn, unlike the unstitched sample FBVEu. The curves of CC and MCC are almost linear and parallel to the slopes but MBT curves are quite apart from them for both dry and wet samples. Once the crack growth has been initiated on FBVEs laminates, the fracture toughness then increases until the stitched zone as shown between 52 mm to 55 mm. It was found that stitching has significantly decreased the fracture toughness propagation due to the arrest of crack propagation in the stitched zone, in comparison to the unstitched. This observation can be explained by placing stitch thread that decreases the stiffness of the composite due to damage caused to fibres and resins when a needle punches in the laminates, as shown in Figure 4.7. Hence, the presence of stitching through-thickness reinforcement caused high stress concentrations and created resin-rich pockets (Dransfield et al. 1994).

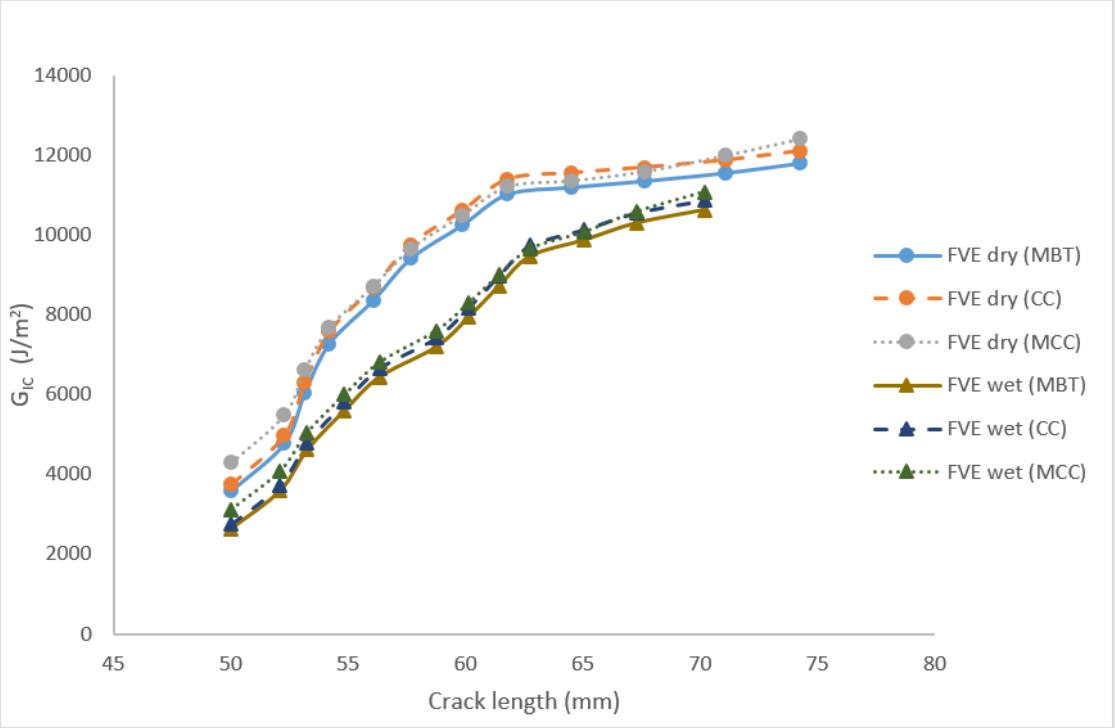


Figure 4.4 Resistance curves (R-curve) of Mode I (DCB) test for both dry and wet samples for FVE composite specimens using MBT, CC and MCC methods.

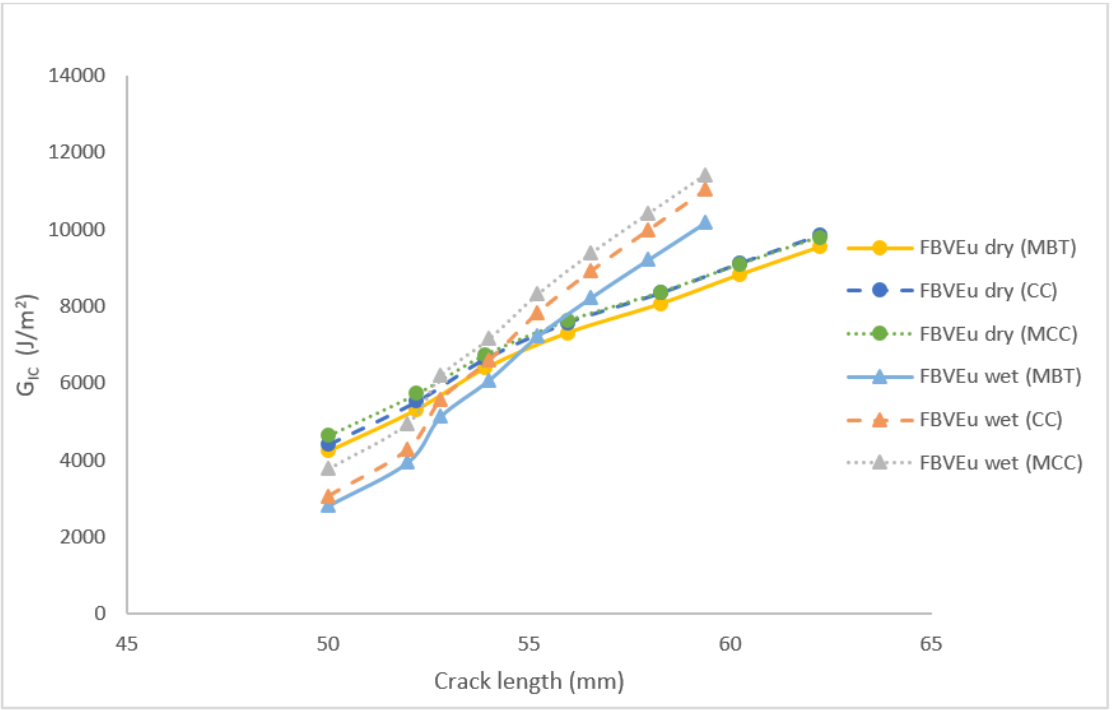


Figure 4.5 Resistance curves (R-curve) of Mode I (DCB) test for both dry and wet samples for FBVEu composite specimens using MBT, CC and MCC methods.

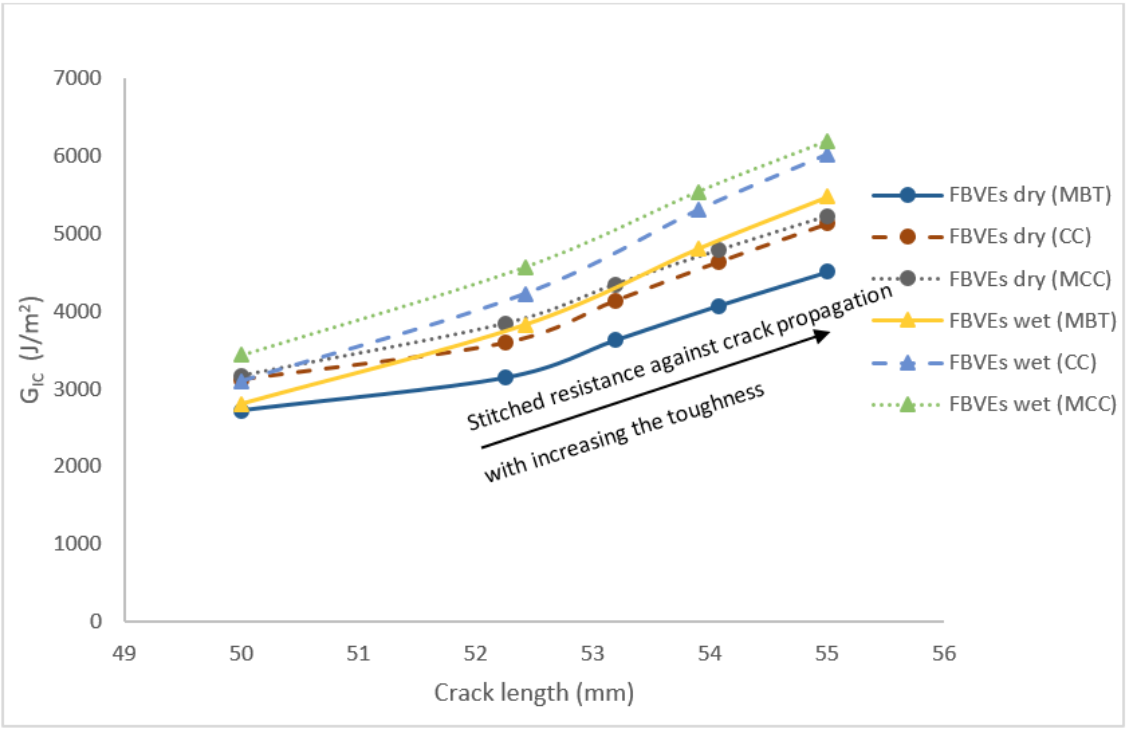


Figure 4.6 Resistance curves (R-curve) of Mode I (DCB) test for both dry and wet samples for FBVEs composite specimens using MBT, CC and MCC methods.

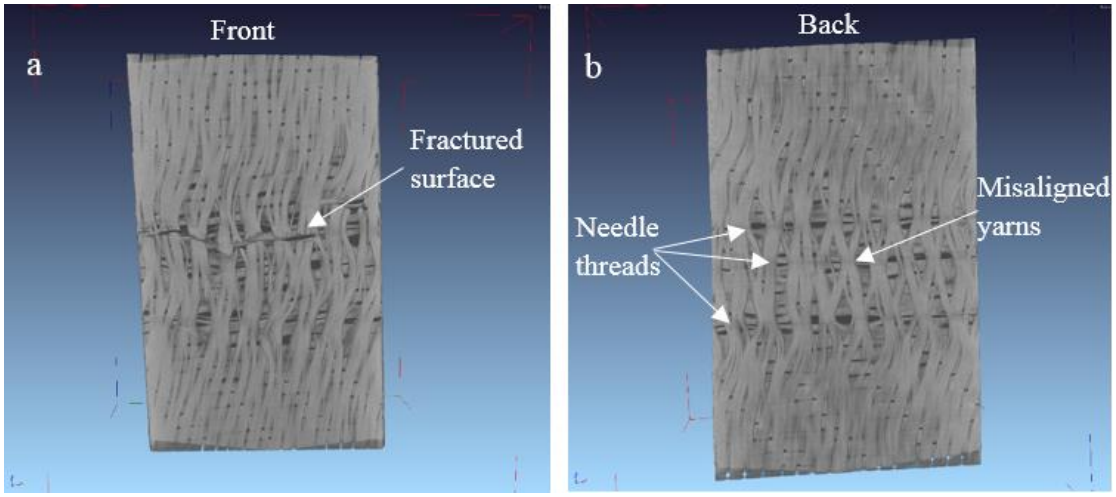


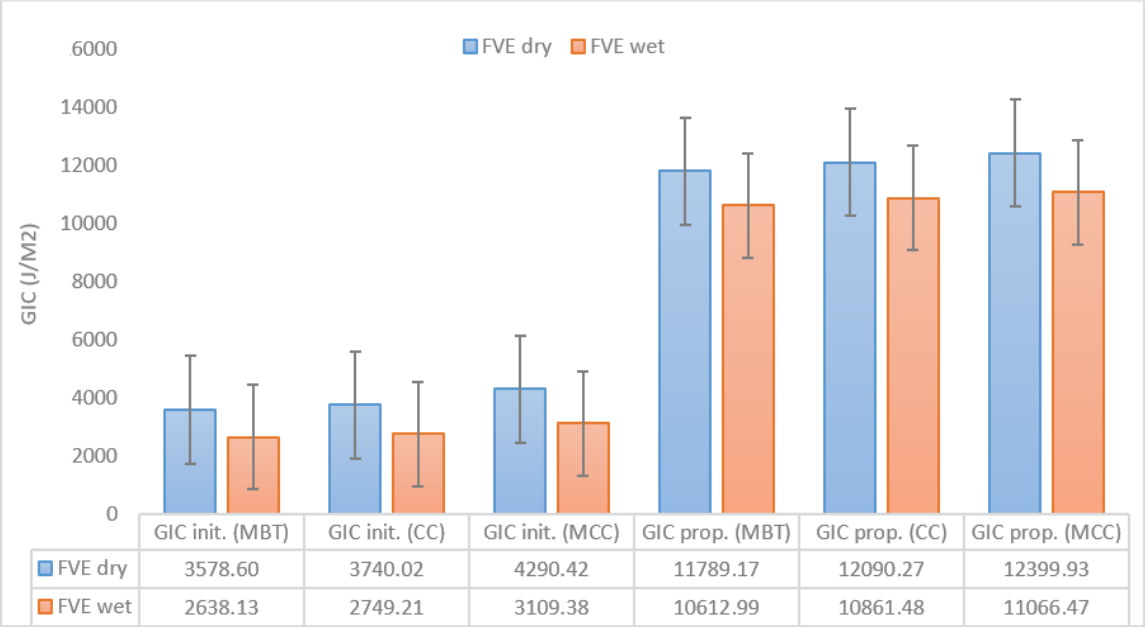
Figure 4.7 Computed micro-tomography (µCT) images of FBVEs samples illustrating the reconstructed 2D slice in x-z plane for a) Front and b) Back face.

4.1.4 Fracture Energy

The average values from Mode I strain energy release rates for $G_{IC\ init.}$ and $G_{IC\ prop.}$ are shown in Figures 4.8 to 4.10 using different reduction MBT, CC and MCC methods of FVE, FBVEu and FBVEs dry and wet composite laminates, respectively. In all cases, the modified beam theory (MBT) has the lowest value for both initiation and propagation toughness. In Figure 4.8,

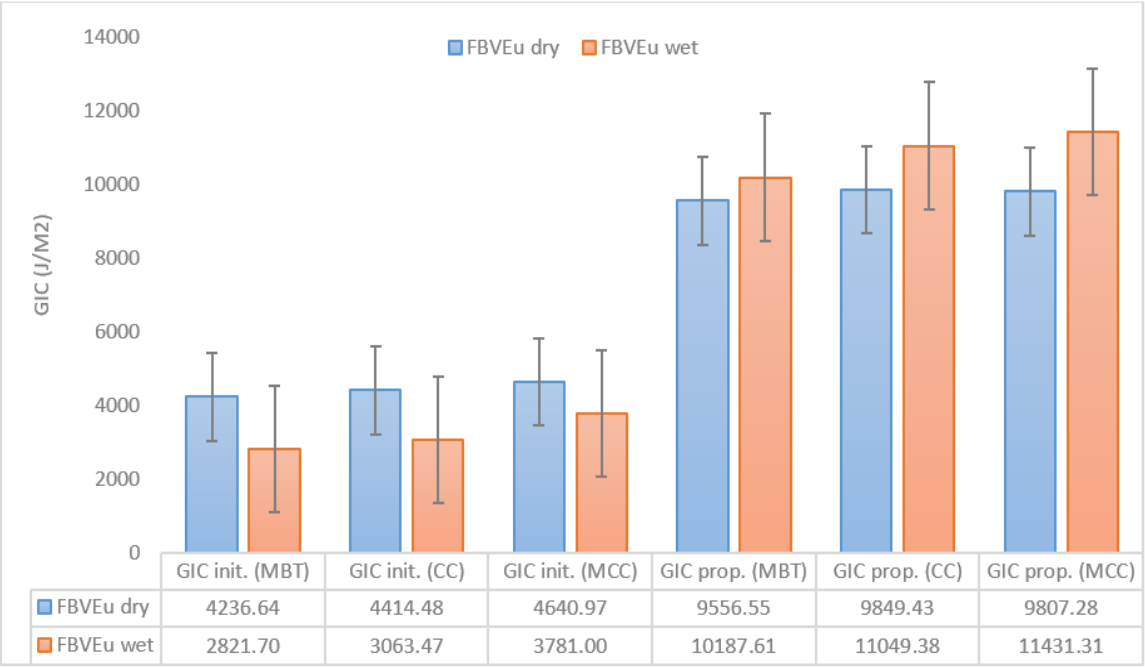
the results showed that the interlaminar fracture toughness of $G_{IC\ init.}$ for FVE wet laminates were significantly decreased by approximately 26.77%; it can be noticed that there is less resistance to crack propagation at the onset of crack tip with water-aged samples. Similarly, the fracture energy of $G_{IC\ init.}$ for FBVEu wet composites was significantly decreased with an average of 23% compared to dry samples, as shown in Figure 4.9. The reason for that could be due to high moisture absorption by flax fibres in the delamination of Teflon inserted through the plies of the composites during water immersion, which leads to the weak fibre-matrix interface. The other factor that might affect the delamination resistance of $G_{IC\ init.}$ for FVE and FBVEu wet composites are poor interfacial bonding between matrix and fibre (Li et al. 2005). With crack growth, the interlaminar fracture toughness of $G_{IC\ prop.}$ for FVE water-immersed specimens were decreased by an average of 10.30%, compared to FVE dry samples. However, the $G_{IC\ prop.}$ of FBVEu wet laminates had increased on average by 15.35%, compared to dry composite laminates, as shown in Figure 4.9. An initial explanation could be attributed to the hybridisation of basalt layers that showed better resistance to crack propagation. The type of resin shows some positive effect on the water absorption. For example, vinyl ester composites have much resistance to water penetration (Kim and Seo 2006).

For stitched samples of FBVEs laminates, the fracture energy of $G_{IC\ init.}$ and $G_{IC\ prop.}$ for wet samples were increased by an average of 4.28% and 19.63% respectively. It was observed that even though basalt hybridisation improved the delamination strength but, because of the high crack closure load exerted by stitches, the interlaminar fracture properties are reduced (Velmurugan and Solaimurugan 2007). This study showed that the presence of stitches led to a notable reduction in the interlaminar fracture toughness of $G_{IC\ init.}$ and $G_{IC\ prop.}$ resulting in the points of initiation and propagation being close to each other, as represented in R-curves shown in Figure 4.10.



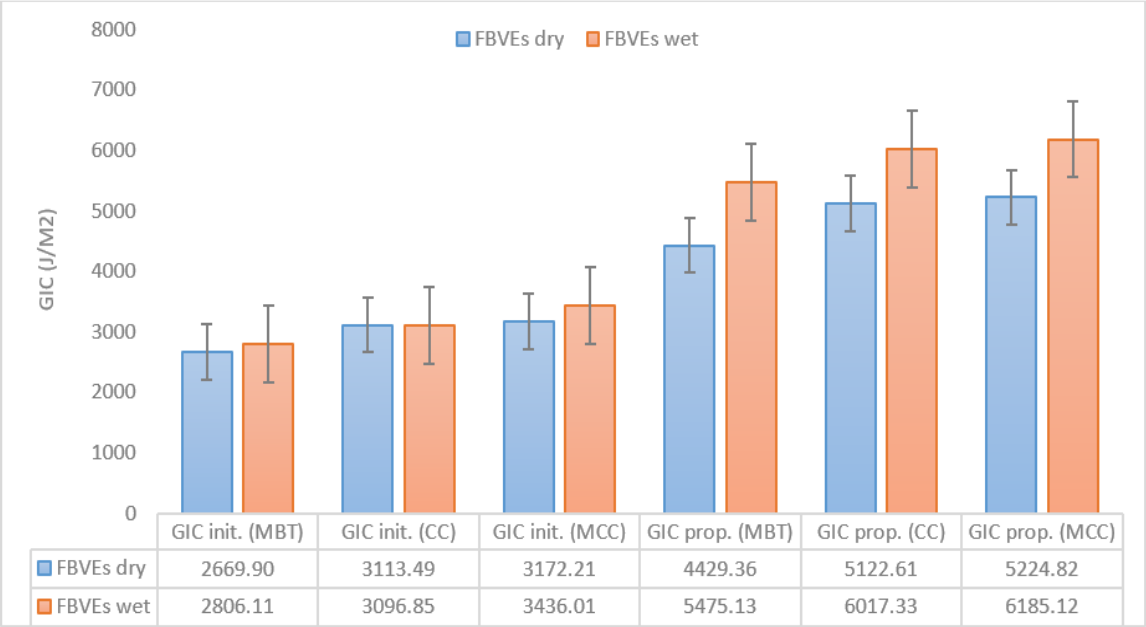
	GIC init. (MBT)	GIC init. (CC)	GIC init. (MCC)	GIC prop. (MBT)	GIC prop. (CC)	GIC prop. (MCC)
FVE dry	3578.60	3740.02	4290.42	11789.17	12090.27	12399.93
FVE wet	2638.13	2749.21	3109.38	10612.99	10861.48	11066.47

Figure 4.8 Mode I strain energy release rates for initiation G_{IC} and propagation G_{IC} toughness obtained from DCB tests for both dry and wet samples for FVE composite specimens using MBT, CC and MCC.



	GIC init. (MBT)	GIC init. (CC)	GIC init. (MCC)	GIC prop. (MBT)	GIC prop. (CC)	GIC prop. (MCC)
FBVEu dry	4236.64	4414.48	4640.97	9556.55	9849.43	9807.28
FBVEu wet	2821.70	3063.47	3781.00	10187.61	11049.38	11431.31

Figure 4.9 Mode I strain energy release rates for initiation G_{IC} and propagation G_{IC} toughness obtained from DCB tests for both dry and wet samples for FBVEu composite specimens using MBT, CC and MCC.



	GIC init. (MBT)	GIC init. (CC)	GIC init. (MCC)	GIC prop. (MBT)	GIC prop. (CC)	GIC prop. (MCC)
FBVEs dry	2669.90	3113.49	3172.21	4429.36	5122.61	5224.82
FBVEs wet	2806.11	3096.85	3436.01	5475.13	6017.33	6185.12

Figure 4.10 Mode I strain energy release rates for initiation G_{IC} and propagation G_{IC} toughness obtained from DCB tests for both dry and wet samples for FBVEs composite specimens using MBT, CC and MCC.

The results of the interlaminar fracture toughness of initiation and propagation for dry and wet composite specimens using MBT, CC and MCC are summarised in data table in Figures 4.8 to 4.10. Fracture toughness of FVE dry composites is the highest at propagation with an average of 12093.12 J/m^2, indicating that woven flax fibres play an important role as toughening material. For FBVEu wet laminates, the fracture toughness of $G_{IC\ prop.}$ was slightly higher than FVE wet composites with an average of 11232.68 J/m^2 and 10846.98 J/m^2 respectively. This could be attributed to the basalt hybridisation that provides a better shield to the swelled flax fibres. In the case of FBVEu wet samples, it is observed that interlaminar fracture toughness initiation has more energy absorbed than FVE and FBVEs wet composites. This can be explained in terms of high amounts of water absorption in the delamination of the starter crack zone before the crack tip causes swelling fibres that fill the gaps between the fibre and polymer matrix and then could lead to increase the interlaminar fracture properties of $G_{IC\ init.}$. This study showed that flax fibre without hybridised and stitched has higher interlaminar fracture toughness. Reported works on the effect of stitching on carbon and glass fibre composites suggest that stitching has contributed towards the improvement on crack arrest and load bearing capability (Tan et al. 2010; Velmurugan and Solaimurugan 2007). With this concept, it was expected that FBVEs laminates should have greater load-bearing capability and higher fracture energy than that of FVE composites. However, this improvement was not observed on the stitched samples. The reasons could have been due to that fact that the stitch thread was strong

to the extent of causing a permanent location of high stress concentration and resin-rich pockets (Dransfield et al. 1994). Hence, the initial and primary crack of the stitched specimen changed to secondary and longitudinal crack these primary-oriented secondary cracks would have caused the final failure. The results are somewhat surprising in view of the fact that the stitching was actually introduced to improve the fracture toughness. In order to find the reason for this reverse behaviour, the crack surfaces of stitched and unstitched samples are compared. It can be seen that the crack propagation was effectively restrained due to the presence of stitching. However, the stich was so strong that it did not let the crack to propagate further for the entire range of applied load. In fact, the purpose of stitch is to decelerate the crack propagation by introducing barriers in the propagation path after regular intervals. However, if these barriers are too strong to let the any further propagation of the crack, the stitch line becomes a permanent location of high stress concentration. Therefore, the secondary cracks start to evolve at this location in the lateral direction. As the lateral dimension of the specimen is much lower than the longitudinal dimension; these laterally oriented secondary cracks would cause the final failure if the specimen before even the primary crack starts to restart its propagation (after breaking the stitch). As a result, the interlaminar fracture toughness of initiation and propagation for FBVEs dry and wet laminates had significantly decreased compared to FVE and FBVEu composites. The µCT evidence shown in Figure 4.11 supports this observation. Clearly, the results of this study are in reasonable agreement with the weft-knitted glass fabrics shown in (Falconnet et al. 2002), indicating that interlaminar fracture toughness of woven flax composites (6 layers) was double than that of glass woven fabric composites (10 layers).

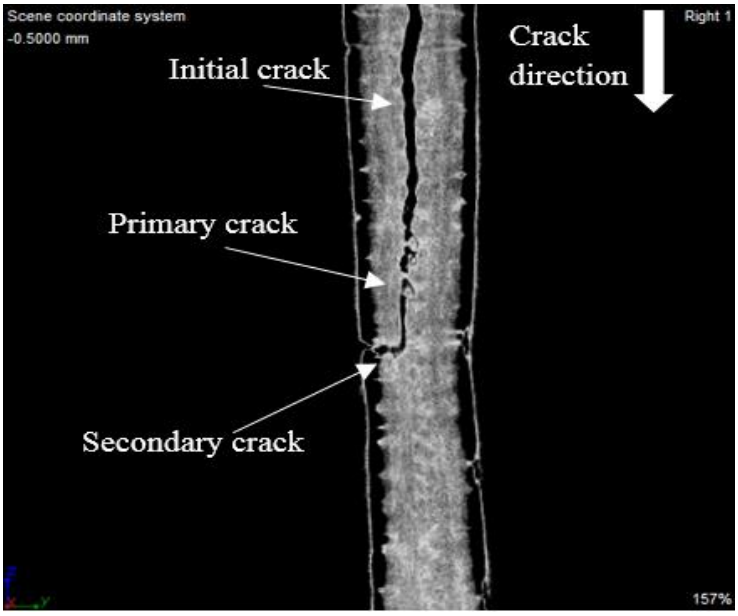


Figure 4.11 X-ray µCT reconstructed cross section of FBVEs sample in y-z plane.

4.2 Morphology Study on Mode I Fractured Surfaces

In order to differentiate fractured surfaces between dry and water-immersed specimens, the delaminated surfaces were observed by using a scanning electron microscope (SEM). Figure 4.8 shows SEM micrographs of the fractured surfaces for dry composites laminates after Mode I (DCB) failure. It is evident that there is more fibre breakage and fracture surfaces in FVE composites resulting from the poor fibre-matrix interfacial bonding; the flax fibres tend to agglomerate into bundles and are then unequally dispersed through the matrix (Figures 4.12 a and b). Fibre pull-out and splitting deformed fibres from the matrix in FBVEu composites could be seen, and there are some broken fibres on the delaminated surfaces shown in Figure 4.12 (c).

Extensive in-plane fibre-bridging exists in the stitched zone after crack growth, high stress concentrations at the interface of FBVEs laminates which caused fibre-matrix debonding and led to unstable crack propagation, are shown in Figure 4.12 (f). This is evidence confirmed by x-ray imaging of stitching through-thickness reinforcement causing localised in-plane fibre damage due to needle penetration of woven fabric (Dransfield et al. 1994). Therefore, the interlaminar fracture toughness of stitched laminates significantly drop compared to unstitched samples. Moreover, further fracture occurred for FBVEs composites and voids induced by fibre pull-out are clearly seen in Figure 4.12 (e). At higher magnification (Figure 4.12 d) large in-plane fracture for fibre bundles of stitched composites can be seen, and a substantial amount of energy was absorbed by fibre breakage and fibre bridging mechanisms during delamination. These micro-scale results commonly occurred on Mode I (DCB) tests (Alif, Carlsson, and Boogh 1998; Ravandi et al. 2016).

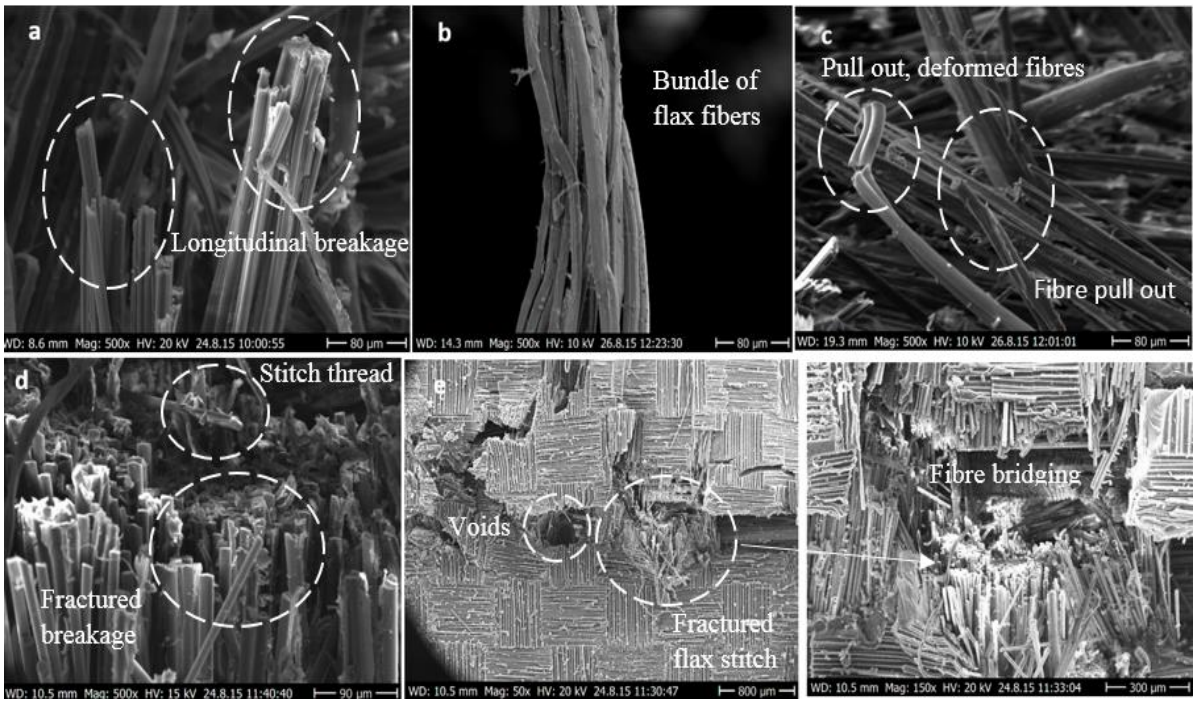


Figure 4.12 SEM micrographs of the fracture surfaces for dry composites showing (a) longitudinal breakage for FVE, (b) bundle of flax fibres, (c) fibre pull out and fibre fractured of FBVEu, (d) fractured breakage and cotton stitch thread of FBVEs, (e) fractured flax stitch and voids, (f) fibre bridging of FBVEs.

SEM micrographs of delaminated surfaces for water-aged samples are shown in Figure 4.13. It can be clearly observed that exposure to moisture without hybridisation results in a decrease in the fracture toughness properties due to degradation and cavities of the fibre-matrix interface. The presence of water in the environment can create moisture-induced cavities and surface degradation as indicated on the fractured surfaces. This scenario can cause micro-cracking and debonding in the composites and reduce the fracture toughness of the composites as a result of a weak fibre-matrix interface. Micro-cracking and debonding caused by large amounts of water ingress for FVE composites as illustrated in Figures 4.13 (a) and (b). As expected, the addition of basalt fibre on flax as hybrid material, the water repellence property has been enhanced. As a result, a large toughness enhancement has arisen from FBVEu specimens. In flax/basalt hybrid specimens (FBVEu), a resistance to delamination has occurred on the surface without much matrix cracking at the fibre-matrix interface, especially in the crack propagation zone (Figure 4.13 c). Fracture and fibre breakage happened mostly at the fibre-matrix interface as revealed by the bare fibres and fibre imprints in the matrix. The delaminated surfaces indicate poor interfacial bonding (Figure 4.13 d) and fibre matrix adhesion as a result of water molecules ingress is the primary mode of failure for water-immersed specimens.

In the case of stitched samples, resin-rich pockets and matrix deformation are observed in Figure 4.13 (e) as a result of needle-punching during the stitching procedure (Aymerich, Onnis, and Priolo 2005). Thus, high stress concentration around stitch fibres caused fibre damage and then reduced the fracture toughness initiation and propagation of FBVEs laminates. A large number of fragmented matrix are observed in this stitched sample which allowed fracture and pull-out of non-aligned fibres (Figure 4.13 f). Furthermore, higher amounts of stitched fibres might cause in-plane fibre misalignment and resin-rich regions (Velmurugan and Solaimurugan 2007).

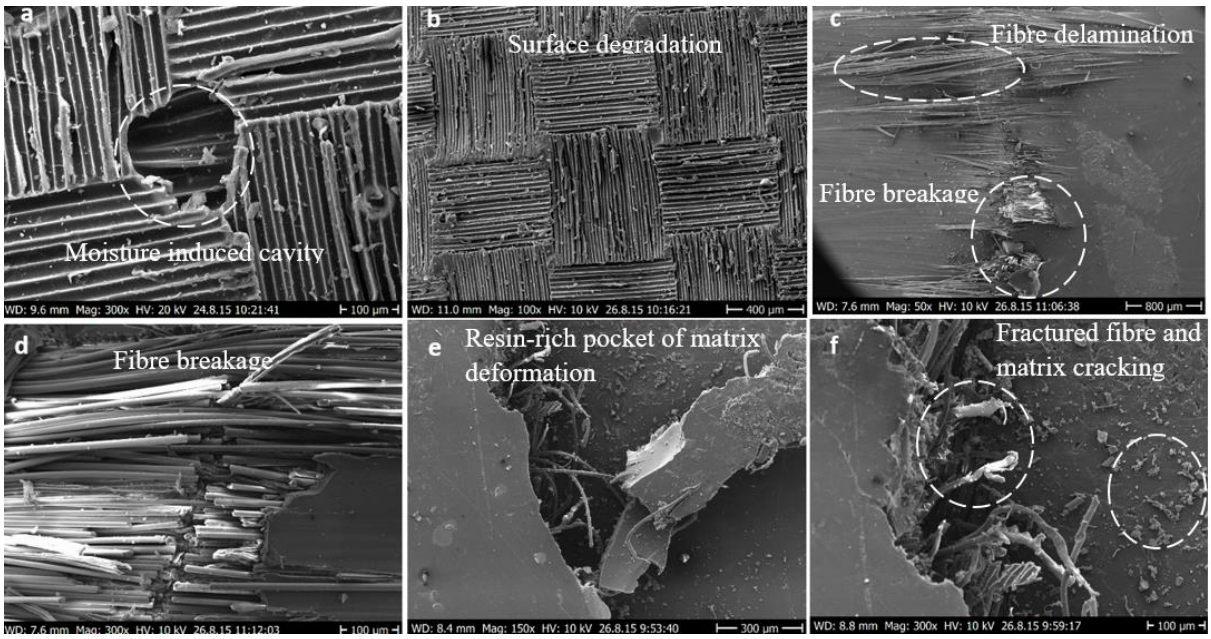


Figure 4.13 SEM micrographs of the fracture surfaces for wet composites showing (a) Moisture induced cavity for FVE composite, (b) surface degradation due to moisture presence of FVE, (c) delamination of FBVEu, (d) fibre breakage of FBVEu, (e) resin rich pocket with matrix cracking of FBVEs, (f) fractured fibre and matrix cracking of FBVEs.

5 Chapter 5: Results and Discussion of Mode II (3ENF)

This chapter focuses on the experimental results that obtained from Mode II (3ENF) tests. In this chapter, the first part evaluates the sorption behaviour and the diffusion coefficient of flax and basalt fibres hybrid composites along with stitched composite specimens. The second part study the effect of hybridisation and stitching on the load and displacement curves under two different conditions. The third and fourth parts investigate the influence of water absorption behaviour and its effects on the Mode II interlaminar fracture toughness of hybrid and stitched composites. In the last part, the fracture damage mechanisms at the surface and delamination of these composite specimens are examined using SEM and micro CT scan.

5.1 Effect of Moisture Absorption on Mode II Interlaminar Fracture Toughness

5.1.1 Sorption Behaviour

The weight gain percentage of four different group of samples (FVE, FBVEu, FBVEs and neat VE) vs. square root of time are shown in Figure 5.1. Saturation moisture uptake and diffusion coefficient are presented in Table 5-1. It was found that the maximum percentage of weight gain for FVE, FBVEu, FBVEs and neat VE composite laminates immersed at room temperature for 1008 hours is 5.24, 3.46, 3.41 and 0.78%, respectively. Without basalt hybridisation, flax fibre composites absorbed higher than FBVEu laminates by approximately 34% higher. This is attributed to high cellulose content (71 to 75 %) in the structure of flax fibre that allowed the water molecules to interact with the hydroxyl groups, which led to poor interface between the fibre and matrix (Yan et al. 2014). FVE samples absorbed larger amount of water ingress than FBVEu composites. Therefore, the external skin layers of basalt fibre prevented the inner core of flax fibres from the degradation and exhibited a greater resistance to water absorption and it has a superior water repellence behaviour compared to FVE composites. Moreover, water accumulation was reduced in FBVE laminates among their interfacial voids due to improved fibre/matrix interfacial bond (Fiore, Scalici, Calabrese, et al. 2016).

As shown in Figure 5.1, there are three-stage mechanisms in different zone for each composite laminates except unreinforced samples with only two stages. At the beginning (stage I), the water absorption rate is rapidly increased with linearity for 15 hours$^{1/2}$ (10 days) in both composites of FVE and FBVE, following a Fickian behaviour at room temperature. After that in (stage II), the curve gradually increased for long time 30 hours$^{1/2}$ (39 days) until saturation

reaches apparent steady state in (stage 3). Water diffusion into polymer composites in phase II involves further displacement of fluid molecules from a region of high concentration to lower concentration. This diffusion is exacerbated through; poor wetting of the fibre, incomplete sizing or grafting, as well as mechanical fatigue. For unreinforced samples, the water uptake process of neat VE composites is linear and slowly increased for just 14 hours$^{1/2}$ (9 days) in (stage I), then quickly reached a stable state because of hydrophobic matrices and do not include any hydrophilic fibres in (stage II). These results of sorption behaviour are an agreement with other results, as reported (Almansour et al. 2017; Fiore, Scalici, Calabrese, et al. 2016).

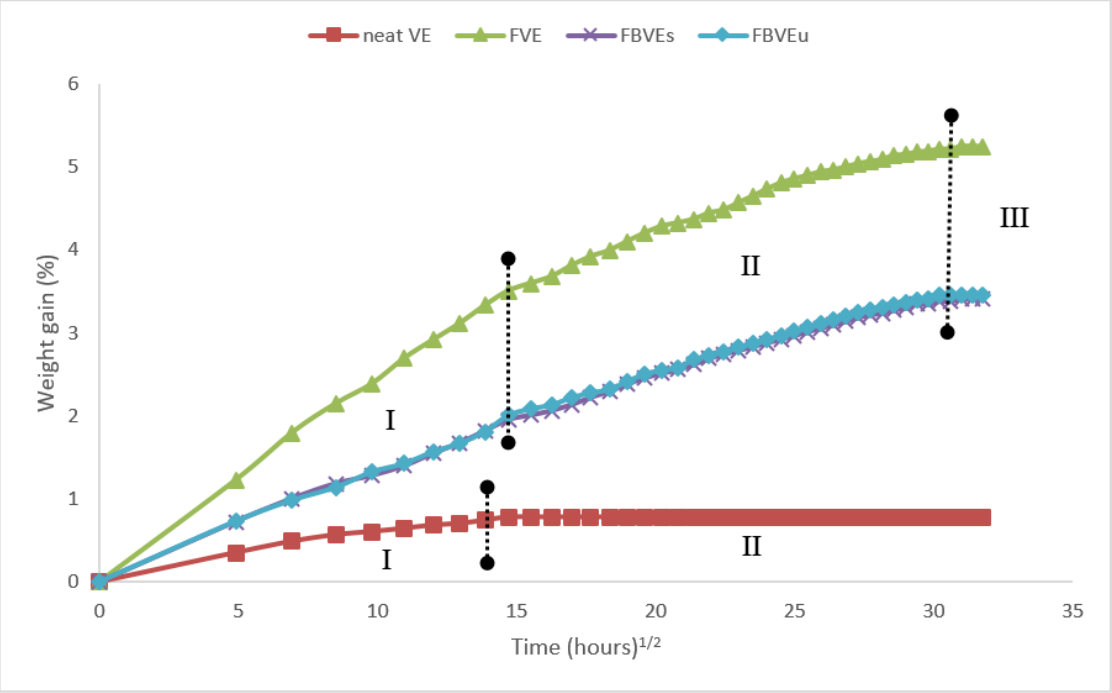


Figure 5.1 Weight gain as a function of time for 3ENF specimens of FVE, FBVEu, FBVE$_S$ and neat VE composite laminates exposed to distilled water at room temperature.

The diffusion properties of composites were calculated by Fick's law in terms of weight gain percentages of dry specimen immersed in water and the initial slope of the weight gain curve versus square root of time in hours (Dhakal et al. 2007). The diffusion coefficient values for FVE, FBVEu, FBVEs and neat VE composite laminates are presented in Table 5.1. It can be observed that the moisture uptake and the diffusion coefficient decreased for FBVEu compared to FVE samples without hybridisation by approximately 34% and 29%, respectively. This is ascribed to the hybridisation of hydrophobic basalt layers that preserved the cellulose core layers of composite laminates from degradation during ageing environmental exposure (Fiore,

Scalici, Calabrese, et al. 2016). The water diffusion in thermosetting polymers was found to cause composite laminates swelling and micro cracking, supported by brittle thermosetting resin used. Thus, water penetrated through micro cracks into the interface of the composites consequently caused composite failure (Pothan and Thomas 2004). For neat VE composite laminates, when saturation moisture uptake decreased, the diffusion coefficient increased. Similar behaviour has been reported for unsaturated polyester (neat UP) composites (Dhakal et al. 2007). The moisture uptake and the diffusion coefficient were decreased for neat VE when compared to neat UP by approximately 12% and 15%, respectively. It was observed that neat VE composites saturated rapidly than neat UP, This has been reported that the water absorption behaviour was not only depend on the fibre, but also on the type of resin used. This could be caused from the void content and the molecular structure of the resin (Kim and Seo 2006).

Table 5-1 Moisture uptake and diffusion coefficient of FVE, FBVEu, FBVES and neat VE composite laminates immersed in distilled water at room temperature.

Type of Sample	Saturation moisture uptake M_m (%)	Initial slope of plot (*k*) *M(t)* versus $t^{1/2}$	Diffusion Coefficient, D, x10-3(m^2/s)
FVE	5.24	0.25	1.50776E-06
FBVEu	3.46	0.15	1.0739E-06
FBVEs	3.41	0.15	1.04705E-06
neat VE	0.78	0.07	4.65357E-06
neat UPE*	0.87	0.10	5.714E-06

*for comparison purpose.

5.1.2 Load and Displacement Curve

The average load and displacement curves of FVE, FBVEu, FBVEs and neat VE composite laminates were obtained from the 3ENF tests. The curves for both dry and wet specimens are shown in Figure 5.2. It can be seen from the figure that the load increased linearly with increase in displacement during the initial stage of loading. These curves show elastic behaviour during deformation, with exception of neat VE samples. For FVE dry composites, the load and displacement increased linearly and then reached to its maximum values of 812 N and 5.2 mm, respectively. However, in the case of FVE wet samples, the displacement continued to increase up to 7.4 mm with decrease in the load by 100 N compared to dry samples. The first reason for this variation is due to the phenomena of plasticisation that could increase the deformation until

the fracture point. Secondly, the weak fibre/matrix interface due to water ingress in the interface region.

In the case of hybridised composites of FBVEu, both water immersed and dry samples exhibited a sudden drop in load after a maximum load of 696 N and 588 N, respectively. This indicates that the strain energy release rate has already reached the fracture toughness of the material for crack propagation. When the displacement reached 4.5 mm, then the compliance of the dry curve gradually declined, which could initiate matrix cracking in the delamination of composite laminates. It is evidenced that FVE wet samples absorbed higher energy before fracture than FVE dry composites. However, with basalt hybridisation of FBVEu wet specimen absorbed lower energy than FBVEu dry composites. This behaviour is related to the external layers of basalt fibre showing greater resistance to water penetration into fibre/matrix interface due to excellent water repellence behaviour (Fiore, Scalici, Calabrese, et al. 2016). It is observed that the crack propagation was stable for all samples including stitched composites, but stick-slip crack occurred by arrest crack after the maximum load of FBVEs for both dry and wet samples. The results showed that all composites exhibited ductile fracture except neat VE which showed brittle fracture without any evidence of plastic yielding prior to fracture. Unreinforced vinyl ester showed ostensibly linear behaviour to the point of fracture because of its brittle nature and has low energy absorption before breaking into two pieces. Load and displacement values of saturated samples of neat VE were increased more than that of unsaturated laminates.

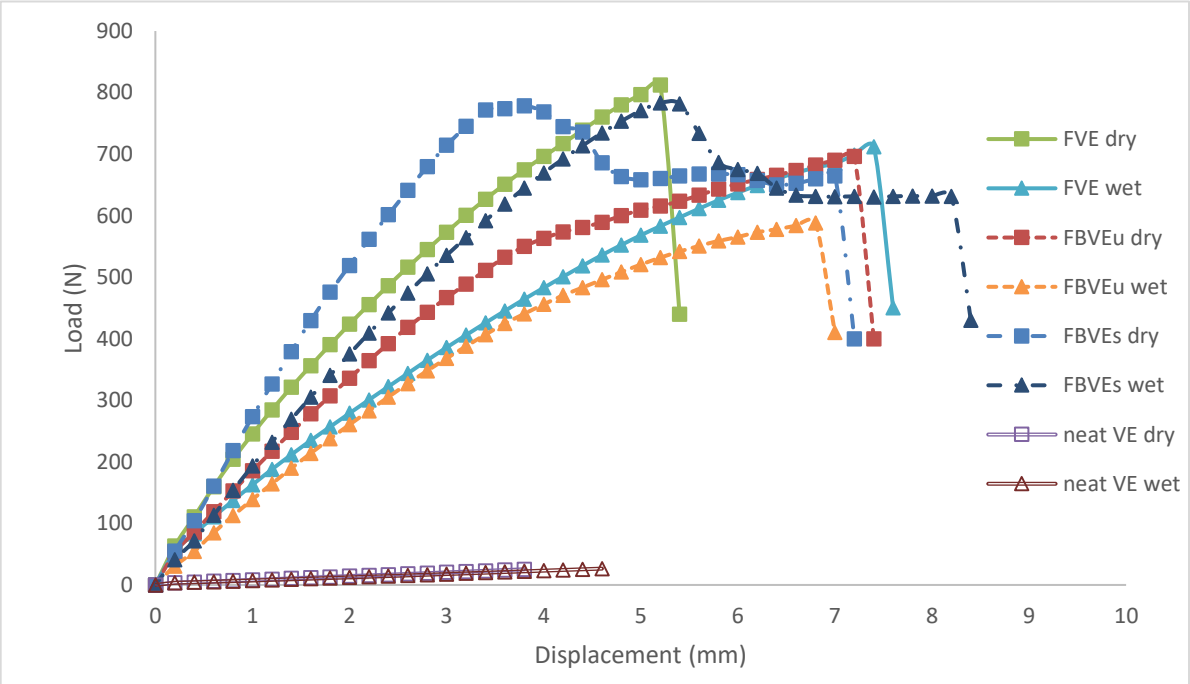


Figure 5.2 Load versus displacement curves of Mode II dry and wet samples for FVE, FBVEu, FBVEs and neat VE specimens.

5.1.3 Delamination Crack Growth Resistance Curve

The experimental results of resistance curves (R-curve) show the relationship between the Mode II strain energy release rate (G_{IIC}) and the delamination length (a). These were obtained to determine the initiation and propagation of a crack length in both conditions; dry and wet. Referring to the published literature on Mode II (3ENF) tests (Hadavinia and Ghasemnejad 2009; Zenasni and Saadi 2006), two data reduction methods of CCM and SBT were used to determine the interlaminar fracture toughness. The crack growth results of resistance curves from this study are presented in Figures 5.3 to 5.5 for samples of FVE, FBVEu and FBVEs composite laminates, respectively. In general, the fracture energy G_{IIC} increased gradually with an increasing delamination growth in all composite laminates and the crack zone was measured between 30 mm and 40 mm. It can be observed that the values obtained from CCM and SBT methods are close to each other and exhibited similar behaviour for both dry and wet composites. However, SBT method had lower values in the fracture energy than CCM of dry composites, whereas in wet samples, the latter showed lower G_{IIC} values than SBT method. This could be related to a large displacement occurred in water-aged samples. As shown in Figure 5.3, the average of R-curve obtained for FVE composites, which shows an increasing trend up to a crack growth of 38 mm and 39 mm for dry and wet composites, respectively.

With basalt hybridised composites in Figure 5.4, the crack length increased from 38 mm to 40 mm compared to FVE dry composites showing that high resistance to delamination due to the external of basalt layers, which contributed to increasing crack propagation resistance. It was observed that the crack length reduced for FBVEu wet laminates from 40 mm to 39 mm compared to FBVEu dry ones. This behaviour could be attributed to the reduction in fibre/matrix interfacial strength due to the moisture absorption resulting in a reduction of crack propagation; this, however, improved the resistance to crack initiation because of increasing in matrix ductility (Nash, Young, and Stanley 2016a). The results for stitched composites of FBVEs are shown in Figure 5.5, it can be seen that the lowest crack length for stitched composites with only increased by 5-6 mm due to the arrest to crack propagation of stitching yarn, while unstitched composites of FBVEu growth up to 9-10 mm.

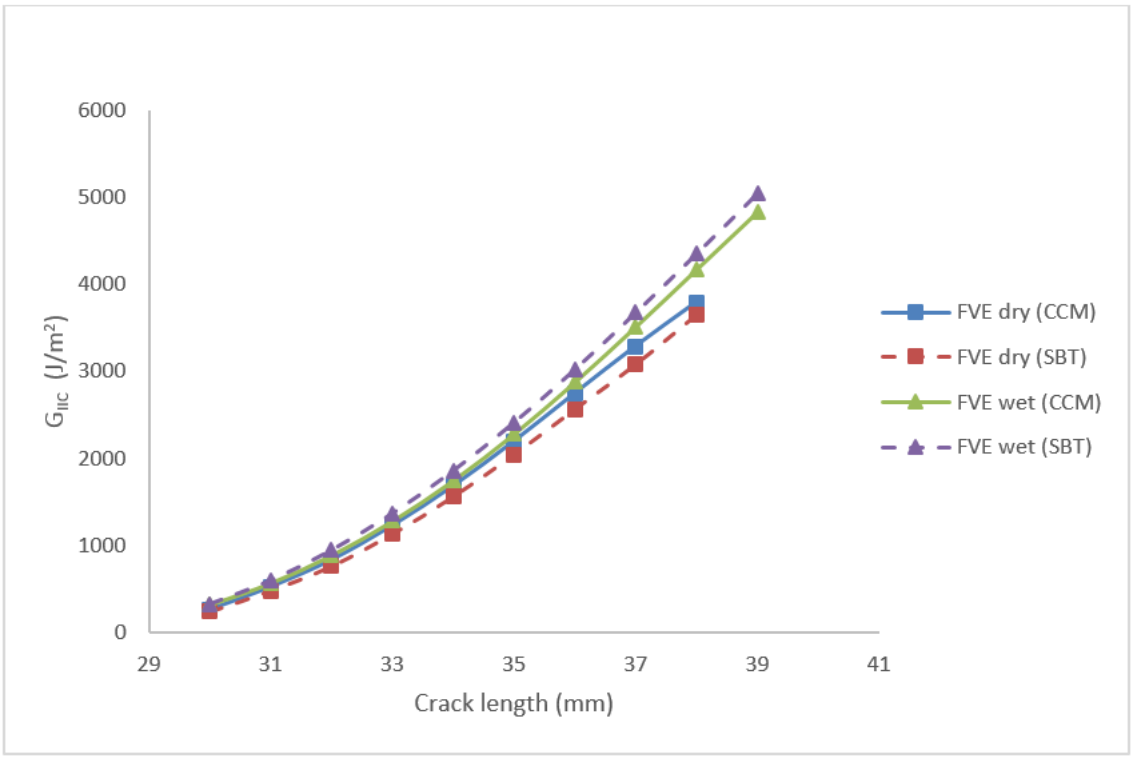


Figure 5.3 Resistance curves (R-curve) of Mode II (3ENF) tests for both dry and wet samples for FVE composite specimens using CCM and SBT methods.

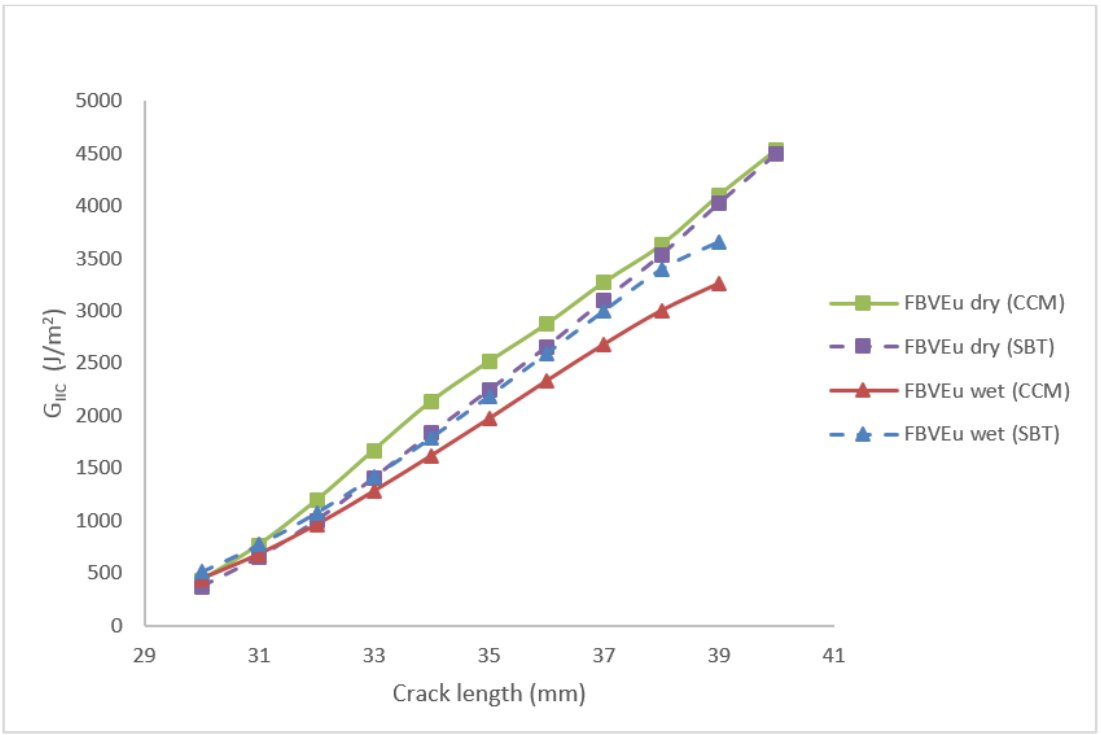


Figure 5.4 Resistance curves (R-curve) of Mode II (3ENF) tests for both dry and wet samples for FBVEu composite specimens using CCM and SBT methods.

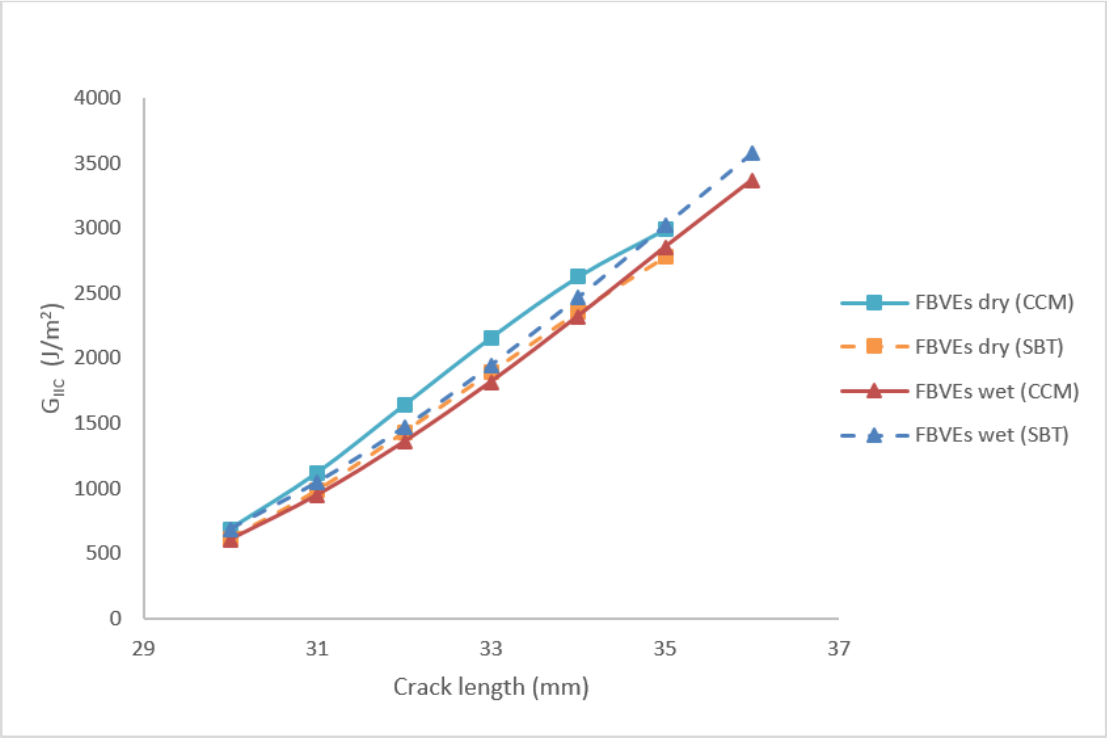


Figure 5.5 Resistance curves (R-curve) of Mode II (3ENF) tests for both dry and wet samples for FBVEs composite specimens using CCM and SBT methods.

5.1.4 Fracture Energy

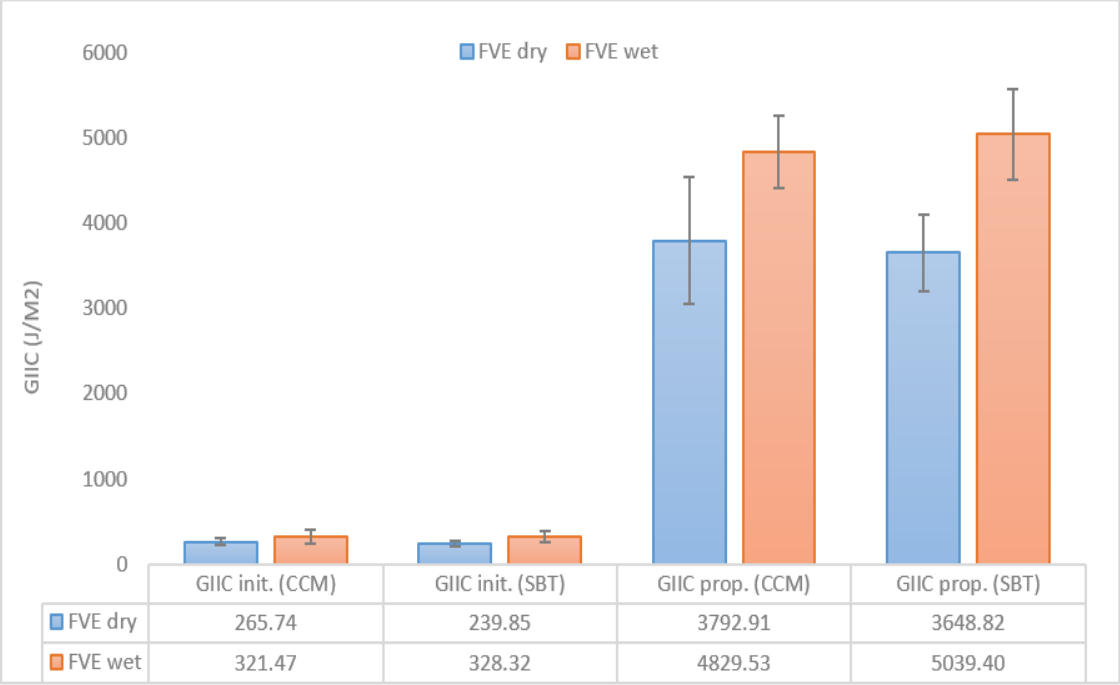
The results from Mode II strain energy release rates of $G_{IIC\ init.}$ and $G_{IIC\ prop.}$ are shown in Figures 5.6 to 5.9, depicting FVE, FBVEu, FBVEs and neat VE composite laminates at dry and wet conditions, respectively. It can be noted that the initiation and propagation of fracture energy increased with increasing the moisture content of FVE wet composites as shown in Figure 5.6. There are several reasons for increase in the strain energy release rate G_{IIC} after water absorption. Firstly water molecules are a plasticiser that influenced the fibres and matrix by distributing the mechanical integrity of composite laminates (Huang and Sun 2007), and secondly, flax fibres are susceptible to absorb high amount of water due to its hydrophilic nature and consist of high cellulose which would effect on the structure and dimension of the fibres (Biagiotti et al. 2008). Similar observations have been reported on the effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated composites for both flexural and tensile strains (Dhakal et al. 2007). With basalt hybridisation in Figure 5.7, the resistance to crack initiation of saturation samples were improved due to matrix ductility; however, this was declined by a reduction in the interfacial strength of fibre-matrix and causing a decreased in the resistance to crack propagation of FBVEu wet composites.

It is clear that in Figure 5.8, the interlaminar fracture toughness of crack growth was reduced significantly due to stitching. This could be ascribed to fibres damage caused by thread when needle punched into the composite laminates during the process of stitching (Almansour et al. 2017). This could also have created a stress concentration region. Therefore, stitched woven composites led to reduce the interlaminar fracture toughness of $G_{IIC\ prop.}$, caused damage to the structural performance under shear fracture and reduces its delamination resistance. This behaviour under stitched samples is in close agreement with our previous experimental results on Mode I interlaminar fracture toughness (Almansour et al. 2017) and also other recently published works on the mechanical properties of low velocity impact test (Ravandi et al. 2017). After water immersion in Figure 5.9, neat VE composites were found the fracture energy is higher than neat VE dry composites.

The average values of the interlaminar fracture toughness of $G_{IIC\ init.}$ and $G_{IIC\ prop.}$ for dry and wet composite specimens using CCM and SBT methods are summarised in Figures 5.6 to 5.9. It was found that hybrid composites of FBVEu improved the interlaminar fracture toughness of the initiation and propagation when compared to FVE dry samples by approximately 58% and 21%, respectively. Consequently, hybridisation with basalt fibres placed in the outer layers improved the Mode II interlaminar fracture toughness of natural fibres reinforced composite laminates as well as superior ageing resistance. Saturation results of $G_{IIC\ init.}$ and $G_{IIC\ prop.}$ for FVE wet composites were increased by 29% and 33%, respectively compared to FVE dry specimens, due to high moisture absorption from the hydrophilic nature of natural fibres; particularly flax fibres which consist of high cellulose about 71-75% (Yan et al. 2014) and the plasticisation of the matrix (Nash, Young, and Stanley 2016b). In addition, the presence of moisture increased the resistance to crack initiation of FBVEu wet composites. However, it tended to cause a reduction in the propagation of fracture energy. This has resulted to reduction in the interfacial strength between the fibres and matrix due to the presence of the water into the interface. Hence, it increased matrix ductility (Nash et al. 2016a).

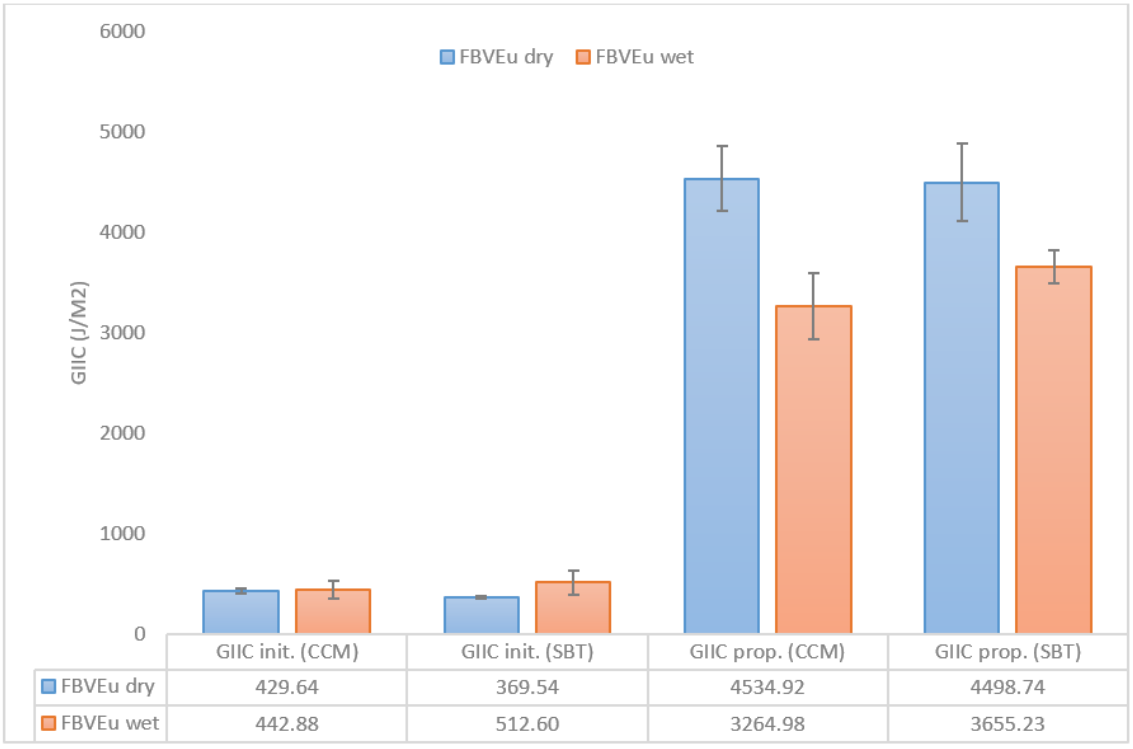
In the case of stitched composites, FBVEs samples had the highest resistance to crack initiation of fracture toughness for both dry and wet composites than unstitched composites. It was observed that stitching of natural fibre composites through-thickness reinforcement can enhanced the interlaminar fracture toughness (Ravandi et al. 2016). However, it was also observed that stitching led to a notable reduction in the in-plane mechanical properties and the delamination resistance to crack propagation (Almansour et al. 2017; Ravandi et al. 2016, 2017). In this study, the interlaminar fracture toughness, $G_{IIC\ prop.}$ of stitched composites were

significantly lower than unstitched composites of FBVEu dry laminates by 36%. The reason is that stitching can create resin-rich pockets at the crack tip zone and cause in-plane fibre damage. As shown in Figure 5.10 (a), misalignment of in-plane fibres around the stitch zone is attributed to large reduction in the interlaminar shear strength of FBVEs samples, whereas in Figure 5.10 (b), there is a good fibres alignment of unstitched composites of FVE. It has been reported that stitching can lead to disruption of the fibre alignment and misaligned yarns between the weft and warp of woven tows (Almansour et al. 2017; Mouritz and Cox 2010). The results in Figure 5.9, is an agreement values with other thermosetting results such as polyester (Hughes et al. 2002); the critical strain energy release rate G_{IIC} of neat polyester and neat VE composites was about 100 J/m^2 and 158 J/m^2, respectively. The fracture energy of $G_{IIC\ init.}$ for example increased for neat VE from 157.84 J/m^2 to 239.85 J/m^2 without hybridisation of FVE composites, while with basalt hybridised of FBVEu specimens increased to 369.54 J/m^2.



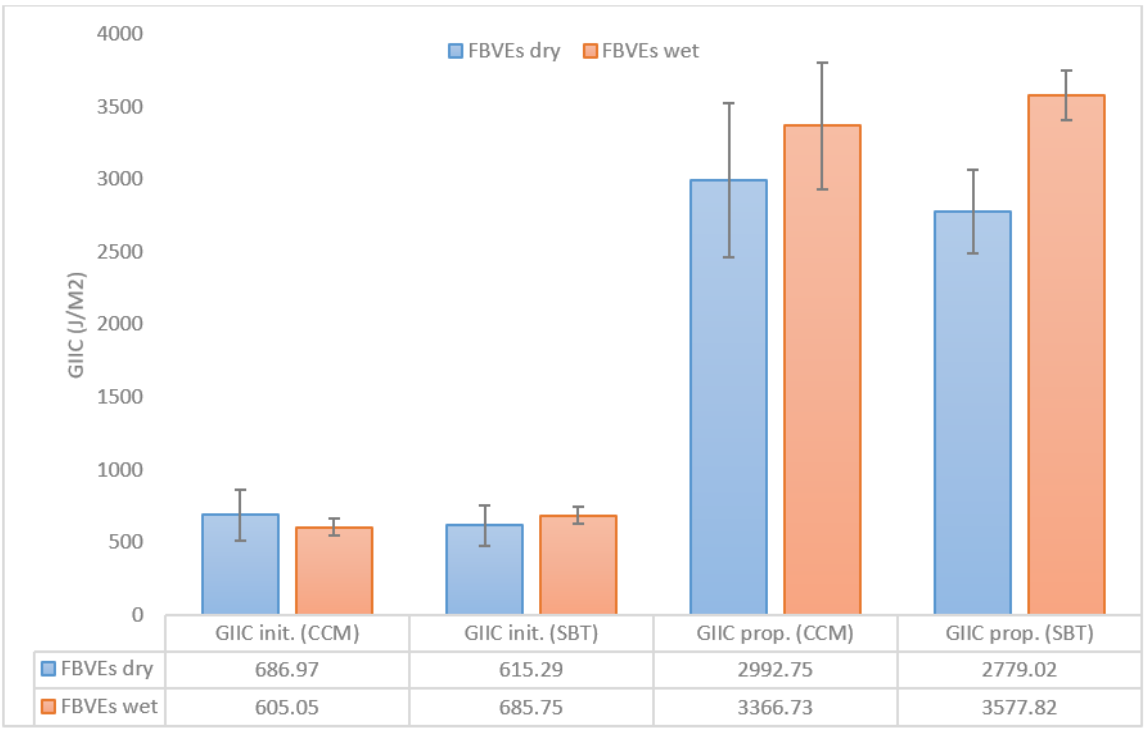
	GIIC init. (CCM)	GIIC init. (SBT)	GIIC prop. (CCM)	GIIC prop. (SBT)
FVE dry	265.74	239.85	3792.91	3648.82
FVE wet	321.47	328.32	4829.53	5039.40

Figure 5.6 Mode II strain energy release rate, G_{IIC} for initiation and propagation toughness obtained from 3ENF tests at dry and wet conditions for FVE composite specimens using CCM and SBT methods.



	GIIC init. (CCM)	GIIC init. (SBT)	GIIC prop. (CCM)	GIIC prop. (SBT)
FBVEu dry	429.64	369.54	4534.92	4498.74
FBVEu wet	442.88	512.60	3264.98	3655.23

Figure 5.7 Mode II strain energy release rate, G_{IIC} for initiation and propagation toughness obtained from 3ENF tests at dry and wet conditions for FBVEu composite specimens using CCM and SBT methods.



	GIIC init. (CCM)	GIIC init. (SBT)	GIIC prop. (CCM)	GIIC prop. (SBT)
FBVEs dry	686.97	615.29	2992.75	2779.02
FBVEs wet	605.05	685.75	3366.73	3577.82

Figure 5.8 Mode II strain energy release rate, G_{IIC} for initiation and propagation toughness obtained from 3ENF tests at dry and wet conditions for FBVEs composite specimens using CCM and SBT methods.

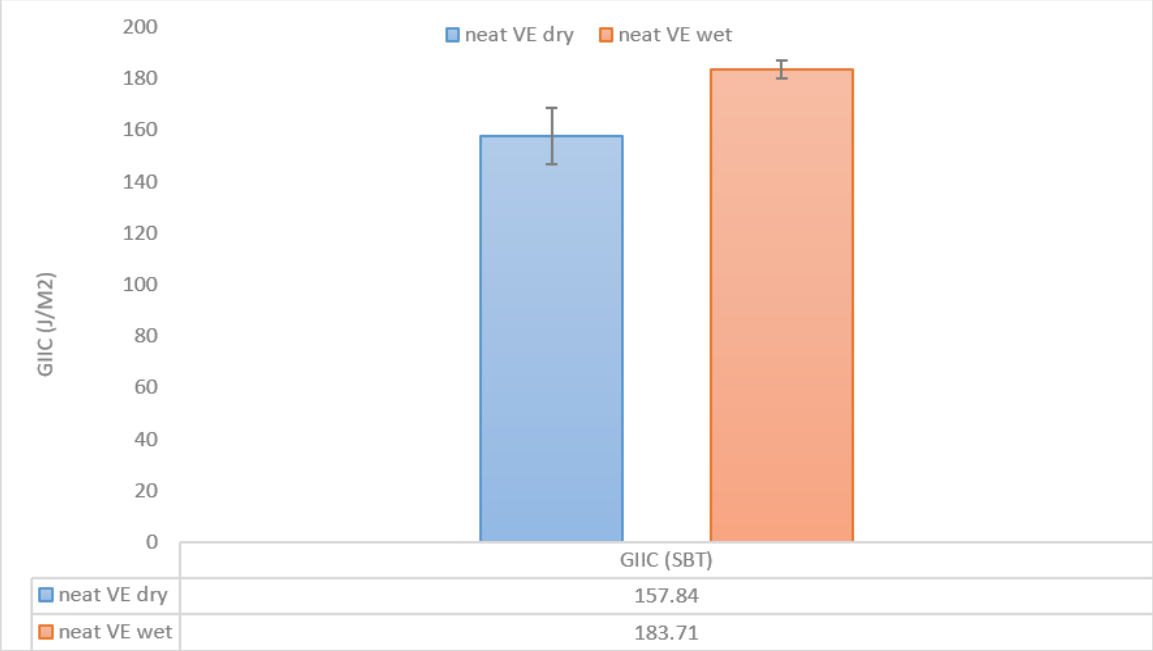


Figure 5.9 Mode II strain energy release rate, G_{IIC} for initiation and propagation toughness obtained from 3ENF tests at dry and wet conditions for neat VE composite specimens using SBT methods.

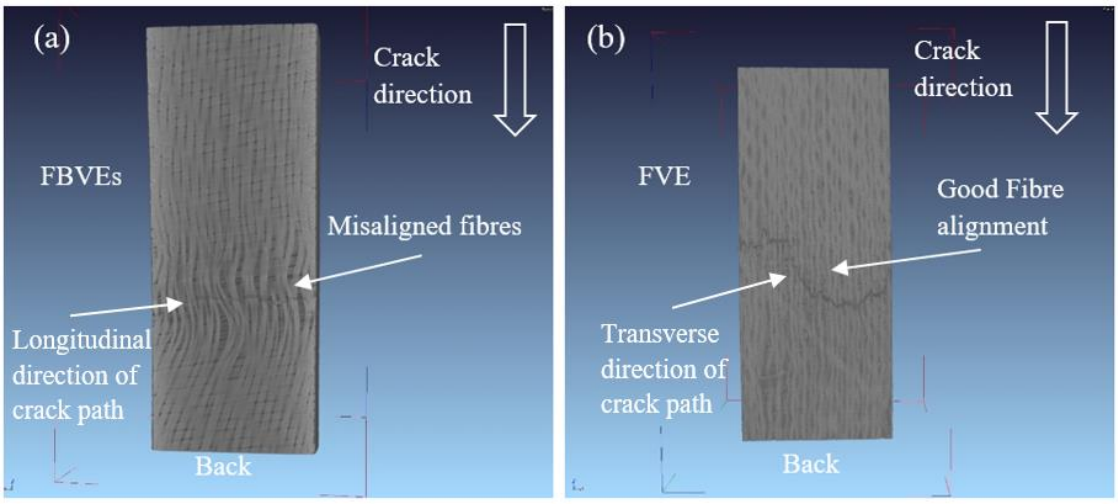


Figure 5.10 Computed micro-tomography (µCT) images of the reconstructed 2D slice in x-z plane from backside for (a) FBVEs and (b) FVE composites.

5.2 Morphology Study on Mode II Fractured Surfaces

The shear fracture surfaces of the 3ENF specimens after testing were evaluated by SEM analysis at dry and wet conditions. Figure 5.13 shows the fracture surfaces of the dry composites after Mode II failure. The shear fracture of deformed fibres is dissipative process which requires more energy and high fracture resistance for FVE composites as shown in Figure 5.13 (a). As stated in the literature that flax fibres possess microstructural defects such as kink bands and nodes or dislocations (Hughes et al. 2007; Yan et al. 2014). At higher

magnification of flax fibres (Figure 5.13 (b)), shear kink bands led to stress concertation in the matrix and fibres resulting into poor internal adhesion. Fracture occurred mostly at the interface of fibre/matrix as revealed on the fracture surfaces by the bare fibres as a consequence of poor interfacial bonding (Suppakul and Bandyopadhyay 2002). Furthermore, micro cracks inside thermosetting matrix facilitated penetration from the moisture of flax fibres that consist mainly of cellulose and hemicellulose which is related to high moisture absorption (Fiore, Scalici, Calabrese, et al. 2016). Therefore, this weak fibre/matrix adhesion led to reduction in the interlaminar fracture toughness of FVE composites. It was observed that the capability to absorb fracture energy is higher for the hybrid composites of FBVEu than flax laminates of FVE, regardless of water immersed specimens. This means that using of basalt fibres as an external reinforcing element shows improvement of the Mode II interlaminar fracture toughness of flax laminates.

It is evident from microscopic images in Figure 5.13 (c) that the presence of basalt fibres increased the resistance to crack propagation despite the increased delamination of FBVEu composites. Hence, lower degradation in the interlaminar fracture toughness properties of FBVEu can be attributed to the properties of basalt fibres when hybridised on the outer layers of the laminates to prevent the internal layers from the degradation. This phenomenon was also reported by (Fiore et al. 2017) on the flexural and impact properties. For stitched composites, the stitch yarn contributed to an increase of interlaminar fracture toughness of $G_{IIC\ init.}$ than unstitched composites, because of the energy dissipated directly to the front of the crack tip. However, when the crack propagated until the stitch zone, the fracture energy of $G_{IIC\ prop.}$ decreased significantly compared to unstitched samples. Thus, matrix cracking occurred in the vicinity of stitch yarn which could create resin pockets and then deteriorate the in-plane properties, as seen in Figure 5.13 (d). These microscopic results commonly occurs on Mode II (3ENF) tests (Compston et al. 2001).

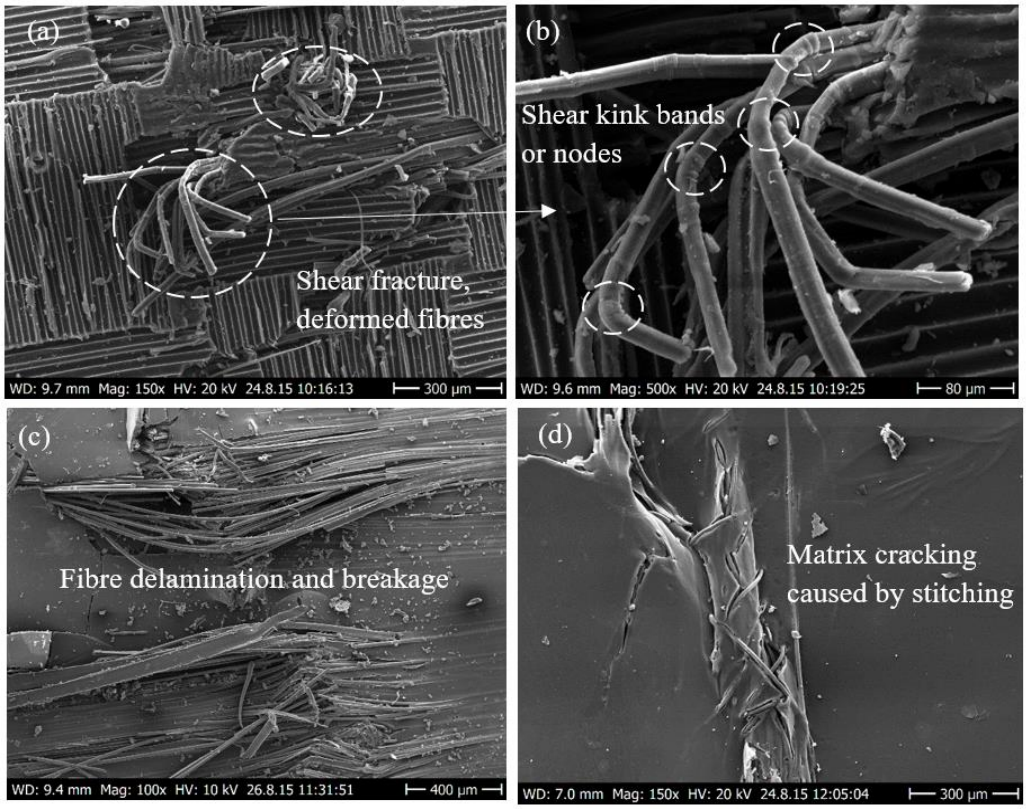


Figure 5.13 SEM images of Mode II fracture surfaces at dry specimens of (a) shear fracture which deformed fibres for FVE. (b) shear kink bands or nodes lead to failure of flax fibres. (c) fibre delamination and breakage of FBVEu. (d) matrix cracking caused by stitching for FBVEs.

SEM micrographs of shear fracture surfaces for water-immersed samples are shown in Figure 5.14. There are some differences between the images of dry and wet samples because of the degradation affected by the presence of water molecules. It shows that the fracture surfaces of water-immersed samples were more exposed than dry composites, especially those samples without hybridisation. In Figure 5.14 (a), voids and cracks on the surface of FVE composites caused penetration damage into the laminates due to the hydrophilic nature of flax fibres. This is an indication of the reduction in the fibre/matrix interfacial strength due to hydrolysis. Basalt hybridisation of FBVEu laminates improved the interlaminar fracture toughness and the water repellence properties. It can be seen that from Figure 5.14. (b), matrix degradation mostly occurred in the matrix interface rather than fibres with no any evidence of voids and cavity on the shear fracture surfaces of FBVEu and FBVEs wet composites. The fractured surface of stitched composites are shown in Figure 5.14 (c). Extensive fibre bundle fracture and fibre bridging can be clearly observed at higher magnification in Figure 5.14 (d). This finding is in agreement with our previous results on Mode I (Almansour et al. 2017).

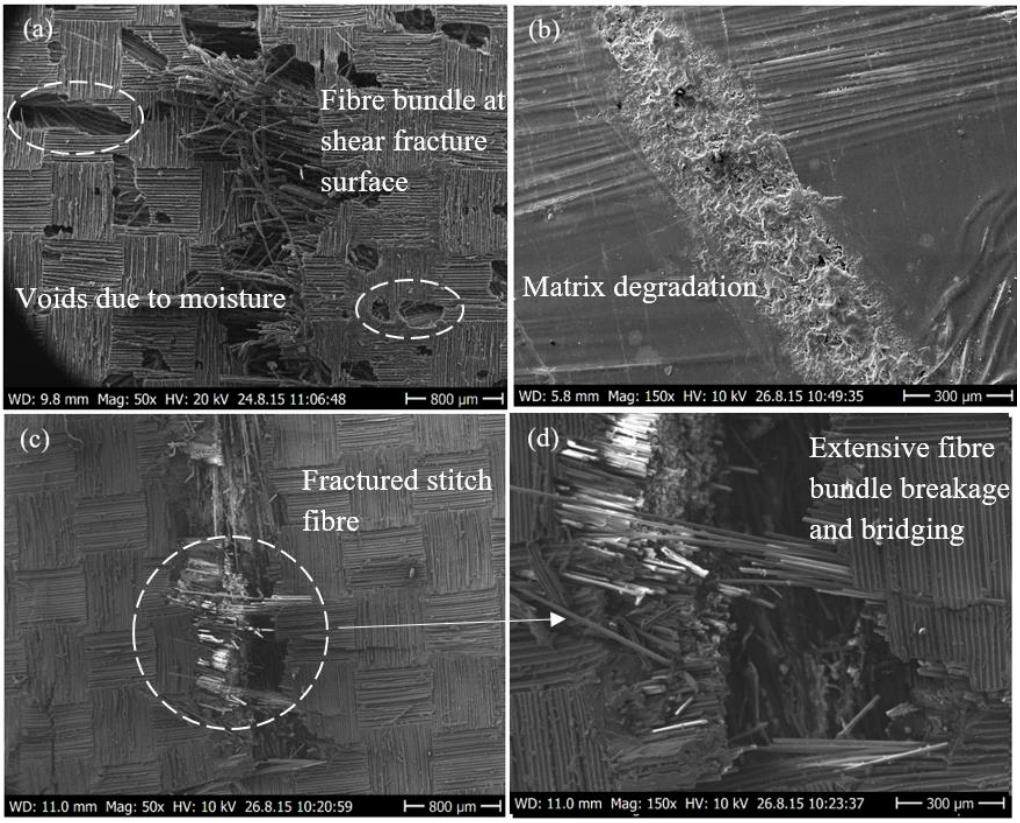


Figure 5.14 SEM images of Mode II fracture surfaces at wet specimens of (a) shear fractured fibres and voids due to moisture for FVE. (b) matrix degrdation of FBVEu. (c) fractured stitch fibres of FBVEs. (d) Extensive fibre bundle breakage and bridging of FBVEs.

6 Chapter 6: Conclusions and Recommendations for Future Work

6.1 Conclusions

A comprehensive literature review and experimental study on interlaminar fracture toughness behaviour of NFRCs have been conducted and presented clear outcomes of this PhD study as outlined in section 1.3. An in-depth understanding of fracture toughness properties of natural fibres reinforced composites enable in providing important information for engineering applications, especially in structural components. Hence, this research study plays an efficacious role in advancing materials and manufacturing technology as well as characterising their failure mechanisms.

Woven flax fibre reinforced and woven flax/basalt hybridised vinyl ester composites were successfully fabricated using vacuum assisted resin infusion technique. The influence of water absorption on the mechanical properties especially the interlaminar fracture toughness behaviour under Mode I and Mode II have been investigated using DCB and 3ENF test methods, respectively.

From the results obtained in this study of FVE, FBVEu, FBVEs and neat VE composite laminates, the following conclusions are drawn:

Mode I Interlaminar Fracture Toughness (DCB)

Mode I interlaminar fracture toughness of FVE, FBVEu and FBVEs composites were examined using MBT, CC and MCC methods to quantify the effects of water absorption on fracture toughness behaviour. The experimental findings showed that the fracture toughness values for initiation and propagation of FVE wet composites without hybridisation were decreased compared to dry samples. However, the fracture toughness for propagation of FBVEu water-aged composites was increased, with decreased crack initiation because of the basalt hybridisation that provided a better shield to the swelled flax fibres. The reason for a decrease in the crack initiation is due to high moisture absorption by flax fibres leading to a weak fibre-matrix interface. The resistance curve (R-curve) of FVE and FBVEu wet composites showed that the crack growth length is shorter than the dry samples. The modified beam theory (MBT) has the lowest and most conservative value for both initiation and propagation toughness for all specimens.

Dry and wet composites of FBVEs have the lowest crack length and growth behaviour from stable propagation to stick-slip instability. It was found that even though basalt hybridisation improved the delamination strength, because of high crack closure loads exerted by the stitches, the interlaminar fracture properties were reduced. Both FVE and FBVE composites showed saturation after 960 hours of ageing time. Moisture absorption and the diffusion coefficient of hybrid composites showed less absorption compared to over non-hybrid composites by approximately 50% and 44%, respectively. The fracture mechanisms showed energy dissipation through matrix deformation, fibre pull-out, fibre debonding, and fibre breakage. The analysed results of this study revealed that using basalt fibre as external layers onto flax reinforced composites improved the interlaminar fracture toughness. This shows that basalt fibre hybridisation can be used as an effective method to enhance the mechanical properties, durability and the moisture resistance of natural fibre composites.

Mode II Interlaminar Fracture Toughness (3ENF)

The present study investigated the effects of water absorption on the interlaminar fracture toughness behaviour of woven flax and flax/basalt reinforced vinyl ester composite laminates. The Mode II experimental works were performed under 3ENF tests. Evaluation of the fracture energy initiation and propagation as well as the crack length under dry and wet conditions using CCM and SBT methods were undertaken.

The results showed that basalt fibre hybridised composites improved the interlaminar fracture toughness for initiation and propagation when compared to FVE dry specimens. Furthermore, the crack length of FBVEu dry composites exhibited high resistance to delamination due to the external of basalt fibre layers and showed an increased crack propagation resistance. It was evidenced that in stitched composites of FBVEs, stitches yarn effectively arrested the delamination and contributed to increase the fracture energy of $G_{IIC\ init}$. by 62% but the interlaminar fracture toughness of $G_{IIC\ prop.}$ decreased by 36%. The fracture energy of $G_{IIC\ init.}$ for neat VE increased about 52% with reinforcement of flax fibre composites. The SBT method showed lower values in the fracture energy than CCM method at dry conditions. It was observed that flax fibre composites without basalt hybridisation absorbed higher moisture uptake than FBVEu laminates with percentage of 34%, and FVE wet samples absorbed higher energy before fracture than FVE dry composites. However, with basalt hybridisation of FBVEu wet specimen absorbed lower energy than FBVEu dry composites. This is attributed to the

external skin layers of basalt fibres, which exhibited a greater resistance to water absorption and prevented the inner core of flax fibres from the degradation.

6.2 Recommendations for Future Work

On the basis of the test results and discussion presented, the following recommendations are proposed for future work:

1. The overall performance of flax fibre reinforced polymer composites is suggested to investigate by considering other intralaminar fracture toughness tests, such as compact tension (CT) and single edge notched bending (SENB) tests. Moreover, Mode II four-point bend end-notched flexure, Mixed Mode (called Mode III) and fatigue tests are suggested to further carry out.
2. Investigation of fracture toughness behaviour of natural fibre reinforced composites at different loading rates (static and dynamic) can also be carried out to further understand the effect of loading rates.
3. It should be taken into account various types of modelling complex geometries that cannot easily be tested or represented by simpler methods. Thus, finite element analysis (FEA) proposed to solve the basic spring equation for segmented regions of a larger body. Modelled stresses can be compared to material strengths to predict failure.
4. In addition, it is recommended to use other types of hybrid laminates configurations.

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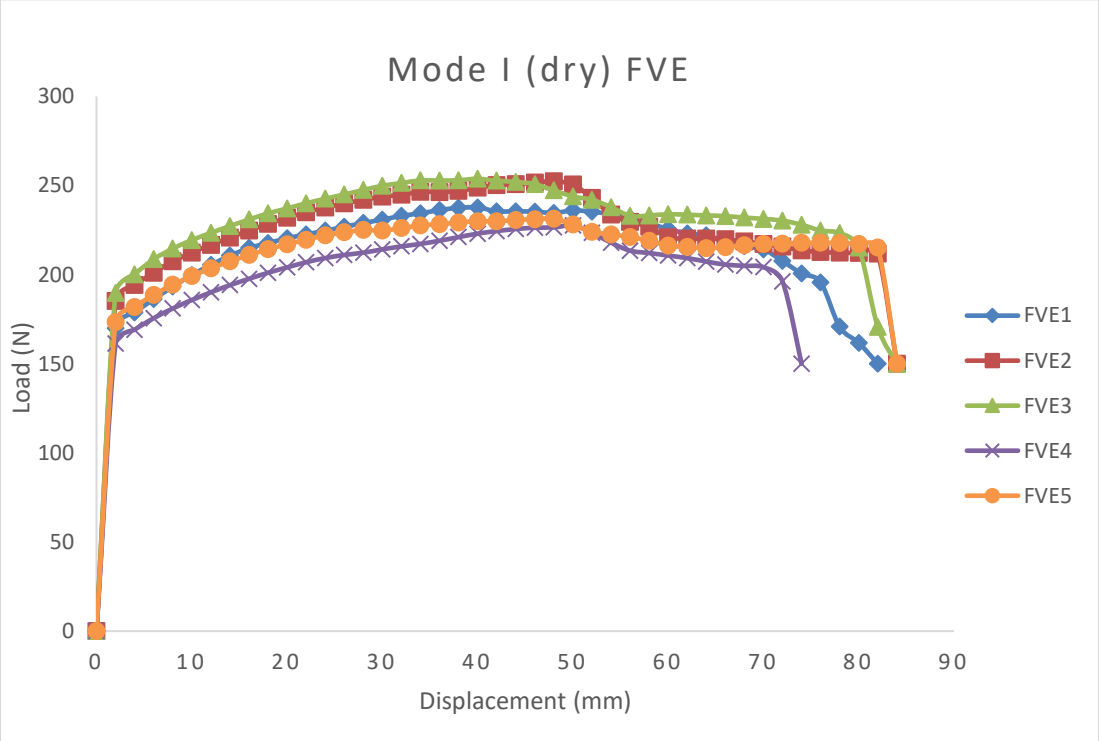
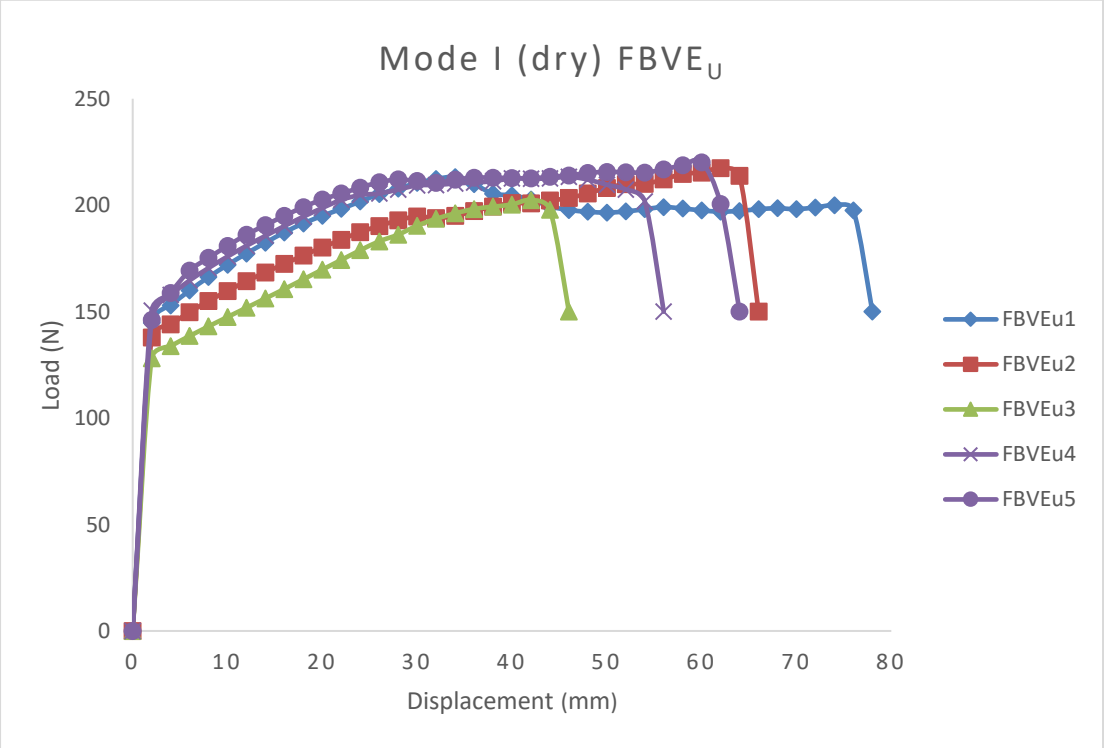
Appendices

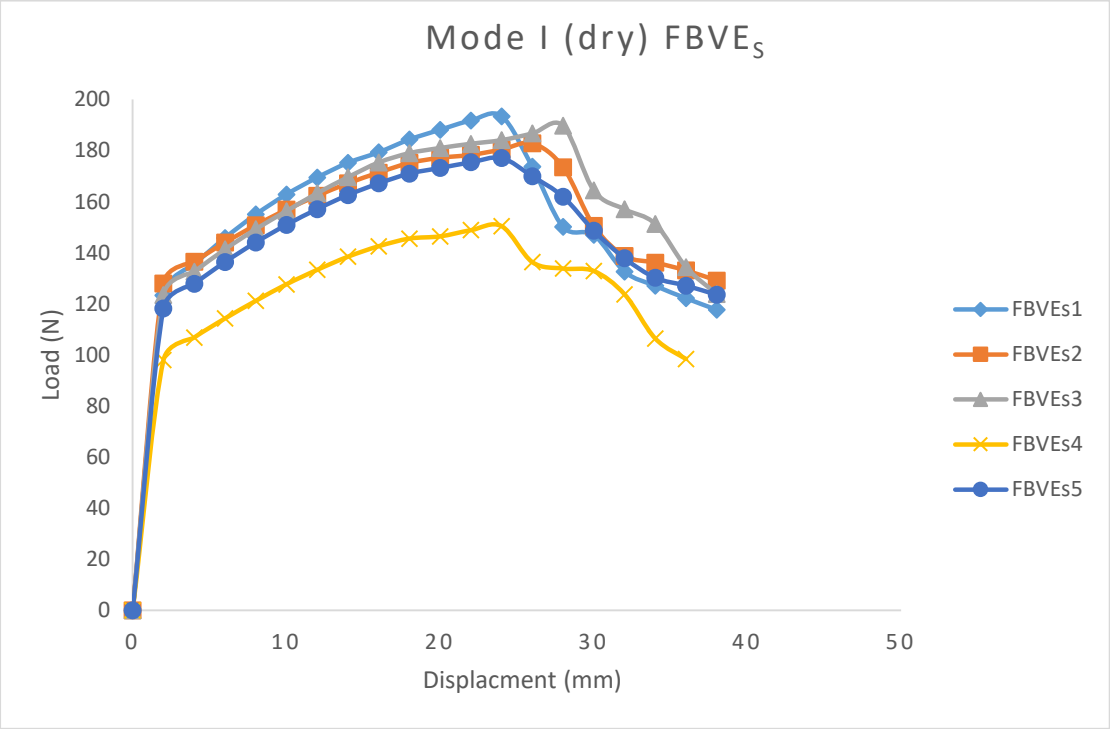
Appendix A Plan of PhD project

	1st Year				2nd Year				3rd Year				4th Year	
Date Plan	Feb-Apr 2014	May-Jul 2014	Aug-Oct 2014	Nov-Jan 2014/2015	Feb-Apr 2015	May-Jul 2015	Aug-Oct 2015	Nov-Jan 2015/2016	Feb-Apr 2016	May-Jul 2016	Aug-Oct 2016	Nov-Jan 2016/2017	Feb-Apr 2017	May-Jul 2017
Review of literature														
Materials selection, mould design, fabrication of composite laminates														
Determination and finalization of geometry and design for mode I and mode II specimens														
Major review														
Specimens; preparation of different sample														
Conduct of fracture toughness testing, Characterisation of all tests					Mode I (DCB) Mode II (3ENF)	Water absorption for both modes	SEM,C-Scan TGA,DSC							
Analysing results														
Annual Review														
Publication of Papers														
PhD Thesis writing														
Doctoral Viva voce examination														

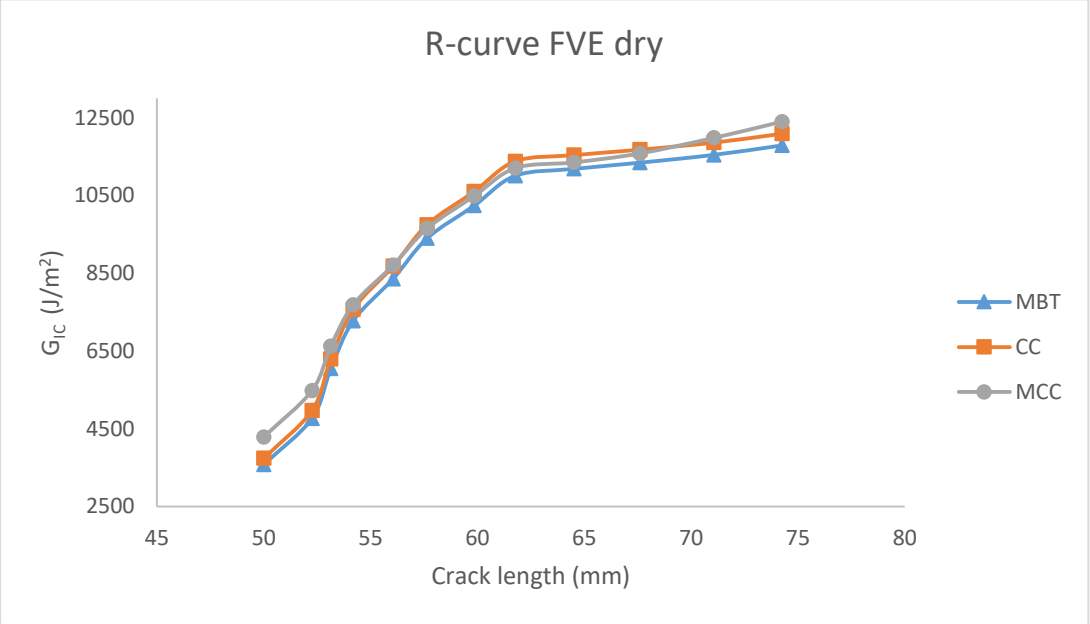
Appendix B Load-displacement curves of dry samples Mode I for FVE, FBVEu and FBVEs laminates

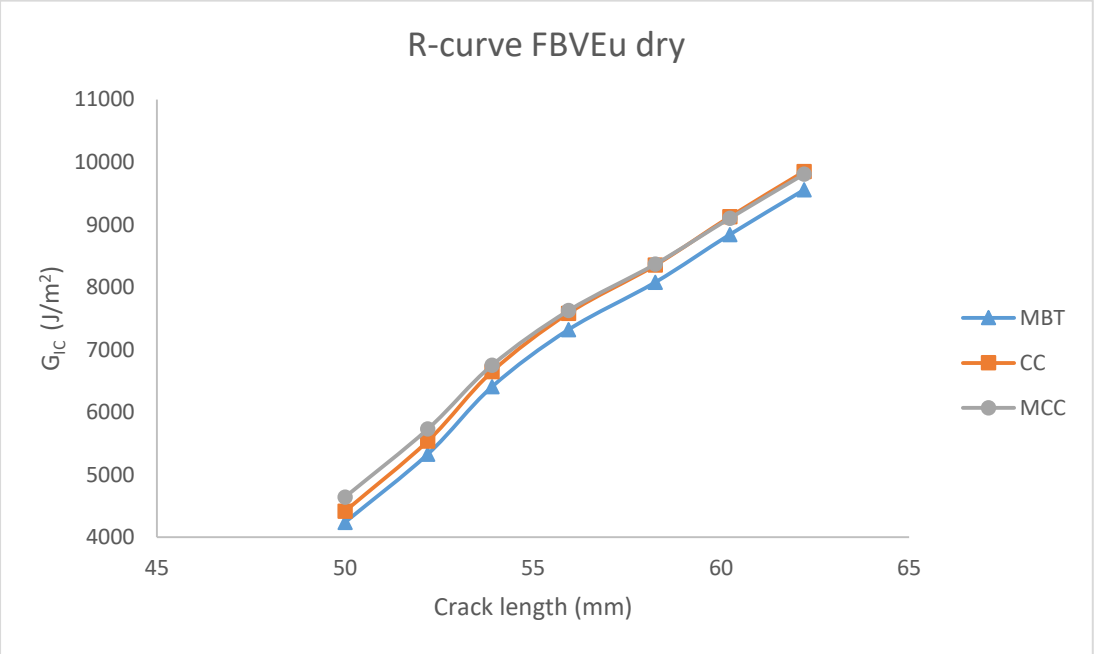


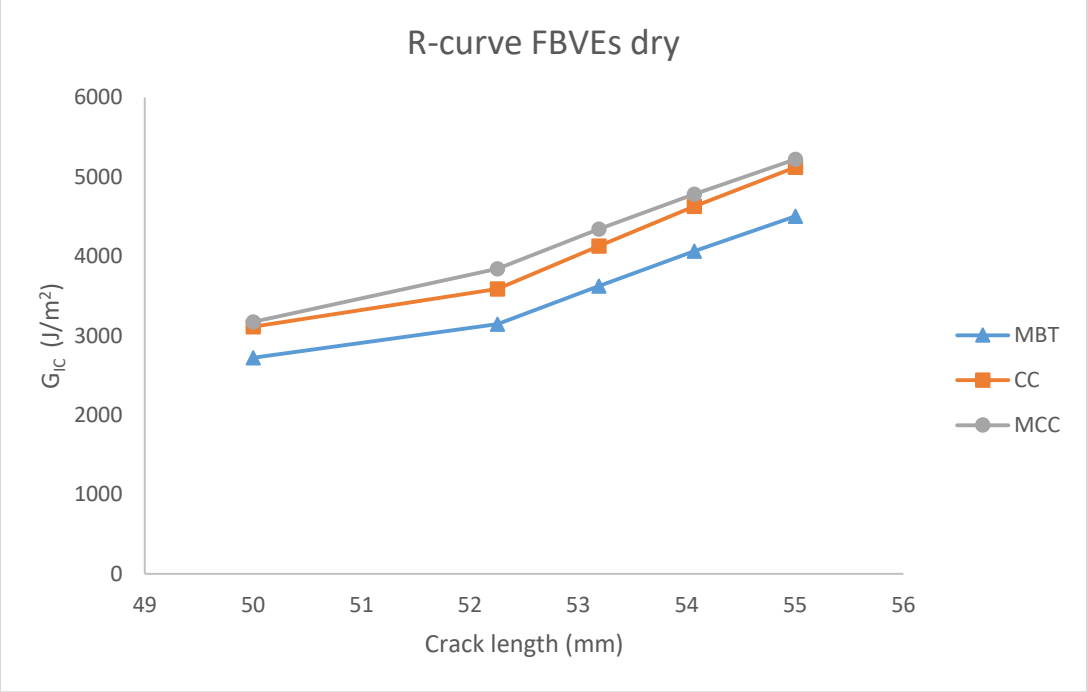



Mode I (dry) FBVE$_S$
Load (N)
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
Displacment (mm)
FBVEs1
FBVEs2
FBVEs3
FBVEs4
FBVEs5

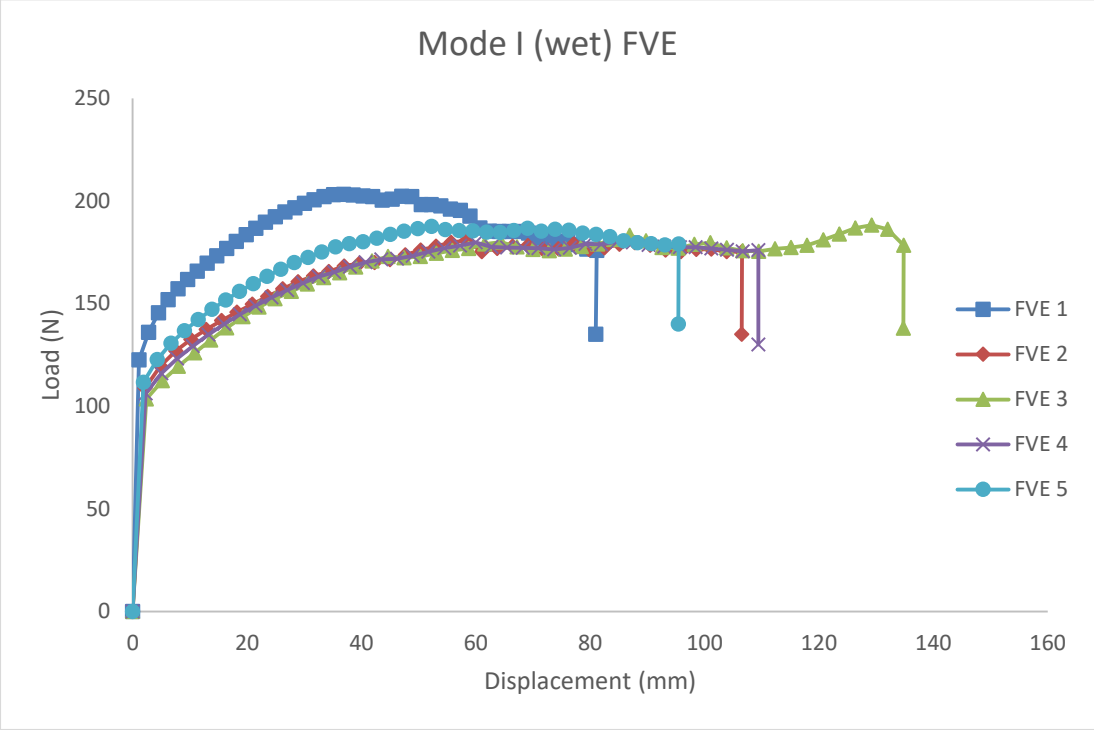
Appendix C Resistance curves (R-curve) for Mode I (dry) Samples of FVE, FBVEu and FBVEs laminates

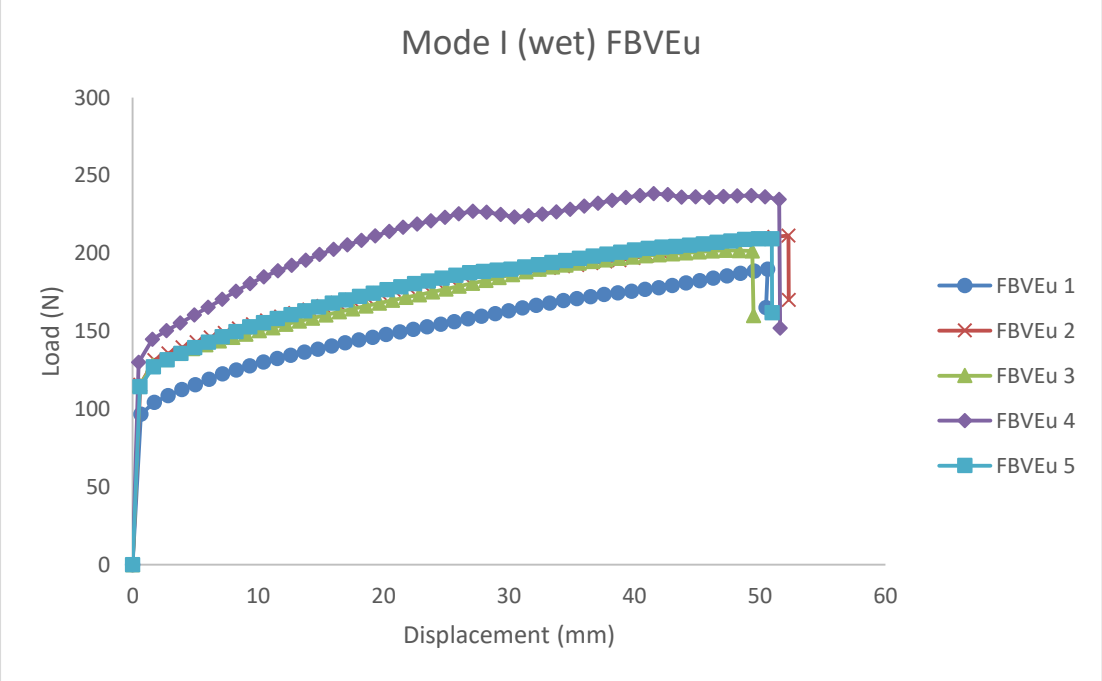


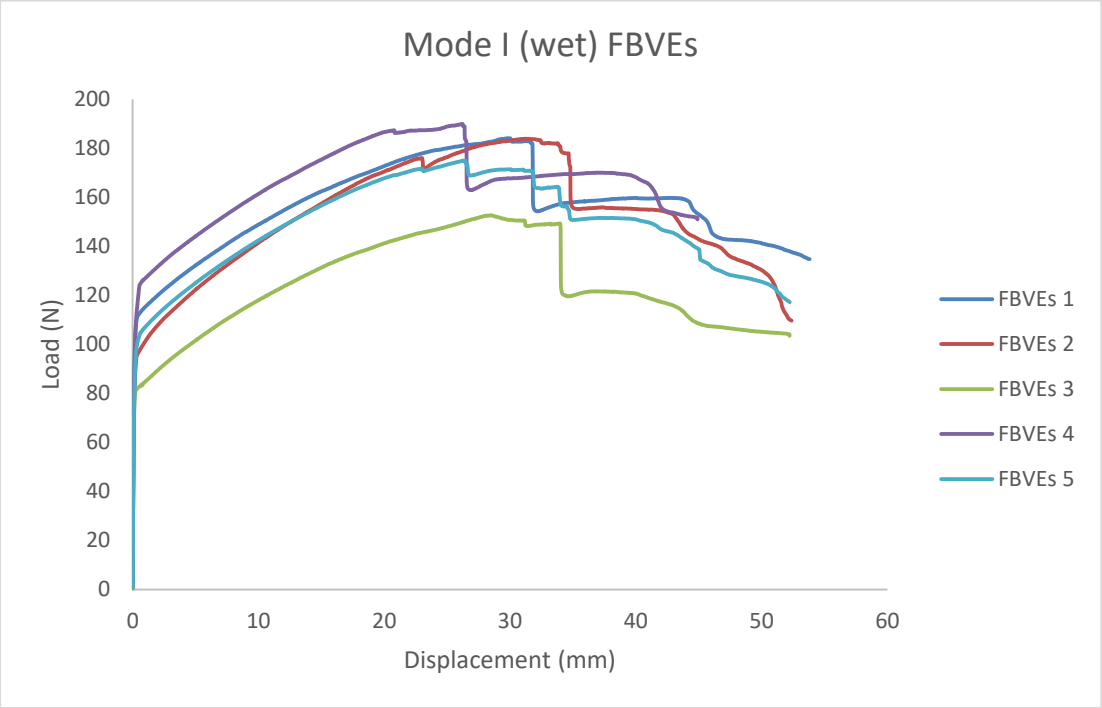



R-curve FBVEs dry
6000
5000
4000
3000
2000
1000
0
G_{IC} (J/m²)
49
50
51
52
53
54
55
56
Crack length (mm)
MBT
CC
MCC

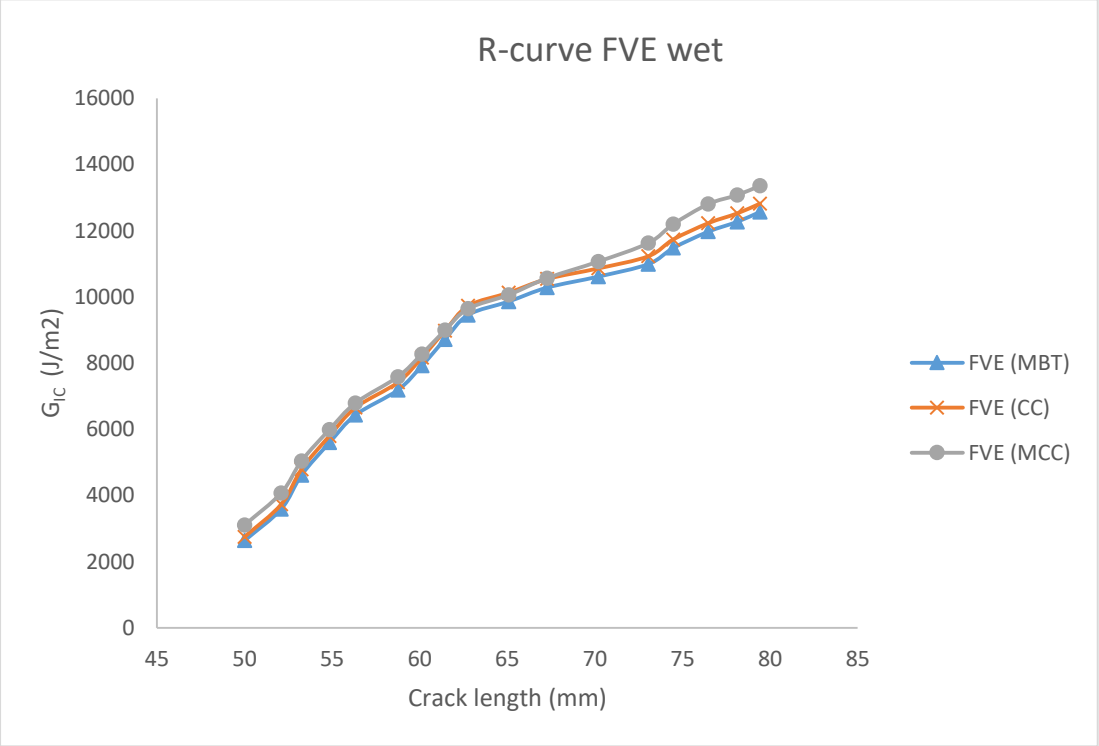
Appendix D Load-displacement curves of wet samples Mode I for FVE, FBVEu and FBVEs laminates

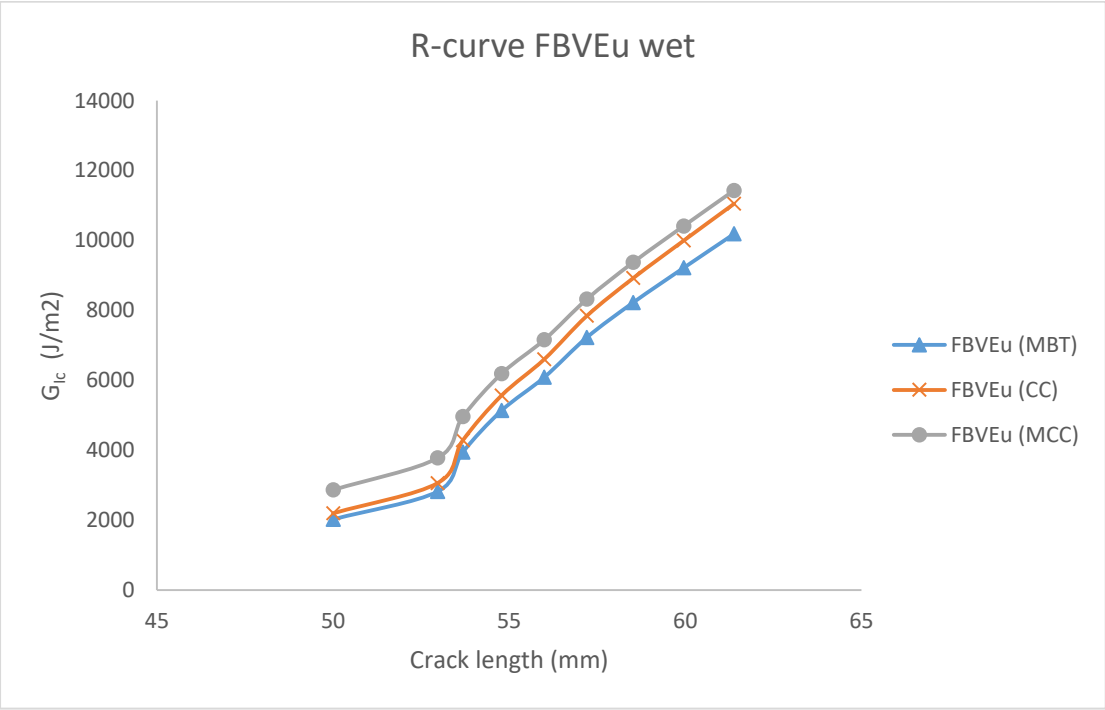


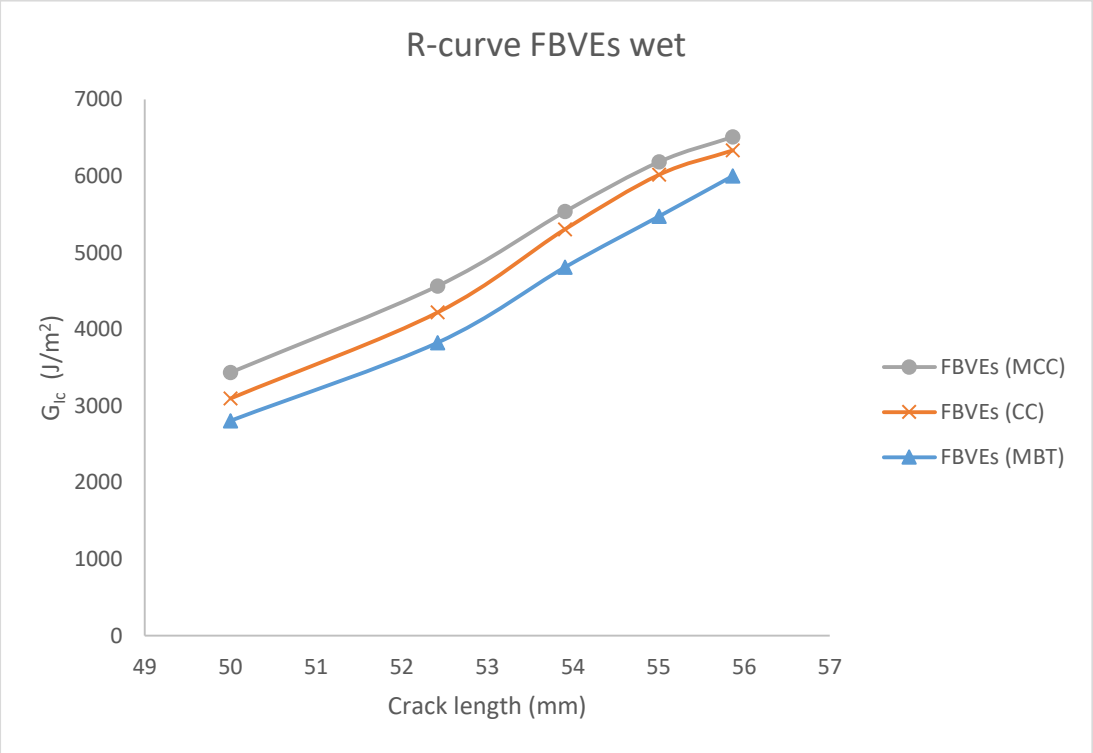



Mode I (wet) FBVEs
Load (N)
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
Displacement (mm)
FBVEs 1
FBVEs 2
FBVEs 3
FBVEs 4
FBVEs 5

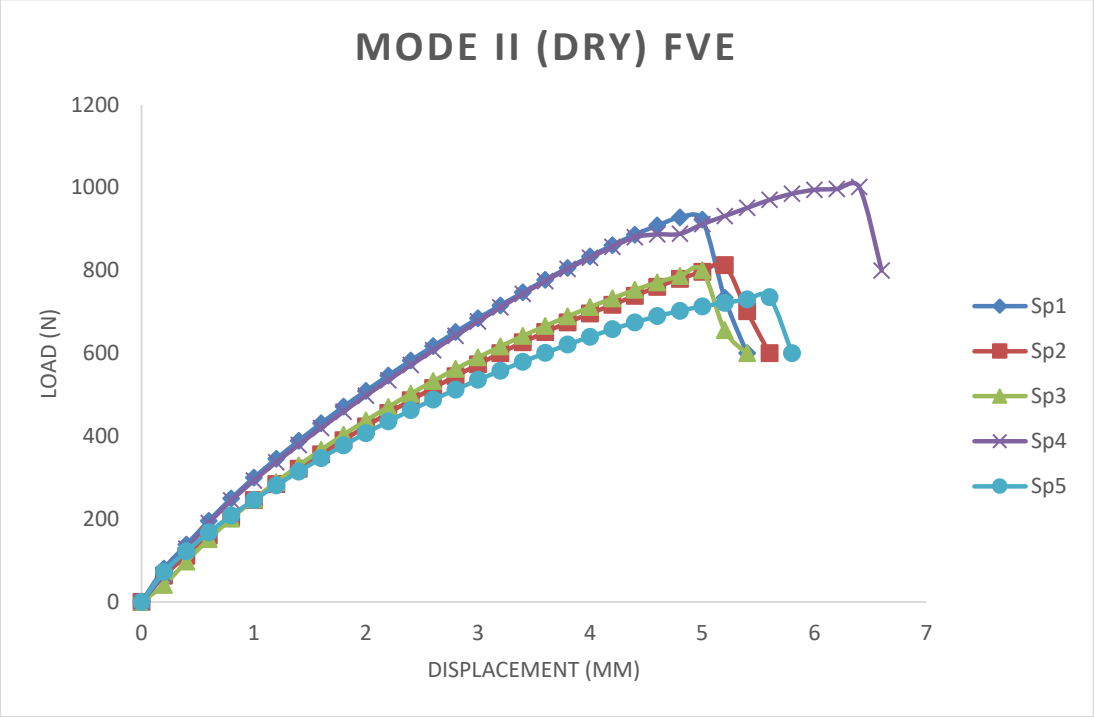
Appendix E Resistance curves (R-curve) for Mode I (wet) Samples of FVE, FBVEu and FBVEs laminates

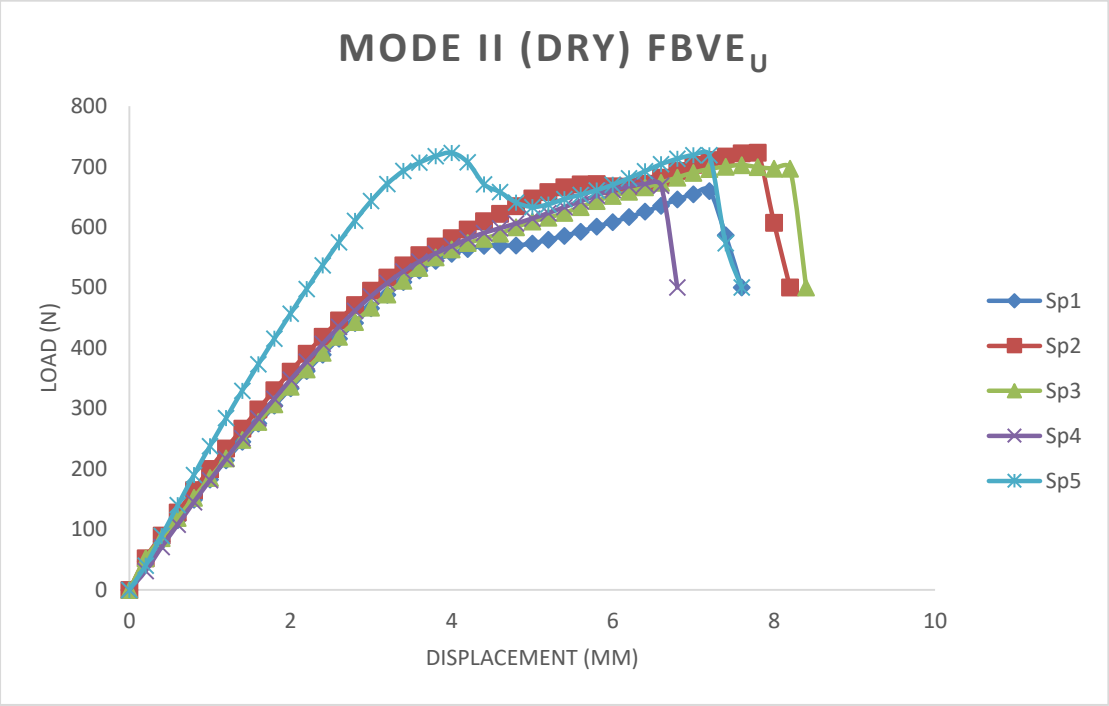


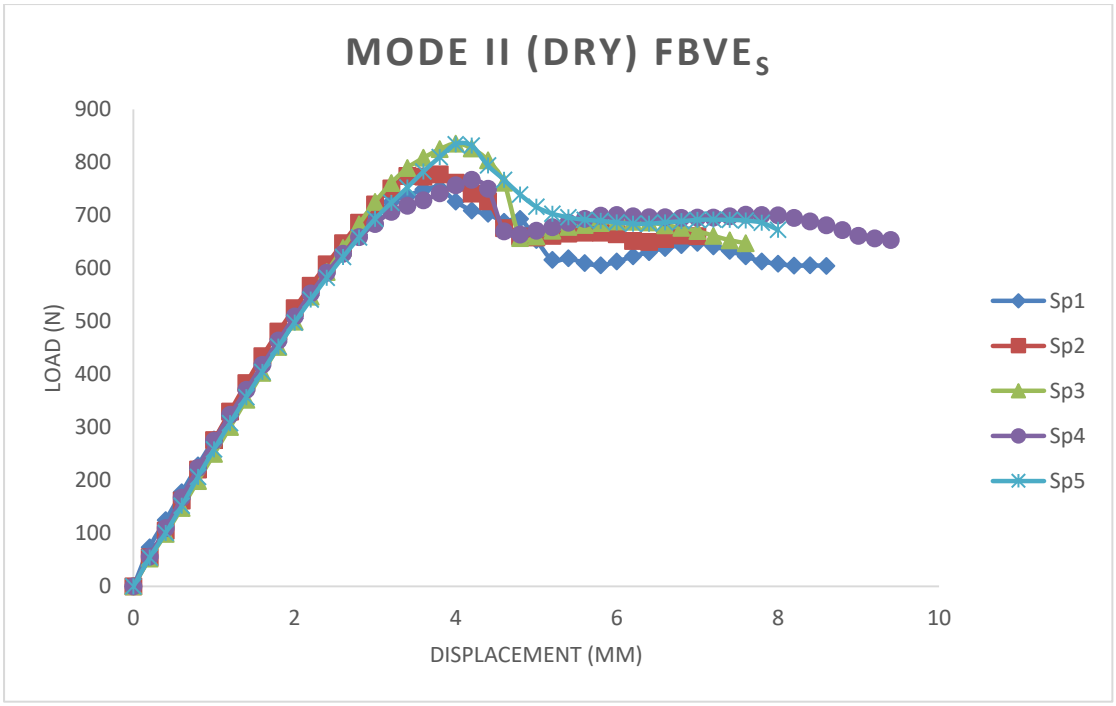


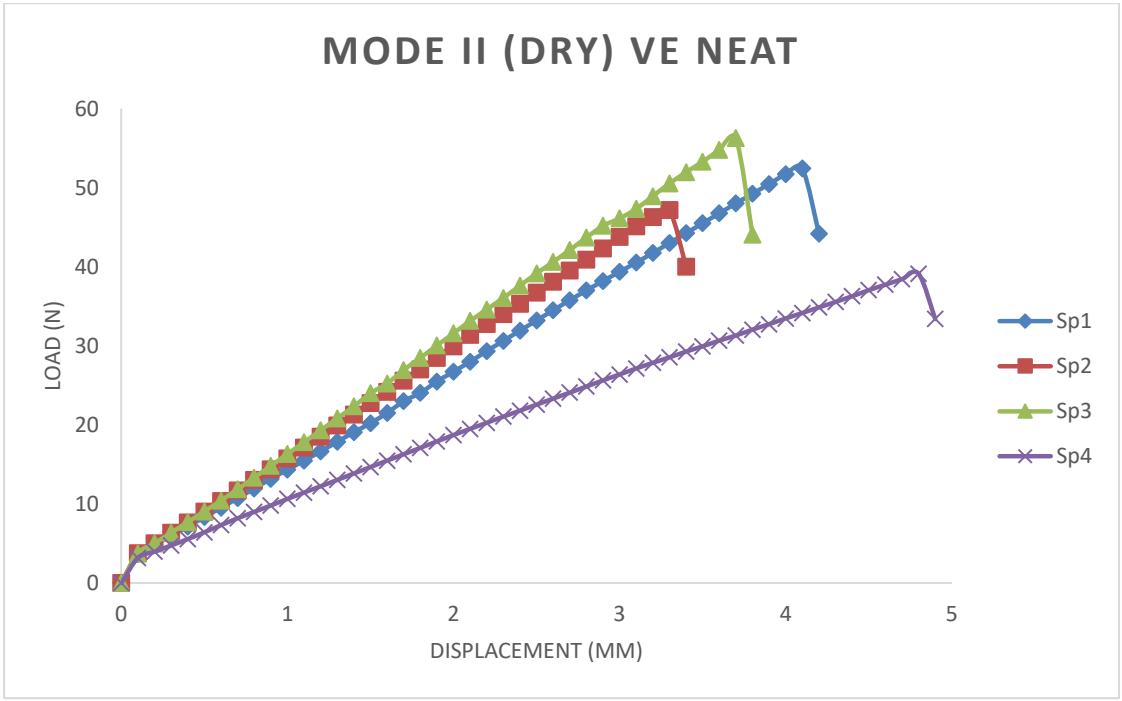

R-curve FBVEs wet
7000
6000
5000
4000
3000
2000
1000
0
G_{Ic} (J/m²)
49
50
51
52
53
54
55
56
57
Crack length (mm)
FBVEs (MCC)
FBVEs (CC)
FBVEs (MBT)

Appendix F Load-displacement curves of dry samples Mode II for FVE, FBVEu, FBVEs and neat VE laminates

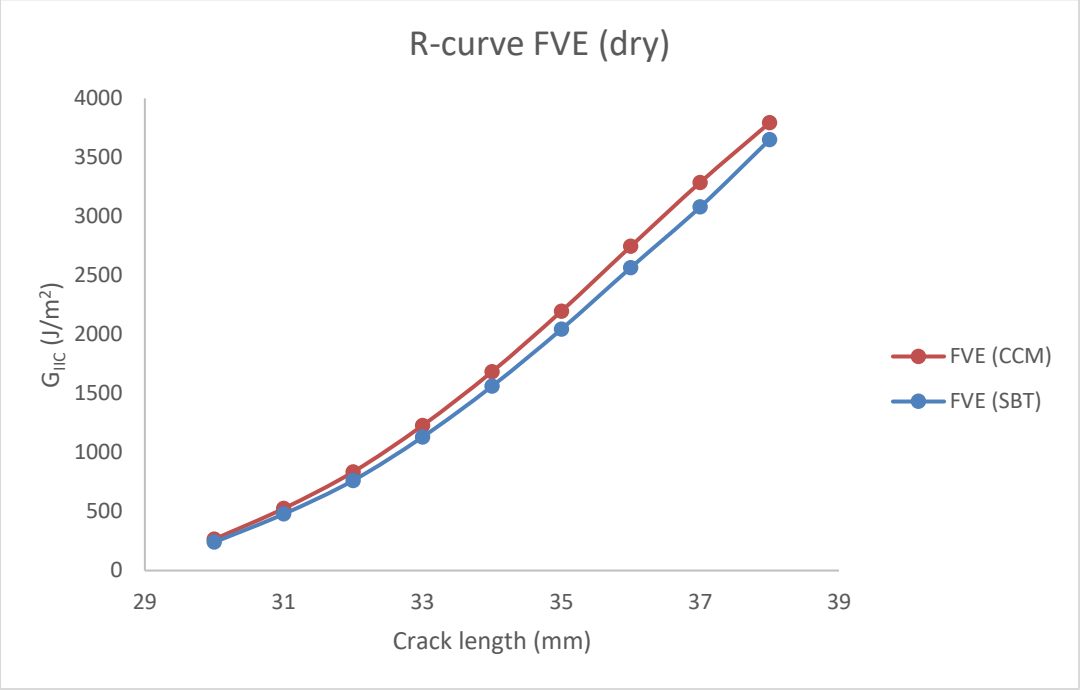


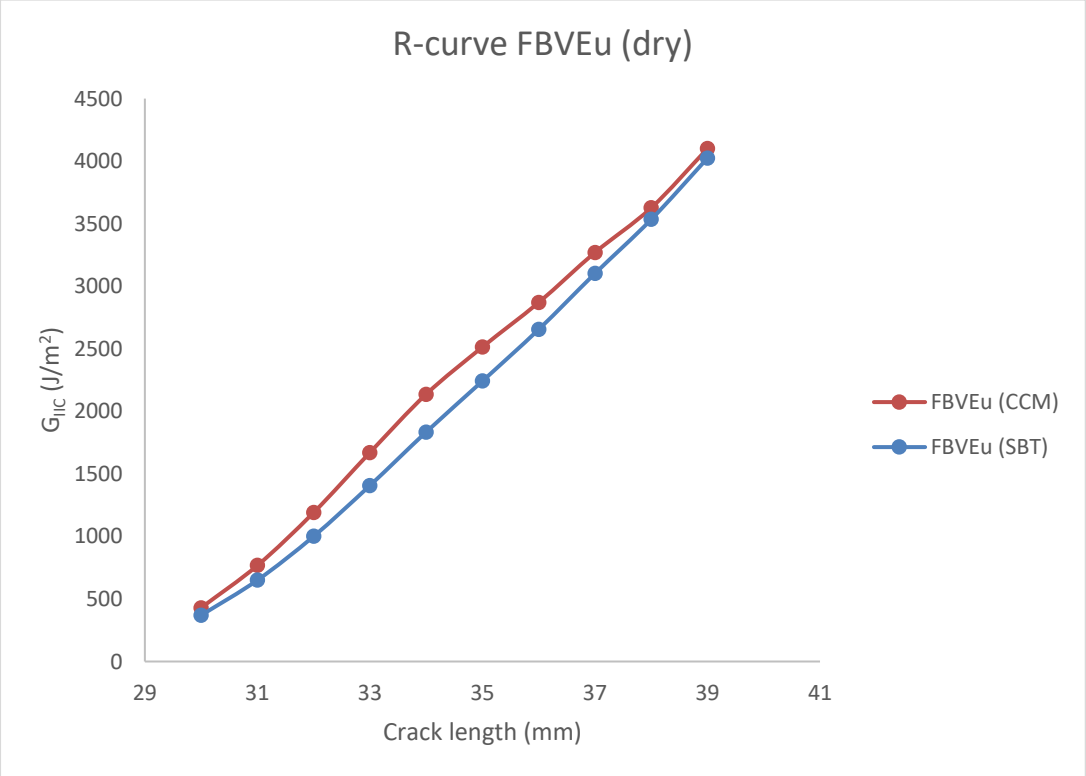


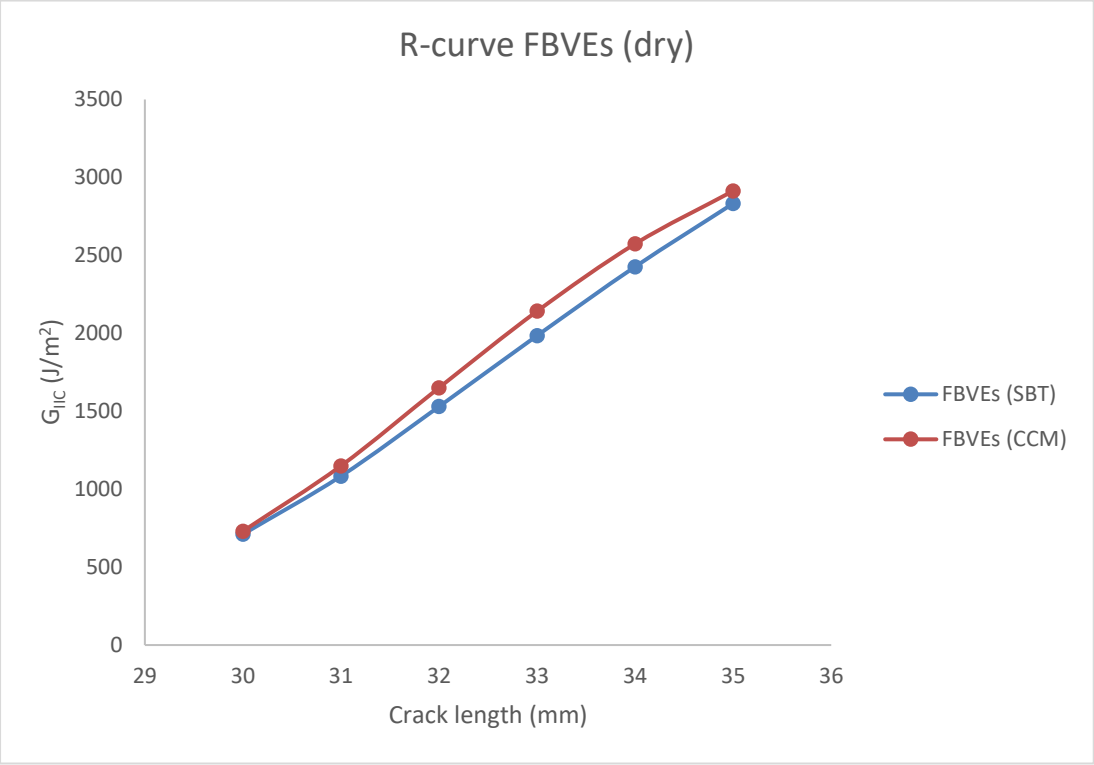

MODE II (DRY) FBVE$_S$
900
800
700
600
500
400
300
200
100
0
LOAD (N)
0
2
4
6
8
10
DISPLACEMENT (MM)
Sp1
Sp2
Sp3
Sp4
Sp5


MODE II (DRY) VE NEAT
60
50
40
30
20
10
0
LOAD (N)
0
1
2
3
4
5
DISPLACEMENT (MM)
Sp1
Sp2
Sp3
Sp4

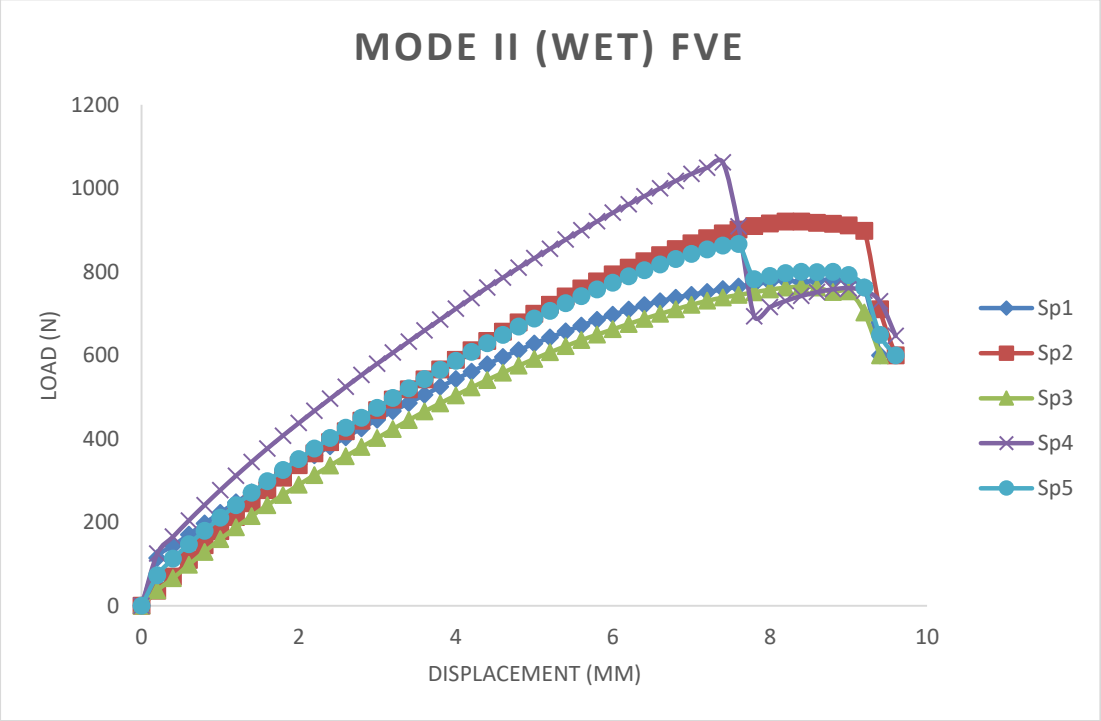
Appendix G Resistance curves (R-curve) for Mode II (dry) Samples of FVE, FBVEu and FBVEs laminates

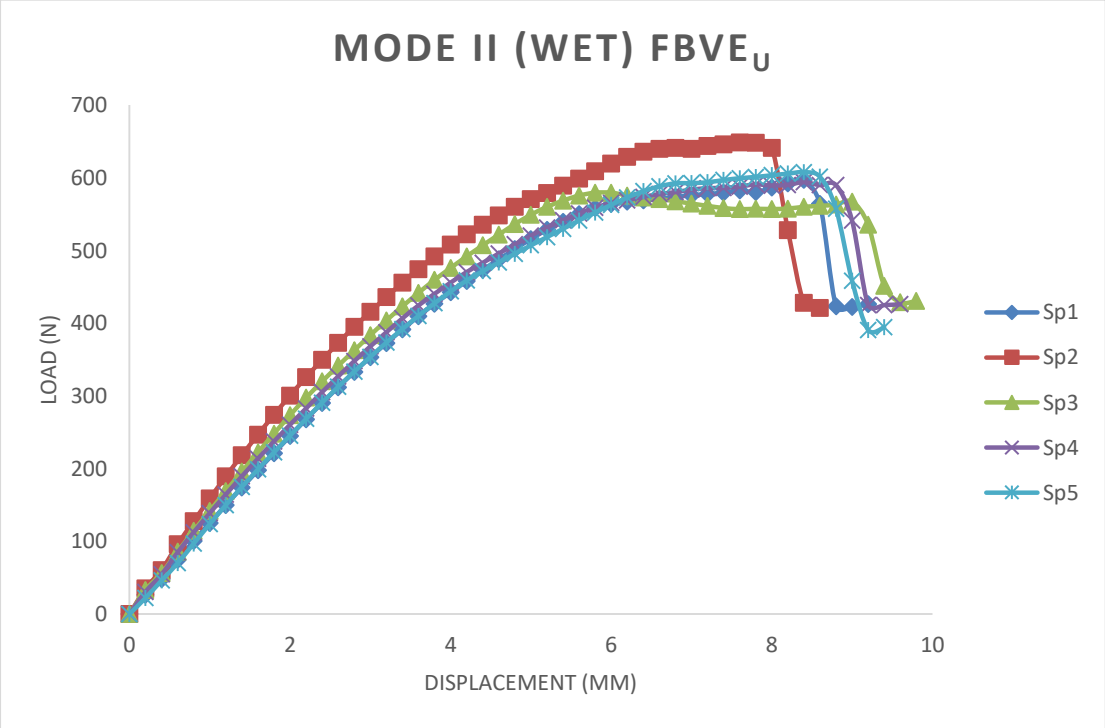


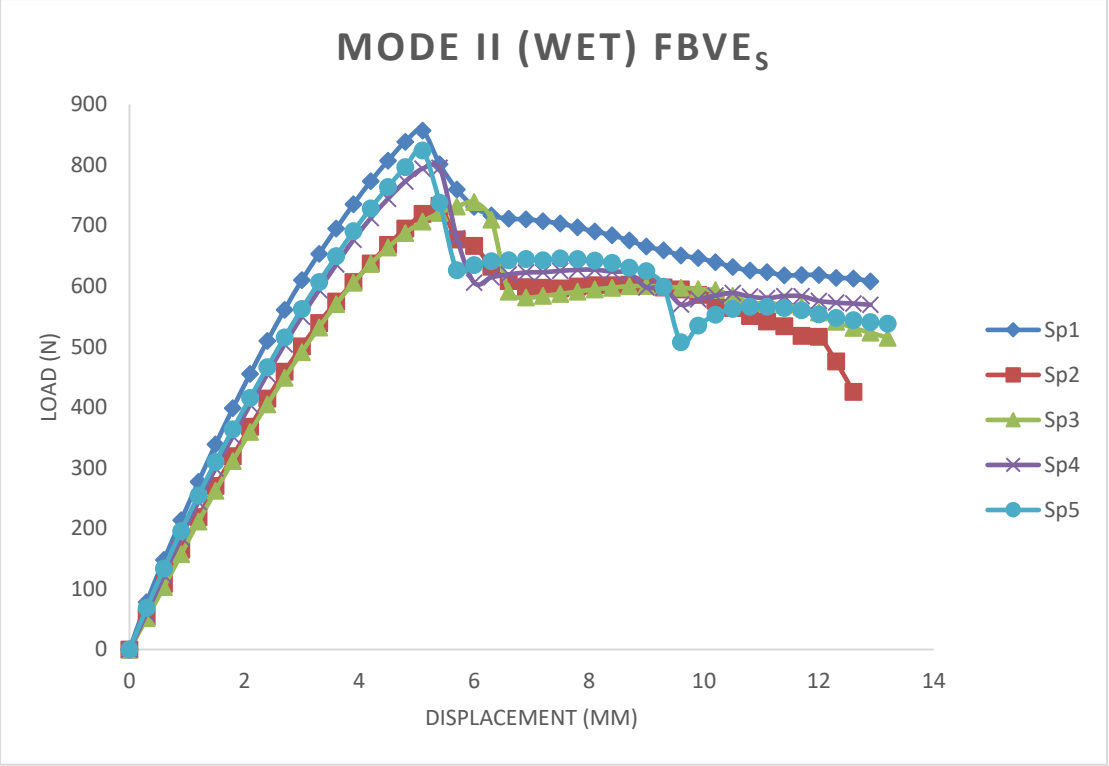


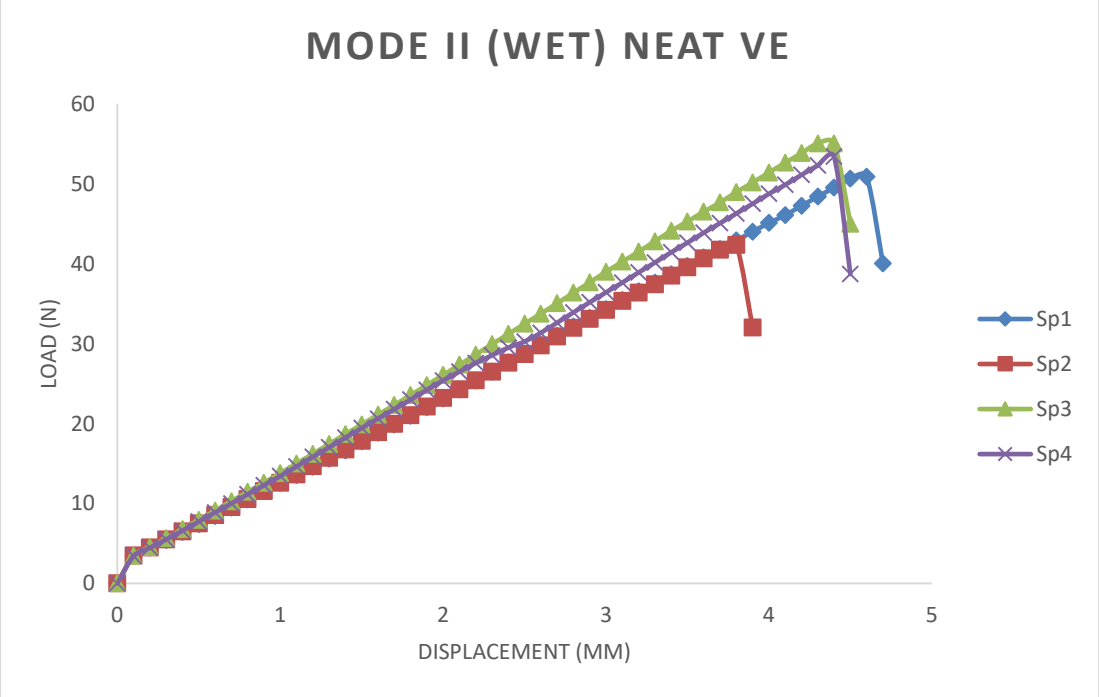

R-curve FBVEs (dry)
3500
3000
2500
2000
1500
1000
500
0
G_{IIC} (J/m^2)
29
30
31
32
33
34
35
36
Crack length (mm)
FBVEs (SBT)
FBVEs (CCM)

Appendix H Load-displacement curves of wet samples Mode II for FVE, FBVEu, FBVEs and neat VE laminates

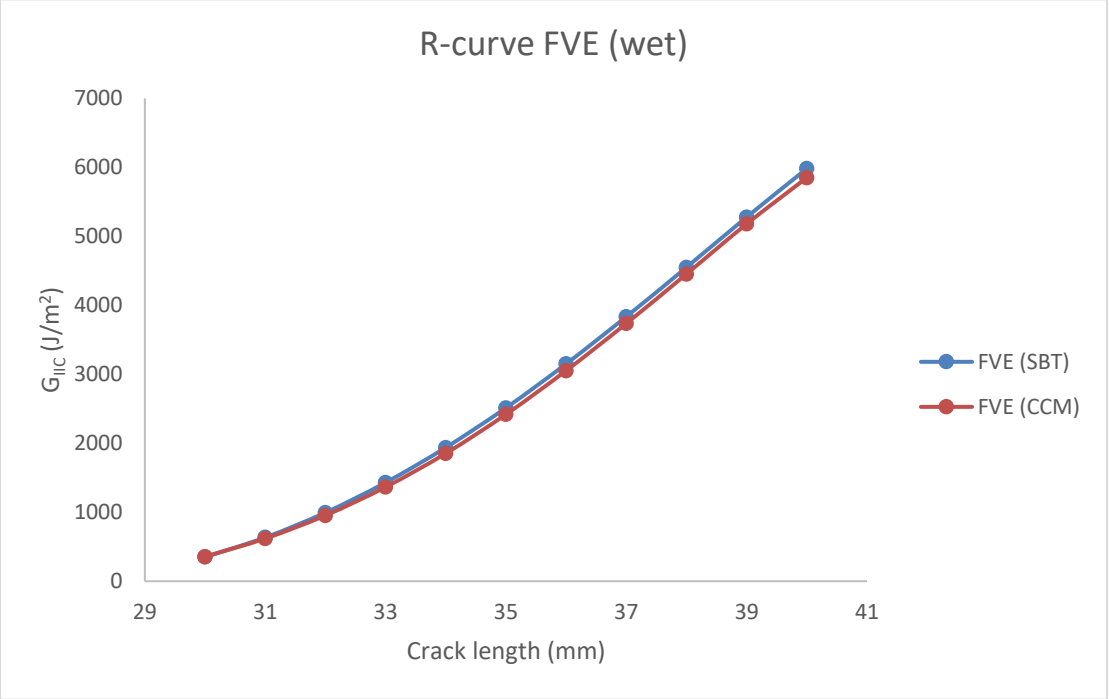


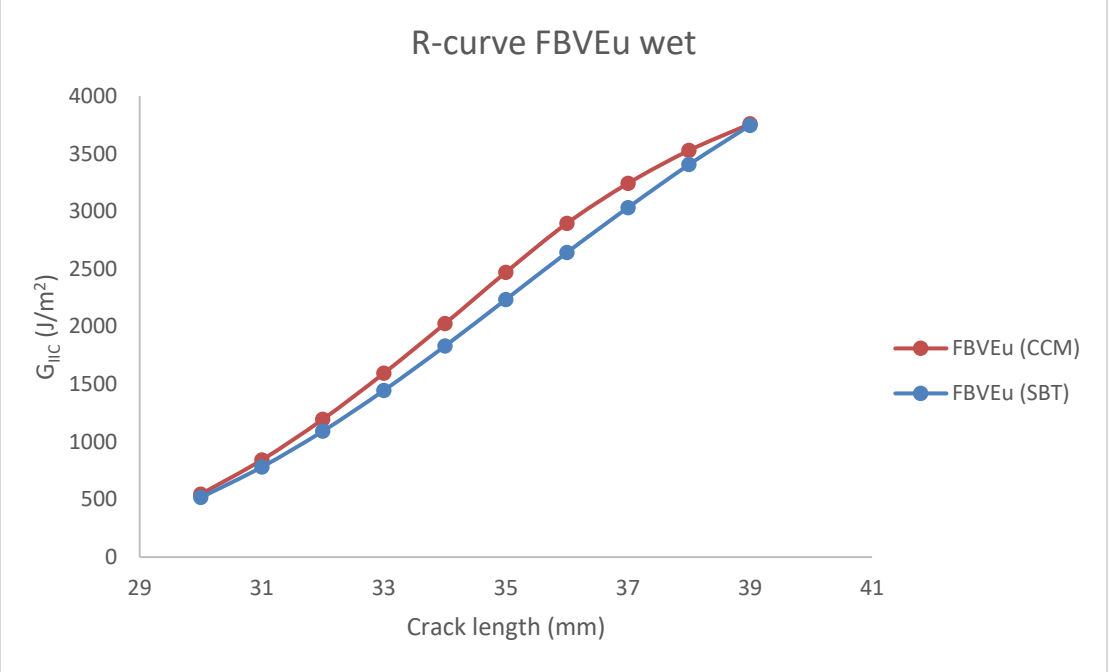


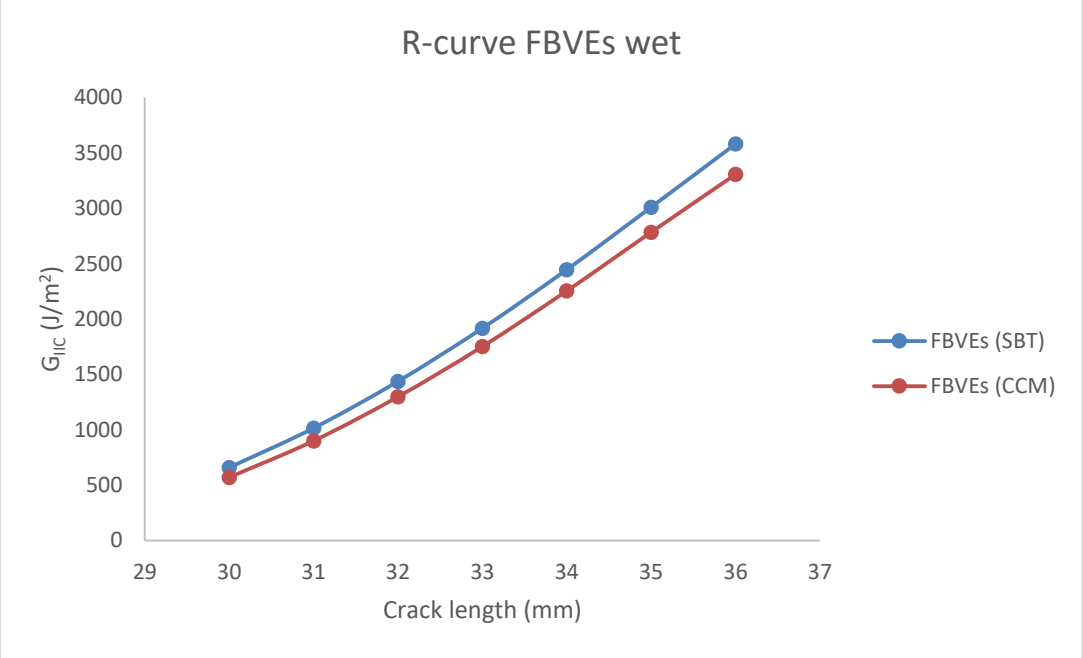

MODE II (WET) FBVE$_S$
LOAD (N)
900
800
700
600
500
400
300
200
100
0
0
2
4
6
8
10
12
14
DISPLACEMENT (MM)
Sp1
Sp2
Sp3
Sp4
Sp5


MODE II (WET) NEAT VE
LOAD (N)
60
50
40
30
20
10
0
0
1
2
3
4
5
DISPLACEMENT (MM)
Sp1
Sp2
Sp3
Sp4

Appendix I Resistance curves (R-curve) for Mode II (wet) Samples of FVE, FBVEu and FBVEs laminates






R-curve FBVEs wet
4000
3500
3000
2500
2000
1500
1000
500
0
G_{IIC} (J/m^2)
29
30
31
32
33
34
35
36
37
Crack length (mm)
FBVEs (SBT)
FBVEs (CCM)

FORM UPR16

Research Ethics Review Checklist

University of Portsmouth

Please include this completed form as an appendix to your thesis (see the Postgraduate Research Student Handbook for more information

Postgraduate Research Student (PGRS) Information							
				Student ID:	626085		
PGRS Name:	Fahad Abdulaziz Almansour						
Department:	School of Engineering		First Supervisor:	Dr.Hom Nath Dhakal			
Start Date: (or progression date for Prof Doc students)	01/02/2014						
Study Mode and Route:	Part-time	☐	MPhil	☐	MD	☐	
	Full-time	☒	PhD	☒	Professional Doctorate	☐	

Title of Thesis:	Interlaminar Fracture Toughness Behaviour of Flax/Basalt Reinforced Vinyl Ester Hybrid Composites
Thesis Word Count: (excluding ancillary data)	45926

If you are unsure about any of the following, please contact the local representative on your Faculty Ethics Committee for advice. Please note that it is your responsibility to follow the University's Ethics Policy and any relevant University, academic or professional guidelines in the conduct of your study

Although the Ethics Committee may have given your study a favourable opinion, the final responsibility for the ethical conduct of this work lies with the researcher(s).

UKRIO Finished Research Checklist:
(If you would like to know more about the checklist, please see your Faculty or Departmental Ethics Committee rep or see the online version of the full checklist at: http://www.ukrio.org/what-we-do/code-of-practice-for-research/)

a)	Have all of your research and findings been reported accurately, honestly and within a reasonable time frame?	YES ☒ NO ☐
b)	Have all contributions to knowledge been acknowledged?	YES ☒ NO ☐
c)	Have you complied with all agreements relating to intellectual property, publication and authorship?	YES ☒ NO ☐
d)	Has your research data been retained in a secure and accessible form and will it remain so for the required duration?	YES ☒ NO ☐
e)	Does your research comply with all legal, ethical, and contractual requirements?	YES ☒ NO ☐

Candidate Statement:

I have considered the ethical dimensions of the above named research project, and have successfully obtained the necessary ethical approval(s)

Ethical review number(s) from Faculty Ethics Committee (or from NRES/SCREC): 144B-0428-15A6-5F88-E72-8D83-2A16-450A

If you have *not* submitted your work for ethical review, and/or you have answered 'No' to one or more of questions a) to e), please explain below why this is so.