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Mechanical Performance of Industrial Hemp Fibre Reinforced Polylactide and Unsaturated Polyester Composites

A thesis submitted in
partial fulfilment of the requirements for the degree of Doctor of Philosophy
in Materials and Process Engineering

by

Moyeenuddin Ahmad Sawpan



THE UNIVERSITY OF
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Te Whare Wānanga o Waikato

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Abstract

This study investigated the effect of fibre content, fibre treatment and fibre/matrix interfacial strength on the mechanical properties of industrial hemp fibre reinforced polylactide (PLA) and unsaturated polyester (UPE) composites.

Surface treatment of hemp fibres was investigated as a means of improving the fibre/matrix interfacial strength and mechanical properties of hemp fibre reinforced PLA and UPE composites. The fibres were treated with sodium hydroxide, acetic anhydride, maleic anhydride and silane. A combined treatment, sodium hydroxide and silane, was also carried out. The average tensile strength of sodium hydroxide treated fibres (ALK) slightly increased compared with that of untreated fibres, which was believed to be as a result of increased cellulose crystallinity. In contrast, the average tensile strength of acetic anhydride, maleic anhydride and silane treated fibres slightly decreased compared with that of untreated fibres, which was believed to be as a result of decreased cellulose crystallinity. In the case of combined treatment with sodium hydroxide and silane, the average tensile strength of the fibres (ALKSIL) slightly decreased compared with that of alkali treated fibres (ALK), which was also thought to be as a result of decreased cellulose crystallinity. The average Young's modulus and thermal stability of all treated fibres increased compared with untreated fibres. This was considered to be as a result of densification of fibre cell walls due to the removal of non-cellulosic components during treatment. It was also thought that the grafted molecules in cellulose chains of the acetic anhydride, maleic anhydride and silane treated fibres enhanced resistance to thermal degradation.

The interfacial shear strength (IFSS) of PLA/hemp fibre samples increased after treatment, except in the case of maleic anhydride treatment. The increase in IFSS could be due to better bonding of PLA with cellulose of treated fibres (except for the maleic anhydride treatment) as a result of removal of non-cellulosic components evidenced by increased PLA transcrystallinity. The highest IFSS was 11.41 MPa which was obtained for PLA/ALK samples. IFSS of UPE/hemp fibre samples increased for all treated fibres. This could be due to the improvement of chemical bonding between the treated fibres and the

UPE as supported by FT-IR results. The highest IFSS (20.3 MPa) was found for the UPE/ALKSIL samples.

Short hemp fibre reinforced PLA composites were fabricated using injection moulding. Alkali and silane fibre treatments were found to improve mechanical (tensile, flexural and impact) and dynamic mechanical (storage modulus) properties which appears to be due to the increase in IFSS and matrix crystallinity. Tensile strength, Young's modulus, flexural modulus, impact strength and storage modulus of the PLA/hemp fibre composites increased with increased fibre content. A 30 wt% short fibre reinforced PLA composite (PLA/ALK) with a tensile strength of 75.5 MPa, Young's modulus of 8.18 GPa, flexural modulus of 6.33 GPa, impact strength of 2.64 kJ/m² (notched) and 28.1 kJ/m² (un-notched) and storage modulus of 4.28 GPa was found to be the best, and better than any in the available literature. However, flexural strength, plane strain fracture toughness (K_{Ic}) and strain energy release rate (G_{Ic}) decreased with increased fibre content. This behaviour could be due to the increase in stress concentration points (number of fibre ends) with increased fibre content. The influence of loading rate and fibre content on the K_{Ic} of random short fibre reinforced PLA composites, lacking from the available literature, was studied. K_Q (trial K_{Ic}) of composites decreased as loading rate increased, until stabilising at a loading rate of 10 mm/min and higher.

UPE based short hemp fibre composites were produced by compression moulding. At 20 wt% fibre content, the tensile strength was not increased above that recorded for unreinforced UPE, but thereafter, the tensile strength increased approximately proportionally to the fibre content, except at the highest fibre content (60 wt%) where a decrease in the tensile strength occurred. K_{Ic} and G_{Ic} reached a minimum value at 30 wt% fibre content and afterwards increased with increased fibre content. The flexural strength was found to decrease with increased fibre content; however, the impact strength and storage modulus increased with increased fibre content. It was also observed that the mechanical and dynamic mechanical properties improved after treatment of fibres. A 50 wt% ALKSIL fibre reinforced UPE composite with a tensile strength of 62.1 MPa, Young's modulus of 13.35 GPa, flexural modulus of 6.11 GPa, impact strength (notched) of 7.12 kJ/m² and storage modulus of 3.5 GPa was found to be the best.

To improve the mechanical and dynamic mechanical properties further, aligned long hemp fibres were used to fabricate PLA/ALK and UPE/ALKSIL composites using compression moulding. The mechanical and dynamic mechanical properties of aligned long fibre reinforced PLA/ALK and UPE/ALKSIL composites were found to be superior to those of short fibre composites. The highest tensile strength of 85.4 MPa, Young's modulus of 12.6 GPa, flexural modulus of 6.59 GPa, impact strength of 7.4 kJ/m² (notched) and 32.8 kJ/m² (un-notched), and storage modulus of 5.59 GPa were found for PLA/ALK composites at a fibre content of 35 wt%. In the case of UPE/ALKSIL composites, the highest tensile strength of 83 MPa, Young's modulus of 14.4 GPa, flexural modulus of 6.7 GPa, impact strength (notched) of 15.85 kJ/m² and storage modulus of 3.74 GPa were found for composites with a fibre content of 50 wt%.

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Publications

Journal papers:

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2. Sawpan, M. A.; Pickering, K. L.; and Fernyhough, A. Characterisation of hemp fibre reinforced poly(lactic acid) composites, *International Journal of Materials and Product Technology* 36 (2009) 229-240.

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2. Sawpan, Moyeenuddin A.; Pickering, K. L.; and Fernyhough, A. Mechanical characterisation of hemp fibre reinforced poly(lactic acid) composites, International Conference on Innovative Natural Fibre Composites for Industrial Applications, University of Rome "La Sapienza", Italy, October 2007.
3. Sawpan, Moyeenuddin A.; Pickering, K. L.; and Fernyhough, A. Influence of loading rate and fibre content on plane-strain fracture toughness of polylactide (PLA) and random short hemp fibre reinforced PLA bio-composites, The 10th International Conference on Wood & Biofiber Plastic Composites, Madison, Wisconsin, USA, May 2009.

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Symbols and Abbreviations

Symbols:

α	Young's modulus ratio of the matrix and to the fibre
σ_c	Composite strength
σ_f	Fibre strength
σ_N	Net compressive stress
σ_m^*	Tensile strength of matrix at failure strain of composite
σ_y	Yield strength
ρ_f	Density of fibre
ρ_m	Density of matrix
ϕ	Energy calibration factor
τ_a	Average interfacial shear strength
ν_m	Poisson ratio of matrix
ν_f	Poisson ratio of fibre
a	Initial crack length
d	Diameter of fibre
$F_{\max}$	Maximum load
E	Young's modulus
E'	Storage modulus
E''	Loss modulus
E_f	Young's modulus of fibre
E_m	Young's modulus of the matrix
f	Geometrical correction factor
G_{Ic}	Strain energy release rate
G_c	Critical strain energy release rate
ΔH_{cc}	Cold crystallisation enthalpy
ΔH_f	Enthalpy of melting
I_{XRD}	Crystallinity index
K	Stress-intensity factor
K_c	Critical stress intensity factor
K_I	Orientation factor
K_2	Stress transfer factor
K_{Ic}	Plane strain fracture toughness
l_c	Critical fibre length
l_e	Embedded length
$P(l)$	Cumulative probability

r	Radius of fibre
t	Specimen thickness
T_g	Glass transition temperature
U	Energy
V_f	Volume fraction of fibre
W_f	Fibre weight fraction
W_{fa}	Weight of fibre in air
W_{fs}	Weight of fibre in liquid
X_{DSC}	Crystallinity
x	Stress transfer factor
Y	Dimensionless geometric factor
ν_m	Poisson's ratio of matrix
ν_f	Poisson's ratio of fibre
$\tan \delta$	Mechanical damping factor
$\tan \delta_{\max}$	Maximum height of $\tan \delta$

Abbreviations:

ASTM	American Society for Testing and Materials
DTA	Differential thermal analysis
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
FT-IR	Fourier Transform Infrared
GPa	Gigapascal
IFSS	Interfacial shear strength
ISO	International Standard Organisation
MPa	Megapascal
MA	Maleic anhydride
MROM	Modified rule of mixtures
PLA	Polylactide
SENB	Single-edge notched bending
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UPE	Unsaturated polyester resin
XRD	X-ray diffraction
wt%	weight percentage

CHAPTER ONE

Introduction

1.1 Background

The potential of natural fibres as reinforcement in composite materials has been well recognised since the Egyptians, some 3,000 years ago, used straw reinforced clay to build walls. With the development of more durable materials such as metals, the interest in “natural” materials decreased. It was not until the early 1900s when natural materials re-emerged as possible future materials for structural applications [1].

Current research findings show that in certain composite applications, natural fibres demonstrate competitive performance to glass fibres. One of the most promising applications of natural fibres is in polymer composites that can be moulded into a variety of flat and complex-shaped components which exploits their reinforcing potential. Additionally, the low density of natural fibres results in lightweight composites, which is of great benefit in automotive and building applications.

Both thermosets and thermoplastics are attractive as matrix materials for polymer composites. Natural fibre reinforced thermoset (e.g. epoxy, polyester and phenolic resins) and thermoplastic (e.g. polyethylene, polypropylene and polystyrene) composites have been addressed in numerous research studies [2-7].

Major drawbacks associated with the use of natural fibres as reinforcement in polymers include the poor wetting and the very weak interface which commonly occur between these fibres and most of the polymers used as matrices. Better interfaces can, however, be obtained by modifying the fibres by physical or chemical treatments. Another way to increase the fibre to matrix interaction is to modify the matrix. The introduction of reactive sites in the matrix with higher chemical affinity toward the fibres can improve fibre/matrix interfacial strength.

1.2 Rationale and objectives of the study

In this dissertation, the renewable resource based thermoplastic, polylactide (PLA), is used to prepare industrial hemp fibre reinforced biocomposites with potential for structural applications. When the work of this dissertation started, only a limited amount of literature focused on the interfacial strength and mechanical properties of natural fibre reinforced PLA composites, which highlighted the need for a systematic investigation of the processing and characterisation of hemp fibre reinforced PLA biocomposites. In addition, the literature review affirmed that no systematic investigation has been conducted on the interfacial strength and mechanical properties of natural fibre reinforced thermoset polyester composites to compare directly with those of natural fibre reinforced thermoplastic polyester composites. It would seem appropriate, therefore, that in any work undertaken, the properties of natural fibre reinforced thermoset polyester composites should be compared with those of natural fibre reinforced thermoplastic polyester composites. For this purpose, an unsaturated polyester resin (UPE) was used to fabricate hemp fibre reinforced thermoset polyester composites.

As can be seen in the literature review section, some physico-mechanical properties of various natural fibres reinforced PLA and UPE composites have been reported. However, a fundamental issue, the role of the interface in the mechanical properties of natural fibre reinforced PLA and UPE composites, has not been explained in the literature. With the aim of a better understanding, this research focused on fundamental issues concerning the behaviour of the industrial hemp fibre reinforced PLA and UPE composites and the underlying mechanisms controlling these. This work investigated the effects of interaction of the materials (fibre and matrix) and the change in chemistry, morphology, and stress transfer that they impart on the hemp fibre reinforced PLA and UPE composites. For this purpose, systematic approaches to the fibre, matrix and composite characterisation (e.g. spectroscopic, optical, thermal and mechanical) were carried out to follow the interactions.

The outlines of the research plan to achieve the above goals were as follows.

- Characterisation of hemp fibre properties.
- Evaluation of fibre/matrix interfacial strength.
- Preparation of hemp fibre reinforced PLA and UPE composites.

- Studies on the effect of fibre properties, fibre content, fibre length and orientation, and processing methods on the performance of composites in particular tensile properties, impact strength, flexural properties and fracture toughness.
- Studies on the relationships between fibre characteristics, fibre treatments, fibre/matrix interfacial properties and end composite properties.

1.3 Structure of the thesis

The layout of this thesis is that of a conventional academic report presenting experimental results. It consists of eight chapters. In this chapter, Chapter One, a general introduction to the subject is presented, in addition to the rationale and research goals, and the outline of the report. Chapter Two presents relevant literature review in support of the remainder of the thesis. This chapter provides a broad understanding of composite materials, general structural organisation and composition of natural fibres, chemistry of PLA and UPE, and an overview of the main composite fabrication methods. In addition, this chapter contains a brief review of recent works on the natural fibre treatment, and natural fibre reinforced PLA and UPE composites.

Chapter Three covers details for materials, methodology of fibre treatment and composite processing, configuration of specimens, instrumentation, techniques for characterisation and testing of fibres and composites. Also included is the methodology for pull-out test sample preparation to assess the fibre/matrix interfacial strength.

The experimental results of this research are presented in three consecutive chapters (namely Chapters Four, Five and Six). Chapter Four covers the results and discussion of the FT-IR, XRD, TGA-DTA, density and tensile properties for the untreated and various chemical treated hemp fibres. Chapter Five presents the results and discussion of the PLA/hemp fibre composite properties. This includes results of the IFSS, tensile properties, impact strength, flexural properties, fracture toughness, DMTA, XRD and DSC analysis. SEM and light microscope images are included to support the above results. Also included are the (i) FT-IR analysis and possible bonding in untreated and treated hemp fibre/PLA composites, and (ii) relationships between the tensile strength, impact strength, flexural strength and plane strain fracture toughness with the IFSS and crystallinity of PLA in the composites. Chapter Six encompasses the results of IFSS, tensile properties, impact

strength, flexural properties, fracture toughness, and DMTA. SEM and light microscope images are presented to support the above results where appropriate. In addition to the above, (i) FT-IR analysis and possible bonding in untreated and treated hemp fibre/UPE composites, and (ii) relationships between the tensile strength, impact strength, flexural strength and plane strain fracture toughness with the IFSS are presented. At the end of this chapter, the IFSS, tensile properties, impact strength, flexural properties, plane strain fracture toughness and strain energy release rate of the hemp fibre/UPE composites are compared with those of the hemp fibre/PLA composites. The error-bars each in the graphs of Chapters Four, Five and Six represent standard deviation.

Chapter Seven draws the main conclusions of this investigation. Finally Chapter Eight suggests a number of issues which are worthy of further investigation.

CHAPTER TWO

Literature Review

2.1 Composite materials

Composites are engineered materials formed from a combination of two or more components which, when combined, retain their identities and properties. Typically, a composite would consist of reinforcing fibre which is the hardest, strongest and stiffest component, embedded in a continuous matrix. The main functions of the matrix are to transmit externally applied loads to the reinforcement and to protect the latter from external mechanical damage [8]. Fibres are commonly classified as to whether they are natural (e.g. hemp, jute and flax fibre) or synthetic (e.g. glass and carbon fibre), whereas the matrix of a composite is commonly classified in term of its generic material which could be ceramic, metal or polymer. In recent years, natural fibre reinforced polymer matrix composites have drawn much attention due to their low density and good specific strength and stiffness.

2.1.1 The composite interface

According to Metcalfe (1974), “An interface is the region of significantly changed chemical composition that constitutes the bond between the matrix and reinforcement” [9]. In composites, the interface plays a key role in transferring the stress from the matrix to the fibre. A weak interface generally results in low strength and stiffness but high resistance to fracture, whereas a strong interface produces high strength and stiffness, but often low resistance to fracture [8, 10].

2.1.1.1 Bonding mechanisms at the interface

Once the matrix has wet the reinforcement, a number of types of bond may be formed, of which more than one may occur at the same time. The principle mechanisms which may be involved in the fibre-matrix bond are [8, 9, 11]:

- Inter-diffusion: A bond may be formed by the inter-diffusion of atoms or molecules between two constituent surfaces. Its strength will depend on the degree of entanglement.
- Electrostatic attraction: Oppositely charged surfaces attract – this phenomenon is used during the application of coupling agents (size) to reinforcements.
- Chemical bonding: This relies on the presence of a chemical group in the matrix and a compatible chemical on the fibre surface.
- Reaction bonding: Reactions occur to form new compounds at the interfacial region. It involves transfer of atoms from one or both constituents to the reaction site near the interface.
- Mechanical bonding: This occurs as a result of physical interlocking and will be stronger with increased fibre wetting.

2.1.1.2 Composite interfacial strength measurement

A large number of analytical techniques have been developed for assessing interfacial strength of fibre reinforced polymer composites. These methods can be broadly classified into three separate categories [12].

- Composite laminate methods: These (e.g. 4-point shear and short beam shear) measure interface sensitive properties from which interfacial strength can be qualitatively assessed.
- Indirect methods: These (e.g. ball compression and slice compression) again provide a qualitative method of ranking fibre/matrix interfacial strength.
- Direct methods: These (e.g. single fibre fragmentation, single fibre pull-out, single fibre microindentation, single fibre compression) not only measure fibre/matrix interfacial strength, but can provide information about the fibre/matrix failure mode. These are the most commonly used methods because of their versatility. Details of these methods are presented in the following sections.

2.1.1.2.1 The single fibre fragmentation test

The single fibre fragmentation test is one of the most popular methods to evaluate the fibre/matrix interface strength. The test specimen has a dogbone shape and consists of one fibre encapsulated in a chosen polymer matrix [see Figure 2.1(a)]. This experiment requires a resin system with a sufficiently higher strain-to-failure than the fibre's. The fibre inside the resin breaks into increasingly smaller fragments at locations where the fibre's

axial stress reaches its tensile strength. The higher the axial strain, the more fractures will be caused in the fibre, but at some level the number of fragments will become constant as the fragment length is too short to transfer enough stresses into the fibre to cause further breakage [13].

The interfacial shear strength (τ_{fi}) can be calculated using the following equation [14]:

$$\tau_{fi} = \frac{\sigma_f d}{2l_c} \quad (2.1)$$

where σ_f is the fibre strength at the critical length, d is the fibre diameter and l_c is the critical fragment length of fibre.

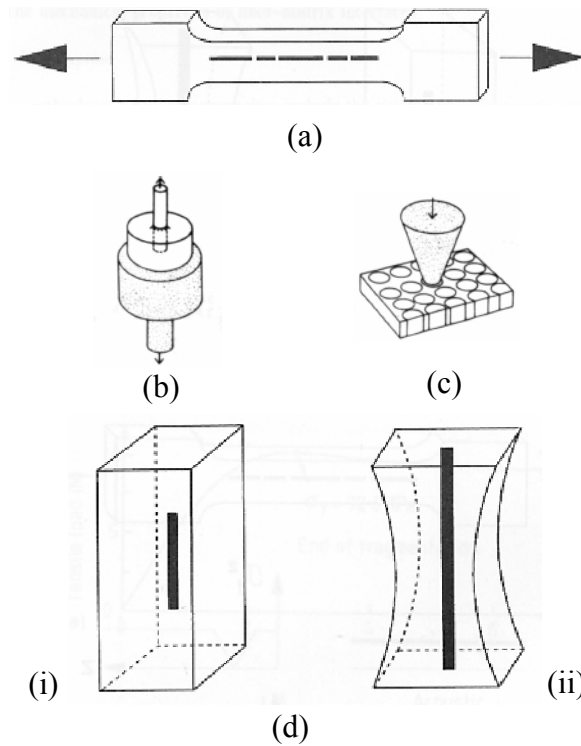


Figure 2.1: Schematic presentation of various specimen geometry for the interfacial strength measurement (a) single fibre fragmentation test; (b) single fibre pull-out test; (c) single fibre microindentation test; and (d) single fibre compression test (i) hexahedral and (ii) curved-necked.

The main advantages of this technique are that it: (i) yields a large amount of information for statistical sampling; (ii) enables observation of failure processes for transparent

samples; and (iii) replicates the composite situation. In contrast, some disadvantages of this technique are: (i) matrix must have a strain limit of at least three times greater than that of the fibres; (ii) matrix must be sufficiently tough to avoid fibre fracture induced failure; and (iii) fibre strength should be known at the critical length [12].

2.1.1.2.2 The single fibre pull-out test

The single fibre pull-out test has been used for measuring the interfacial bond strength between reinforcing fibres and polymer matrices for more than four decades and has become the most popular technique for interface strength characterisation [15]. In a typical pull-out test, an individual fibre is embedded to a predetermined distance in a polymer plug [see Figure 2.1(b)]. The forces required to extract the fibre from the plug is then recorded. The interfacial shear strength (τ_{po}) can be calculated using the following equation [15, 16]:

$$\tau_{po} = \frac{F_{\max}}{\pi d l_e} \quad (2.2)$$

where $F_{\max}$ is the maximum load, d is the fibre diameter and l_e is the embedded length.

The shape of the force/displacement curves from pull-out test depends on the intrinsic characteristics of the interface. In general, three types of curves can be observed for brittle fibre/matrix systems (see Figure 2.2) [17]. In the first case [see Figure 2.2(a)], the stored energy within the system is high enough to extract the fibre immediately after the initiation of interface failure, and only the maximum force during the pull-out can be obtained. This type of curve is commonly seen for strong fibre/matrix interfaces. A second type of curve [see Figure 2.2(b)] is usually observed with a weakly bonded interface. In this case, after interfacial failure, the fibre may be extracted progressively and frictional pull-out can be seen until failure. Both the maximum pull-out load and the frictional load can be obtained from this type of curve. In the third case [see Figure 2.2(c)], peaks in the ascending region of the curve are due to the frictional damage as the debonded region develops along the fibre/matrix interface.

The major advantages of this technique are: (i) the force at onset of debonding can be measured; and (ii) this technique can be used for almost any fibre/matrix combination. On the other hand, a limitation of this technique is that the longer embedded length cause fibre fracture [9, 12].

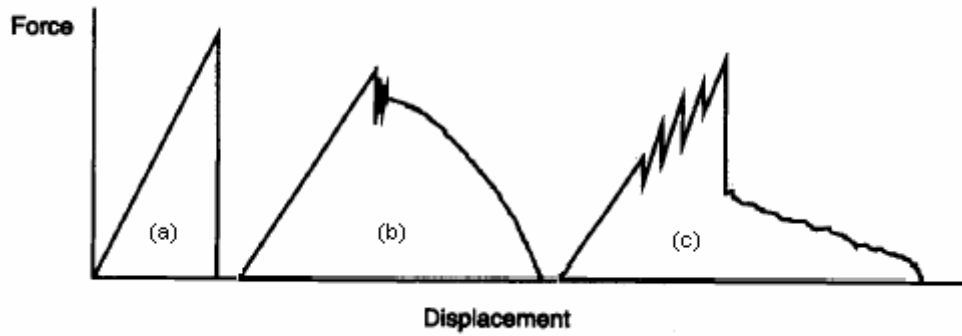


Figure 2.2: Schematic illustrations of possible force/displacement curves for the single fibre pull-out test [17].

2.1.1.2.3 The single fibre microindentation test

The single fibre microindentation test is capable of examining fibres embedded in the actual composite. This technique utilizes a micro-indenter to apply a compressive force to push against a fibre end into polished surface of a matrix block [see Figure 2.1(c)]. The load versus displacement curve is monitored until the fibre debonds from the matrix, and the debonding load can be used to calculate interfacial shear strength (τ_{mi}) [12].

$$\tau_{mi} = \frac{F}{\pi dt} \quad (2.3)$$

where F is the load, d is the fibre diameter and t is the specimen thickness.

The advantages of this technique are that it: (i) allows in situ measurement of debonding force; and (ii) allows probing of the interface in the ‘real’ environment. The disadvantages are: (i) the failure mode cannot be observed; (ii) there exists the possibility of introducing impurities by the surface preparation procedure; and (iii) crushing of fibres can be occurred, limiting the variety of fibres to be tested [12].

2.1.1.2.4 The single fibre compression test

The single fibre compression test was first developed to measure the bond strength of glass fibres and transparent polymer matrices [18]. Two geometries of the specimen namely, hexahedral and curved-necked are used for this testing [see Figure 2.1(d)]. When the parallel-sided specimen is loaded in longitudinal compression, shear stresses build up from the fibre ends due to the difference in elastic properties and lead to debonding at fibre ends. The curved-neck specimen under longitudinal compression causes interfacial debonding to occur in the transverse direction (i.e. tensile debonding) due to the transverse expansion of the matrix when its Poisson's ratio is greater than that of the fibre [9].

The equations used to calculate the interface bond strengths for shear debonding (τ_{ct}) in the parallel-sided specimen and for tensile debonding (σ_b) in the curved-necked specimen are [9]:

$$\tau_{ct} \approx 2.5\sigma_N \quad (2.4)$$

$$\sigma_b = \frac{\sigma_N(\nu_m - \nu_f)}{(1 - \nu_m) + \alpha(1 - \nu_f - 2\nu_f^2)} \quad (2.5)$$

where σ_N is the net compressive stress at the smallest cross-section obtained upon interface debonding, α is the Young's modulus ratio (E_m / E_f) of the matrix and to the fibre, and ν_m and ν_f are Poisson's ratios of the matrix and fibre, respectively.

Single fibre compression testing has not commonly been used due to its limitation in materials selection and specimen preparation. For this testing, transparent matrices are required and determining the onset of debonding is difficult.

2.1.2 Factors affecting composite properties

2.1.2.1 Fibre volume fraction

Fibre volume fraction is one of the most important factors controlling the strength, stiffness and many other physical/mechanical properties of the composites. For a composite system where matrix failure strain is greater than fibre failure strain, two possible failure regimes exist depending on whether the fibre volume fraction (V_f) is above or below a minimum

value ($V_{\min}$). When $V_f < V_{\min}$, the polymer matrix is able to carry the applied load after fibre fracture. Failure of the fibres does not lead to composite failure but merely increases the stress in the matrix. The failed fibres, which now carry no load, can be regarded as holes in the polymer matrix. When $V_f > V_{\min}$, failure of the fibres leads to failure of the whole composite, since the polymer matrix is unable to support the additional load which is transferred into the matrix from the fibres. Thus, the critical volume fraction (V_{crit}) for the composite system is the amount of fibres necessary to ensure the composite strength is at least greater than that of the matrix. At very high volume fractions, the strength of composites starts to decrease due to insufficient filling of the matrix materials [19, 20].

2.1.2.2 Fibre aspect ratio

Fibre aspect ratio (length/diameter) is an important parameter in a composite material. A critical fibre aspect ratio is necessary for efficient strengthening and stiffening of the composites. This critical fibre aspect ratio of a composite can be calculated using the following equation [8]:

$$\frac{l_c}{d} = \frac{\sigma_f}{2\tau_i} \quad (2.6)$$

where d is fibre diameter, σ_f is tensile strength of fibre, τ_i is fibre/matrix interfacial strength and l_c is critical fibre length. This critical fibre length (l_c) is defined as the minimum length of the fibre required for the stress to reach the fracture stress of the fibre [8]. Fibres shorter than the critical length will not carry the maximum possible load and are thus unable to function efficiently.

During extrusion and injection moulding, considerable fibre breakage results from fibre-matrix interaction, fibre-fibre interaction and fibre contact with surfaces of the processing equipment. The average fibre length also decreases with the increase of fibre volume fraction due to increased damage. During extrusion, lower screw speeds results in longer mixing times and leads to length reduction. The fibre attrition is more severe in injection moulding. In order to maintain a high fibre aspect ratio in the final product, low injection speeds and back pressures, and generous gate and runner dimensions are utilised [21].

2.1.2.3 Fibre orientation

Of equal importance to the length of fibres is their orientation. The fibre orientation depends on the processing route. When continuous fibres are used, orientation can be controlled to give predictable end properties for the composite in terms of strength and stiffness. Short fibre reinforced injection moulded composites are more randomly oriented but commonly show preferential fibre alignment in matrix flow direction or a layered structure with distinct fibre alignments in different layers. Changes in fibre orientation are related to a number of factors, such as viscoelastic properties of the fibre filled matrix, mould design and the change in shape of the material produced by the processing operation [8].

2.1.3 Composite strength and Young's modulus predictions

A great number of theoretical models have been developed to predict tensile strength and Young's modulus of the composites [22-24]. Some of these models are briefly discussed in this section.

The simple 'Rule of Mixtures' can predict the tensile properties of unidirectional, continuous fibre-reinforced composites in the axial direction. According to this model, the equation for the tensile properties is as follows:

$$X_c = X_f V_f + X_m V_m \quad (2.7)$$

where X is either tensile strength or Young's modulus, V is the fibre volume fraction, and subscripts c , f and m indicate composite, fibre and matrix, respectively. Equation 2.7 is also known as the Parallel model. On the other hand, the series model (Equation 2.8) is used to predict the transverse tensile properties of the composites which can be expressed as follows:

$$X_c = \frac{X_f X_m}{X_m V_f + X_f V_m} \quad (2.8)$$

The Parallel model can be regarded as an upper bound and the Series model represents the lower bound of the achievable tensile properties [25].

The Hirsch model (Equation 2.9) is a combination of both of the parallel and series models that can be used for more randomly oriented composites. An empirical parameter x is introduced in the Hirsch model that characterises the stress transfer between the fibre and matrix. The value of x can be varied from 0 to 1 to give the best fit.

$$X_c = x(X_m V_m + X_f V_f) + (1-x) \left(\frac{X_f X_m}{X_m V_f + X_f V_m} \right) \quad (2.9)$$

The Rule of Mixtures model for tensile strength has been further modified (Equation 2.10) to account for the influence of fibre orientation, fibre/matrix interfacial strength and fibre length. According to this model (the Modified Rule of Mixtures model) [25, 26]:

$$\sigma_c = \sigma_m^* V_m + \sigma_f V_f K_1 K_2 \quad (2.10)$$

where σ_c , σ_f are the tensile strength of composites and fibres, respectively; σ_m^* is the tensile strength of the matrix at the failure strain of composites; V_f and V_m are the volume fractions of the fibre and matrix, respectively; K_1 is an orientation factor, and K_2 is a factor depends on the stress transfer between matrix and fibres. K_1 has the value of unity for the aligned fibres, and K_2 has the value of unity for a perfect interface. The fibre volume fraction (V_f) can be calculated from the fibre weight fraction (W_f) using the following equation [27]:

$$V_f = \left(1 + \frac{\rho_f}{\rho_m} \frac{1 - W_f}{W_f} \right)^{-1} \quad (2.11)$$

where ρ_f is the density of fibre and ρ_m is the density of matrix.

2.1.4 Composite fracture toughness

Fracture toughness is used to predict when brittle fracture will occur based on the effect of defects in structural components. It is a very important material property since the occurrence of flaws is unavoidable during processing, fabrication or service of a material.

In an early work (1920), Griffith suggested that fracture occurs when sufficient energy is released from the stress field during growth of a crack to supply the requirements of new fracture surfaces [25]. The energy released comes from stored elastic energy of the loading system and can, in principle, be calculated for any type of test piece. It was demonstrated that, for a crack of length $2a$ contained in an infinite plate of brittle material, with stress applied normal to the plane of the crack, the following relationship exists between fracture stress (σ_{fs}), crack length and surface energy (γ_s) [28]:

$$\sigma_{fs} = \left(\frac{2\gamma_s E}{\pi a} \right)^{1/2} \quad (2.12)$$

where E is the Young's modulus.

This development applies only to completely brittle materials and was later extended by Irwin (1948) to encompass tougher materials [25]. In this approach, the surface energy term 2γ is supplemented by other contributions to the energy absorbed in the vicinity of an advancing crack tip. A new term ('energy release rate', G) was subsequently introduced in Equation 2.12 and expressed as [25]:

$$G = \frac{\sigma_{fs}^2 \pi a}{E} \quad (2.13)$$

For fracture to occur, this must exceed a critical value which represents the total energy absorbed per unit of crack advance area and is often termed as the 'critical energy release rate', G_c . Thus, the stress necessary to cause spontaneous fracture in a component with a pre-existing crack can be written as [25]:

$$\sigma_{fs} = \left(\frac{G_c E}{\pi a} \right)^{1/2} \quad (2.14)$$

This approach, therefore, provides a measure of the energy required to extend a crack over unit area.

The stress distribution around a sharp crack in a linear elastic material is uniquely defined by a parameter named stress-intensity factor, K , and can be expressed as [28]:

$$K = Y\sigma\sqrt{\pi a} \quad (2.15)$$

where Y is a dimensionless geometric factor of the crack and specimen; and σ is the applied stress.

A critical value of K can be identified, corresponding to the case where the associated value of G reaches G_c [28]:

$$K_c = Y\sigma_c\sqrt{\pi a} \quad (2.16)$$

where K_c is known as ‘critical stress intensity factor’.

The stress fields near crack tips can be divided into three basic types, each associated with a local mode of deformation, as shown in Figure 2.3. Opening mode is associated with a local displacement in which the crack surfaces move directly apart. Shearing mode is characterised by displacements in which the crack surfaces slide over one another. In tearing mode, the crack surfaces slide with respect to one another parallel to the leading edge.

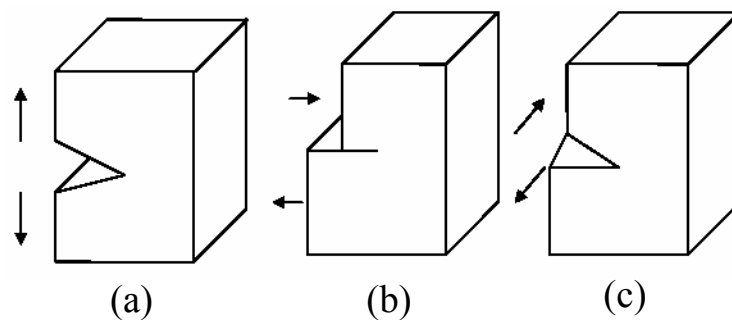


Figure 2.3: Schematic depiction of the crack modes (a) opening mode (Mode I); (b) shearing or edge-sliding mode (Mode II); (c) antiplane strain or tearing mode (Mode III).

2.2 Overview of natural fibres

Natural fibres, often referred to as vegetable or plant fibres, are extracted from plants and categorised into the following [29, 30]:

- Seed fibres: Fibres collected from seeds or seed cases, e.g. cotton and kapok.
- Leaf fibres: Fibres collected from leaves, e.g. sisal and agave.
- Bast fibres: Fibres are collected from the skin or bast surrounding the stem of their respective plant. Some examples are jute, kenaf, industrial hemp, ramie, rattan, soybean fibre, and even vine fibres and banana fibres.
- Fruit fibres: Fibres are collected from the fruit of the plant, e.g. coconut (coir) fibre.
- Stalk fibres: Fibres are actually the stalks of the plant, e.g. straws of wheat, rice, barley, and other crops including bamboo and grass. Tree wood is also such a fibre.

The application of natural fibres is being driven by various reasons such as [31]:

- They are renewable resource and the production requires little energy.
- Low density, which results in a higher specific strength and stiffness than synthetic fibres.
- Recycling is possible, where glass causes problems in combustion furnaces.
- Good thermal and acoustic insulating properties.

2.2.1 Composition and chemistry of natural fibres

Natural fibres consist mainly of cellulose, hemicellulose and lignin in different proportions. These components comprise 80-90% of the dry material. The rest consists of mainly minerals, pectin, waxes and water-soluble components [32]. Although fibres from different plant species can appear quite different, their chemical compositions are fairly similar. Chemical compositions of some natural fibres are presented in Table 2.1. Details of some important chemical composition of natural fibres are given in the following section.

2.2.1.1 Cellulose

Cellulose is the reinforcing material within the plant cell wall. It is defined chemically as a linear, semicrystalline polysaccharide, consisting of β -D-anhydroglucopyranose units, bound with β -(1 $\rightarrow$ 4) glycosidic linkages, as shown in Figure 2.4. The repeating unit in the cellulose chain is strictly speaking cellobiose, consisting of two anhydroglucose units.

The basis of the cellulose structure is the chair-conformed anhydroglucose. Furthermore, cellulose chain has a direction since the terminal groups on the chain ends are different: non-reducing end with closed ring structure and reducing end with aliphatic structure and a carbonyl group in equilibrium with cyclic hemiacetals. The degree of polymerisation (number of glucose units) in plant cellulose lies in the range 4,000-8,000. The glucose monomers in cellulose form hydrogen bonds both within its own chain (intramolecular) forming fibrils and with neighbouring chains (intermolecular), forming microfibrils. These hydrogen bonds lead to the formation of a linear crystalline structure [33-35].

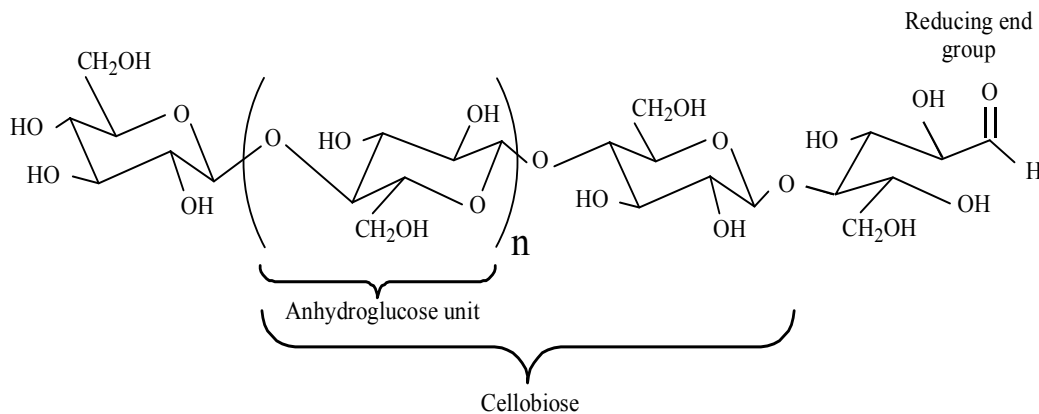


Figure 2.4: The Howorth projection formula of cellulose. Anhydroglucose is the monomer of cellulose, cellobiose is the dimer [31, 34].

Table 2.1: Chemical composition of selected natural fibres [31, 33, 36].

Fibre	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Pectin (%)	Ash (%)
Abaca	56-63	7-9	15-17	-	3
Coir	30-35	40-45	-	-	-
Flax	65-85	1-4	18-20	2.3	-
Hemp	57-77	3-13	14-22	0.9	0.8
Henequen	70-80	12-14	4-8	-	-
Jute	45-63	12-25	4-10	0.2	1-2
Kenaf	31-57	15-19	21-23	-	2-5
Ramie	68-91	0.6-0.7	5-17	1.9	-
Sisal	47-78	7-11	10-24	10	0.6-1
Softwood	40-45	26-34	0-1	-	-
Hardwood	40-50	20-30	0-1	-	-

2.2.1.2 Hemicellulose

Hemicelluloses are imbedded in the cell walls of plants, sometimes in chains that form a ‘ground’ - they bind with pectin and cellulose to form a network of cross-linked fibres. It is a heterogeneous branched polysaccharide, composed of many different sugar monomers. Hemicelluloses extracted from different plant sources are rarely identical. Unlike cellulose, the constituents of hemicellulose differ from plant to plant [31]. Typically, degree of polymerisation is only around 200. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes [37].

2.2.1.3 Lignin

Lignin is essentially a disordered, polyaromatic and crosslinked polymer [see Figure 2.5(a)] arising from free radical polymerisation of p-coumaryl, coniferyl and sinapyl alcohols [see Figure 2.5(b)] [31]. Lignin acts like adhesive material in natural fibres by gluing the fibrils together to form a stiff structure. The dissolution of lignin using chemical aids causes fibre separation. When exposed to ultraviolet light, lignin undergoes photochemical degradation.

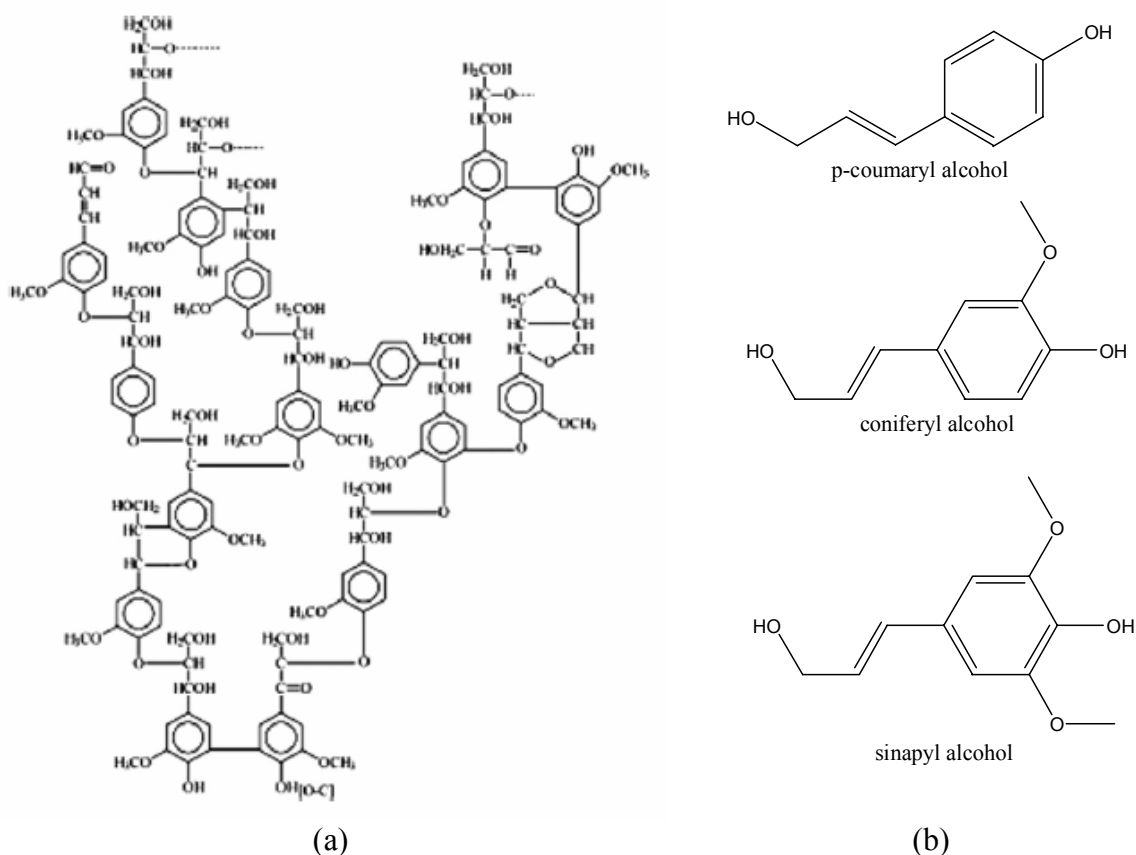


Figure 2.5: Schematic chemical structure of (a) lignin [38] and (b) monomers of lignin.

2.2.1.4 Pectin

Pectin is a complex branched structure of acidic polysaccharides. The structure mainly consists of homopolymeric acid and partially of methylated poly- α -(1-4)-D-galacturonic acid residues. It is the most hydrophilic compound in natural fibres due to the carboxylic acid groups and easy degradation by enzymes.

2.2.2 Structural organisation of natural fibre cell wall

One of the most important distinguishing features of plant cells is the presence of a cell wall (see Figure 2.6). The plant cell wall serves as a variety of functions. Along with protecting the intracellular contents, the structure bestows rigidity to the plant, provides a porous medium for the circulation and distribution of water, minerals, and other nutrients, and houses specialised molecules that regulate growth and protect the plant from disease.

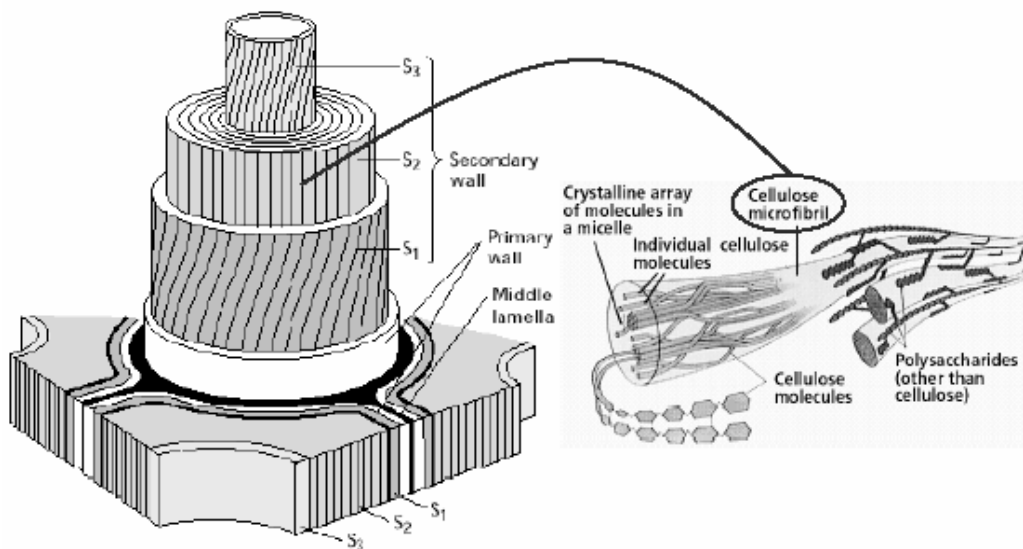


Figure 2.6: Schematic architecture of plant cell wall [37].

The basic fibrous building element of the cell wall may be regarded the microfibril. The microfibril can itself be viewed as a composite, in which crystalline cellulose forms the ‘reinforcement’ core, surrounded by a ‘matrix’ of amorphous cellulose, hemicellulose and pectin. The cell walls differ in their composition and orientation (spiral angle). The spiral angle of fibrils and the content of cellulose, generally determines the mechanical properties of natural fibres.

Plant cell walls consist of three types of layers:

- Middle lamella: This is the first layer formed during cell division. It makes up the outer wall of the cell and is shared by adjacent cells. It is composed of pectic compounds and protein.
- Primary cell wall: This is formed after the middle lamella and consists of a rigid skeleton of cellulose microfibrils embedded in a gel-like matrix composed of pectic compounds, hemicellulose, and glycoproteins.
- Secondary cell wall: This is formed after cell enlargement is completed. The secondary wall is mainly for support and is comprised primarily of cellulose and lignin. The secondary wall may be further sub-divided into S_1 , S_2 and S_3 - which differ in the orientation, or direction, of the cellulose microfibrils.

2.2.3 Industrial hemp fibres

Hemp is a distinct variety of the plant species *cannabis sativa L.* Due to the similar leaf shape, hemp is frequently confused with marijuana. Although both plants are from the species *cannabis*, hemp contains virtually no THC (delta-9-tetrahydrocannabinol), the active ingredient in marijuana [1].

There are broadly three groups of *cannabis* varieties being cultivated today:

- Varieties primarily cultivated for their fibre, characterised by long stems and little branching, more generally called industrial hemp;
- Varieties grown for seed from which hemp oil is extracted; and
- Varieties grown for medicinal purposes.

The fibre is one of the most valuable parts of the hemp plant. It is commonly called bast, which refers to the fibres that grow on the outside of the woody interior of the plant's stalk, and under the most outer part (the bark). Bast fibres give the plants more strength, which is especially true with the hemp plant. Bast fibres account for 20-30 percent of the stalk.

There are two types of bast fibres:

- Primary bast fibres: Primary bast fibres make up approximately 70 percent of the fibres and are long, high in cellulose and low in lignin. These fibres can be spun and woven to a fine, crisp, linen-like fabric and used for apparel textiles, home furnishing textiles and carpeting.

- Secondary bast fibres: Secondary bast fibres make up the remaining 30 percent of the bast fibres and are medium in length and higher in lignin.

Hemp crops are harvested at different times for different hemp products.

- Harvesting stalks for high quality primary fibre occurs as soon as the crop is in flower.
- Harvesting for seed production and stalks occurs 4 - 6 weeks after flowering, when male plants begin to shed pollen.

Once a hemp crop has matured and been harvested, hemp primary fibres are separated from the hemp stalk through the "retting" process. For "dew retting", the cut stalks are left in the field for several weeks to allow natural humidity and bacteria to decompose the fibre-binding pectin. Other ways to separate the fibre from the core are: water retting, warm water retting and chemical retting. When the retting process is complete, the fibres are readily separated from the core, and processed for specific products. Depending on the processing used to remove the fibre from the stem, the hemp naturally may be creamy white, brown, gray, black or green.

The most rapidly expanding application for hemp fibre is as reinforcement in composites. Typical applications include automotive interior substrates, furniture and other consumer products.

2.2.4 Treatment of natural fibres

Natural fibres are highly hydrophilic due to the presence of hydroxyl groups (OH). However, fibres are covered with non-cellulosic components (e.g. pectin and wax), thus hindering the hydroxyl groups reacting with hydrophilic matrices, and forming poor interfacial adhesion with hydrophobic matrices. Therefore, for better adhesion with matrices, fibres are chemically treated to remove the non-cellulosic components. Chemical treatment also brings about an active surface by introducing some reactive groups. Many chemicals have been screened in laboratory experiments for potential to enhance fibre/matrix interface, such as sodium hydroxide, peroxide, organic and inorganic acids, silane, anhydrides and acrylic monomers [39-48]. A brief review of some important chemical treatment is presented in the following section.

2.2.4.1 Literature works on chemical treatment of natural fibres

2.2.4.1.1 Alkali treatment

Alkali treatment is believed to remove non-cellulosic components away from fibre surface and activates hydroxyl groups [49]. However, the surface properties of treated fibres depend on various factors such as alkali concentration, fibre immersion time and temperature. Mwaikambo *et al.* [36] reported the effect of alkali concentration on the crystallinity and thermal properties of hemp, sisal, jute and kapok fibres. They found that the crystallinity index initially increased but then declined at high alkali concentration. The authors argued that lower alkali concentration improves packing of cellulose chains, on the other hand, higher alkali concentrations causes damage to the fibre cell wall. Das *et al.* [50] also found similar behaviour for alkali treated bamboo fibres. Borysial *et al.* [51] investigated the effect of alkali concentration and treatment time on the cellulose crystallinity and polymorphic transformation (from cellulose type I to cellulose type II) of flax fibres. They found that the cellulose crystallinity of alkali treated fibres decreased compared to untreated fibres. They also observed that with the increase in alkali concentration (from 10% to 16%), the amount of cellulose II increased and the highest growth of cellulose II took place up to the 7.5 minutes.

Gassan *et al.* [52] studied the tensile properties of alkali treated jute yarn. They found that this treatment leads to an increase in yarn tensile strength and Young's modulus of 120% and 150% respectively. Ray *et al.* [53] also found that the tensile strength and Young's modulus of alkali treated jute fibres increased by 45% and 79%, respectively. In another report, Pickering *et al.* [39] found that the tensile strength of alkali treated hemp fibres increased by 11%. On the other hand, Arsène *et al.* [48] reported that the alkali treatment does not significantly influence the tensile strength of vegetable fibres (e.g. banana trunks and sugar cane residues).

2.2.4.1.2 Acetylation

Acetylation is an attractive method of modifying the plant fibre surface making it more hydrophobic by introducing acetyl group ($\text{CH}_3\text{CO}-$). This chemical modification is known as esterification. During esterification the hydroxyl groups of fibre react with an acid anhydride. The majority of work in the area of esterification deals with acetic anhydride

treatment. This treatment has been shown to improve resistance to fungal attack, dimensional stability, and thermal and UV resistance of the fibres [46].

Acetylation of natural fibres was reported by several researchers. For instance, Zafeiropoulos *et al.* [54] reported that the acetylation causes removal of non-crystalline constituents of flax fibres. They also found that the acetylation increases the surface energy of the fibres. Acetylation of flax, hemp and wood fibre was reported by Tserki *et al.* [55]. They achieved the highest extent of the esterification reaction for the wood fibres due to their high lignin and hemicellulose content. Nair *et al.* [56] acetylated pre-treated (alkali treated) flax fibres used to reinforce polystyrene matrix. They found that the thermal and dynamic mechanical properties of the treated fibre composites were better than those of untreated fibre composites. Mechanical, hygrothermal and aging properties of acetylated plant fibre (e.g. oil palm empty fruit bunch, coconut fibre, oil palm frond, jute, and flax) reinforced polyester composites were reported by Khalil *et al.* [57]. They found that the tensile strength and Young's modulus of treated fibre reinforced composites were greater than those of untreated fibre reinforced composites.

2.2.4.1.3 Silane treatment

Silane coupling agents are a unique class of organic silicon compounds. A typical general structure is



where RO is a hydrolysable group, such as methoxy, ethoxy or acetoxy, and X is an organofunctional group, such as amino, methacryloxy, epoxy. These chemicals are hydrophilic compounds with different groups appended to silicon, such that one end will interact with hydrophilic groups and the other end will react with hydrophobic groups. Therefore, hydrophilic and hydrophobic materials can be coupled together with silane coupling agent acting as a bridge between them. A simplified coupling mechanism scheme of silane treated fibre and polymer matrix is shown in Figure 2.7.

Silane coupling agents are generally applied to fibres to improve the overall performance of fibre reinforced composites. Although this type of treatment is well established with glass fibre, its effect on natural fibre has also been reported by many researchers [4, 58-61]. Silane uptake is very dependent on a number of factors including hydrolysis time,

organofunctionality of silane, temperature and pH. Herrera-Franco *et al.* [43, 59] used vinyltris (2-methoxy-ethoxy) silane to promote the interfacial strength between henequén fibres and high density polyethylene matrix. They found that the interfacial shear strength (IFSS) increased after fibre treatment. Pickering *et al.* [61] studied the effect of silane coupling agents (γ -amino-propyltriethoxysilane and dichlorodiethylsilane) on radiata pine wood fibre. They found that the fibre treatment improved the strength of polyethylene and wood fibre composites due to better adhesion. Li *et al.* [62] used two silane coupling agents to modify the surface of sisal fibres. They found that the silane treatment did not affect the fibre strength significantly. It was also found that the IFSS between γ -methacryloxy-propyltrimethoxy silane treated fibre and vinyl ester resin was greatly improved as a result of chemical bonding between the fibre and matrix. On the other hand, 3-aminopropyltriethoxy silane was found to react only with the fibre but not the matrix, so that IFSS was not improved significantly.

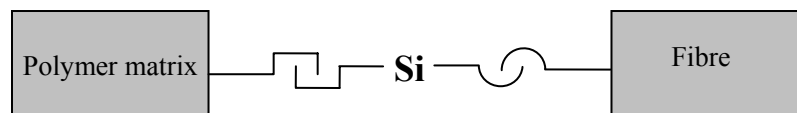


Figure 2.7: Schematic representation of silane coupling mechanism in fibre reinforced composite.

The interfacial adhesion between silane treated flax fibre reinforced epoxy matrix composites was studied by van de Weyenberg *et al.* [63]. They found that the treatment of the fibres with silane leads to an improvement of the composite flexural properties. Mehta *et al.* [64] treated hemp fibre mats with silane to improve mechanical and dynamic mechanical properties of unsaturated polyester resin composites. It is reported that the tensile strength of treated fibre reinforced composites was 48% higher than that of untreated reinforced fibre composites. Rong *et al.* [65] investigated the effect of silane treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. They observed that crystallinity index of the silane treated sisal fibres decreased. They also observed a decrease in treated fibre tensile strength, which is consistent with the changes in cellulose crystallinity. In addition, it was found that the tensile and flexural strength of treated fibre/epoxy laminates was higher than those of untreated fibre/epoxy laminates. Abdelmouleh *et al.* [66] fabricated silane treated bleached pulp reinforced unsaturated

polyester and epoxy composites. They used four different silane coupling agents. It was observed that the flexural properties of various silane treated fibre reinforced composites depended on the type of silane applied for fibre treatment.

2.2.4.1.4 Maleation

Maleic anhydride (MA) is an important interface modifier to improve composite strength. Interactions between maleic anhydride and hydroxyl groups of natural fibres can overcome the incompatibility problem with hydrophobic matrices. For instance, wettability and flexural properties of MA treated flax fibre reinforced polypropylene composites was reported by Cantero *et al.* [67]. They found that this treatment increases the contact angle of flax fibre with water, consequently decreases its polarity. It was also found that the flexural strength and flexural modulus of maleated fibre/polypropylene (PP) composites are better than those for the untreated fibre/PP composites.

Nenkova *et al.* [68] modified wood and wood flour with 5, 10 and 15% solution of maleic anhydride. They observed that the modified wood shows good anti-swelling effect and high increase of impact strength. Composites prepared with modified wood flour reinforced PP composites showed better tensile and impact strength compared to unmodified wood flour PP composites. Misra *et al.* [7] reported the effect of maleic anhydride on mechanical properties of a novolac resin and banana, hemp and sisal fibre composites. They found significant improvement in Young's modulus, flexural modulus, impact strength and Shore-D hardness of the treated fibre reinforced composites compared with those of the untreated fibre composites.

2.2.4.1.5 Miscellaneous treatments

A number of other chemical treatments of natural fibre have also been reported by several authors. For instance, Mishra *et al.* [69] used sodium chlorite (a bleaching agent) to modify sisal fibre. They found that the tensile strength of bleached sisal fibre-polyester composite was less than the other chemical treated (e.g. alkali treated) fibre composites. In another work, graft co-polymerisation of acrylonitrile and pineapple leaf fibre has been studied by Mohanty *et al.* [70]. It was shown that this treatment improves thermal stability of fibres. To improve the dynamic mechanical properties of sisal fibre/polypropylene composites, Joseph *et al.* [71] treated sisal fibres with urethane derivate of toluene diisocyanate/poly(propylene glycol). The performance of the modified fibre reinforced

composites was improved due to the formation of urethane linkage between OH group of the fibre and -N=C=O group of the derivate.

The above studies demonstrate that chemical treatment of natural fibres can be beneficial for improved wetting and/or bonding between fibre and matrix, resulting in improvement of composite properties.

Chemical residues left by fibre surface treatments can be treated in the following methods before disposal:

- (a) Residue from NaOH treatment can be passed through a membrane filter to remove the solid residue before draining.
- (b) A fractional distillation column can be used to recover the solvent (e.g. acetone) from the silane and maleic anhydride residues, and the reaction by-product (e.g. acetic acid) from acetic anhydride residue.

2.3 Polymer matrices

Polymer matrices used for fibre reinforced composites are divided into two groups namely thermoset and thermoplastic. In thermoset resins, polymer molecules are interlinked by covalent bonds and possess a three dimensional network structure. Thermoplastics, on the other hand, do not possess a network structure. Linear or branched molecular chains in thermoplastics are linked together mainly through physical bonding (e.g. van der Waals force and hydrogen bonding) [72]. In this thesis, polylactide, a bioderived thermoplastic polyester, is compared as a matrix with a synthetic unsaturated thermoset polyester.

2.3.1 Polylactide as a matrix material

Polylactide (PLA) was the first commodity plastic produced from annually renewable resources. For a long time, PLA was mainly used in surgical and biomedical applications because of its high production cost. However, recent developments in the manufacturing of its monomer (i.e. lactic acid) economically from agricultural products (e.g. corn, potato and cane sugar) have placed this material at the forefront of the emerging biodegradable plastic industries [1, 73, 74].

Lactic acid exists in two stereoisomeric forms namely L (Levorotatory)-lactic acid and D (Dextrorotatory)-lactic acid (see Figure 2.8). These lactic acids can be produced from

petrochemicals and agricultural products. Petrochemical based chemically synthesised lactic acid exists as a 50/50 mixture of the L and D forms. In contrast, agricultural product based fermentation derived lactic acid exists almost exclusively as L-lactic acid [75]. Nowadays, the majority of lactic acid used in PLA production is produced by fermentation from agricultural products [76]. There are two main methods which can be used to produce PLA from lactic acid. The first method involves direct condensation polymerisation of lactic acid under high vacuum and temperature. With this route, however, only low molecular weight PLA can be produced, mainly because of the presence of water which is a by-product [77]. The second method (see Figure 2.9) starts with condensation polymerisation of lactic acid to produce low molecular weight PLA prepolymer which is then catalytically depolymerised to form lactide intermediate (i.e. dimer of lactic acid). Finally, the lactide is polymerised using solvent free ring-opening polymerisation to produce high molecular weight PLA. This process was patented by Cargill Inc. in 1992 [76].

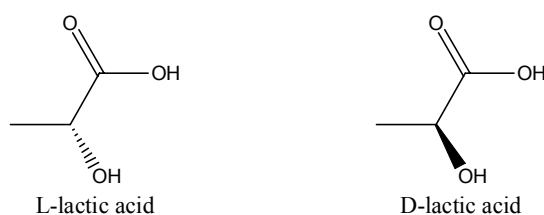


Figure 2.8: Stereo-isomeric chemical structures of lactic acid.

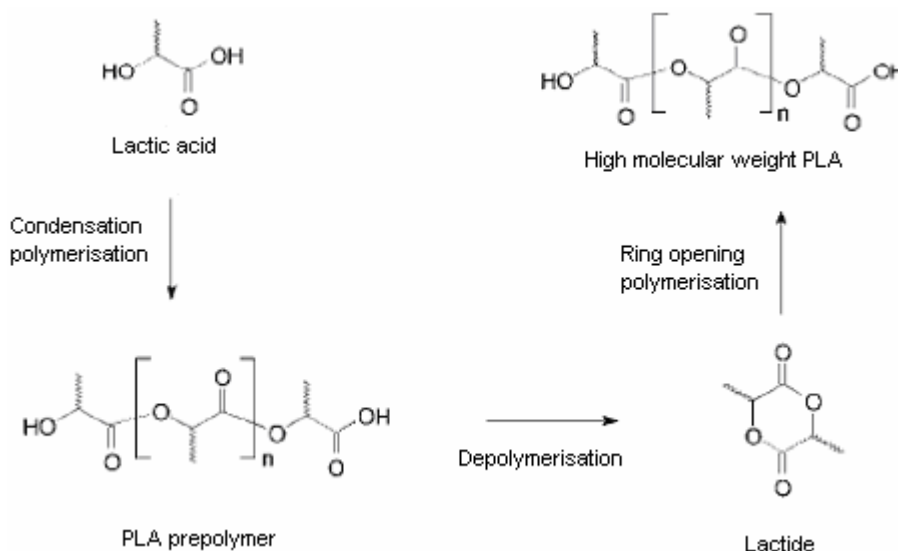


Figure 2.9: Schematic production method of PLA via prepolymer and lactide.

PLA has appealing mechanical properties including improved strength and stiffness compared to standard plastics such as polyethylene, polypropylene and polystyrene. Moreover, PLA can be used to produce injection stretch-blow moulded bottles, film, extrusion-thermoformed containers and fibres [74]. However, one of the limitations for using PLA is its processing instability, i.e., thermal, oxidative and hydrolytic degradations may occur during processing – leading to the cleavage of polymer chains, and hence to a decrease in molecular weight. All of these degradation processes result in a deterioration of PLA properties. Another shortcoming of PLA is its low toughness. However, this can be improved through blending and copolymerisation [78, 79].

2.3.1.1 Natural fibre reinforced polylactide composites

The main purpose of this section is to summarise research on PLA composites where natural fibre is a reinforcing phase.

Oksman *et al.* [80] produced flax fibre reinforced PLA composites by extrusion and compression moulding. They found that tensile strength of the composites increased slightly at 30 wt% fibre content (53 MPa) compared to PLA only samples (50 MPa). But tensile strength of 40 wt% fibre samples decreased to 44 MPa. This decrease in tensile strength at higher fibre content may be due to (i) inadequate amounts of matrix to wet the fibres and (ii) reduction of fibre length during processing. Young's modulus at 30 and 40 wt% fibre content was found to be 8.3 and 7.3 GPa, respectively, which was significantly higher than that of PLA only samples (3.4 GPa). They also found that addition of a plasticiser (glycerol triacetate ester) in the composites decreased tensile strength and Young's modulus. In another study, Bax *et al.* [81] also used flax fibres to reinforce PLA (PLA was in the form of fibre) by hot-pressing followed by pelletising and injection moulding. It was found that tensile strength of the composites increased from 44.5 to 54.1 MPa and Young's modulus increased from 3.1 to 6.31 GPa as the fibre content increased from 0 to 30 wt%. The above findings were fairly consistent with other research work [80]. It was also observed that impact strength (unnotched samples) of the composites at all fibre contents was lower than the PLA only samples.

Garcia *et al.* [82] fabricated PLA composites reinforced with kenaf fibre using extrusion and injection moulding. They also added maleated-PLA in the composites as compatibiliser. It was found that tensile strength of the composites reinforced with 30 wt%

fibre decreased about 10% compared to unreinforced PLA samples, which was inconsistent with other works [80, 81]. This could be due to the difference in reinforcement type and processing method. However, for the same composites, Young's modulus increased about 71%, which was consistent with other reports [80, 81]. They also found that impact strength of notched samples increased from 7.4 to 12.2 J/m with increased fibre content (0 to 30 wt%) but decreased in the case of unnotched samples (from 76 to 52 J/m). This trend in impact strength of the unnotched composite samples was in general agreement with other researchers [81]. Serizawa *et al.* [83] also used kenaf fibres to fabricate PLA composites by extrusion and injection moulding. They did not present any tensile property data. However, they showed that flexural modulus increased from 4.5 to 7.6 GPa as the fibre content increased from 0 to 20 wt%; on the other hand, flexural strength decreased from 132 to 93 MPa. Impact strength of the notched samples also decreased from 4.4 to 3.1 kJ/m² as the fibre content increased from 0 to 20 wt%, which did not agree with Garcia's findings [82]. Suggestion was made that instead of using a twin screw extruder, composite impact strength can be improved by compounding the materials with a single-screw extruder which prevents the fibre from being ground (crushed particles) during processing. Furthermore, impact strength was found to be increased by adding compatibiliser (copolymer of lactic acid and aliphatic polyester) in composites.

Mathew *et al.* [84] used microcrystalline cellulose (MCC), wood flour and wood pulp to reinforce PLA matrix using similar processing methods to Oksman *et al.* [80]. They found that tensile strength of MCC reinforced composites decreased (from 49.6 to 36.2 MPa) with increased MCC content (0 to 25 wt%) whereas Young's modulus increased significantly (from 3.6 to 5 GPa) as for Garcia *et al.* [82] with kenaf fibre. They also observed that the tensile strength, Young's modulus and storage modulus of wood flour and wood pulp reinforced composites were higher (for wood flour composites tensile strength and Young's modulus were 45.2 MPa and 6.3 GPa, respectively, and for wood pulp composites tensile strength and Young's modulus were 45.2 MPa and 6 GPa, respectively) than those of MCC reinforced composites at similar level of reinforcement. In another study, Lee *et al.* [85] reinforced PLA with bamboo fibres using batch mixing and compression moulding. They also found that Young's modulus increased with increased fibre content (10 to 50 wt%) but tensile strength decreased. In addition, they found that tensile strength and Young's modulus improved at all fibre contents when maleic anhydride treated bamboo fibres (5 wt%) were used as a compatibiliser and

dicumyl peroxide as a free radical initiator. In a later report, Lee *et al.* [86] applied a bio-coupling agent (i.e. lysine-based diisocyanate) as compatibiliser in the PLA/bamboo fibre composites using similar processing method of [85]. Like Lee's findings [85], they observed that Young's modulus of the composites increased with increased fibre content (0 to 50 wt%) but tensile strength decreased. In addition, tensile strength and Young's modulus improved at all fibre contents in the presence of coupling agent. In a more recent report, Takatani *et al.* [87] used cellulose esters (2 wt%), RCOO-cellulose (where R = CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₁₁H₂₃), as compatibiliser for PLA/wood fibre (20 wt%) composites fabricated by mixing (details not given) and hot pressing. It was shown that flexural modulus and storage modulus of PLA/wood fibre composites increased due to inclusion of cellulose esters.

Vila *et al.* [88] used eucalyptus wood fibre and rice husks to reinforce PLA using extrusion and injection moulding. They did not observe any notable increase in tensile strength (specific data was not presented) for the composites reinforced with 30 wt% wood fibre or rice husks compared to PLA only samples but Young's modulus increased significantly [57% increase for PLA/wood fibre and 45% increase for PLA/rice husks composites]. Pill *et al.* [89] used silane treated pine wood flour (PWF) to fabricate PLA composites by kinetic mixing and compression moulding. It was observed that tensile strength of the untreated fibre composites was unchanged (55.5 MPa) at 20 wt% PWF content but decreased (51.7 MPa) at 40 wt% PWF content when compared with that of PLA matrix (55.5 MPa). Young's modulus was found to be increased significantly with increased PWF content (0.63 GPa for PLA, 0.86 GPa for 20 wt% PWF/PLA composites and 1.18 GPa for 40 wt% PWF/PLA composites). They did not find notable change in tensile strength and Young's modulus for the composites reinforced with 20 wt% silane treated fibre compared to the untreated fibre composites. However, they found that tensile strength of the silane treated fibre reinforced composites (57.1 MPa) slightly increased at 40 wt% fibre content but with no significant change in Young's modulus compared to the untreated fibre composites.

Shibata *et al.* [90] treated abaca fibres with acetic anhydride, butyric anhydride, alkali and cyanoethylation to reinforce PLA matrix by melt mixing and injection moulding. They found that flexural strength decreased with increased fibre content (0 to 20 wt%) but flexural modulus increased. They also observed that flexural strength and flexural modulus

of treated fibre reinforced composites did not increase significantly compared with those of untreated fibre composites. Iwatake *et al.* [91] prepared micro-fibrillated cellulose (10 wt%) reinforced PLA composites by kneading and compression moulding. They found that tensile strength and Young's modulus of the composites increased by 25 and 40%, respectively, compared to PLA only samples. They also observed that further addition (15 wt%) of micro-fibrillated cellulose caused a decrease in tensile strength.

Wong *et al.* [92] produced PLA/flax fibre (50% by volume) composites by solution mixing and compression moulding. They found that storage modulus of the composites increased markedly in the presence of plasticisers (triethyl citrate, tributyl citrate and glycerol triacetate). Shanks *et al.* [93] used acrylate monomers to treat unwashed and washed flax fibres to reinforce PLA matrix. Composites were fabricated by solution mixing and compression moulding, similar to work by Wong *et al.* [92]. They showed that the washed acrylated fibre composites had higher storage modulus than the unwashed acrylated composites.

Masirek *et al.* [94] fabricated PLA/hemp fibre composites by melt mixing and compression moulding. They found that Young's modulus of the composites increased markedly (from 3.7 to 4.2 GPa) with increased fibre content (0 to 20 wt%) but tensile strength decreased (from 56.8 to 33.9 MPa). It was also observed that the plasticiser (polyethylene glycol) did not improve tensile strength and Young's modulus of the composites, which was consistent with other work [80]. Pan *et al.* [95] used kenaf fibres to reinforce PLA matrix using extrusion and compression moulding. Like other report [82], they found that tensile strength of the composites decreased (from 47.4 to 35.5 MPa) with increased fibre content (0 to 30 wt%) but Young's modulus increased (from 1.43 to 1.86 GPa).

Plackett *et al.* [96] fabricated aligned long jute fibre mat (40 wt%) reinforced PLA composites, which were first pressed and consolidated under vacuum at different temperatures (180 to 220°C) then compression moulded. They found that tensile strength and Young's modulus of the composites increased significantly compared to PLA only samples (tensile strength 55 MPa and Young's modulus 3.5 GPa) at all processing temperatures. Composites processed at 210°C had the highest tensile strength (100.5 MPa) and Young's modulus (9.4 GPa). This significant increase in tensile strength and Young's modulus compared to other findings [80, 81, 97] appears to be due to the alignment of

fibres in loading direction. They also observed that there was a trend towards decreasing molecular weight of PLA with increasing processing temperature.

The above studies indicate that generally Young's modulus, flexural modulus and storage modulus of PLA composites can be improved by adding fibres. This is because natural fibres are very stiff compared to PLA matrix. However, tensile and impact strength of the composites can greatly be influenced by the variety of fibres and processing methods.

2.3.2 Unsaturated polyester resin as a matrix material

Unsaturated polyester (UPE) resin is a condensation polymer formed by the reaction of polyol and polycarboxylic acid. The polyol and polycarboxylic acid are usually dihydric alcohols (e.g. ethylene glycol and propylene glycol) and difunctional acids (e.g. phthalic and maleic acid), respectively. Monomers such as styrene and methyl methacrylate possessing double bonds are used as crosslinking agents [98]. Catalysts (e.g. methyl-ethyl ether ketone peroxide) and accelerators (e.g. cobalt octoate) are used to promote the crosslinking reaction. A schematic chemical structure for an unsaturated polyester resin is presented in Figure 2.10.

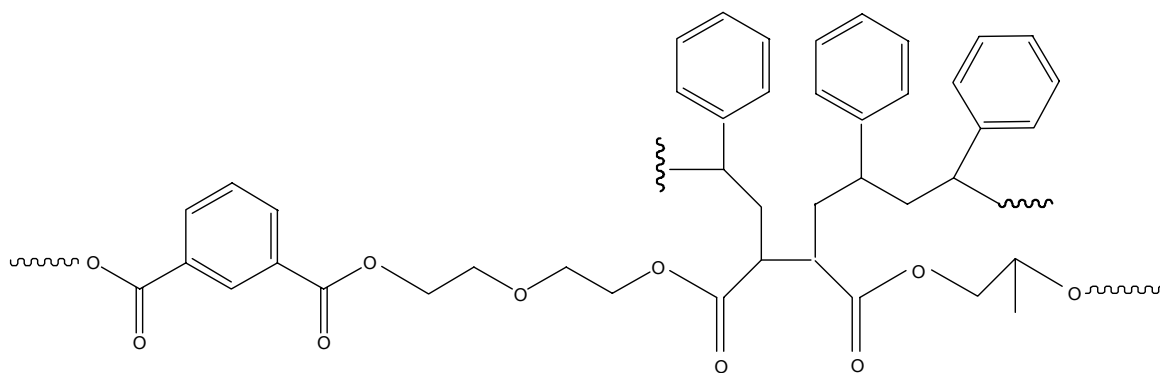


Figure 2.10: Schematic chemical structure of UPE.

2.3.2.1 Natural fibre reinforced unsaturated polyester resin composites

UPE resins are the most frequently used thermoset matrices owing to their low cost and adaptability to be transformed into large composite structures. Recently, natural fibre reinforced UPE composites have drawn much attention due to their low density and good specific strength and stiffness [99].

Mehta *et al.* [64] used alkali, silane, UPE resin and acrylonitrile treated randomly oriented nonwoven hemp fibre mats [90% hemp fibre (1-2 inches long) and 10% polyethylene terephthalate as binder] to produce UPE composites by compression moulding. Tensile strength (about 39 MPa) and Young's modulus (about 6 GPa) of untreated hemp fibre (30% by volume) composites were 45 and 325%, respectively, higher than that of UPE only samples (tensile strength and Young's modulus were approximately 26 MPa and 2.3 GPa, respectively). Tensile strength of alkali, silane, UPE resin and acrylonitrile treated fibre reinforced composites were 34, 48, 57 and 80%, respectively, higher than that of untreated fibre composites. Young's modulus of silane treated fibre composites had enhancement of 6% as compared with that of untreated fibre composites, while UPE resin modified fibre composites had an enhancement of 4%, and acrylonitrile treated fibres had a 25% enhancement compared with that of untreated fibre composite. Treated fibre composites had 10-16% enhancement in flexural strength and 140-225% increment in flexural modulus compared to UPE only samples (flexural strength and flexural modulus were approximately 105 MPa and 6 GPa, respectively). There was an improvement of 82% in impact strength for untreated hemp fibre composites, 49% for alkali treated fibre composites, 94% for silane treated fibre composites, 120% for UPE resin treated fibre composites and 180% for acrylonitrile treated fibre reinforced composites as compared to unreinforced UPE (about 10 J/m). The above results suggest that fibre/matrix interfacial bonding increased due to the treatment of fibres.

In another study, Sèbe *et al.* [100] fabricated non-woven hemp fibre mat (fibre orientation was not mentioned) reinforced UPE composites by resin transfer moulding (RTM). They found that flexural strength and flexural modulus of the composites increased with increased fibre content (0 to 36 wt%). At 36 wt% fibre content, flexural strength and flexural modulus increased by 220 and 100%, respectively, compared to UPE only samples (flexural strength and flexural modulus were approximately 30 MPa and 3 GPa, respectively). This increase in flexural strength was higher than Mehta's findings [64], on the other hand, flexural modulus was lower. The above discrepancy in flexural properties of two research works may be due to the difference in fibre orientation and/or fibre quality. Impact strength of unnotched samples was found to decrease slightly at low fibre content (11 wt%) then increased with increased fibre content. At 36 wt% fibre content, impact strength was found to be 14 kJ/m², which was more than double that for the unreinforced UPE only samples.

Ahmed *et al.* [101] prepared composites of woven jute fabric (43.8 wt%) by compression moulding. Results showed that tensile strength (80.2 MPa) and Young's modulus (9.5 GPa) of the composites were 83.96 and 118.7%, respectively, higher than those of unreinforced UPE samples (tensile strength = 43.5 MPa and Young's modulus = 4.3 GPa). Flexural strength (121.8 MPa) and flexural modulus (7.64 GPa) of the composites found to be 31.8 and 209%, respectively, higher than those of UPE only samples (flexural strength = 92.3 MPa and flexural modulus = 2.4 GPa). This increase in tensile and flexural properties was in general agreement with other work [64].

Kiran *et al.* [102] used randomly oriented sun hemp, banana and sisal fibre to fabricate UPE composites by compression moulding. In this work, composites were prepared with various fibre lengths (10 to 70 mm) and fibre content (1 to 70 wt%). Results showed that composite tensile strength increased gradually with increased fibre length up to 30 mm then decreased. The maximum tensile strength (59.4 MPa) was obtained with 56 wt% sun hemp fibre (fibre length 30 mm) reinforced composites. Composite Young's modulus was not presented. In another study, Mwaikambo *et al.* [103] produced untreated and alkali treated (pre-treated with petrol) cotton-kapok fabric reinforced UPE composites using compression moulding. They found that tensile strength of untreated fabric reinforced composites decreased (from 57.4 to 53.2 MPa) with increased fibre content (from 58 to 65% by volume) but Young's modulus did not show a general trend with respect to fibre content. They also found that tensile strength of alkali treated fibre composites was lower than that of untreated fibre composites but Young's modulus of treated fibre composites was found to be higher than that of untreated fibre composites. This decrease in tensile strength of alkali treated fibre composites may be due to pre-treatment of fibres with petrol prior to alkali treatment which caused damage to the fibres.

Aziz *et al.* [104] used aligned long and random short hemp and kenaf fibres to reinforce UPE resin by compression moulding. Flexural strength of long and short hemp fibre composites (60% by volume long fibre and 55% by volume short fibre) was found to be about 77 and 40 MPa, respectively, with flexural modulus about 7 and 3.5 GPa, respectively. In contrast, flexural strength of long and short kenaf fibre composites (67% by volume long fibre and 56% by volume short fibre) was found to be about 30 and 25 MPa, respectively, and flexural modulus found to be about 3.5 and 2 GPa, respectively. They also reported that alkali treated fibre composites had significantly higher flexural

strength and flexural modulus (about 12 to 300% increases) compared with those of untreated fibre composites, which may be due to increased interfacial bonding between the treated fibres and the resin.

Hill *et al.* [105] used non-woven mats of random coir and oil palm fibres (0 to 55 wt%) to reinforce UPE by compression moulding. They found that tensile strength and Young's modulus of all the composites decreased slightly at low fibre content (15 wt%) then increased with increased fibre content, except at the highest fibre content where tensile strength and Young's modulus decreased again. The initial decrease in tensile properties may be due to non-homogeneous stress distribution in the composites during tensile loading and the decrease in tensile properties at the highest fibre content may be due to lack of sufficient matrix to wet the fibres. Composites reinforced with 45 wt% coir fibres had the highest tensile strength (39.8 MPa) and Young's modulus (5.2 GPa). They also found that tensile strength and Young's modulus of the silane and acetylated fibre reinforced composites slightly higher (2-4%) than the untreated fibre composites. Flexural strength of all the composites found to be lower than UPE only samples (52 MPa) at all fibre contents but flexural modulus showed a trend similar to Young's modulus with respect to fibre content. Composites reinforced with 45 wt% coir fibres had the highest flexural modulus (4.97 GPa). Impact strength of all the composites showed a trend similar to tensile strength with respect to fibre content. Composites reinforced with 45 wt% oil palm fibres had the highest impact strength (18.7 kJ/m²).

Acha *et al.* [106] used bidirectional jute fabrics (46 to 56 wt%) to reinforce UPE composites by compression moulding. They studied the effect of jute fabric treatment (e.g. acetone and detergent wash) and fabric orientation (e.g. 0, 30 and 45°) with respect to applied force on composite tensile properties. Results showed that Young's modulus of all the composites increased significantly (40-160%) compared to UPE only samples but tensile strength decreased (tensile strength and Young's modulus of UPE samples were 55 MPa and 3 GPa, respectively). When the fibres were oriented at 0°, tensile strength and Young's modulus of untreated fibre composites found to be higher than that of treated fibre composites. At 30 and 45°, it was shown that there was no general trend (increase or decrease) in tensile strength and Young's modulus of untreated fibre composites with respect to treated fibre composites.

Idicula *et al.* [107] used randomly oriented short banana and sisal fibres to produce hybrid fibre reinforced UPE composites. In the composites, the total volume fraction of banana and sisal fibres was kept constant to 0.4 volume fraction. It was found that tensile strength and Young's modulus increased with increased banana fibre content from 0 to 65% by volume. Further increase in banana fibre content caused decrease in tensile strength and Young's modulus. At the optimum banana fibre content (65% by volume), tensile strength and Young's modulus of the composites were about 58.5 MPa and 1.5 GPa, respectively (tensile strength and Young's modulus of UPE resin were 33 MPa and 0.95 GPa, respectively). The authors suggested that the improved reinforcing efficiency of banana fibres compared to sisal fibres was due to micro-fibril angle of banana fibre (11°) being less than that of sisal fibre (20°). It was also seen that impact strength of the composites decreased with increased volume fraction of banana fibres. The authors suggested that lumen size of sisal fibres is greater than that of banana fibres which increases the porous nature of the fibre and explain improved impact strength.

Hughes *et al.* [108] reported fracture toughness of nonwoven aligned long hemp and jute fibre (16 to 45% by volume) reinforced UPE composites fabricated by compression moulding. They found that fracture toughness of the composites increased with increased fibre content. This may be due to increased debonding and pull-out of fibres with increased fibre content. Composites reinforced with 45% hemp and jute fibre had fracture toughness of 5.92 and 5.31 MPa-m^{-1/2}, respectively, whereas fracture toughness of UPE only samples was 0.6 MPa-m^{-1/2}.

The works reviewed in this section indicate that mechanical performance of the UPE composites can greatly be influenced by the variety of fibres, similar to the PLA composites as discussed in section 2.3.1.1. In general, Young's modulus and flexural modulus of the UPE composites can be increased by adding fibres, analogous to PLA composites. In addition, it is also seen that bonding between natural fibre and UPE matrix can be improved by the treatment of fibres.

2.4 Polymer composite processing

Processing of thermoset matrix composites can be divided into open mould (e.g. hand lay-up and filament winding) and closed mould (e.g. compression moulding, vacuum bag moulding, resin transfer moulding and pultrusion). Injection moulding and hot pressing are

the two most widely used thermoplastic composite processing methods. Brief details of these methods are presented in the following sections.

2.4.1 Open moulding

- **Hand lay-up:** This is the simplest way of processing thermoset resins into final products. Prior to lamination, the mould is cleaned carefully and release agent is applied to the mould. Subsequent layers of reinforcement are added to build laminate thickness. The laminating resin is applied by pouring, brushing, spraying, or using paint rollers. Paint rollers, or squeegees are used to consolidate the laminate, thoroughly wetting the reinforcement, and removing entrapped air. The curing of a product takes usually 4 – 12 hours, depending on the size, thickness and complexity of the product. After curing the product is taken out of the mould.
- **Filament winding:** In this process, continuous strand roving is fed through a resin bath and wound onto a rotating former. The roving feed runs on a trolley that traverses the length of the former. The filament is laid down in a predetermined geometric pattern to provide maximum strength in the directions required. When sufficient layers have been applied, the laminate is cured on the former. The moulded part is then stripped from the former. Filament winding is used in the manufacture of hollow, generally cylindrical products such as chemical and fuel storage tanks, pipes, stacks, pressure vessels, and rocket motor cases.

2.4.2 Closed moulding

- **Compression moulding:** In this process, a weighed charge of moulding compound is placed in the open mould. The two halves of the mould are closed and pressure is applied. Curing time depends on thickness, size, and shape of the part. The mould is opened and the finished part is removed.
- **Vacuum bag moulding:** In this process, a flexible film (nylon or polyethylene) is placed over the wet lay-up, the edges sealed, and a vacuum drawn. By reducing the pressure inside the vacuum bag, external atmospheric pressure exerts force on the bag. The pressure on the laminate removes entrapped air, excess resin, and compact the laminate. A higher percentage of fibre reinforcement is the result. Vacuum bag processing can produce laminates with a uniform degree of consolidation, while at the same time removing entrapped air, thus reducing the finished void content.

- **Resin Transfer Moulding:** In this process, reinforcement is positioned in the mould and then the mould is closed and clamped. Afterwards, the resin is injected under pressure, using mix/meter injection equipment, and the part is cured in the mould. Vacuum assistance can be used to enhance resin flow in the mould cavity. This process can be automated and is capable of providing rapid cycle times.
- **Pultrusion:** This is a continuous process for the manufacture of products having a constant cross section, such as rod stock, structural shapes, beams, channels, pipe, tubing, fishing rods, and golf club shafts. In this process, continuous strands roving, mat, cloth, or surfacing veil is impregnated in a resin bath, and then pulled through a steel die, by a powerful tractor mechanism. The steel die consolidates the saturated reinforcement, sets the shape of the stock, and controls the fibre/resin ratio. The die is heated to rapidly cure the resin.

2.4.3 Injection moulding

This process requires the transfer of the materials in powder or granule form from a feed hopper to a heated barrel. In the barrel, the material is melted and then injected into a mould with some form of plunger arrangement. The mould is clamped shut under pressure within a platen arrangement and is held at a temperature well below the thermoplastic melt point. The molten materials solidify quickly within the mould, allowing ejection of the component after a pre determined period of cooling time [25].

2.4.4 Hot pressing

The first stage in fabrication is the production of a pre-preg by melt impregnation of the fibres, which may be in the form of aligned or random mats. Afterwards, the pre-preg sheets are stacked in the required orientations and hot pressed. The temperature is usually set to the minimum necessary for the matrix to melt and flow sufficiently for consolidation to occur [25].

CHAPTER THREE

Experimental

3.1 Introduction

In this research, industrial hemp fibres were used to produce polylactide and unsaturated polyester matrix composites; both short and long fibres were employed. Surface modification of fibres was investigated as a means of improving the fibre/matrix interfacial and mechanical properties of composites. A set of physical, mechanical and thermal tests for the fibres and composites was adopted to obtain a thorough understanding of composites behaviour to help identify the possible ways in which performance might be improved.

This chapter describes in brief the materials, fibre treatment methods and characterisation techniques, composite processing and testing methods.

3.2 Materials

3.2.1 Matrices

NatureWorks[®] PLA (polylactide) polymer 4042D, from NatureWorks LLC, USA was used as a thermoplastic matrix. PLA was provided in a pellet form with a density of 1.25 g/cc.

A standard unsaturated polyester resin (Crystic P489 from Nuplex, New Zealand) of 60% styrene content was used as thermoset matrix. The polymer is based on isophthalic acid and maleic anhydride, with mono propylene glycol and diethylene glycol. The resin also contains fumed silica as a viscosity control agent, and is preaccelerated with a combined cobalt/amine promoter system. The viscosity of the resin at 25°C was 600 cps.

3.2.2 Fibres

In this work, two different batches of industrial hemp fibres were used. The fibres were grown in the UK and supplied by Hempcore Ltd, UK. The first batch was received in 2004 and the second batch was received in 2007. According to the supplier, these fibres had been dew retted and mechanically decorticated, prior to chopping and baling.

3.2.3 Chemicals

The chemicals used in this work are listed in Table 3.1.

Table 3.1: List of the chemicals.

Chemical	Source/supplier
Acetic anhydride	AnalaR
Acetone	Merck
Acetic acid	AnalaR
Benzene	AnalaR
Dichloromethane	Merck
Ethanol	AnalaR
Hydrochloric acid (HCl)	AnalaR
Maleic anhydride	Sigma
Methylether ketone peroxide	Fibreglass International
Potassium bromide (KBr)	Merck KGaA
Sodium hydroxide (NaOH)	Scharlau Chemie S.A.
Sulphuric acid (H ₂ SO ₄)	Ajax Finechem Pty Ltd
[3-(2-aminoethyl amino)propyl]trimethoxy silane	Aldrich

3.3 Methods

3.3.1 Fibre treatment

Nomenclature for the fibres (untreated and treated) used in this work is listed in Table 3.2. For the two batches of hemp fibre (FB1 and FB2), tensile strength of FB2 fibres was found to be higher than that for FB1 fibres (see chapter four); accordingly FB2 fibres were selected for treatment with different chemicals namely sodium hydroxide, acetic anhydride, maleic anhydride and silane. A combination treatment of alkali and silane was also carried out. The rationale behind the selection of these treatments was that these treatments have been found to enhance interfacial and mechanical strength with the other polyester matrices [29, 62, 64, 99, 104, 109-114]. Prior to the treatments, fibres were washed with hot water (50°C) to remove dirt and impurities. Afterwards, fibres were dried in an oven at 80°C for 48 hours.

3.3.1.1 Alkali treatment

Pre-dried fibres were soaked in 5% sodium hydroxide (NaOH) solution at ambient temperature, maintaining a liquor ratio of 20:1 (by weight). The fibres were kept immersed in the solution for 30 minutes. After treatment, fibres were copiously washed with water to remove any traces of alkali on the fibre surface and subsequently neutralised with 1%

acetic acid solution. The neutrality was checked with litmus paper. The treated fibres (ALK) were then dried in an oven at 80°C for 48 hours.

3.3.1.2 Silane treatment

A solution of 0.5 wt% silane coupling agent [3-(2-aminoethyl amino)propyl trimethoxy silane] was prepared in acetone. Acetone was used in preference to water to promote hydrolysis to take place with the moisture on the surface of the fibres rather than within the carrier. It is also reported that acetone promotes swelling of the fibre and so increases the fibre surface area exposed to treatment [115]. The pH of the solution was adjusted to 3.5 with acetic acid and stirred continuously for 5 minutes. Fibres (6-7 wt% moisture content) were then immersed in the solution for 45 minutes. After treatment, fibres were removed from the solution and dried in oven at 65°C for 12 hours. Fibres were then thoroughly washed with acetone and dried again in air. Finally, the fibres were thoroughly washed with water to remove chemical residues until a pH of 7 was obtained and then dried in an oven at 80°C for 48 hours. Similar silane treatment procedures also employed for fibres that were previously alkali treated.

3.3.1.3 Maleic anhydride treatment

Fibres were treated with maleic anhydride at a concentration of 5 wt% with respect to the weight of fibres. For this esterification, pre-dried fibres were placed in a round-bottom flask equipped with a water condenser. The calculated amount of maleic anhydride and acetone was added in the flask, maintaining a fibre to solution ratio of 1:20. The flask was refluxed on a heating mantle maintained at a temperature of 65°C for 3 hours. Thereafter, the fibres were separated from the solvent and washed with acetone to remove unreacted maleic anhydride. Finally, the treated fibres (MA) were washed thoroughly with water to remove residual chemicals and then dried in an oven at 80°C for 48 hours.

3.3.1.4 Acetylation

Fibres (4-5 wt% moisture content) were placed in a glass beaker with a sufficient amount of acetic anhydride ensuring that all fibres were totally covered with the reagent to enable the moisture present in the fibres to hydrolyse the acetic anhydride to acetic acid. In addition to chemical modification acetic acid also improves swelling of fibres increasing the accessibility of hydroxyl groups of the fibres, and eliminating the need for a solvent [54]. A few drops of sulphuric acid were added to promote the reaction. After 15 minutes,

the fibres were removed from the beaker and placed in a pre-heated (120°C) oven for 2 hours to complete the esterification reaction. Lastly, treated fibres (ACY) were thoroughly washed with water to remove residual chemicals until a pH of 7 was obtained, and then dried in an oven at 80°C for 48 hours.

Table 3.2: Nomenclature used for untreated and various treated hemp fibres.

Abbreviation	Fibres
FB1	Untreated fibres (batch 1, received in 2004)
FB2	Untreated fibres (batch 2, received in 2007)
	<u>Treatment of FB2 fibres</u>
ALK	Alkali (Sodium hydroxide) treated fibres
SIL	Silane treated fibres
ALKSIL	Fibres first treated with alkali solution and then with a silane solution
MA	Maleic anhydride treated fibres
ACY	Acetic anhydride treated fibres

3.3.2 Fabrication of composites

The nomenclature for the different untreated and treated hemp fibres reinforced PLA and UPE composites are listed in Table 3.3.

Table 3.3: Nomenclature used for various treated and untreated hemp fibres reinforced composites.

Abbreviation	Composites
PLA/FB1	FB1 fibre reinforced polylactide composites
PLA/FB2	FB2 fibre reinforced polylactide composites
PLA/ALK	ALK fibre reinforced polylactide composites
PLA/SIL	SIL fibre reinforced polylactide composites
PLA/ALKSIL	ALKSIL fibre reinforced polylactide composites
PLA/MA	MA fibre reinforced polylactide composites
PLA/ACY	ACY fibre reinforced polylactide composites
UPE/FB2	FB2 fibre reinforced unsaturated polyester composites
UPE/ALK	ALK fibre reinforced unsaturated polyester composites
UPE/SIL	SIL fibre reinforced unsaturated polyester composites
UPE/ALKSIL	ALKSIL fibre reinforced unsaturated polyester composites
UPE/MA	MA fibre reinforced unsaturated polyester composites
UPE/ACY	ACY fibre reinforced unsaturated polyester composites

3.3.2.1 PLA/short fibre composites

Prior to processing, chopped fibres (average length 4.9 mm) and PLA were dried in an oven at 80°C overnight. PLA/hemp fibre composites were compounded (10, 20 and 30 wt% fibre) in a ThermoPrism TSE-16-TC twin screw extruder [screw diameter (D): 15.6 mm, L/D = 25:1, where L is barrel length]. The extruded composite material was pelletised and dried at 80°C for 24 hours and then injection moulded using a BOY15-S injection moulding machine. No processing aids or other additives were used. The processing parameters are shown in Table 3.4. A photograph of the untreated and various treated hemp fibre reinforced PLA composites (tensile specimens) is shown in Figure 3.1.

Table 3.4: Processing parameters for extrusion and injection moulding.

Extrusion	Injection moulding
Temperature profile	Temperature profile
Feeding zone: 110°C Mixing zone: 175-185°C Metering zone: 190 °C Die: 185 °C	Feeding section: 155°C Compression section: 175-185°C Metering section: 190°C Nozzle: 180 -185°C Mould: 25-30°C
Screw speed: 100 rpm Torque: 45-55 (%)	Residence time in mould: 25 seconds Screw speed: 160 rpm

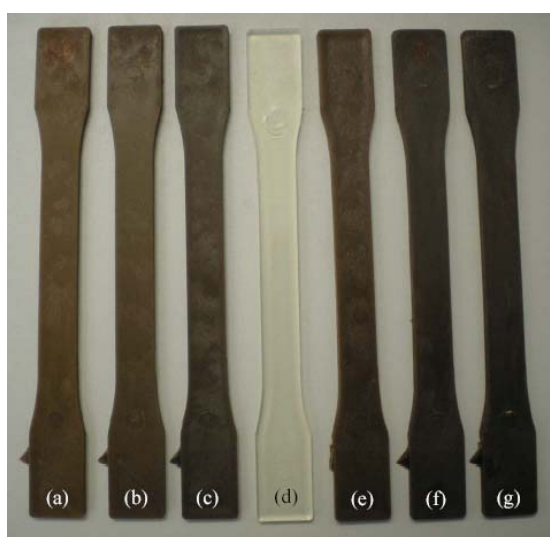


Figure 3.1: Injection moulded short fibre reinforced (30 wt% fibre) PLA composites; (a) PLA/ALKSIL, (b) PLA/SIL, (c) PLA/ALK, (d) PLA, (e) PLA/FB2, (f) PLA/ACY, and (g) PLA/MA.

It was noted that with reinforcement above 30 wt% processing became difficult due to poor melt flow of the compounded materials. Similar behaviour has also been reported by the other researchers; it has been observed that reinforcement of PLA with risk husks and wood fibres above 30 wt% was difficult to obtain by conventional injection moulding equipment [88].

3.3.2.2 PLA/long fibre composites

PLA and aligned long fibre (average length 65 mm) composites were produced by compression moulding using the film-stacking method at three different fibre contents (30, 35 and 40 wt%). Dried long fibres were aligned using a hand carding machine from Ashford Handicrafts Limited, New Zealand. PLA films were produced from dry pellets, using an extruder equipped with a coat hanger die. The thickness of the films was approximately 0.5 mm. PLA sheets and fibres were weighed prior to composite fabrication so as to determine the weight percentage (wt%) of fibres and matrix of the resulting composites. Stacks of PLA films and fibres were prepared by placing alternately PLA films and aligned fibre mats in a parallel array. Before pressing, these were placed between two Teflon sheets in a stainless steel matched-die mould (220 x 150 x 3.5 mm³).



Figure 3.2: Aligned long hemp fibre reinforced PLA composites fabricated by compression moulding.

The ready stacks of PLA and fibres were pre-pressed at 185°C for 5 minutes keeping a constant pressure of 2 MPa using a hot press machine, and afterwards compacted at elevated pressure of 5 MPa for 3 minutes. The assembly was consolidated under a pressure

of 5 MPa until the mould was naturally cooled down to ambient temperature. Long aligned hemp fibre reinforced PLA composites are shown in Figure 3.2.

3.3.2.3 UPE/short fibre composites

In this study, hemp fibre reinforced unsaturated polyester resin composites were fabricated by compression moulding due to simplicity. Prior to composite fabrication, chopped fibres (fibre length 3-5 mm) were dried in an oven at 80°C overnight. A mould releasing agent was sprayed onto a tissue and smeared evenly onto the surface of the mould. Dried fibres were weighted to give 20, 30, 40, 50 and 60 wt% and randomly oriented by hand in the mould cavity (220 x 150 x 3.5 mm³), and polyester prepolymer along with 1% (w/w) MEKP (methylether ketone peroxide) was poured over the fibres. The mould was then closed and curing was carried out at room temperature for 5 hours at a pressure of 5 MPa. The composites were post-cured at 80°C in an oven for 3 hours.

3.3.2.4 UPE/long fibre composites

Dried long fibres (average length 65 mm) were aligned according to method described in the section 3.3.2.2. Aligned long fibre/UPE composites at three different fibre contents (30, 40 and 50 wt%) were produced according to the method described in section 3.3.2.3.

All composite plaques (described in section 3.3.2.2, 3.3.2.3 and 3.3.2.4) were cut to desired shapes using a computer numerical controlled (CNC) mill.

3.4 Characterisation and testing of fibres and composites

3.4.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR measurements were performed using a Digilab FTS-40 FT-IR spectrometer equipped with a DTGS detector. A total of 30 scans were taken for each sample with a resolution of 4 cm⁻¹. Grounded dried sample and KBr (2 mg sample per 150 mg KBr) was pressed into a disk for FT-IR measurement.

3.4.2 X-ray diffraction (XRD)

A Philips X-ray diffractometer, employing CuK α ($\lambda = 1.54$) radiation and a graphite monochromator with a current of 40 mA and a voltage of 40 mV was used. The diffraction intensity was in the range of 12 to 45° of 2 θ (Bragg angle), and the scanning speed was 0.02°/sec.

3.4.2.1 Cellulose crystallinity index

The use of XRD counts offers a simple and fast method to calculate the crystallinity index of fibres by means of the empirical Segal equation (Equation 3.1) [51, 116-118].

$$I_{XRD} (\%) = \frac{I_{002} - I_{amp}}{I_{002}} \times 100 \quad (3.1)$$

where I_{XRD} crystallinity index, I_{002} is the maximum intensity of the 002 lattice diffraction plane at a 2θ angle of between 22° and 23° ($22^\circ \leq 2\theta \leq 23^\circ$) and I_{amp} is the intensity diffraction at an angle 2θ close to 18° representing amorphous materials in cellulosic fibres. For the measurements, about 15 mg of fibres were cut and pressed into a disk using a cylindrical steel mould with an applied pressure of 10 MPa in a laboratory hydraulic press.

3.4.3 Single fibre tensile strength measurement

Single fibre tensile strength of hemp fibres was measured according to the ASTM D3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials [119]. Specimens were prepared by separating fibre bundles by hand, and then attaching single fibres to cardboard mounting-cards using polyvinyl acetate glue with 10 mm holes punched into them to give a gauge length of 10 mm (see Figure 3.3). The mounted fibres were then placed in the grips of an Instron 4204 tensile testing machine, and a hot-wire cutter was used to cut the supporting sides of the mounting cards.

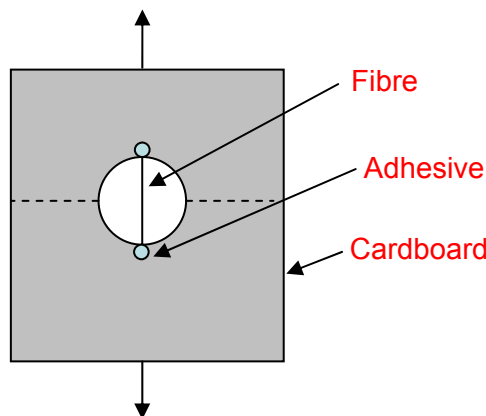


Figure 3.3: Schematic diagram of single fibre mounting for tensile testing.

Tensile testing of the fibres was carried out at a cross-head speed of 0.5 mm/min using a 10 N-load cell. The fibre was assumed to have a cylindrical shape. The diameter was measured at five points along each fibre using an optical microscope with a calibrated eye-piece, and the average diameter was used to calculate the tensile properties of fibres. Average strength was obtained using the results from thirty five specimens.

3.4.4 Interfacial strength measurement by pull-out test

The single fibre pull-out test is the most extensively used test method because of its simplicity and versatility and the fact that it can be used to evaluate a number of interfacial parameters [120]. The procedure for pull-out specimen preparation depends on the physical state of the matrices. For instance, thermoset pre-polymers are usually liquid at room temperature and it is easy to prepare specimens for pull-out testing. On the other hand, thermoplastics are generally solid at room temperature and require heat for melting to give higher viscosity liquids and are thus more difficult to prepare samples from.

3.4.4.1 PLA/hemp fibre specimen preparation

In this work, a simple new procedure of pull-out specimen preparation for PLA/hemp fibre samples was implemented. The sample preparation method is as follows. A hole of 6 mm diameter was made in a silicon rubber mould (18mm x 24mm x 3 mm) from the top side of mould using a punch (see Figure 3.4). Along the 18 mm length side of the mould wall a slot was cut to a depth of 2.5 mm. The mould was flexed to open the cut to allow the introduction of a fibre and then released to grip the fibre. The desired embedded length was obtained by drawing the fibre through the cut under optical light microscope. Fibre diameters were measured using an optical microscope with a calibrated eye-piece. Then the mould was kept on a piece of Teflon sheet on a glass plate, and two pieces of PLA pellets were placed into the mould cavity. The samples were obtained by placing the ready moulds in a pre-heated oven (180°C) for 5 minutes and then allowed to cool in air at room temperature. The samples were prepared with a range of embedded lengths from 0.25 mm to 2 mm and a free-fibre length of approximately 5 mm. The free-fibre end was glued to a piece of cardboard.

Pull-out testing was performed on an Instron machine. The sample was held on the upper cross-head and the paper cardboard was gripped with the stationary bottom part. The force was measured with an accuracy of ± 0.1 mN.

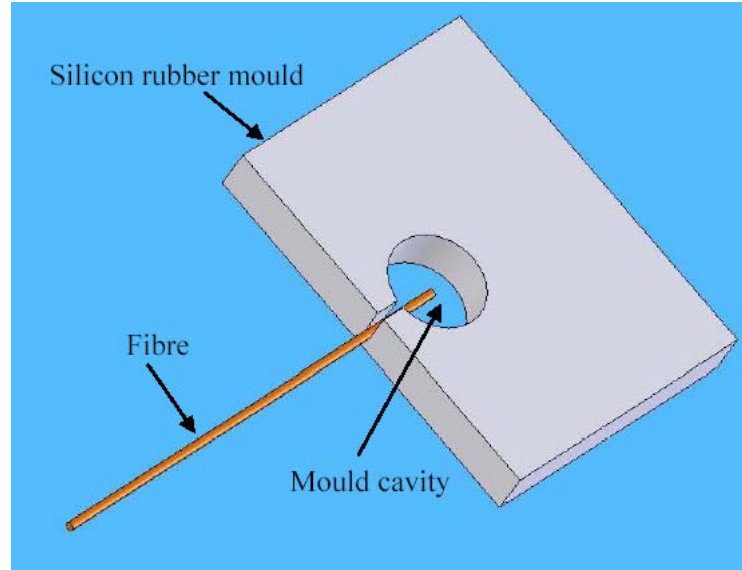


Figure 3.4: Illustration of specimen preparation for pull-out testing.

3.4.4.2 UPE/hemp fibre specimen preparation

UPE/hemp fibre pull-out specimen preparation and testing were achieved using the same procedure described in section 3.4.4.1, except pre-heating the UPE resin. The samples were cured at room temperature for 5 hours followed by post-curing in a pre-heated (80°C) oven for 3 hours.

3.4.5 Fibre length distribution

Fibre length distribution in the injection moulded short fibre composites was measured according to the following procedure: specimens were dissolved in dichloromethane and then some suspended fibres were cast on a microscope glass slide. The fibres were observed with an optical microscope and fibre length was measured by direct analysis of the micrographs using ImagePro AMS 6.0 software. About 250-300 fibres were measured for each sample and their length were statistically analysed to obtain the cumulative distribution function $P(l)$ [121]:

$$P(l) = \frac{\sum_{i=0}^l N_i}{\sum_{i=0}^{\infty} N_i} \quad (3.2)$$

where $P(l)$ is the cumulative probability to find fibres with length shorter or equal to l and N_i is the number of fibres with length i .

3.4.6 Density measurement of fibres

Density of the untreated and treated hemp fibres was measured according to the ASTM D 3800-99 Standard Test Method for Density of High-Modulus Fibres [122]. Benzene was used as immersion liquid [123]. Prior to the measurements, the samples were dried overnight in an oven at 80°C. The density of the fibres was calculated using Equation 3.3.

$$\rho_f = \frac{\rho_l W_{fa}}{W_{fa} - W_{fs}} \quad (3.3)$$

where ρ_l is the density of benzene (0.8765 g/m³), W_{fa} is the weight of fibre in air and W_{fs} is the weight of fibre in liquid.

3.4.7 Mechanical testing of composites

Prior to testing, all samples were conditioned for 48 hours at 50% (± 5) relative humidity and a temperature of 23°C (± 2) [124].

3.4.7.1 Tensile testing

Tensile testing was carried out according to the ASTM D 638-03 Standard Test Method for Tensile Properties of Plastics [125]. Samples were tested by an Instron 4042 tensile test machine fitted with 50 kN-load cell. The cross-head speed was 5 mm/min. Load versus extension data were acquired by computer, which was also facilitated machine control. Strain was measured with an extensometer, attached to the central portion of the test specimen with clips. Five samples were evaluated for each batch of samples.

3.4.7.2 Flexural testing

Flexural testing was performed using a LLOYD LR 100K universal testing machine according to the ASTM D 790-03 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials [126]. Specimen coupons of dimensions 100 x 12.7 x 3.5 mm³ were utilised. The sample span-to-depth ratio was 16:1 and the cross-head speed was 1.5 mm/min. Five samples were assessed for each batch of samples.

3.4.7.3 Impact testing

The impact testing was carried out according to the EN ISO 179 Plastics – Determination of Charpy impact strength [127]. Ray-Ran Pendulum Charpy Impact System machine was used to measure the impact strength of the composites. The impact velocity was 2.9 m/s and the hammer weight of 0.475 kg. Dimensions of the samples were 80 x 8 x 3.5 mm³ with a single notch of 0.25 mm. Five replicates were evaluated for each batch of samples.

3.4.7.4 Fracture toughness testing

Mode I fracture toughness testing was carried out using single-edge-notched-bend (SENB) specimen according to the ASTM D 5045-99 Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials [128]. LLOYD LR 100K universal testing machine was used for this purpose. Four samples were evaluated for each batch of sample. Specimen length (L), span length (S), width (W) and thickness (B) of the testing samples are given in Table 3.5. Specimen dimensions satisfy the condition $2B < W < 4B$ which is standardised for SENB specimens used in plane-strain fracture toughness of plastics. Specimen configuration is shown in Figure 3.5.

Table 3.5: Dimensions of SENB specimens.

Composites	Length (L) (mm)	Width (W) (mm)	Thickness (B) (mm)	Span length (S) (mm)
PLA/hemp fibre	55.88	12.7	3.5	50.8
UPE/hemp fibre	61.6	14	5	56

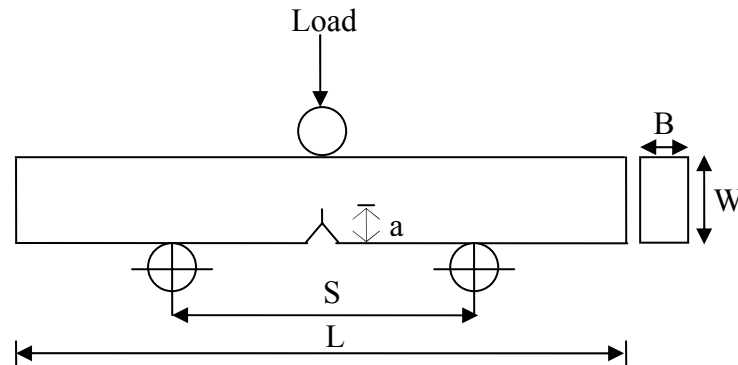


Figure 3.5: Illustration of specimen configuration and experiment setup of the single-edge-notched-bend (SENB) fracture toughness testing.

Mode I plane-strain fracture toughness (K_{Ic}) of single-edge-notch-bending (SENB) specimens can be calculated with the following relations [128]:

$$K_Q = \left(\frac{P_Q}{BW^{1/2}} \right) f(x) \quad (3.4)$$

and

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}} \quad (3.5)$$

where K_Q is the trial K_{Ic} , P_Q is the load, $f(x)$ is the geometrical correction factor ($0 < x < 1$) expressed as a/W and a is the initial crack length. P_Q can be measured from the load versus deformation curve.

In order for K_Q to be considered as plane-strain fracture toughness (K_{Ic}), the following size criterion must be satisfied:

$$B, a, (W-a) > 2.5(K_Q / \sigma_y)^2 \quad (3.6)$$

where σ_y is the yield strength of the specimen. Then,

$$K_Q = K_{Ic} \quad (3.7)$$

Tensile testing should be performed in such a way that loading rate and temperature are same as the fracture toughness testing.

Strain energy release rate (G_{Ic}) can be derived from integration of the load versus displacement curve up to the same load point as used for K_{Ic} . The general formula for G_{Ic} calculation of bend specimens is given in Equation 3.8.

$$G_{Ic} = \frac{U}{BW\phi} \quad (3.8)$$

where U is the energy and ϕ is the energy calibration factor. ϕ may be computed from the Equation 3.9.

$$\phi = \frac{A + 18.64}{dA/dx} \quad (3.9)$$

where

$$A = \left[\frac{16x^2}{(1-x)^2} \right] \left[\begin{array}{l} 8.9 - 33.717x + 79.616x^2 - 112.952x^3 \\ + 84.815x^4 - 25.672x^5 \end{array} \right] \quad (3.10)$$

and

$$\begin{aligned} dA/dx = & \left[\frac{16x^2}{(1-x)^2} \right] \left[-33.717 + 159.232x - 338.856x^2 + 339.26x^3 - 128.36x^4 \right] \\ & + 16 \left[8.9 - 33.717x + 79.616x^2 - 112.952x^3 + 84.815x^4 - 25.672x^5 \right] \\ & \left\{ \frac{[2x(1-x) + 2x^2]}{(1-x)^3} \right\} \end{aligned} \quad (3.11)$$

3.4.8 Thermal analysis

Thermal analysis is defined as a group of methods based on the determination of changes in chemical or physical properties of material as a function of temperature in a controlled atmosphere. In this study, Dynamic mechanical thermal analyser, Differential scanning calorimeter and Thermogravimetric analyser were used to assess thermal properties of the fibres and composites.

3.4.8.1 Dynamic mechanical thermal analysis (DMTA)

DMTA is a sensitive testing method that characterises the mechanical responses of a material by monitoring dynamic property changes as a function of frequency, temperature or time. The technique applies an oscillating force to test a sample and the sinusoidal stress and strain curves are recorded as a function of time (see Figure 3.6).

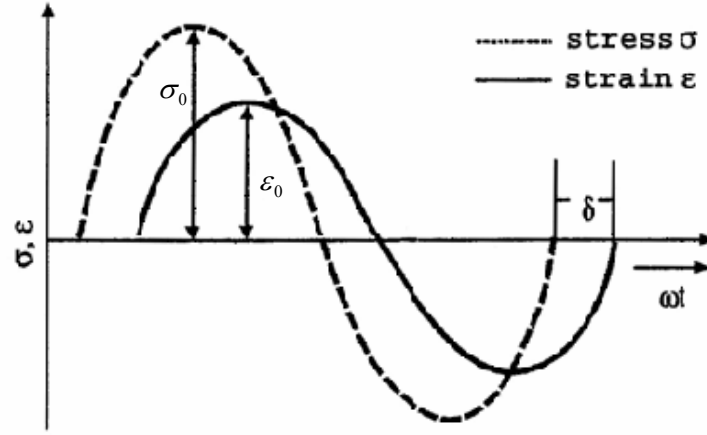


Figure 3.6: Schematic diagram showing sinusoidal oscillation and the phase angle difference at an applied frequency (f), where angular frequency, $\omega = 2\pi f$.

An oscillating stress (σ_A) can be expressed as:

$$\sigma_A = \sigma_0 e^{i\omega t} \quad (3.12)$$

Due to the loss of energy during the loading cycle the strain (ϵ_A) in the sample will exhibit a phase shift relative to the applied stress, thus

$$\epsilon_A = \epsilon_0 e^{i(\omega t - \delta)} \quad (3.13)$$

where, δ is the phase shift angle between dynamic stress and dynamic strain in a visco-elastic material that is exposed to a sinusoidal load.

The modulus of the material can therefore be expressed as:

$$E = \frac{\sigma_A}{\epsilon_A} = \frac{\sigma_0 e^{i\omega t}}{\epsilon_0 e^{i(\omega t - \delta)}} = \frac{\sigma_0 e^{i\delta}}{\epsilon_0} \quad (3.14)$$

$$\text{Again, } e^{i\delta} = \cos \delta + i \sin \delta \quad (3.15)$$

Therefore, from the Equation 3.14 it can be written as:

$$E = \frac{\sigma_0}{\varepsilon_0} \cos \delta + i \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (3.16)$$

or,

$$E^* = E' + iE'' \quad (3.17)$$

where E^* , E' and E'' are the complex modulus, storage modulus and loss modulus, respectively [12, 129].

The important parameters that can be obtained during a dynamic mechanical test are: (i) storage modulus (E'), which is a measure of the maximum energy, stored in the material during one cycle of oscillation, (ii) loss modulus (E''), which is proportional to the amount of energy that has been dissipated as heat by the sample and (iii) mechanical damping factor ($\tan \delta$), which is the ratio of the loss modulus to storage modulus and is related to the degree of molecular mobility in the polymer material. The damping or loss factor ($\tan \delta$) is very useful to describe the damping properties of a material. A high $\tan \delta$ is characteristic of a material with a more non-elastic behaviour, while a low value of $\tan \delta$ is characteristic of a more elastic material [130].

In this work, dynamic mechanical properties of the composite samples were measured by using a DMT analyser (DMTA V: Rheometric Scientific Inc.) in tensile mode. The analyser was operated at 1 Hz from 20 to 120°C at a heating rate of 2°C/min. The strain amplitude was 0.05%, which was well within the linear viscoelastic region. The samples were rectangular coupons with dimensions of about 30 x 4 x 2.7 mm³.

3.4.8.2 Differential scanning calorimetry (DSC)

The thermal behaviour of polylactide and composites was assessed using a DSC 2920-TA Instruments machine. All DSC scans were carried out at a scan rate of 10°C/min from room temperature to 200°C in the presence of air using samples of approximately 10 mg.

The percent crystallinity (X_{DSC}) of PLA was calculated by using Equation 3.18 [89]:

$$X_{DSC}(\%) = \frac{\Delta H_f - \Delta H_{cc}}{\Delta H_f^o} \times \frac{100}{w} \quad (3.18)$$

where $\Delta H_f^o = 93$ J/g for 100% crystalline PLA, ΔH_f is the enthalpy of melting, ΔH_{cc} is the cold crystallisation enthalpy and w is the weight fraction of PLA in the composite.

3.4.8.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using an SDT 2960 Simultaneous DTA-TGA analyser. The weight of each specimen was around 10mg. Measurements were taken at a constant heating rate of 10°C/min whilst maintaining a static air flow of 150 mL/min. The samples were heated in the temperature range of 25 to 500°C.

3.4.9 Microscopy

3.4.9.1 Scanning electron microscope (SEM)

In this study, fibre surface topography and composite fracture surface morphology was studied using Hitachi S-4000 and S-4700 field emission scanning electron microscopes. Hitachi S-4000 was operated at 5 kV and Hitachi S-4700 was operated between 5 to 20 kV. All samples were ion sputter-coated with platinum and palladium to provide enhanced conductivity. Samples were mounted with carbon tape on aluminium stubs and then sputter coated with platinum and palladium to make them conductive prior to SEM observation.

3.4.9.2 Optical light microscope (OLM)

In this work, Olympus BX60F5 optical light microscope and a WILD M3B stereo microscope were used for several investigation purposes. For examples, (i) fibre diameter for single fibre tensile testing, (ii) fibre embedded length and diameter for pull-out testing, (iii) crystal morphology of PLA in microcomposites and (iv) composite fracture surfaces.

Both light microscopes were fitted with a Nikon camera (Digital Sight DS-U1).

CHAPTER FOUR

Results and Discussion: Part I - Hemp Fibre Treatment and Characterisation

4.1 Introduction

This chapter covers results for the:

- microscopic analysis of the structural organisation of industrial hemp fibres, defects analysis of fibres and surface topography of untreated and various treated hemp fibres;
- crystallinity index (by X-ray diffraction) of fibres and its relation with tensile properties;
- FT-IR analysis of untreated and various treated hemp fibres;
- density of untreated and treated hemp fibres;
- thermogravimetric analysis of untreated and various treated hemp fibres; and
- tensile properties of untreated and various treated hemp fibres.

4.2 Microscopic analysis of hemp fibre morphology

4.2.1 Structural organisation

Figure 4.1 presents SEM micrographs of the transverse cross section of hemp fibres. As can be seen in Figure 4.1(a), the hemp fibre bundle is composed of a few technical fibres, bonded together by a relatively weak interphase, which mainly consists of pectin and lignin [131]. Technical fibres consist of a bundle of elementary fibres which are the single plant cells. The elementary fibres are glued together by an interphase mainly consisting of pectin and hemicellulose, which are a mixture of different low molecular weight branched polysaccharides [132].

Elementary fibres consist of a primary cell wall, a secondary cell wall and a lumen. The primary cell wall is relatively thin, in the order of 0.1 μm [32]. It can be seen in Figure 4.1(b) that the secondary cell wall of elementary hemp fibres has a composite like structure. This secondary cell wall makes up most of the fibre diameter, and is made mainly from cellulose and hemicellulose [133]. The cellulose crystallites (microfibrils) in

the secondary cell wall are oriented and glued together by the amorphous hemicellulose phase. Thygesen *et al.* [134] reported that secondary cell wall of a hemp fibre is composed of a 100-130 nm thick S1 layer and a 3-13 μm thick S2 layer. The cellulose aggregates in the S1 and S2 layer beneath are oriented perpendicular and parallel to the fibre axis, respectively. The lumen is an open channel in the centre of the fibre as can be observed clearly in Figure 4.2.

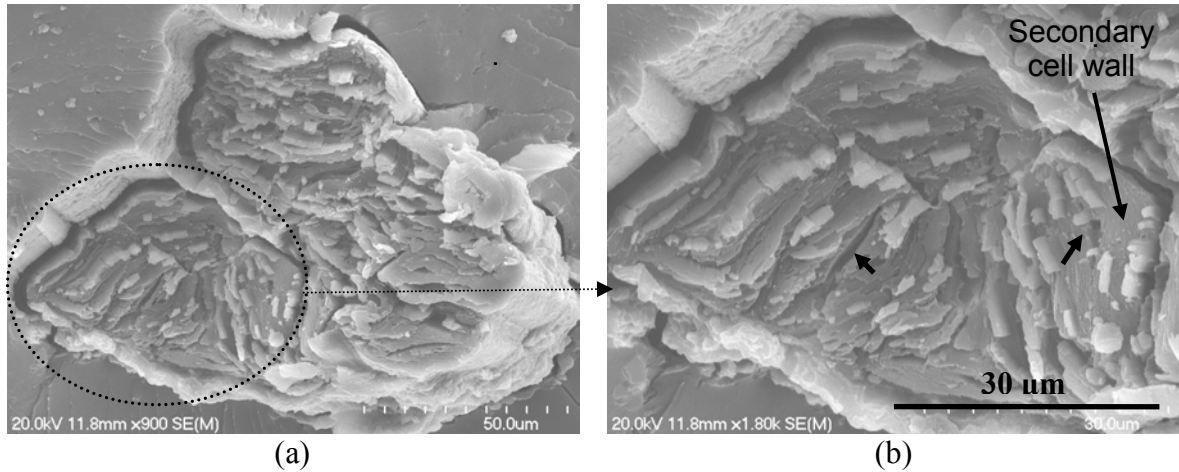


Figure 4.1: SEM micrographs of the transverse cross section of hemp fibres; (a) hemp fibre bundle and (b) technical fibre (small solid arrow sign indicating lumen).

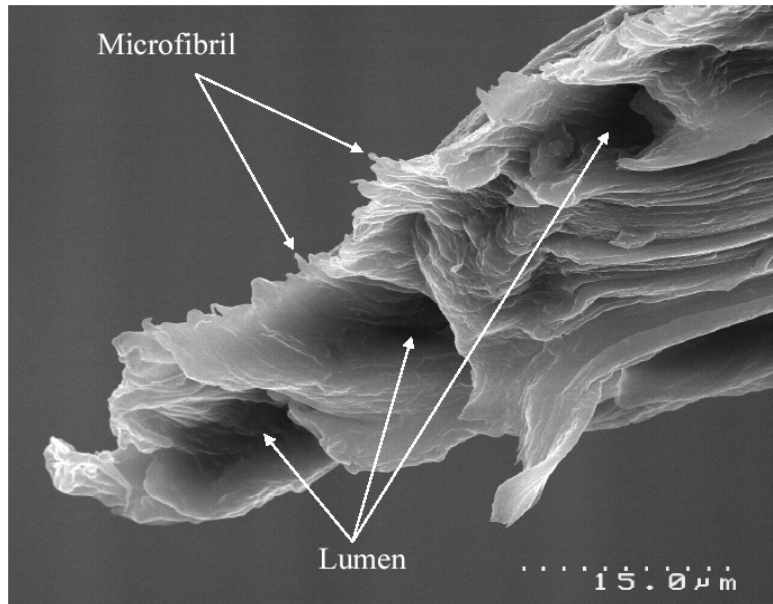


Figure 4.2: SEM micrographs of the transverse cross section of a technical hemp fibre showing the lumens in the elementary fibres.

4.2.2 Defects in fibres

One general feature of natural fibres is their non-uniform geometry. The cell walls of natural fibres contain defects, known as kink bands and micro-compressive defects [135]. At the defect region, the angle of the microfibrils relative to the fibre axis differs from the angle of the surround cell wall, which corresponds to the change of crystalline orientation [135, 136].

In general, defects in natural fibres arise from two different sources namely (1) during growth, and (2) during the process of decortication by which the fibres are separated from the plant. In a typical decortication process, retted basts are passed between fluted rollers and/or fed through a bladed thresher to break up the woody core and separate the fibres. This results in a high level of introduced defects in the elementary fibres. Such defects significantly retard fibre strength and are responsible for much of the variability in fibre properties. A manifestation of these defects, when fibres are used as composite reinforcement, is that they lead to stress concentrations in the matrix in the vicinity of the defects when the composite is loaded parallel to the axis of the fibre [137]. Therefore, it is important to investigate the fibres to assess any features which might affect the mechanical properties of the composites.

A number of features, similar to those seen in other natural fibres [131, 135], were noted in hemp fibres of the present study. For example, the presence of kink bands in hemp fibres can be seen in Figure 4.3(a) which were often found at the same place on various fibres of a bundle. It is reported that the kink bands are the most likely area to break during the tensile tests of fibres. Kink bands would suggest a loss of tensile strength in the fibres [135]. In Figure 4.3(b), micro-cracks in fibre cell wall along the fibre length were evident (shown in small box). It was unclear how deep the crack penetrated into the fibre cell wall. Light microscope images of micro-compressive defects (indicated by arrows) in hemp fibres are shown in Figure 4.4. The damage appeared to be extensive, occurring at frequent intervals along the length of the fibre.

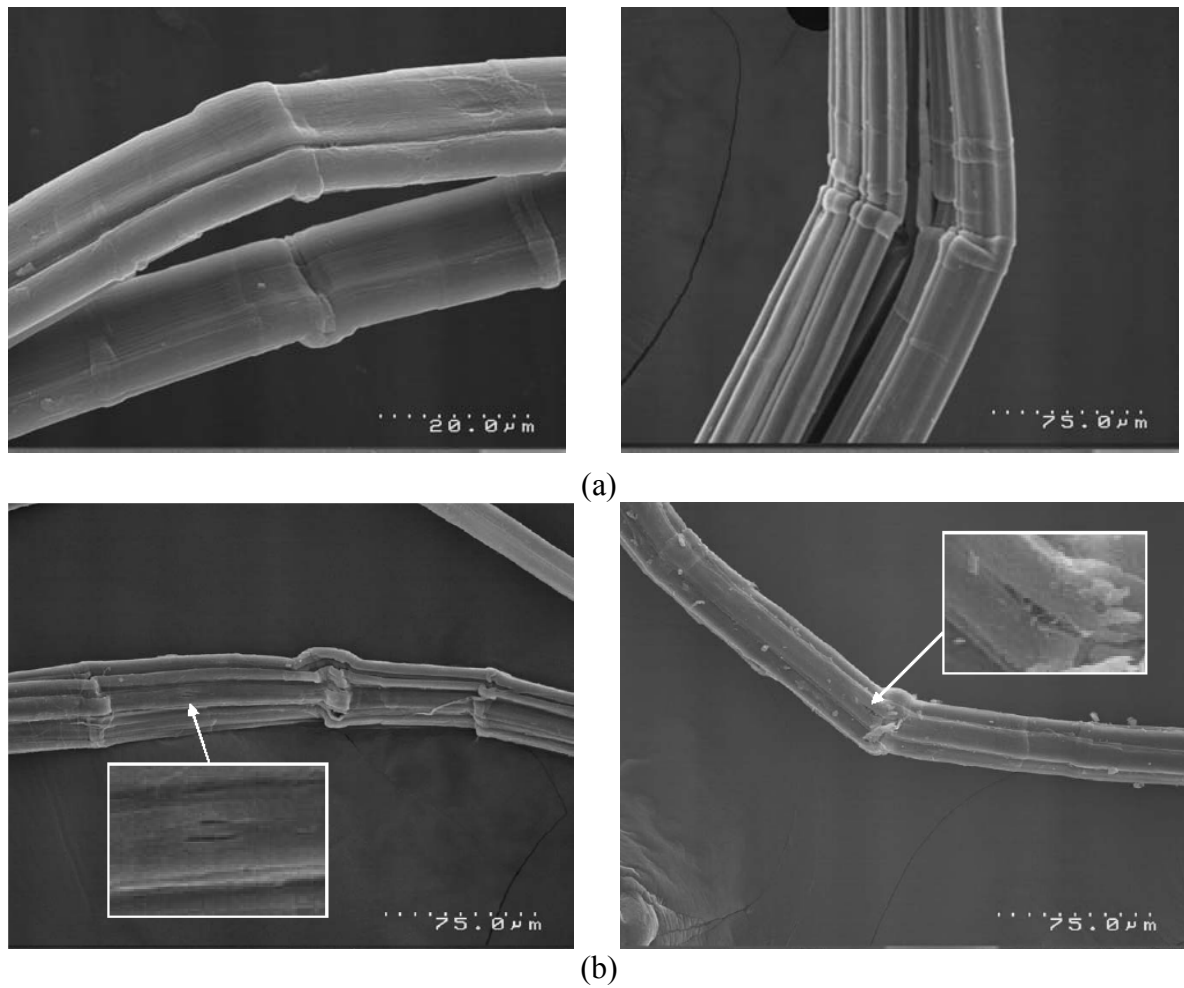


Figure 4.3: SEM micrographs showing the defects in hemp fibres; (a) kink bands and (b) micro-cracks.

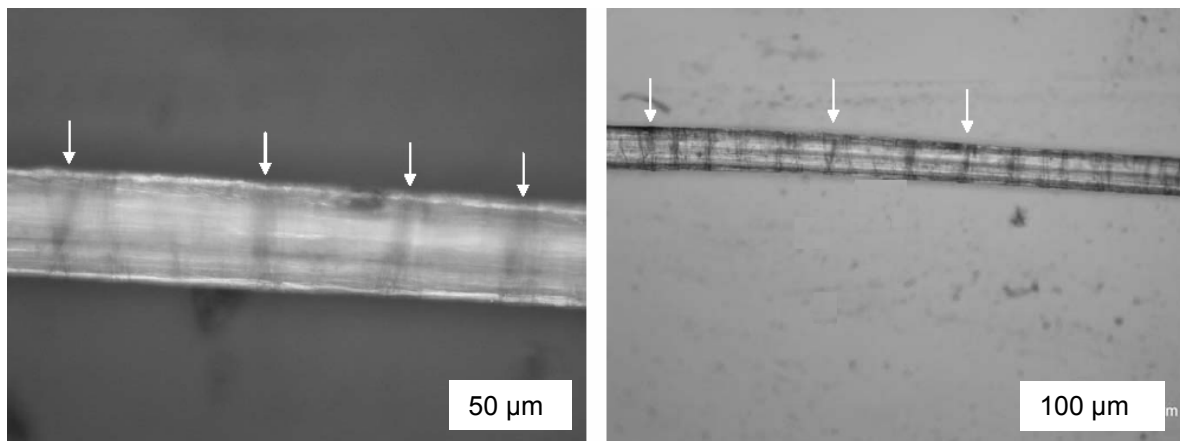


Figure 4.4: Light microscopic images of the micro-compressive defects in hemp fibres.

Hughes *et al.* [138] have shown that micro-compressive defects can be present in both ‘green’ (separated by hand) and ‘processed’ (by decortication) hemp fibres. Micro-compressions in wood pulp fibres have been shown to result in decreased tensile strength

and Young's modulus of the fibres [139]. It has also been shown that the elastic modulus of paper was reduced by the presence of fibre micro-compressive defects, crimps and curls [140]. More recently, Bos *et al.* [141] determined the tensile strength of flax fibres isolated by hand and compared to the strength of decorticated fibres. They found mean ultimate tensile stress values of 1834 ± 900 MPa and 1522 ± 400 MPa, respectively. In another report, Davies and Bruce [142] studied the relationship between tensile properties and the amount of defects for flax and nettle fibres. They observed that tensile properties of the fibres decreased to some extent as the number of defects increased.

4.2.3 Surface morphology of untreated and treated hemp fibres

SEM micrographs of the bundles of FB1 fibres are shown in Figure 4.5. The fibre bundles were approximately 80-110 μm in diameter. The fibre surfaces appeared to be covered with noncellulosic components namely wax and pectin. In addition to the above, some cavities (indicated by circles) on the surface of fibres appeared to be present. It was thought that naturally occurring fungi might have etched (or degraded) the fibres and created the holes during storage. These holes acted as flaws to decrease the tensile properties of fibres. This observation helps to explain the lower tensile properties of FB1 fibres than those of FB2 fibres as observed in the single fibre tensile tests here (see section 4.7).

SEM micrographs of FB2 fibres are shown in Figure 4.6. As can be seen in Figure 4.6(a), each fibre bundle was composed of many single fibres cemented to each other. The single fibres do not appear as well bonded to each other as for FB1 fibres, and indeed they could be easily separated. An uneven deposit of pectin and wax on the fibre can be seen in Figure 4.6(b). In contrast, alkali treated fibres appeared to have clean surfaces with a rough texture (see Figure 4.7), which is in agreement with other reports [35, 39, 143]. The extraction of alkali-soluble materials observed in SEM micrographs clearly corroborated the FT-IR results of the alkali treated fibres as discussed in section 4.3. Alkali treatment led to the separation of the fibre bundles into single fibres by dissolving the cementing materials. This breaking down of fibre bundles into single fibres was believed to increase the effective surface area available for matrix wetting. It was also expected that the number of free hydroxyl groups on the surface increased, thus providing a greater number of active sites on the fibre surface. Accordingly, bonding between the fibre and the matrix at the interface would be expected to improve.

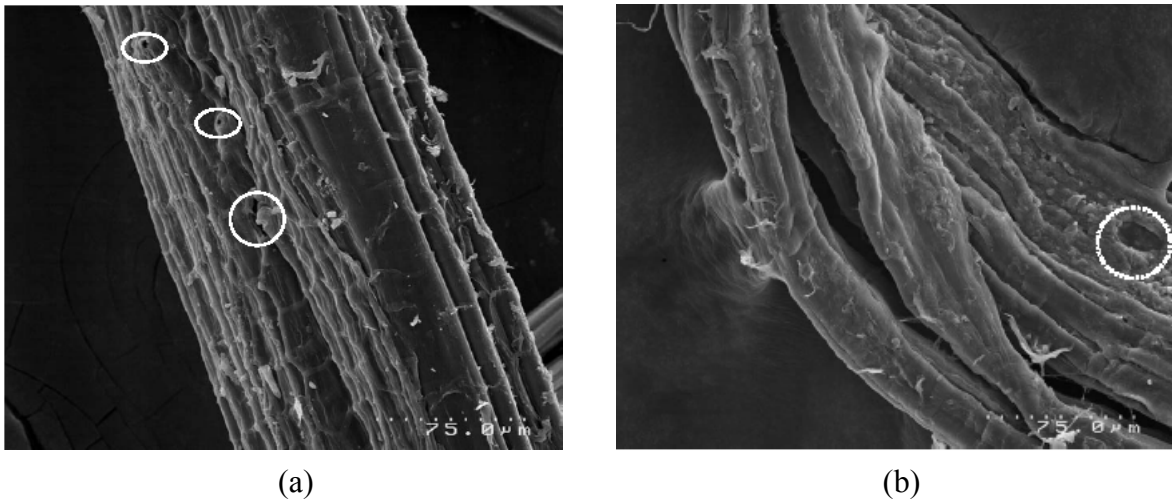


Figure 4.5: SEM micrographs of the surface morphology of FB1 fibres.

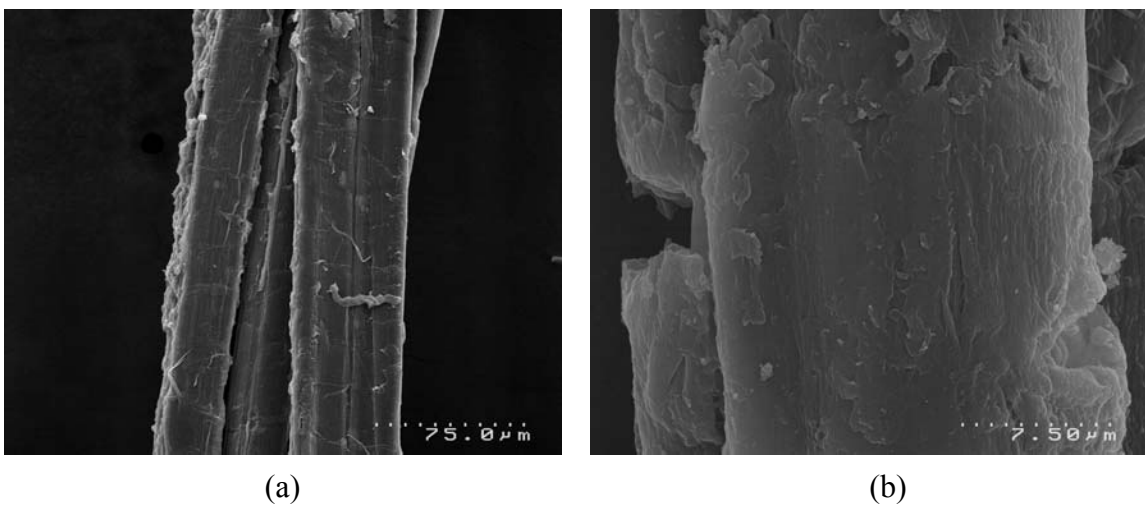


Figure 4.6: SEM micrographs of the surface morphology of FB2 fibres.

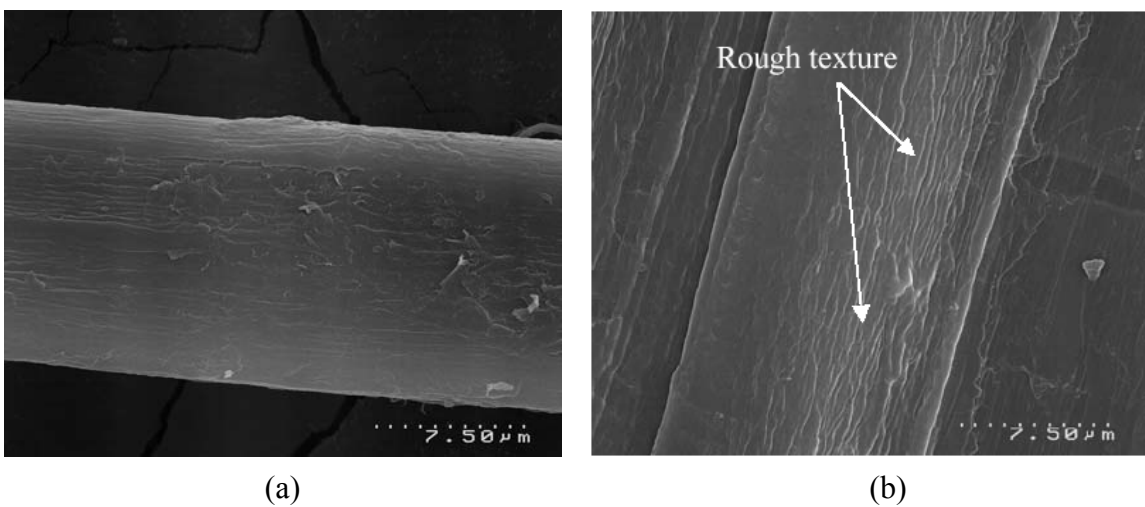


Figure 4.7: SEM micrographs of the surface morphology of ALK fibres.

Surface morphology of acetic anhydride and maleic anhydride treated hemp fibres are shown in Figures 4.8 and 4.9, respectively. It can be observed that nearly all external impurities were removed from the surfaces which appeared to be smooth. Dissolution of waxy materials from the surfaces and addition of new chemical groups (as confirmed by FT-IR) could explain smoothing of the fibre surfaces after esterification. This observation found to be in general agreement with other researchers [55, 109, 144].

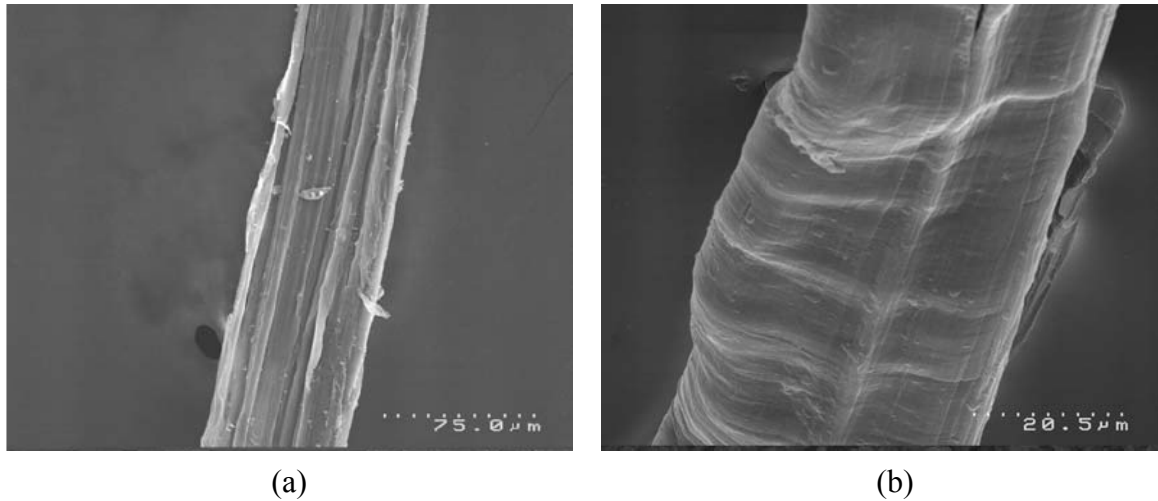


Figure 4.8: SEM micrographs of the surface morphology of ACY fibres.

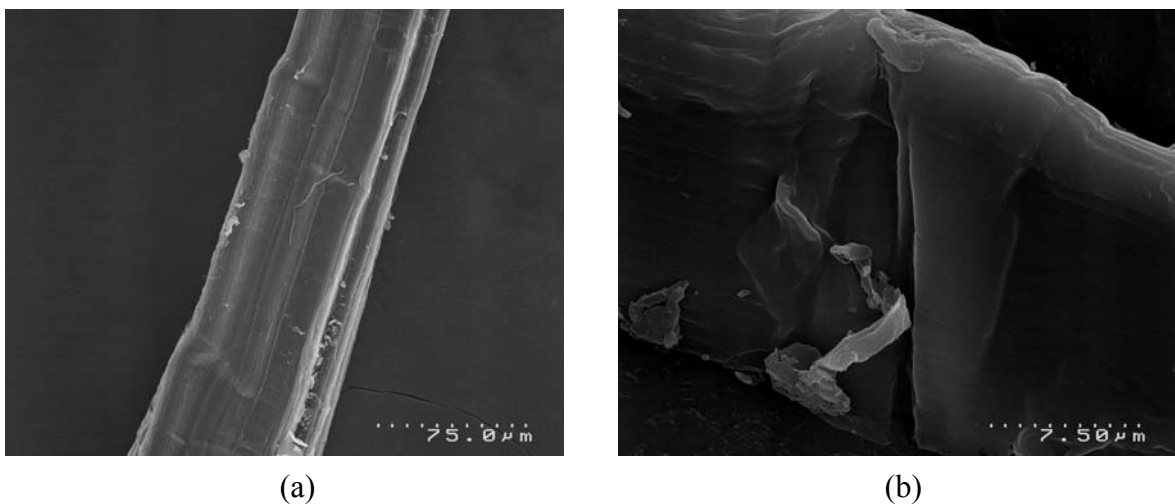


Figure 4.9: SEM micrographs of the surface morphology of MA fibres.

Figure 4.10 shows the surface topography of silane treated hemp fibres (SIL and ALKSIL) which appeared to be smooth. This could be due to the deposition of siloxane to some extent. However, there was no appreciable morphological difference found in the SIL and ALKSIL fibres in the SEM micrographs.

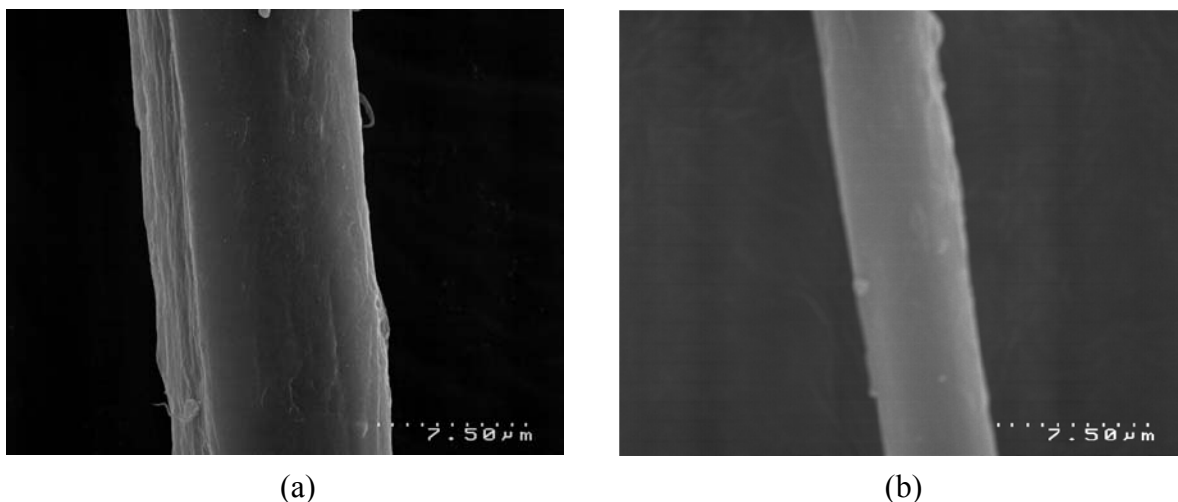


Figure 4.10: SEM micrographs of the surface morphology of (a) SIL and (b) ALKSIL fibres.

4.3 FT-IR analysis of untreated and treated hemp fibres

Figure 4.11 shows the FT-IR spectra of the untreated hemp fibres (FB2). The characteristic peaks obtained for the untreated fibres are as follows. The strong peak at 3410 cm^{-1} was characteristic of the hydrogen bonded OH (hydroxyl group) stretching vibration. The peak at 2916 cm^{-1} was due to C-H stretching vibration in cellulose and hemicellulose. A shoulder band observed at 1732 cm^{-1} was due to the absorption of carbonyl (C=O) stretching of fatty acids present in the fibre. The peaks appeared at 1425 and 1322 cm^{-1} corresponded to the aromatic skeletal vibrations and ring breathing with C-O stretching in lignin. The band at 1247 cm^{-1} was due to -C-O-C- bond in the cellulose chain. A small sharp band at 892 cm^{-1} arisen from β -glucosidic linkages between the sugar units in hemicellulose and cellulose [53, 145]. A summary of the characteristic peaks is presented in Table 4.1.

FT-IR spectra of alkali, acetic anhydride and maleic anhydride treated hemp fibres are shown in Figure 4.12. In general, the spectrum of alkali treated hemp fibres (ALK) was similar to that of the untreated hemp fibres. However, the peak at 1732 cm^{-1} seen in untreated fibres disappeared after alkali treatment. This was due to the removal of pectin and hemicellulose present in the fibres. In alkali treatment, other substances associated with the celluloses, namely fats, wax and pectin also dissolved out as observed in the SEM micrographs. A similar observation has also been made by the other researchers [36, 145]. As mentioned earlier, the removal of surface impurities from plant fibres is advantageous

for fibre/matrix adhesion as it facilitates both mechanical interlocking and bonding reaction due to the exposure of the hydroxyl groups to the matrix [146].

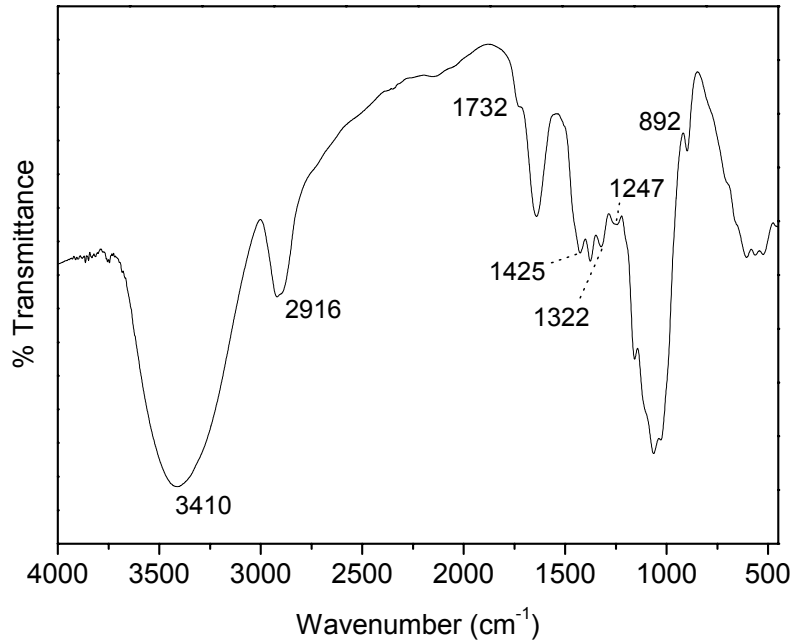


Figure 4.11: FT-IR spectrum of untreated hemp fibre.

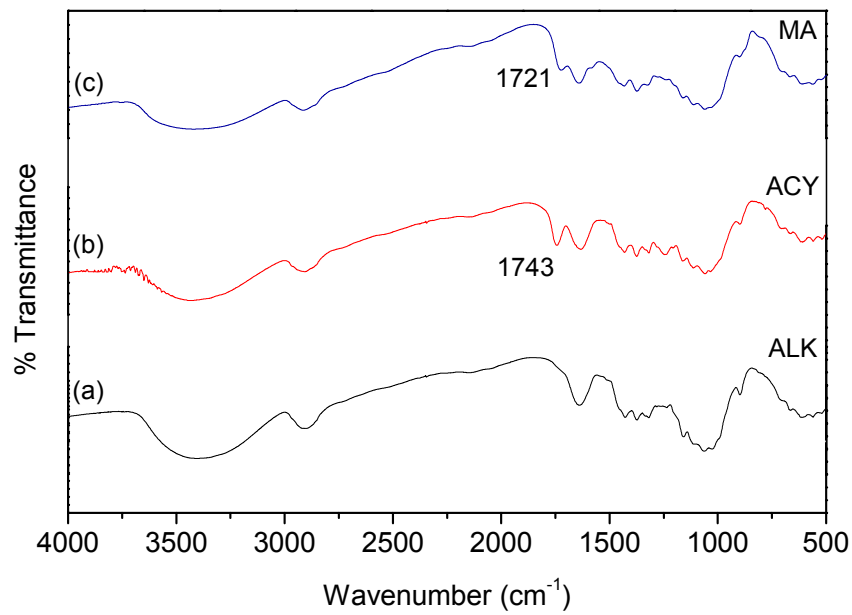


Figure 4.12: FT-IR spectra of different treated hemp fibres; (a) alkali, (b) acetic anhydride and (c) maleic anhydride.

Esterification of fibres leads to chemical reaction between the hydroxyl groups of fibres and the anhydride groups by transforming them to ester-type groups [58]. The reaction scheme of acetic anhydride with hemp fibres is shown in Figure 4.13. Acetylation of hemp fibres with acetic anhydride led to the appearance of a new peak at 1743 cm^{-1} . This was attributed to the C-O stretching of the ester carboxyl group. The lowering in intensity of OH stretching band at 3410 cm^{-1} in the spectra also confirms acetylation of hemp fibres [55, 147].

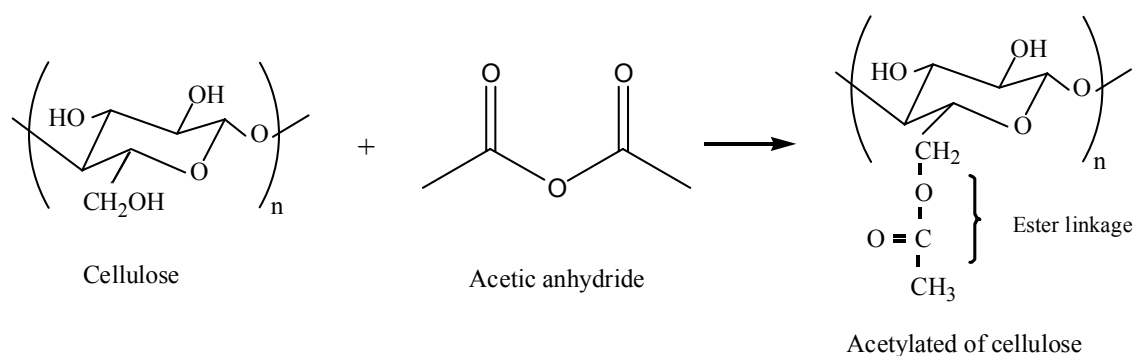


Figure 4.13: Acetylation reaction scheme for the cellulose of hemp fibres.

The reaction scheme of hemp fibres with maleic anhydride is presented in Figure 4.14. A peak at 1721 cm^{-1} in the maleated hemp fibres indicated the presence of the ester groups. There was also a remarkable decrease in the intensity of OH stretching band at 3410 cm^{-1} in the spectra, which further confirmed the maleation of hemp fibres [67, 68].

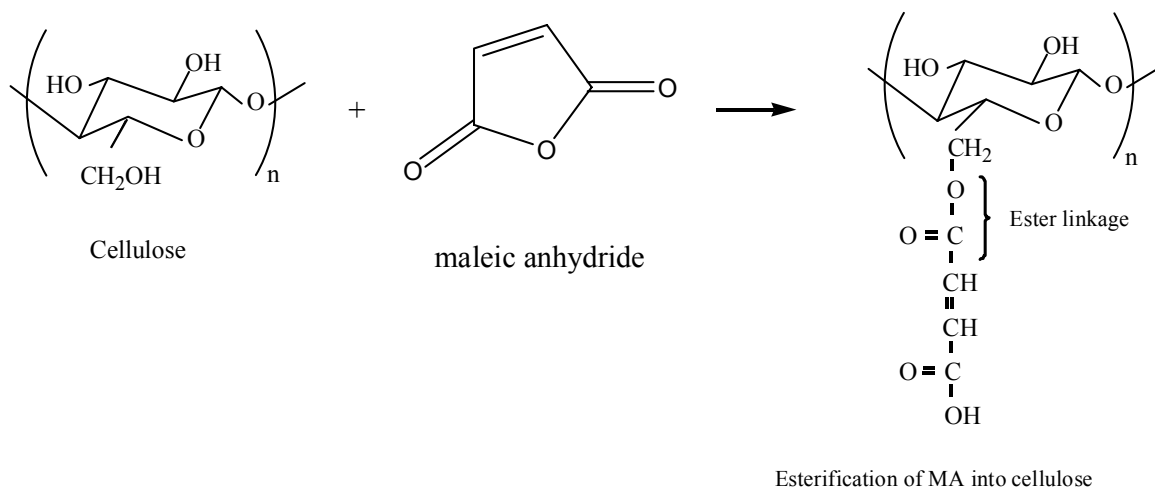


Figure 4.14: Reaction scheme between cellulose of hemp fibres and maleic anhydride.

The silane [3-(2-aminoethyl amino)propyl trimethoxy silane] used in this work, had two functional groups, a hydrolysable group able to condense with the hydroxyl group of hemp

fibres and a primary amino group capable of interacting with polymer matrix. The reaction mechanisms of silane and fibre can be explained as follows. First silane reacted with water to form silanol and an alcohol. Then the silanol reacted with hydroxyl group of cellulose of the fibres through an ether linkage with removal of water. The reaction scheme for adhesion of the silane to fibre is presented in Figure 4.15.

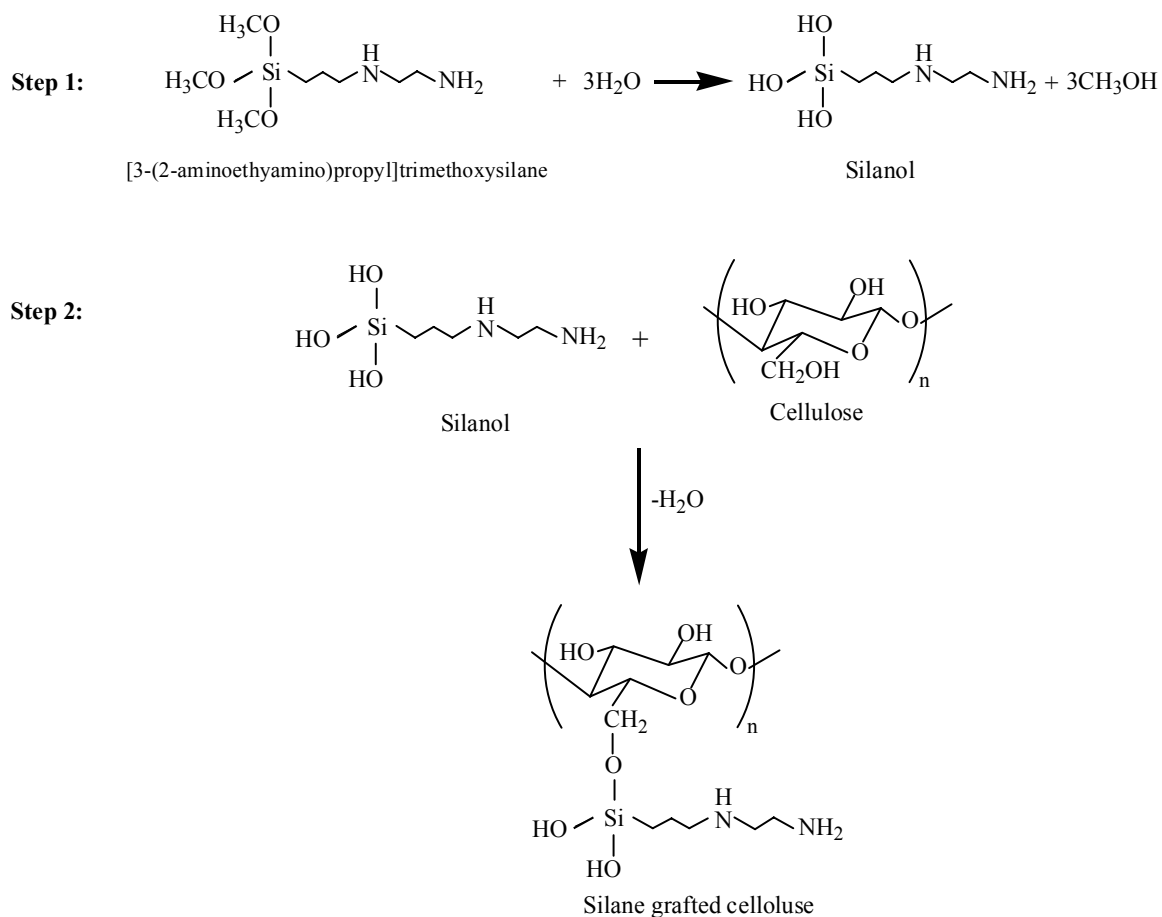


Figure 4.15: Reaction scheme for silane grafting onto cellulose of hemp fibres.

Figure 4.16 shows the FT-IR spectra of silane treated hemp fibres. For both treatments, the characteristic band at 708 cm^{-1} was corresponding to the $-\text{Si-O-Si}-$ symmetric stretching and the band at 780 cm^{-1} was corresponding to the $-\text{Si-C}-$ symmetric stretching. The former bond was indicative of the polysiloxanes deposited on the fibres and latter points to a condensation reaction between silane and hemp fibres. The well-defined band at 1203 cm^{-1} was associated to the $-\text{Si-O-C}-$ bond confirmed the reaction between hydrolysed silane and cellulose of hemp fibres [4, 43, 145]. However, for ALKSIL fibres, the intensity of the band at 1203 cm^{-1} was higher than that of SIL fibres which suggested that the efficiency of

silane grafting onto hemp fibres was higher for the alkali treated fibres compared to the untreated fibres. Gonzalez *et al.* [43] also made a similar observation for the henequen fibres and silane system.

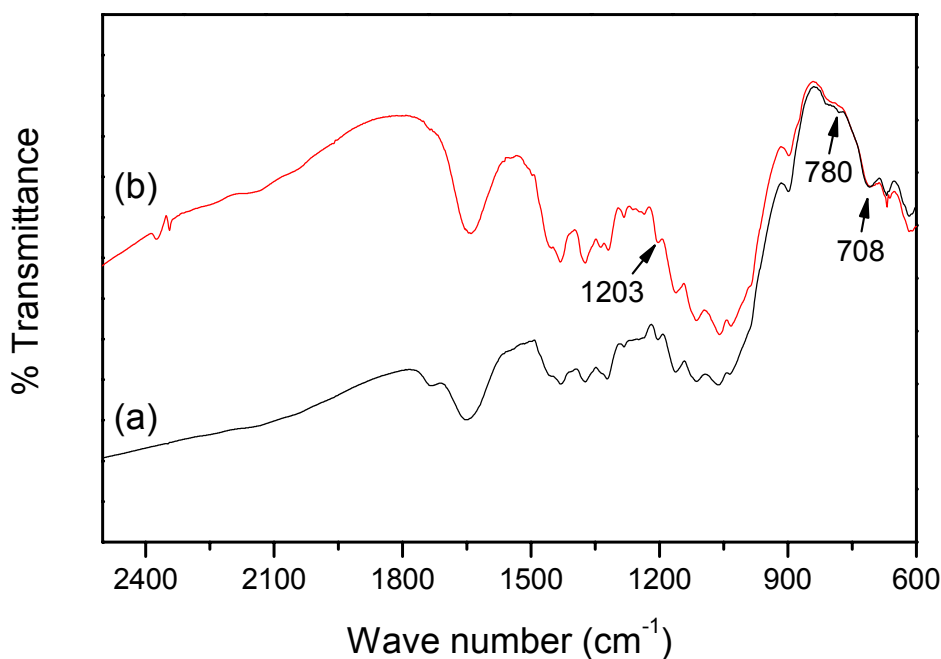


Figure 4.16: FT-IR spectra of silane treated hemp fibres; (a) SIL and (b) ALKSIL.

Table 4.1: FT-IR transmittance peaks for untreated and treated hemp fibres.

Possible assignments	Transmittance peak (cm ⁻¹)
-OH bond stretching	3410
C-H stretching vibration	2916
>C=O stretching of carboxylic acid or ester	1732
=CH bending of lignin	1425
C-O stretching of lignin	1322
-C-O-C bond stretching of cellulose chain	1247
β-glucosidic linkage	892
>C=O stretching of ester (in ACY fibres)	1743
>C=O stretching of ester (in MA fibres)	1721
-Si-C- symmetric stretching (in silane treated fibres)	780
-Si-O-Si- symmetric stretching (in silane treated fibres)	708
-Si-O-C- stretching (in silane treated fibres)	1203

4.4 XRD analysis of untreated and treated hemp fibres

Cellulose crystallinity index (I_{XRD}) of the untreated and treated hemp fibres were measured according to the method described in section 3.4.2 and 3.4.2.1. The X-ray diffractograms of the treated and untreated fibres are shown in Figure 4.17. As can be seen, all the samples showed the characteristics peak of cellulose I ($22^\circ \leq 2\theta \leq 23^\circ$), which correspond to the 002 crystallographic plane [148]. This means that the treatment conditions (time, temperature and concentration) applied to the hemp fibres did not modify the crystal packing chains of native cellulose I (chains aligned in parallel) to cellulose II (anti-parallel). It is reported that the tensile strength of plant fibre decreases when the cellulose I transforms to cellulose II [116].

The other two major peaks at 15.2° and 16.6° correspond to the 101 and $10\bar{1}$ crystallographic planes, respectively. When looking at the diffractograms, these two peaks of the treated fibres appeared to be better defined than those of untreated fibres. This is because untreated fibres contained large amounts of amorphous materials (e.g. lignin, hemicellulose and amorphous cellulose). Thus, these two peaks are smeared, appearing as one broad peak.

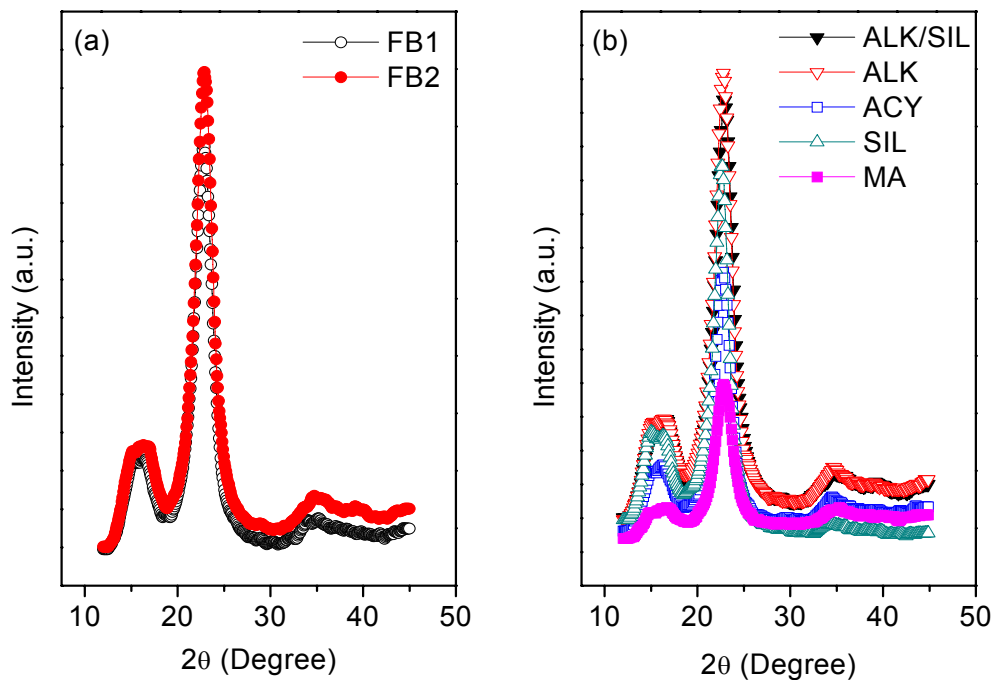


Figure 4.17: X-ray diffractogram of untreated (a) and treated (b) hemp fibres.

The measured crystallinity index of the treated and untreated hemp fibres is illustrated in Figure 4.18. The results showed that the crystallinity index of FB2 fibres (87.9%) was approximately 12% higher than that of FB1 fibres (78.2%). As mentioned earlier, FB1 fibres were suspected to be degraded, and thus the low crystallinity index of FB1 fibres could be due to the presence of excessive amounts of degraded amorphous materials.

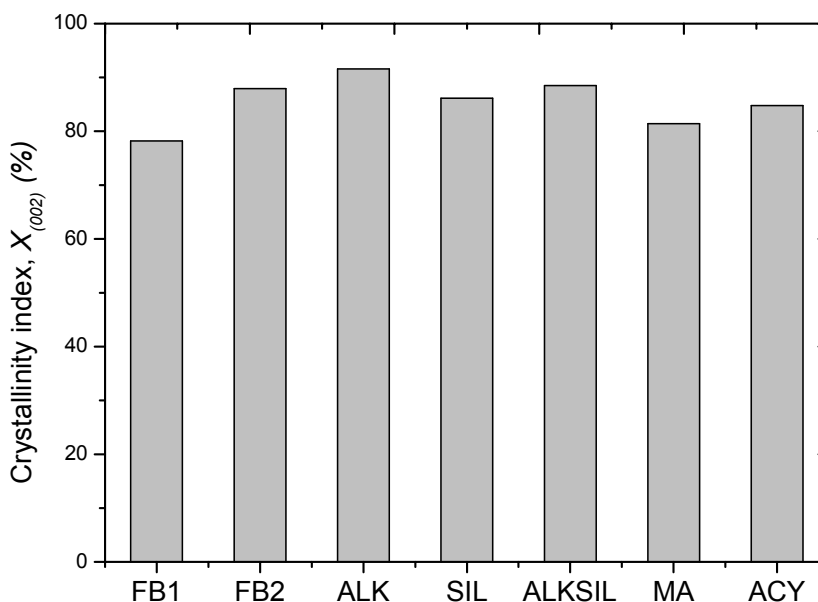


Figure 4.18: XRD crystallinity index of untreated and treated hemp fibres.

The treated fibres showed the following order of crystallinity index: ALK (91.6%) > ALKSIL (88.5%) > FB2 (87.9%) > SIL (86.1%) > ACY (84.8%) > MA (81.8%). The improved crystallinity index of ALK fibres compared to FB2 fibres suggests that under the applied treatment conditions non-crystalline (amorphous) components are removed from the fibres to some extent. The increase of crystallinity index after alkali treatment was also observed elsewhere [36, 39, 53, 149], and explained by the removal of non-cellulosic materials enabling better packing of cellulose chains. On the other hand, the crystallinity index of the SIL, ACY and MA fibres decreased compared with that of FB2 fibres. This was probably due to the increase of amorphous cellulose content upon chemical treatment. The crystallinity of ALKSIL fibres also decreased compared with that of control fibres (ALK). This was again thought to be due to the increase of amorphous cellulose content. It is reported that the reaction of cellulose with different chemical reagents takes place in the

amorphous regions and proceeds at two different rates (rate of diffusion and rate of chemical reaction). The reagent first reacts with the chain ends on the surface of the crystallites, as it cannot diffuse into the crystalline region, resulting in the opening of some of the hydrogen-bonded cellulose chains. This procedure results in some new amorphous cellulose to be formed. The reagent then diffuses into this newly produced amorphous section, reacting with the cellulose and simultaneously generating more amorphous cellulose [55].

4.5 Density of untreated and treated hemp fibres

Density of the untreated and treated hemp fibres were measured according to the method described in the section 3.4.6, and the results are presented in the Table 4.2. It can be observed that the density of hemp fibres increased after treatment. This could be due to the (i) densification of fibre cell wall as a result of removal of impurities (less dense fats and wax) by the solvent and (ii) increase in weight of fibres by filling up the pores with grafted molecules (except the alkali treated fibres).

Table 4.2: Density of the untreated and treated hemp fibres.

Sample	Density (g/cm ³)
FB1	1.338 ($\pm$ 0.0017)
FB2	1.401 ($\pm$ 0.0011)
ALK	1.423 ($\pm$ 0.0009)
ACY	1.437 ($\pm$ 0.0013)
MA	1.431 ($\pm$ 0.0010)
SIL	1.447 ($\pm$ 0.0008)
ALKSIL	1.459 ($\pm$ 0.0011)

From Table 4.2, it may be observed that the densities of the silane treated fibres (ALKSIL and SIL) were higher than that of the other treated fibres. This was because the molecular weight of the grafted silane molecule was higher than that of the other grafted molecules. Density of the ALKSIL fibres was found to be higher than that of the SIL fibres. This could be due to higher amounts of silane absorbed onto the alkali treated fibres compared to the untreated fibres. The difference in the amounts of absorbed silane could be due to the fact that the alkali treated fibres contain large amounts of exposed hydroxyl groups on the surface compared to the untreated fibres, resulting in higher absorption of hydrolysed silane [43].

The density of ACY fibres was found to be higher than that of MA fibres. This was thought to be due to the addition of large amounts of $\text{CH}_3\text{-CO-O-}$ group to fibres during acetylation, which in turn increased the weight of the treated fibres. The density of alkali treated fibres (ALK) was higher than that of untreated fibres. This could be due to the removal of alkali soluble materials which caused cell wall densification of the fibres.

Mwaikambo *et al.* [150] found that the density of hemp fibres increased upon alkali treatment. In another work, Varma *et al.* [151] treated jute fibres with various chemicals and also found that the fibre density increased after treatment.

4.6 Thermal properties of untreated and treated hemp fibres

Thermal properties of untreated and treated hemp fibres were measured according to the method described in section 3.4.8.3. Figure 4.19 shows TGA (thermogravimetric analysis) and DTA (differential thermal analysis) thermograms of the untreated hemp fibres (FB1 and FB2). As can be seen in the TGA thermogram [Figure 4.19 (a)], degradation behaviour of the fibres can be divided into several steps. A slight decrease in weight was observed as the temperature increased to 100°C. This could be attributed to the loss of moisture from the fibres. The weight loss showed nearly steady behaviour up to a temperature of around 245°C, and was characterised by the loss of carbon-dioxide and traces of low molecular weight organic compounds. Between 245 and 370°C, fibres lost over 65% of their initial weight, and could be attributed to the start of cellulose degradation. Finally, around 25% by weight was lost at the temperatures between 345 and 455°C leaving behind ash and indigestible minerals. The weight loss of untreated and treated hemp fibres at different stages of thermal degradation is presented in Table 4.3.

In Figure 4.19(b), the DTA curves for FB1 and FB2 fibres showed two main exotherms. The first exotherm has a peak temperature at 335°C for FB1 fibres and 365°C for FB2 fibres, and was likely caused by the decomposition of cellulose leading to the formation of volatile products. The second exotherm has a peak temperature at 455°C for FB1 fibres and 465°C for FB2 fibres, which could be attributed to the oxidation of volatile and charred products. The above greater exothermic peak temperatures of FB2 fibres indicated their better thermal stability when compared to the FB1 fibres. This might be due to the degradation of FB1 fibres during storage as mentioned earlier.

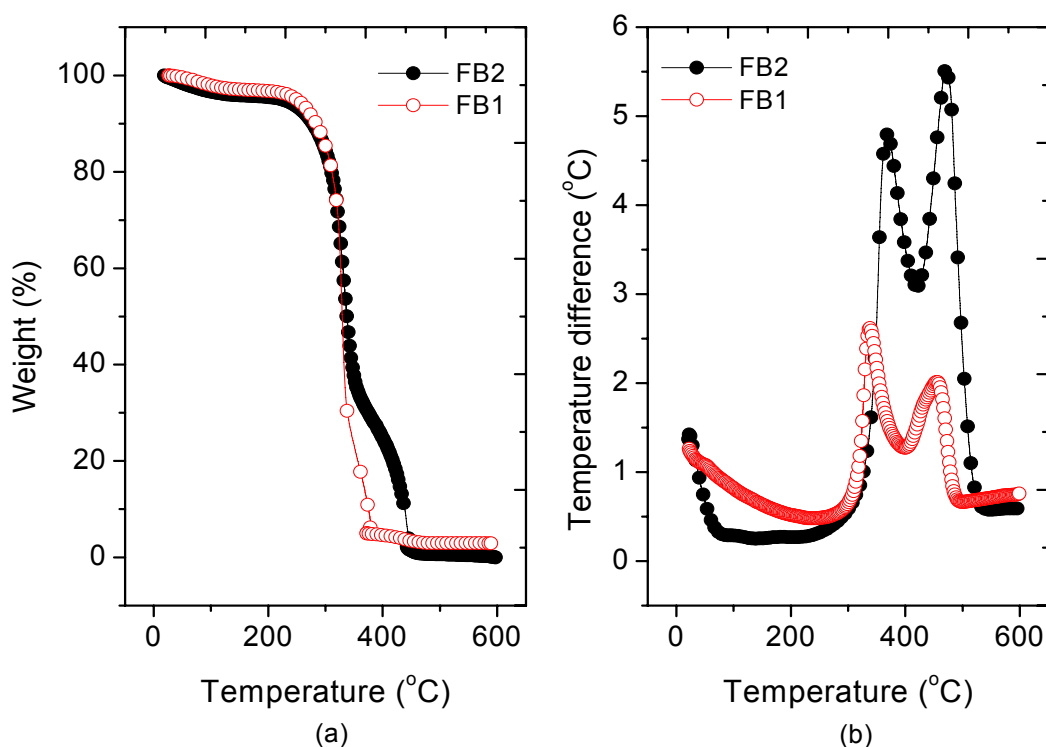


Figure 4.19: (a) TGA and (b) DTA thermograms of untreated hemp fibres.

TGA and DTA thermograms of the treated hemp fibres are depicted in Figure 4.20. Like the TGA thermogram of FB2 fibres, different treated fibres showed a similar degradation pattern with respect to temperature as can be seen in Figure 4.20(a). However, the major thermal degradation (i.e. weight loss) of all the treated fibres started around 290°C, which was higher than that of FB2 fibres. This finding certainly indicates enhanced thermal stability of the treated fibres. A possible explanation of this behaviour is that the removal of non-cellulosic components and the addition of new side group in the cellulose chains of treated fibres increased rigidity of the cellulose body and hindered the mobility of the system [58, 152-154].

DTA thermograms of the treated fibres are shown in Figure 4.20(b). Exothermic peak temperatures of the treated fibres were found to depend on treatment type. The order of the first exothermic peak temperature for various treated fibres is: ALKSIL (381°C) > SIL (377°C) > ALK (375°C) > ACY (372°C) > MA (367°C). In the case of second exothermic peak temperature, the order is: ALK/SIL (487°C) > SIL (481°C) > ACY (477°C) > MA (475°C) > ALK (469°C).

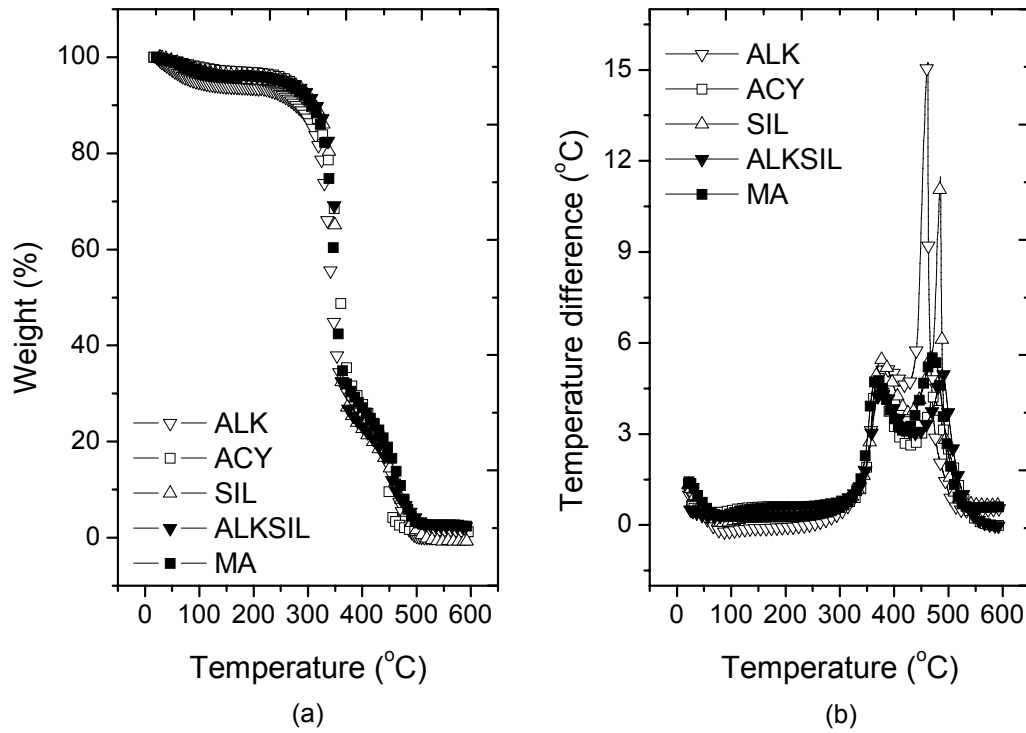


Figure 4.20: (a) TGA and (b) DTA thermograms of various treated hemp fibres.

Table 4.3: Weight loss of untreated and treated hemp fibres at different stages of thermal degradation.

Sample	Weight loss (%)				Residue
	Temperature range (°C)				
	25-100	101-220	221-360	361-500	
FB1	3.4	1.3	70.3	24.7	0.3
FB2	5.4	1.2	69.6	23.3	0.5
ALK	3.3	1.2	73.1	21.5	0.9
ACY	2.8	1.1	71.4	23.3	1.4
MA	3.5	1.4	68.7	24.9	1.5
SIL	3.4	1.1	65.8	26.2	3.5
ALK/SIL	2.6	1.1	67.5	25.1	3.7

Activation energy (E_a) for various stages of thermal degradation of the untreated and treated fibres were calculated by the Broido formula (Equation 4.1) [155, 156].

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{RT} + \ln\left(\frac{RZ}{E_a\beta}T_m^2\right) \quad (4.1)$$

where y is the fraction of initial material not yet decomposed, T_m is the temperature at the maximum reaction rate, β is the heating rate, Z is the frequency factor, and R is the universal gas constant.

A plot of $\ln[\ln(1/y)]$ versus $1/T$ (see Figure 4.21), was used to calculate the activation energy from the slope of the plot. A high value of E_a points to a stable substance because it is the energy needed for the reaction (i.e. thermal degradation) of the substance. Activation energies of the untreated and treated fibres are presented in Table 4.4. As expected, activation energy of the treated fibres was greater than that of the untreated fibres.

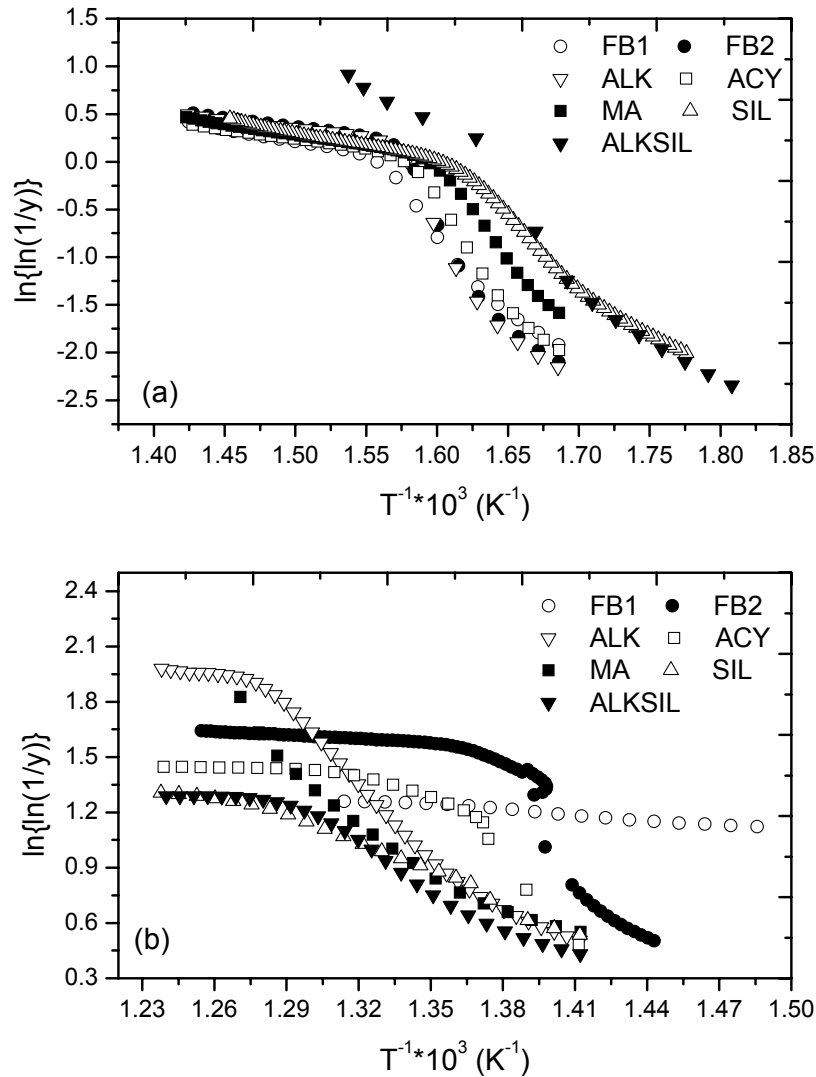


Figure 4.21: Plots of $\ln[\ln(1/y)]$ versus $T^{-1} \cdot 10^3$ for (a) the first exothermic peak and (b) for the second exothermic peak of untreated and treated hemp fibres.

Table 4.4: Activation energy of the untreated and treated hemp fibres.

Sample	1 st exothermic peak			2 nd exothermic peak		
	T (°C)	T_m (°C)	E_a (kJ/mol)	T (°C)	T_m (°C)	E_a (kJ/mol)
FB1	280-385	334	30.3	400-490	453	20.2
FB2	290-415	365	55.3	420-525	470	39.5
ALK	320-430	375	67.2	435-535	471	41.2
ACY	320-430	371	87.3	435-535	472	49.1
MA	320-430	370	72.4	435-535	470	42.7
SIL	320-430	376	90.9	435-535	485	86.4
ALK/SIL	320-430	372	110.3	435-535	488	74.7

4.7 Single fibre tensile properties of untreated and treated hemp fibres

The tensile properties of single hemp fibres were measured according to the method described in the section 3.4.3. The average diameter of the untreated and treated fibres is presented in Table 4.5. Figure 4.22 shows typical stress-displacement curves for single fibres. From these curves, it is evident that the stress versus displacement graphs were essentially linear until fracture. The failure strain of single fibres is found to be approximately 1-2%.

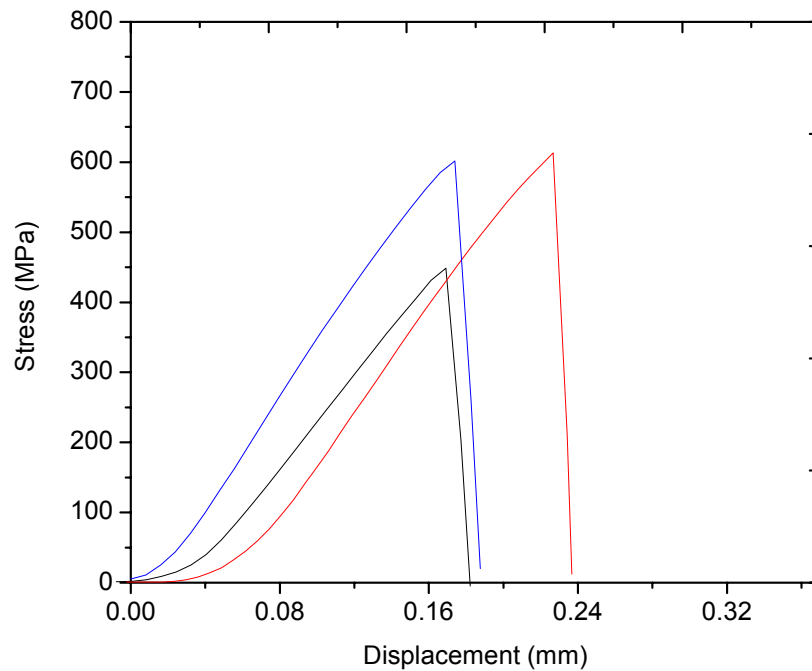


Figure 4.22: Typical stress-displacement curves of single hemp fibres.

The average tensile strength and Young's modulus of the untreated fibres (FB1 and FB2) is depicted in Figure 4.23. From the results it can be seen that the average tensile strength of FB2 fibres was 577 MPa, which was approximately 30% higher than that of the FB1 fibres (442 MPa). Similarly, the average Young's modulus of FB2 fibres (26.5 GPa) was found to be 14% higher than that of FB1 fibres (23 GPa). To assess the significance of the difference in tensile strength and Young's modulus of FB1 and FB2 fibres, the data was statistically analysed using a two sample t-test at a confidence level of 95%. Tensile strength and Young's modulus of FB1 fibres were found to be significantly lower than those of FB2 fibres. Compared to FB2 fibres, the lower tensile properties of FB1 fibres are thought to be largely due to degradation of the fibres during storage as supported by SEM.

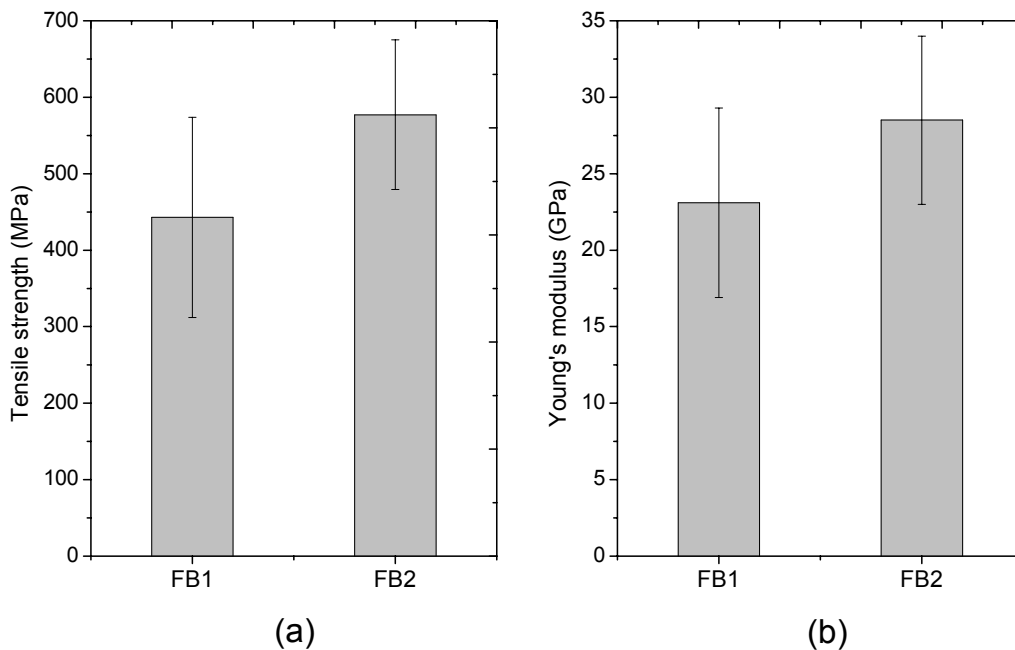


Figure 4.23: Tensile properties of untreated hemp fibres; (a) tensile strength and (b) Young's modulus.

The average tensile strength and Young's modulus of the treated hemp fibres is illustrated in Figure 4.24. It can be seen that the alkali treatment appeared to slightly increase tensile strength of treated fibres in relation to those of untreated fibres, whereas the other treatments appeared to slightly reduce the tensile strength of hemp fibres. The order of average tensile strength is: ALK (598 MPa) > FB2 (577 MPa) > ALK/SIL (565 MPa) > SIL (554 MPa) > ACY (546 MPa) > MA (538 MPa). On the other hand, the Young's moduli of various treated fibres appeared to slightly increase when compared with that of

untreated fibres. The order of average Young's modulus is: ALK (33.8 GPa) > ALK/SIL (31.7 GPa) > SIL (29.9 GPa) > ACY (29.1 GPa) > MA (28.3 MPa) > FB2 (26.5 GPa). However, statistical analysis did not support a significant difference in tensile strength and Young's modulus of the different treated fibres when compared with those of the untreated fibres.

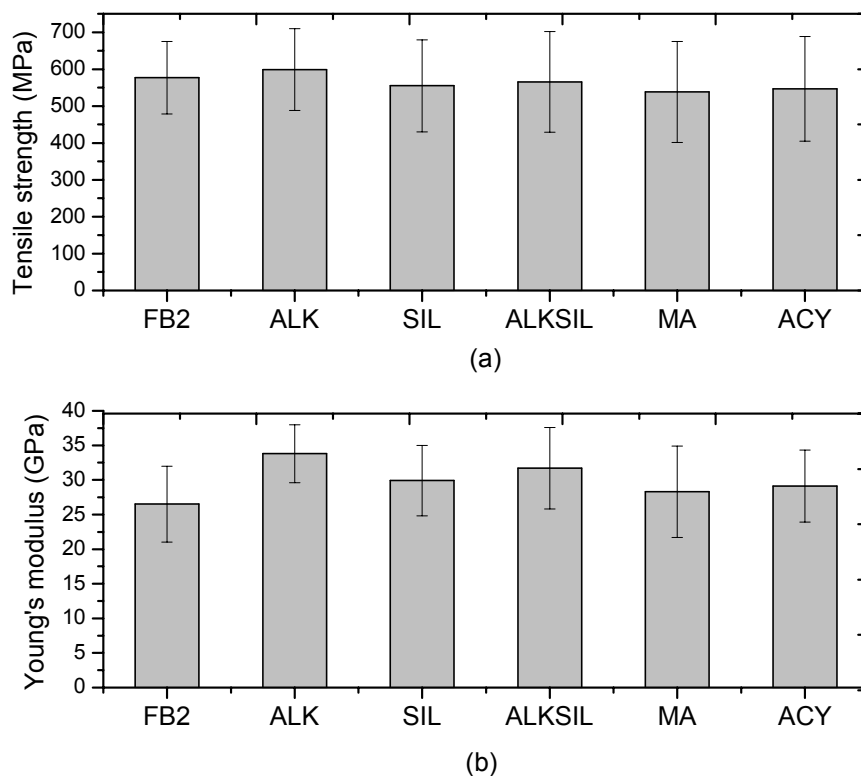


Figure 4.24: Tensile properties of different chemically treated hemp fibres; (a) tensile strength and (b) Young's modulus.

The slight increase in tensile strength of ALK fibres thought to be due to the improvement of cellulose chain packing order. As stated in the literature [157], the alkali treatment of natural fibre causes a reduction in the spiral angle of cellulose microfibrils which in turn allowed for the rearrangement of the cellulose chains and consequently improves tensile strength. Unlike alkali treatment, silane and acetylation were carried out in acidic medium. This acidic medium could catalyse the cleavage of β -1,4-glycosidic bonds between the two anhydroglucose units. Thus cellulose chain reduction could be the reason for lower tensile strength of hemp fibres after treatment [143]. In the case of maleic anhydride modified fibres (MA), fibres were heated in the presence of a solvent (e.g. acetone). The decrease in tensile strength of MA fibres was thought to be due to the weak interfibrillar interaction in

the celluloses that occurred during heating in the presence of the solvent. Weakening (or softening) of the interfibrillar interaction in MA fibres adversely affected the stress transfer between the fibrils and thereby the overall stress development in the fibres under tensile deformation [150]. Fibre treatment caused dissolution of soft materials (e.g. wax, gum and pectin) as confirmed by SEM. So a slight increase in Young's modulus of the treated fibres thought to be due to fibre cell wall densification by the elimination of soft materials.

Table 4.5: Average diameter of the untreated and treated hemp fibres.

Sample	Diameter (μm)
FB2	31.5 (± 7.3)
ALK	25.8 (± 5.2)
ACY	28.1 (± 6.5)
MA	27.7 (± 5.8)
SIL	28.4 (± 6.1)
ALKSIL	25.3 (± 5.5)

It can also be observed that a large uncertainty appeared in the tensile properties for both untreated and treated fibres. This behaviour could be explained as follows. The transverse cross-sectional area of the fibres was assumed to be circular, although the single hemp fibres were polygonal shape as can be seen in Figure 4.25. This assumption would be a source of error in the measured tensile properties of the untreated and treated fibres which could have increased variability. It was also seen earlier that the fibres had many defects along their length. These defects could be another reason for the large scatter in tensile strength and Young's modulus results.

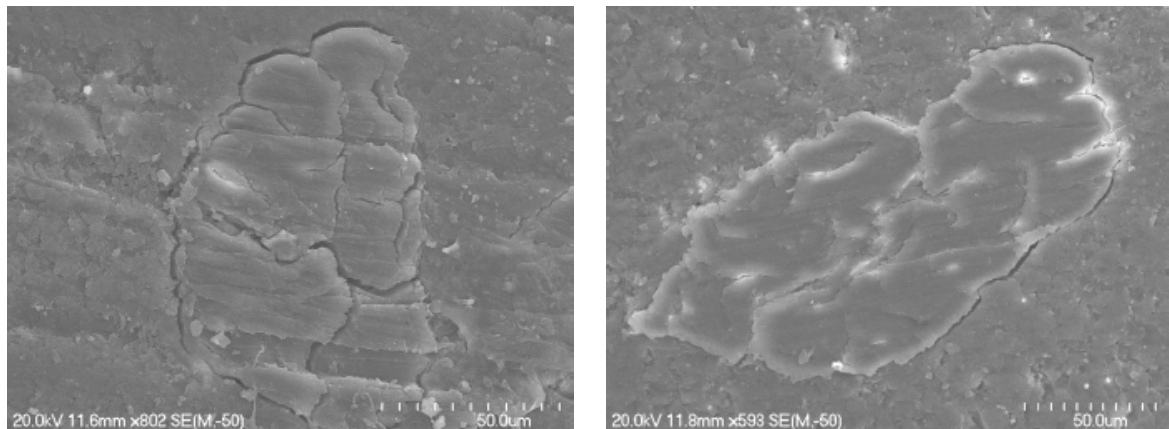


Figure 4.25: SEM micrographs of transversal cross-section of hemp fibres showing variability of shape and size.

Relationships between the tensile properties and crystallinity index of the treated and untreated hemp fibres are shown in Figure 4.26 (solid line indicating the trends only). As can be observed, tensile strength and Young's modulus of hemp fibres increased with increased crystallinity index. Similar type of relation between the tensile strength of alkali treated jute fibre and crystallinity index also referred to as the crystallinity ratio was reported by Gassan *et al.* [52]. They also found that the tensile strength of jute fibres increased with increased crystallinity index. On the other hand, Mwaikambo *et al.* [158] found a contradicting result, which showed that the tensile strength and Young's modulus of alkali treated sisal fibres decreased with increased crystallinity index. These contradicting behaviours demonstrate that different plant fibre types exhibit different structure-property relationships.

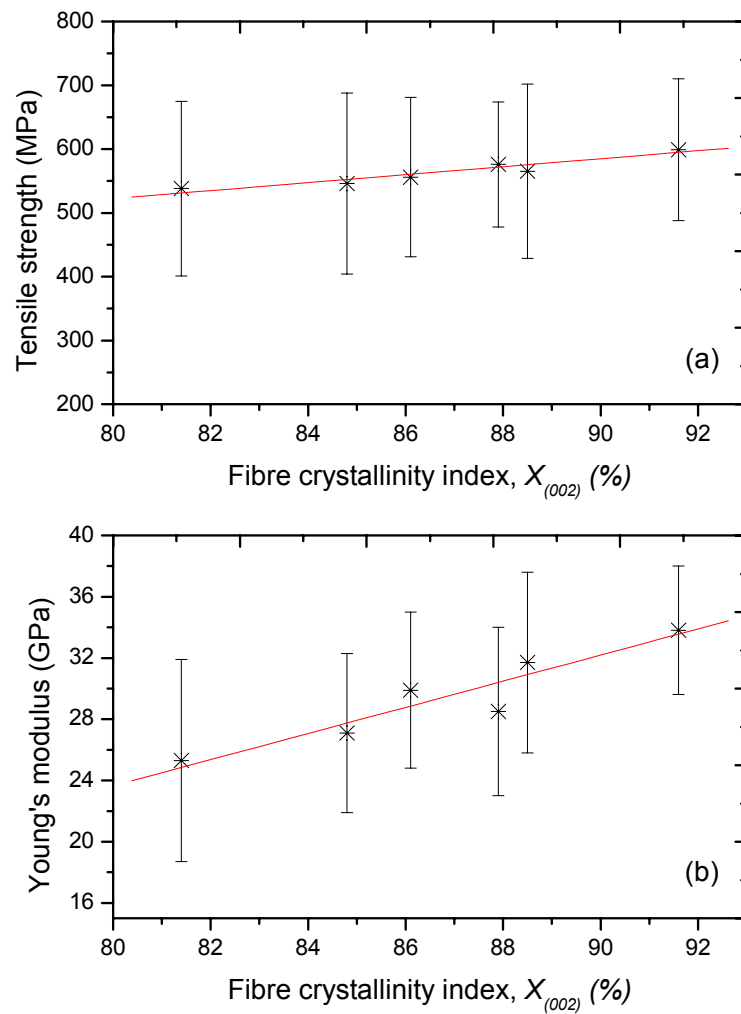


Figure 4.26: Relationships between tensile properties and crystallinity index; (a) tensile strength versus crystallinity index, and (b) Young's modulus versus crystallinity index.

CHAPTER FIVE

Results and Discussion: Part II – Polylactide/Hemp Fibre Composites

5.1 Introduction

This chapter covers results for the:

- FT-IR analysis of polylactide (PLA) and hemp fibre (untreated and treated) reinforced PLA composites;
- interfacial shear strength (IFSS) between hemp fibre (untreated and treated) and PLA;
- influence of fibre content and fibre treatment on the tensile properties, impact strength, flexural properties, plane strain fracture toughness, strain energy release rate and dynamic mechanical thermal properties of short and long hemp fibre reinforced PLA composites;
- effect of loading rate on plane strain fracture toughness of short fibre PLA composites;
- microscopic analysis of the fracture surface of PLA/hemp fibre composites;
- influence of fibre content and fibre treatment on the crystallinity of PLA in PLA/hemp fibre composites;
- comparison of experimental with theoretical tensile strength and Young's modulus for the PLA composites of different treated fibres.

5.2 FT-IR analysis of PLA and PLA/hemp fibre composites

A typical FT-IR spectrum of the PLA is presented in Figure 5.1. The principal absorbance peaks obtained for the PLA are as follows: (i) the peak around 3500 cm^{-1} was attributed to the hydroxyl (OH) stretching, (ii) the strong peaks at 2998 and 2944 were assigned to the asymmetric and symmetric mode of C-H stretching, respectively, (iii) the C=O stretching (from ester linkage) was observed at 1756 cm^{-1} , (iv) the peak at 1456 cm^{-1} was characterised by the CH_3 band, (v) the C-H deformation appeared at 1386 cm^{-1} , (vi) the O-C asymmetric mode of the ester groups was observed at 1083 cm^{-1} , and (vii) the peaks

appeared at 956 and 922 cm^{-1} could be attributed to the rocking mode of CH_3 [76, 159, 160].

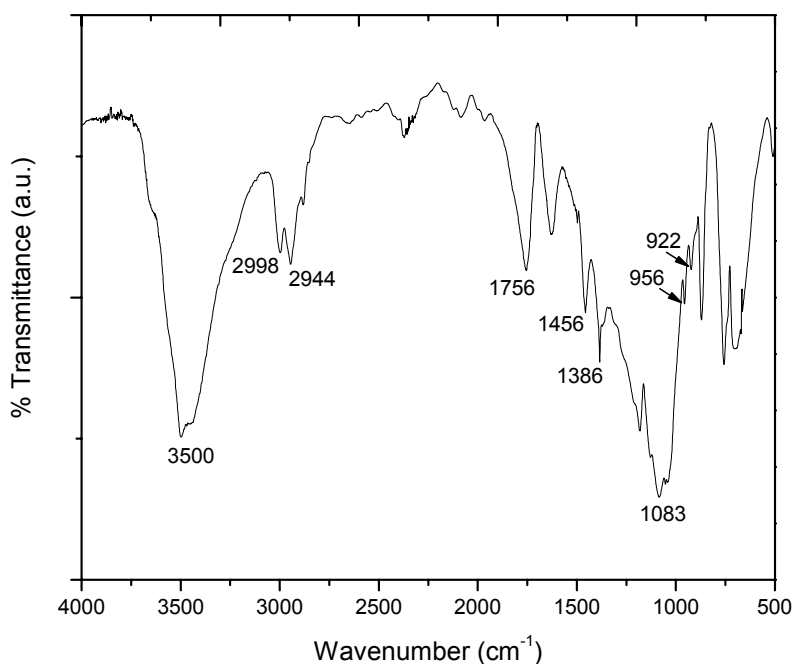


Figure 5.1: FT-IR spectrum of PLA.

FT-IR spectrum of the PLA/FB2 composites is shown in Figure 5.2. The spectra of FB2 fibre and PLA are presented for comparison. As can be seen, the OH stretching in the composite that appeared at 3437 cm^{-1} , was found to be different to that of the FB2 fibres (3410 cm^{-1}) and the PLA (3500 cm^{-1}). This indicates that in the PLA/FB2 composites, the OH groups (from fibres) formed hydrogen bonds with the carbonyl groups ($\text{C}=\text{O}$) of PLA. A similar observation has also been reported for the PLA/rice starch composites by other researchers [161]. In addition, it was also evident that the intensity of $\text{C}=\text{O}$ (1756 cm^{-1}) stretching in the PLA/FB2 composites was significantly higher than that of the PLA. This was due to the esterification between OH groups of hemp fibres and terminal carboxylic acid groups (COOH) of PLA. This agrees with the work reported by Semba *et al.* [162] who showed that the peak intensity of the $\text{C}=\text{O}$ group increased due to the chemical reaction between the dicumyl peroxide and the PLA in a PLA/polycaprolactone blend.

FT-IR spectra of various treated hemp fibre reinforced PLA composites are shown in Figure 5.3. In general, the spectra of all the treated hemp fibre reinforced PLA composites were similar to that of the untreated fibre reinforced composites (PLA/FB2). However, the

intensity at around 1756 cm^{-1} (C=O stretching) was found to depend on fibre treatment, which increased in the order: PLA/MA < PLA/FB2 < PLA/ACY < PLA/SIL < PLA/ALKSIL < PLA/ALK. The physical and chemical bonding of PLA with the untreated and various treated hemp fibres could be explained as follows. Since cellulose is the main component of hemp fibres, it could be speculated that most bonding interactions occurred between the OH groups of cellulose of hemp fibres with the carbonyl (C=O) and carboxylic acid (COOH) groups of PLA. The possible sites of interaction between the cellulose of hemp fibres and PLA are shown in Figure 5.4.

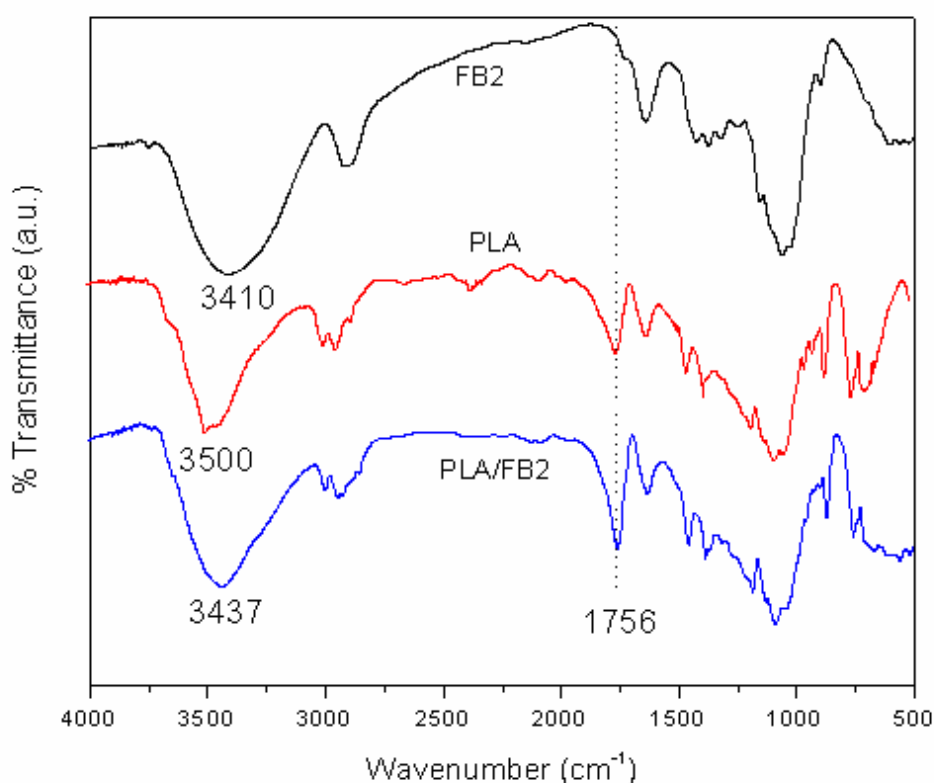


Figure 5.2: FT-IR spectrum of PLA/FB2 fibre composites. Spectra of FB2 fibre and PLA are shown for comparison.

As seen in section 4.2.3, the untreated hemp fibres contain impurities (e.g. wax and pectin) on their surfaces. Therefore, it is reasonable that only a limited number of OH groups (from fibres) were exposed for bonding with C=O and COOH groups of PLA. In contrast, for the alkali treated fibres (ALK), the number of available OH groups increased due to the removal of impurities from the surfaces. Thus, it could be believed that the increased exposure of the OH groups of fibres provided improved potential for hydrogen and

covalent bonding with the carbonyl (C=O) and carboxyl (COOH) groups of PLA, respectively.

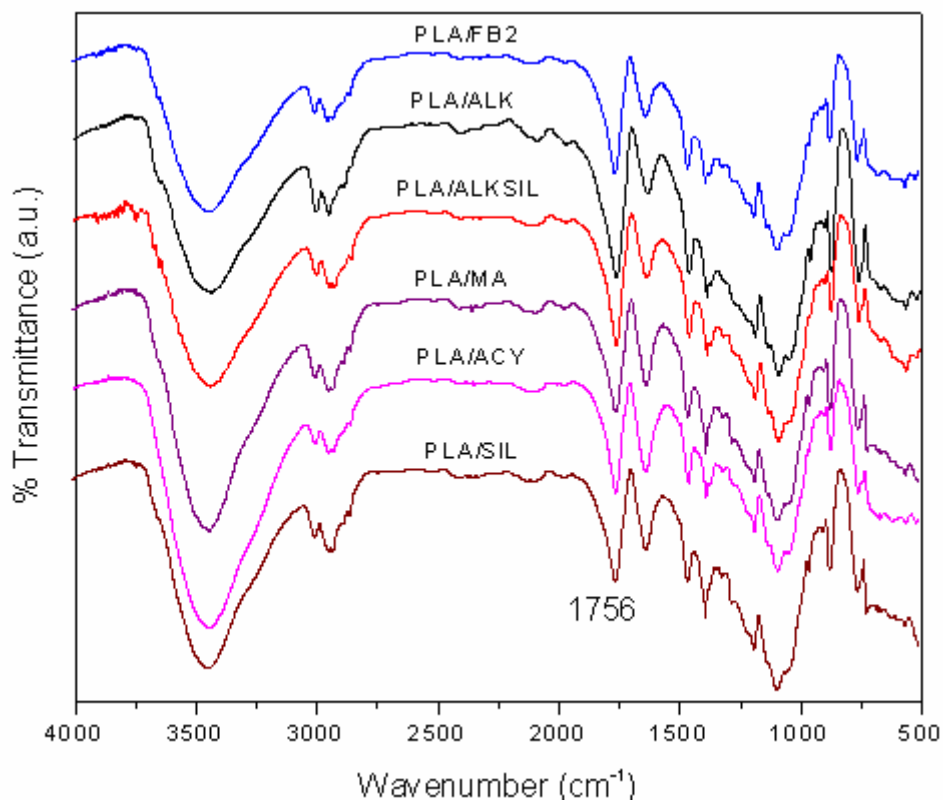


Figure 5.3: FT-IR spectra of various treated hemp fibres reinforced PLA composites. Spectrum of PLA/FB2 fibre composites is shown for comparison.

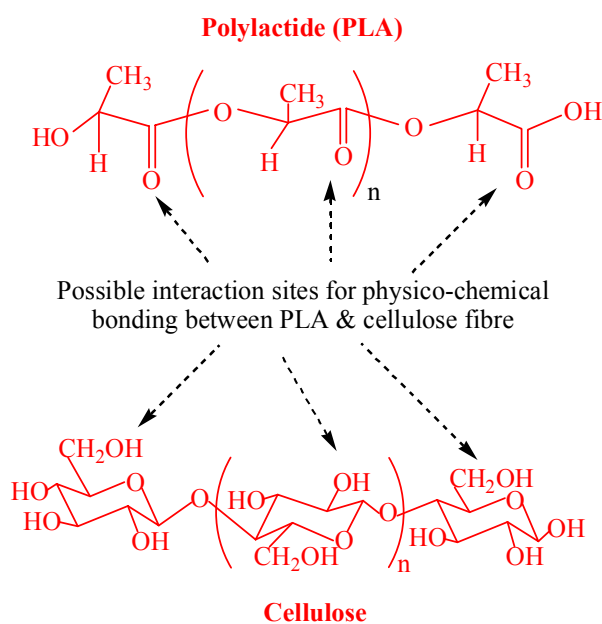


Figure 5.4: Schematic illustration for the possible bonding sites of PLA and cellulose of hemp fibres.

The silane grafted hemp fibres (SIL and ALKSIL) possessed various functional groups namely hydroxyl (OH), primary amine ($-NH_2$) and secondary amine ($=NH$) (see section 4.3), which would be able to form hydrogen bonds and covalent bonds with the carbonyl ($C=O$) and carboxyl ($COOH$) groups of PLA, respectively. It seems likely that a greater degree of bonding has occurred between the silane grafted hemp fibres and the PLA. The possible sites of interaction between the silane grafted hemp fibres and the PLA are depicted in Figure 5.5. Huda *et al.* [163, 164] suggested similar bonding interaction for the silane grafted kenaf and pineapple leaf fibre reinforced PLA composites. In another study, Zhang *et al.* [165] also indicated that the silane modified hydroxyapatite has the capability to form hydrogen and covalent bonds with PLA.

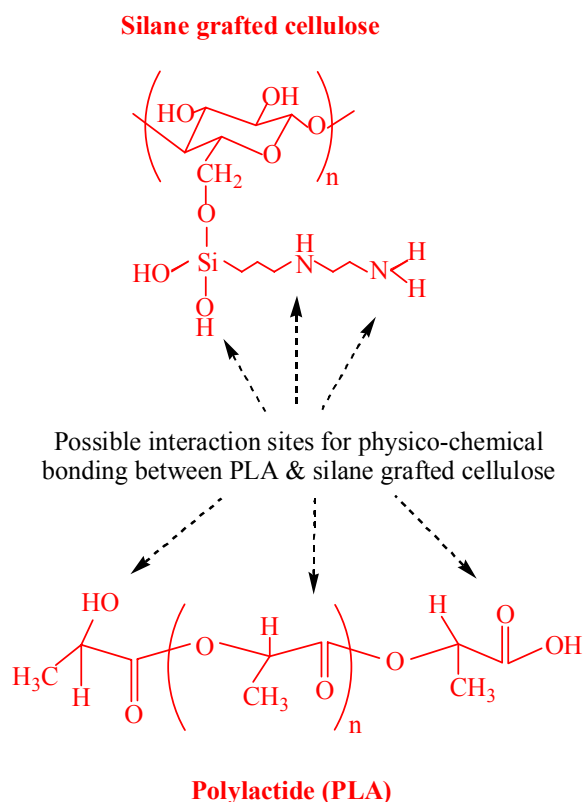


Figure 5.5: Schematic illustration for the possible bonding sites of PLA and silane grafted cellulose of hemp fibres.

Acetylation of hemp fibres would be expected to replace OH groups with $COCH_3$ groups to some extent as supported by the FT-IR analysis in section 4.3. This decreased the number of available OH groups in the acetylated fibres. Thus, it could reasonably be said that a lower degree of chemical bonding has occurred between the ACY fibres and the

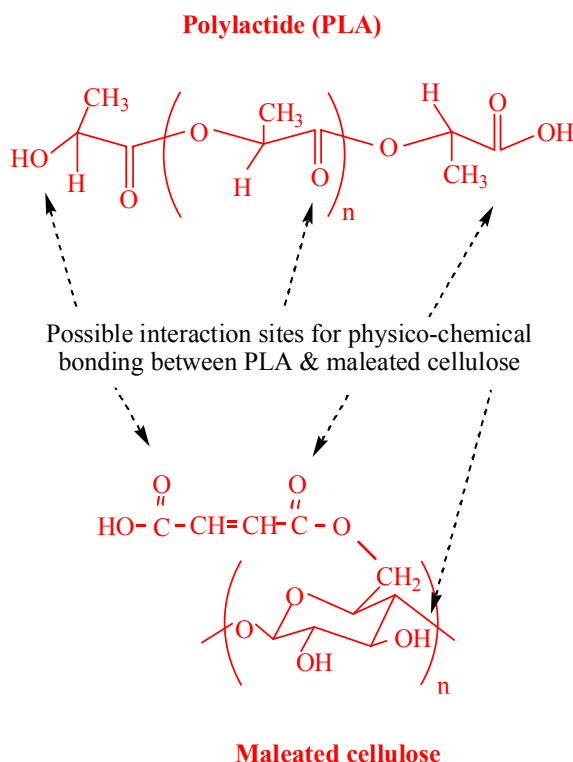


Figure 5.7: Schematic illustration for the possible interaction sites of PLA and maleated cellulose of hemp fibres.

5.3 Interfacial shear strength (IFSS) of PLA/hemp fibre samples

As noted in the literature review (see section 2.1.1.2), a few experimental techniques have been developed to evaluate fibre/matrix interfacial strength. In this work, the pull-out method was adopted to assess the interfacial strength of PLA/hemp fibre composites. This was because the failure strain of PLA was very small (see section 5.6.1) which limited the selection of testing method. The detailed procedures of the specimen preparation and the pull-out test method are given in section 3.4.4.1. A SEM micrograph of a pull-out test specimen is shown in Figure 5.8.

The typical load-displacement curves of the PLA/hemp fibres samples from the pull-out tests are illustrated in Figure 5.9. It can be seen that the load increased gradually until initial debonding occurred, which indicates debonding was neither complete nor sudden. Complete debonding was seen as the load reached the maximum, then dropped abruptly. This maximum debonding force depends on the fibre/matrix interfacial adhesion [166].

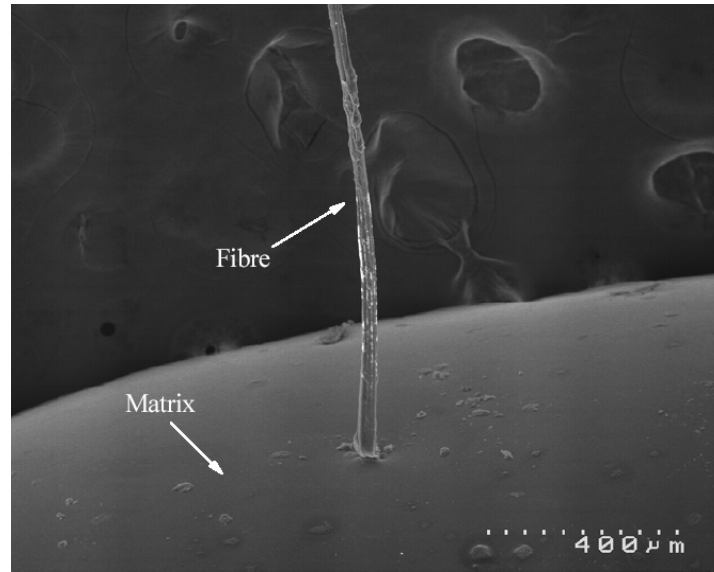


Figure 5.8: SEM micrograph of single fibre pull-out test specimen (PLA/ALK).

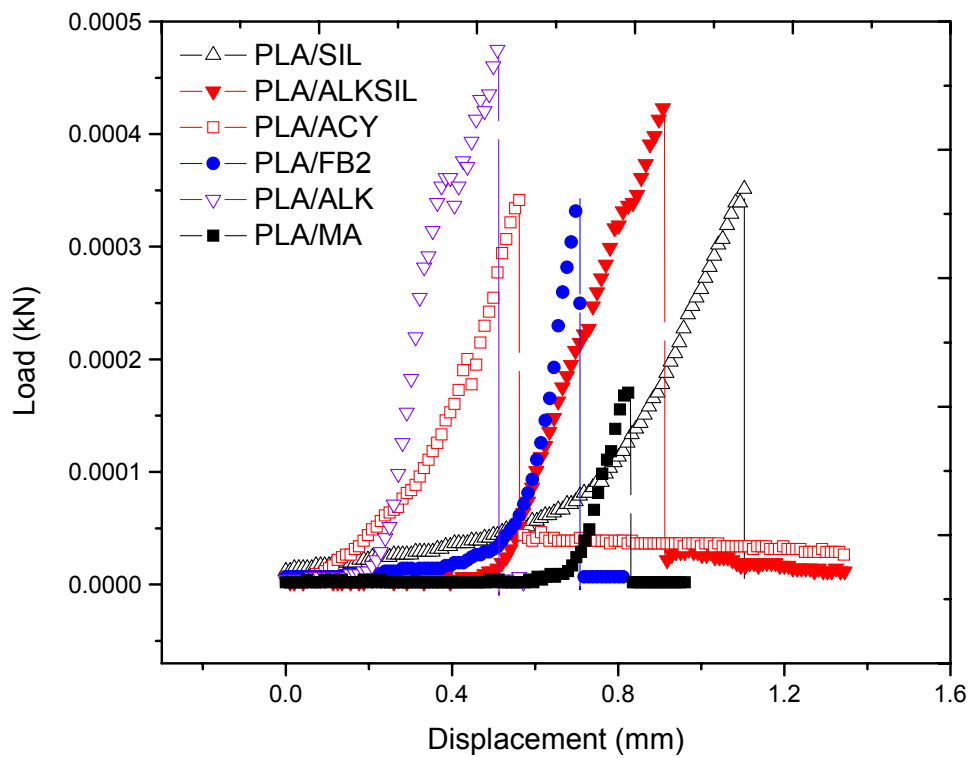


Figure 5.9: Typical load-displacement curves for pull-out tests of PLA/hemp fibre (untreated and treated) samples.

Figure 5.10 shows the debonding forces of the PLA/hemp fibres samples as a function of fibre embedded length. The straight lines in the figure are only an indicator of the trend. As can be seen, the debonding force showed a reasonably linear relationship with the

embedded fibre length, which was in good agreement with other work elsewhere [167, 168].

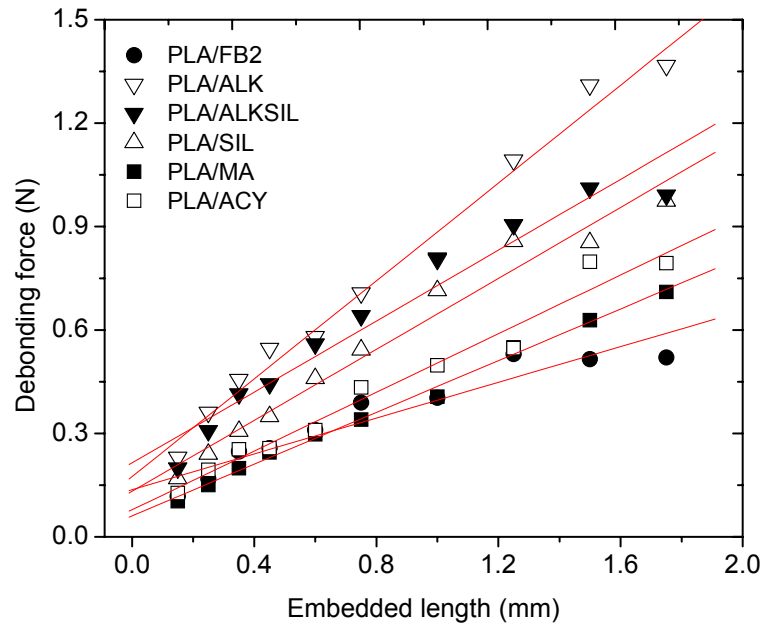


Figure 5.10: Debonding force versus embedded fibre length of PLA/hemp fibre (untreated and treated) samples.

From the debonding forces, the interfacial shear strength (IFSS) of the samples was calculated using Equation 2.2. The IFSS of the PLA/hemp fibre samples as a function of fibre embedded length is depicted in Figure 5.11. As can be seen, the IFSS with respect to the embedded fibre length showed a non-linear relationship, which indicated a brittle-like interface fracture as reported in literature [169]. This brittle-like interface fracture as observed by the pull-out tests could be explained by the requirements of a critical crack length, which, once achieved, requires no further increase of stress for the longer embedded fibre length. Similar interface failure behaviour has also been reported for flax fibre/high density polyethylene [169] and carbon fibre/poly(phenylene sulfide) [170] samples.

The average IFSS of each of the PLA/hemp fibre (untreated and treated) samples is shown in Figure 5.12. The average IFSS increased in the following order: PLA/MA (5.33 MPa) < PLA/FB2 (5.55 MPa) < PLA/ACY (6.29 MPa) < PLA/SIL (8.22 MPa) < PLA/ALKSIL (9.87 MPa) < PLA/ALK (11.41 MPa). This trend was found to be similar with the trend in chemical bonding as seen in the FT-IR results for composites.

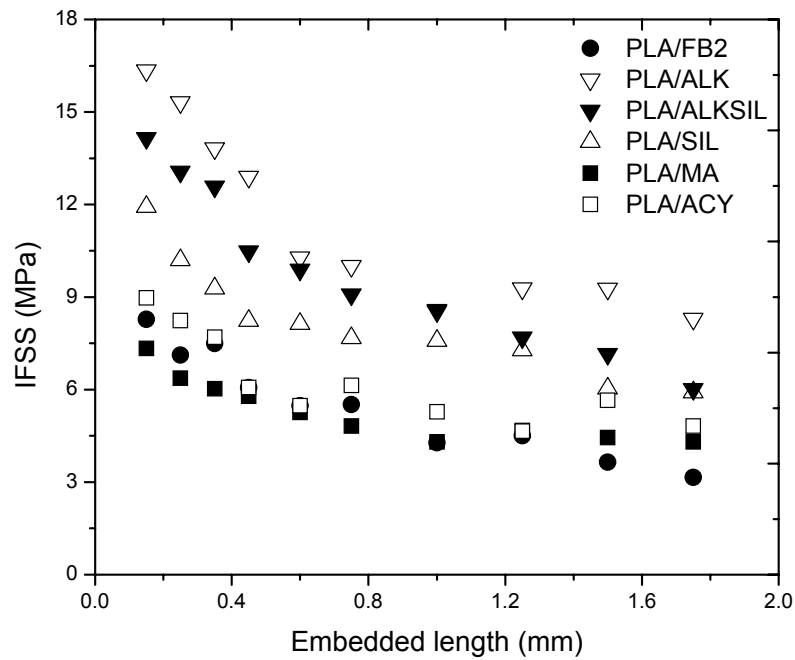


Figure 5.11: IFSS versus embedded fibre length of PLA/hemp fibre (untreated and treated) samples.

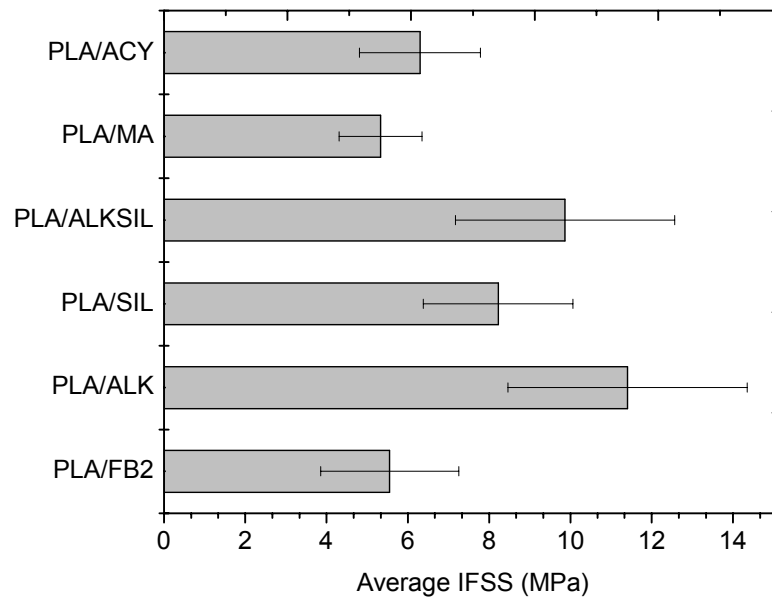


Figure 5.12: Average IFSS of untreated and treated hemp fibre/PLA samples.

The IFSS results obtained in this work were reasonable and agreed quite well with the reported IFSS of PLA and other natural fibre samples. For instance, Tokoro *et al.* [171] reported the IFSS (measured by micro-droplet test) of PLA and three different types of

bamboo fibre namely ‘Short fibre bundle’ (SFB), ‘alkali treated filament’ (ATF) and ‘steam-exploded filament’ (SEF). They found that the IFSSs of PLA/SFB, PLA/ATF and PLA/SEF were 4.3, 9.8 and 12.6 MPa, respectively. In another work, Cho *et al.* [172] reported the average interfacial strength (measured by microbond test) of PLA with jute and kenaf fibres. They found that the average IFSS of jute/PLA and kenaf/PLA were approximately 5.5 and 10.5 MPa (from graphs), respectively. They also treated the fibres with water by static (STW) and dynamic (DTW) soaking. For treated jute fibres, the average IFSSs of STW/PLA and DTW/PLA were approximately 9.5 and 13 MPa (from graphs), respectively, and for the treated kenaf fibres, the average IFSSs of STW/PLA and DTW/PLA were approximately 11.5 and 11 MPa (from graphs), respectively. In contrast, Hubber *et al.* [173] observed a very weak interface (no data available) between flax fibres and PLA. They tested the samples by the single fibre fragmentation method, and did not see any fragmentation of flax fibres which was an indication of poor adhesion between the flax fibres and the PLA. From the aforesaid discussion, it could reasonably be said that the interfacial strength between the PLA and the natural fibres strongly depends on the type of fibre and nature of treatment applied to the fibres.

5.3.1 Estimation of critical fibre length

The critical fibre length (l_c) of the untreated and treated hemp fibres was estimated using Equation 2.6, where the gauge length of the tested fibre strength was 10 mm [133, 174, 175].

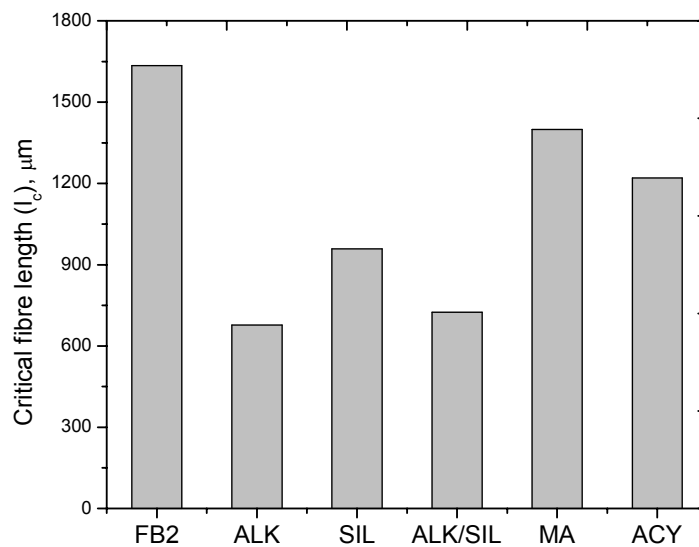


Figure 5.13: Estimated critical fibre length of untreated and treated fibres.

The estimated critical fibre length for the untreated and different treated hemp fibre reinforced PLA composites is depicted in Figure 5.13. The order of the critical fibre length for different samples was: FB2 (1634 μm) > MA (1398 μm) > ACY (1220 μm) > SIL (958 μm) > ALKSIL (724 μm) > ALK (677 μm). These results were in general agreement with the reported critical fibre length of other natural fibre reinforced polymer samples [176].

5.4 Crystallinity of PLA in PLA/hemp fibre composites

5.4.1 Microscopic analysis

Natural fibres can induce crystallisation (transcrystallinity) from their surfaces in a semicrystalline polymer [35, 177]. A schematic transcrystalline layer on a fibre surface is illustrated in Figure 5.14. In this study, micro-composites of PLA and hemp fibres (untreated and treated) were prepared between two glass slides by embedding the fibre into molten PLA. The samples were isothermally crystallised at 110°C for 15 minutes and then cooled to room temperature. An optical light microscope was used to examine the samples.

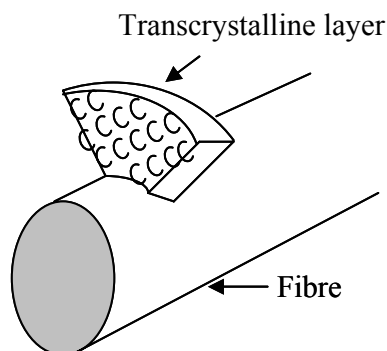


Figure 5.14: Schematic transcrystal layer at fibre/matrix interface.

The influence of fibre treatment on the PLA crystallinity at the fibre/matrix interface is presented in Figure 5.15. As can be seen, a discontinuous transcrystalline layer of PLA was formed on the surface of untreated fibres (FB2). This could be due to the presence of impurities (e.g. wax and pectin), which acted as barriers to nucleate the PLA. However, a highly dense transcrystalline layer of PLA was formed in the case of ALK fibres. This could be because impurities were removed from the fibres by the alkali treatment, which in turn increased the number of nucleating sites (i.e. crystalline portion of cellulose [35]) of the fibres. The density of the nucleating sites of SIL, ALKSIL, ACY and MA fibres

seemed not to be sufficiently high to form a highly dense transcrystalline layer of PLA. This was because crystalline cellulose of the SIL, ALKSIL, ACY and MA fibres decreased due to the destruction of hydrogen bonds in the crystalline cellulose structures (i.e. increase of amorphous cellulose portion [55, 117]) as supported by the XRD results (see section 4.4).

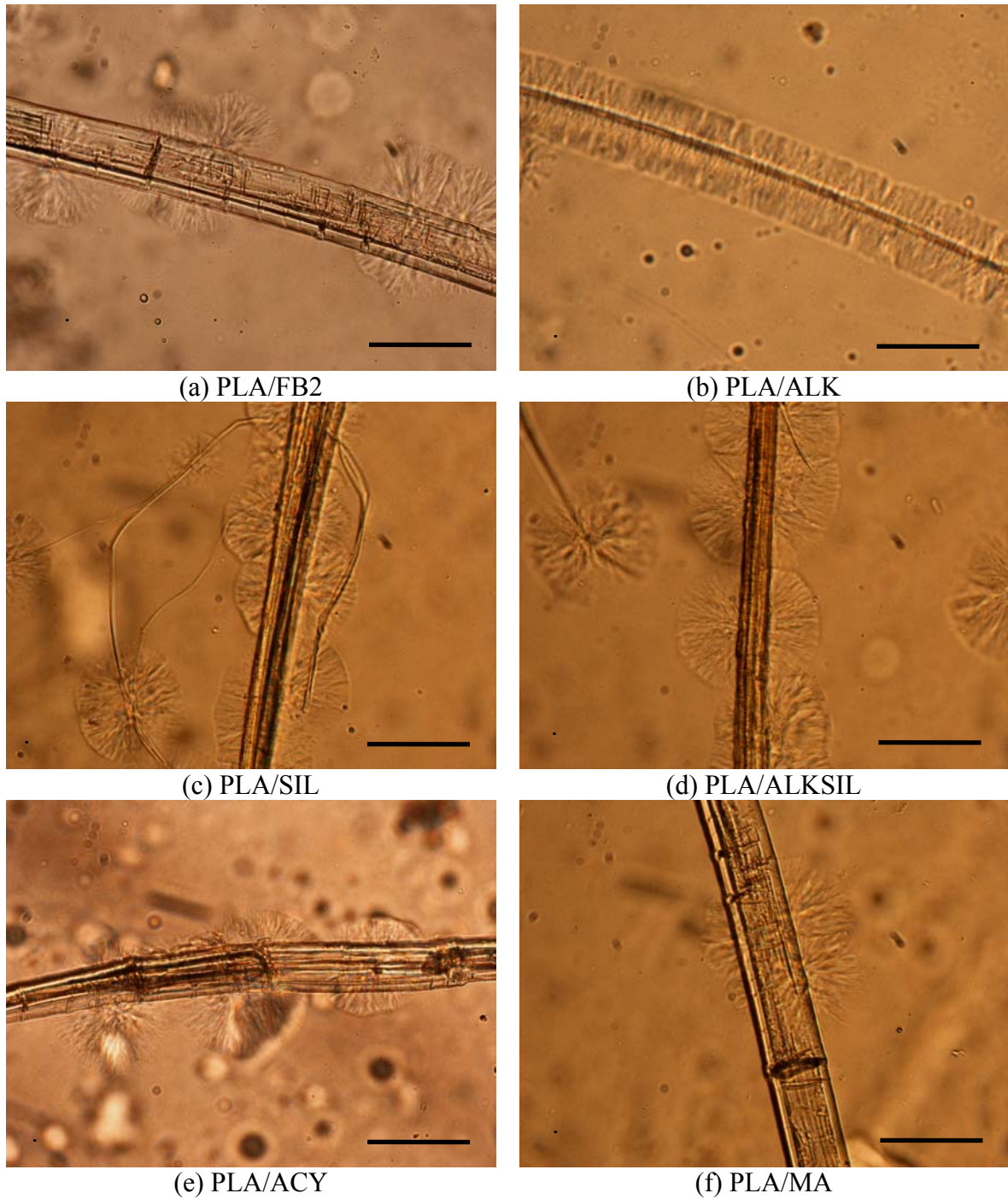


Figure 5.15: Optical light micrographs showing transcrystalline layer of PLA from hemp fibre (untreated and treated) surfaces (scale bar = 50 μm).

5.4.2 X-ray diffraction (XRD) analysis

XRD analysis of injection moulded PLA and composites were carried out according to the method described in section 3.4.2. Figure 5.16 shows the diffraction patterns of PLA and PLA/FB2 composites at 10, 20 and 30 wt% fibre loads. It can be seen that PLA alone exhibited a trace of crystallinity which can be identified by the broad peak close to $2\theta = 16.4^\circ$ [84]. This broad peak indicated that the PLA chains were poorly ordered (i.e. low degree of crystallinity). This could be due to the rapid cooling of PLA during injection moulding. A similar XRD spectrum for injection moulded PLA has been reported by other researchers [178]. Diffractograms for PLA/FB2 composites revealed that the intensity of the peak at 16.4° increased considerably with increased fibre content as a result of increased PLA crystallinity in the composites. This behaviour was expected, because hemp fibres act as nucleating sites to crystallise the PLA. Another prominent peak at $2\theta = 23.4^\circ$ corresponds to the cellulose material which increased sharply with the increase of fibre content.

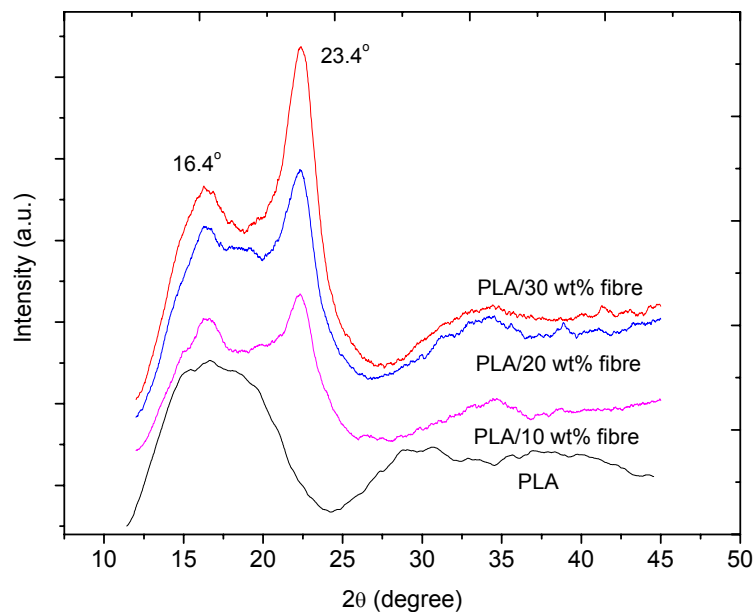


Figure 5.16: X-ray diffractograms of PLA and PLA/FB2 composites at different fibre contents.

Figure 5.17 presents the diffractograms of the different treated hemp fibre (30 wt%) reinforced PLA composites along with untreated fibre composites (PLA/FB2) for comparison. The intensity of the peak at 16.4° for different composites increased in the following order: PLA/MA < PLA/ACY < PLA/FB2 < PLA/SIL < PLA/ALKSIL <

PLA/ALK. This trend suggested that the alkali and silane treated fibres (ALK, SIL and ALKSIL) induced better crystallisation in the PLA compared to the untreated fibres (FB2). In contrast, the intensity of the peak at 16.4° for the PLA/ACY and PLA/MA composites is lower than that of the PLA/FB2 composites, which suggested that the acetylated and maleic anhydride treated fibres (ACY and MA) did not enhance the crystallinity of PLA compared to the untreated fibres (FB2).

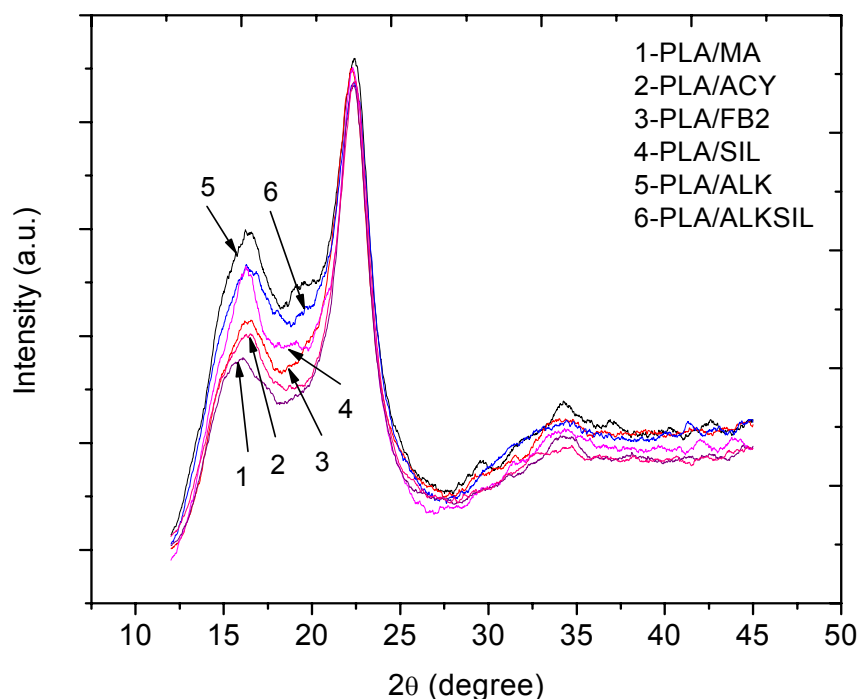


Figure 5.17: X-ray diffractograms of different treated hemp fibre/PLA composites at 30 wt% fibres loading.

5.4.3 Differential scanning calorimetry (DSC) analysis

DSC analysis of injection moulded PLA and composites were carried out according to the method described in section 3.4.8.2. The DSC heating thermograms of PLA and PLA/FB2 composites recorded in the range of 25-200°C are shown in Figure 5.18. On heating, the samples displayed three main successive transitions: a glass transition (T_g), a cold-crystallisation exotherm (T_{cc}) and a melting endotherm (T_m). These are given for all the composites in Table 5.1. As can be seen in Table 5.1, PLA exhibited the T_g , T_{cc} and T_m around 57.8, 122.7 and 152.3°C, respectively. The T_g of PLA in the PLA/untreated fibre (FB1 and FB2) composites did not change noticeably with increased fibre content, a

finding consistent with other research studies [89, 94]. The ability of PLA to recrystallise on heating above the T_g improved with increased fibre content. In fact, the cold-crystallisation temperature decreased significantly for the composites when compared with PLA only samples. The presence of double melting peak in the DSC thermograms of the composites could be due to the existence of two populations of crystallites differing in size [179]. The heat of melting (ΔH_m) of the composites also increased with increased fibre content, which indicated an increase in the degree of PLA crystallinity.

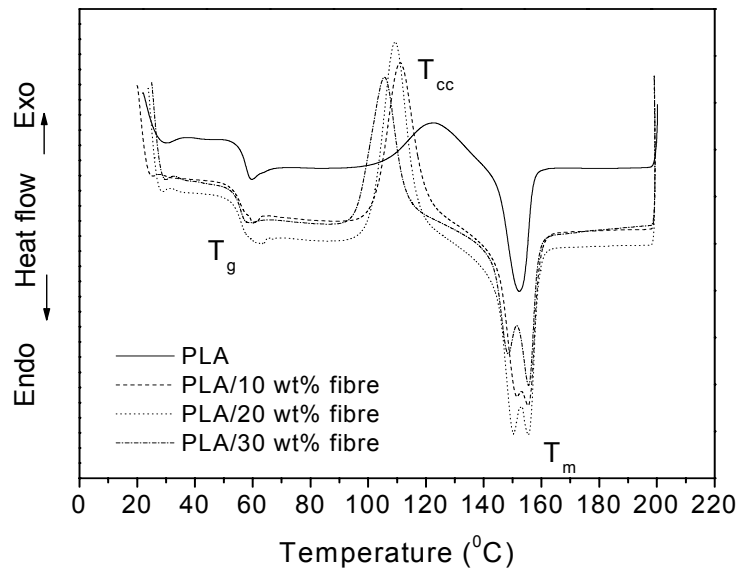


Figure 5.18: DSC thermograms of PLA and PLA/FB2 composites.

PLA crystallinity in composites was calculated using Equation 3.18. In Figure 5.19, it is apparent that the crystallinity of PLA in composites increased with increased fibre content which could be due to the increased availability of nucleation sites leading to the formation of increased transcrystallinity. However, the increase of crystallinity was smaller as the fibre content increased from 20 to 30 wt% which could be due to the decrease of PLA content or space limitation. It can be seen that the crystallinity of PLA in the PLA/FB2 composites was higher than that for the PLA/FB1 samples. This was because cellulose crystallinity (i.e. nucleating sites) of FB2 fibres was higher than that of FB1 fibres (see Figure 4.18). It is apparent that the crystallinity of PLA in the PLA/ALK, PLA/ALKSIL and PLA/SIL composites increased compared with that of the PLA/FB2 composites. Other researchers also found that the crystallinity of PLA enhanced in the presence of alkali and

silane treated fibres [89, 171]. In contrast, the crystallinity of PLA in the PLA/ACY and PLA/MA composites decreased compared with that of the PLA/FB2 composites. The above findings were consistent with the XRD results (see section 5.4.2).

Table 5.1: Thermal properties of PLA and PLA/hemp fibre composites.

Sample	Fibre content (wt%)	T_g ($^{\circ}\text{C}$)	T_{cc} ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
PLA	-	57.8	122.7	152.3	7.90
PLA/FB1	10	56.5	116.7	150.1-154.9	8.12
	20	57.8	105.1	149.2-155.6	12.36
	30	56.9	108.6	148.6-154.1	13.51
PLA/FB2	10	56.2	110.9	152.4-155.3	14.33
	20	56.3	109.2	150.3-155.5	18.27
	30	55.5	105.5	149.7-155.5	19.20
PLA/ALK	10	56.8	98.5	150.6-157.3	20.66
	20	56.3	98.7	147.8-156.9	27.28
	30	57.8	97.3	146.1-156.6	27.18
PLA/ACY	10	56.7	111.7	148.2-155.9	13.38
	20	55.5	109.9	150.1-155.1	15.59
	30	57.8	107.2	146.1-155.7	18.89
PLA/SIL	10	55.9	107.6	148.3-155.7	17.56
	20	56.2	108.9	147.2-156.3	21.77
	30	56.1	103.6	149.3-155.4	22.88
PLA/MA	10	55.9	114.5	147.7-155.8	9.41
	20	55.3	110.4	150.4-155.1	12.76
	30	56.7	110.9	148.9-155.5	14.43
PLA/ALKSIL	10	55.9	102.7	148.9-154.8	19.23
	20	56.6	105.4	147.7-156.9	23.11
	30	57.3	103.9	149.1-156.9	23.79

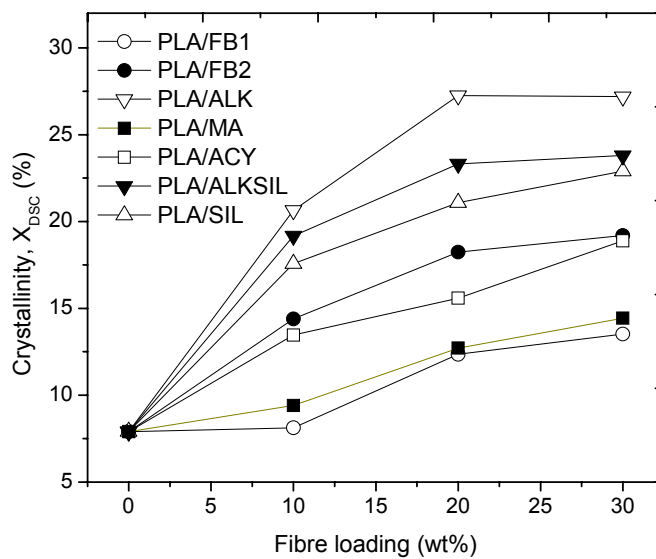


Figure 5.19: DSC crystallinity of PLA and composites.

5.5 Fibre length distribution and fibre orientation in short hemp fibre/PLA composites

The mechanical properties of short fibre composites depend critically on the fibre length distribution and fibre orientation [180-182]. In this context, fibre length distribution and fibre orientation in the injection moulded hemp fibre/PLA composites were analysed to better understand the mechanical properties of short hemp fibre/PLA composites.

5.5.1 Fibre length distribution

The distribution of fibre length before and after processing was evaluated according to the method described in section 3.4.5. Figure 5.20 presents the cumulative distribution of the chopped fibre length before processing to produce composites. As can be seen, nearly 90% of the fibres were well above the critical fibre length (about 1.6 mm for FB2 fibres) before processing. It could be assumed that other chopped fibres (treated) had almost similar length distribution before processing. Thus, for the treated fibres, it could be speculated that approximately all the fibres were above the critical length before processing, because the estimated critical length of treated fibres was lower than that of the untreated fibres.

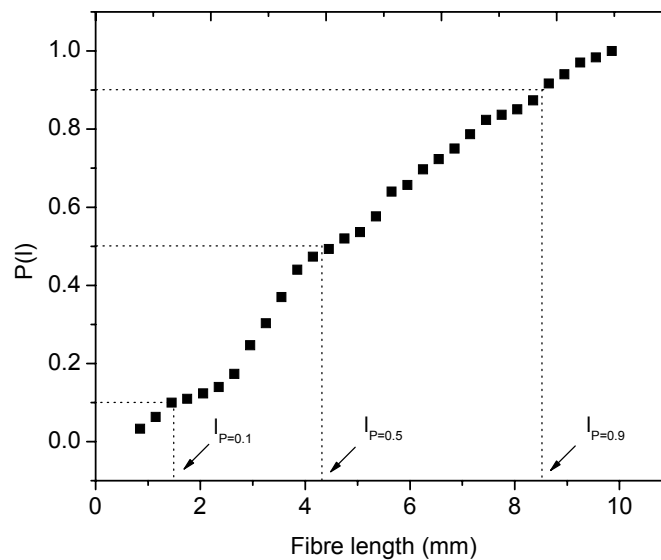


Figure 5.20: Cumulative fibre length distribution before processing for the FB2 fibres.

The cumulative fibre length distribution after the processing of composites is presented in Figure 5.21 and the probability (%) of fibre length below the critical fibre length is given

in Table 5.2. It is evident that the fibre length distribution narrowed and shifted to shorter lengths as the fibre content increased. It is well known that fibre breakage results from the fibre/polymer interaction, fibre/fibre interaction and fibre contact with the surfaces of processing equipment [180]. As mentioned in literature, fibre shortening inevitably occurs during extrusion and injection moulding of the composites containing both natural [133, 171] and synthetic fibres [180], due to the strong shear stresses that act in the viscous molten polymer. So, in the present case, as the fibre content increased, the probability of the fibre/fibre interaction and fibre/equipment wall also increased, resulting in an increase of short fibre populations in the composites as observed in Figure 5.21.

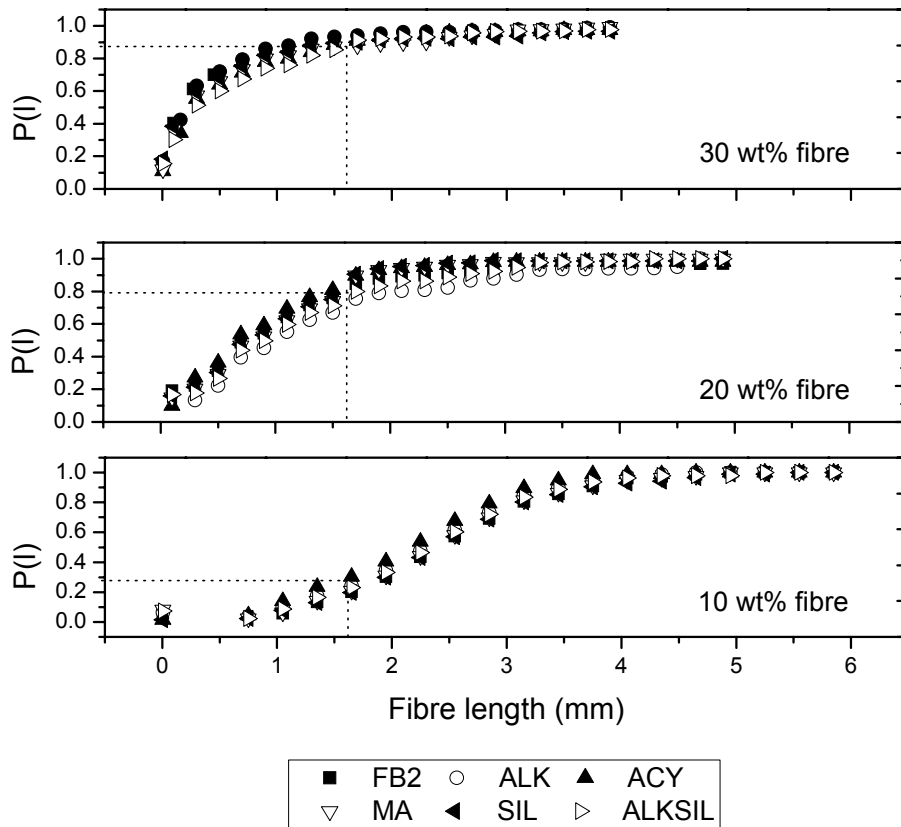


Figure 5.21: Cumulative fibre length distribution after processing.

Table 5.2: Probability (%) of fibre length below the estimated critical fibre length in the composites.

Sample	Fibre content (wt%)		
	10	20	30
PLA/FB2	20.1	76.1	91.3
PLA/ALK	3.4	39.6	67.3
PLA/ACY	17.2	58.7	86.8
PLA/MA	19.5	69.3	88.1
PLA/SIL	5.5	52.3	82.7
PLA/ALKSIL	3.9	47.5	76.5

5.5.2 Fibre orientation

Figure 5.22 shows light microscope images of transverse cross sections of PLA/hemp fibre composites. It was apparent that the fibres arranged themselves in a three-layer structure. There were two surface layers of fibres preferentially aligned parallel to the mould filling direction and a core layer of fibres preferentially aligned perpendicular to the mould filling direction. A schematic drawing of fibre orientation in the X-Y-Z plane is given Figure 5.23.

As can be seen in Figure 5.22, the thickness of the core layer increased with increased fibre content, i.e. more fibres became aligned perpendicular to the mould filling direction. The origin of such microstructures in the injection moulded samples is related to the viscosity of compounding melt. As said in literature [182], the core layer becomes thick when the viscosity of the melt increased. In the present case, the viscosity of the composite compounding melt increased with increased fibre content; consequently, the thickness of the core layer also increased with increased fibre content.

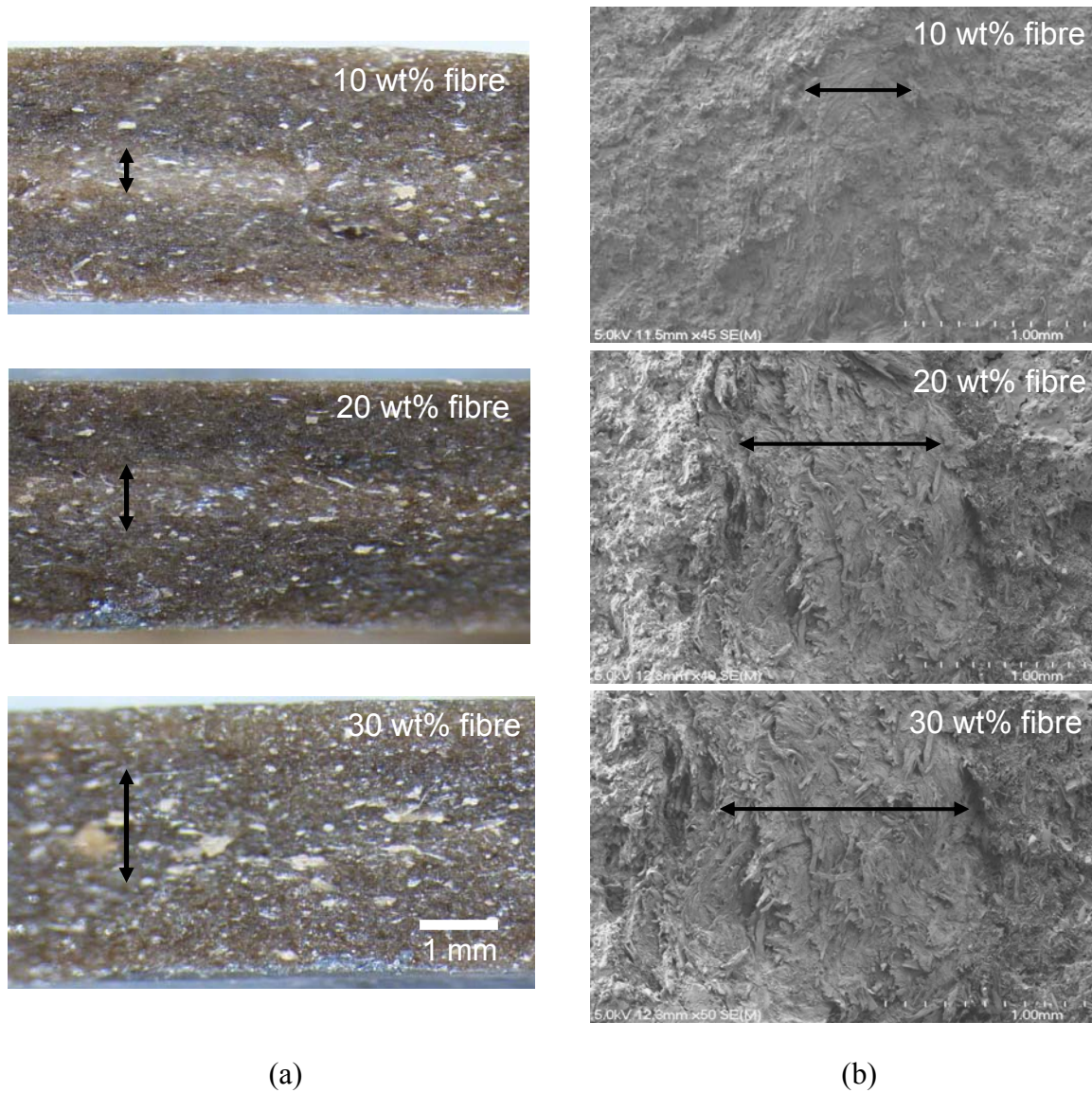


Figure 5.22: Orientation of fibre in the injection moulded samples (a) light microscope images and (b) SEM micrographs (arrow signs are indicating thickness of core layers).

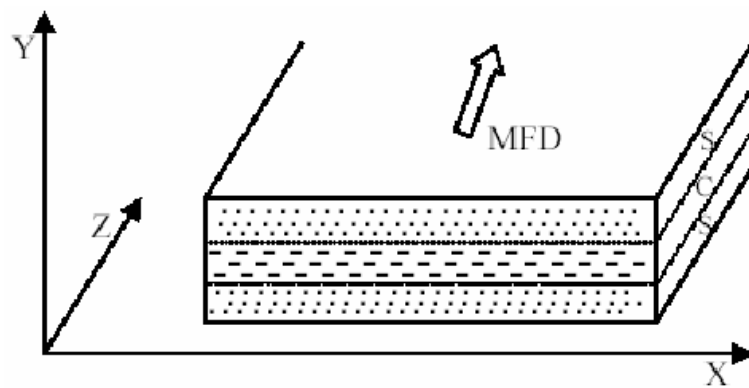
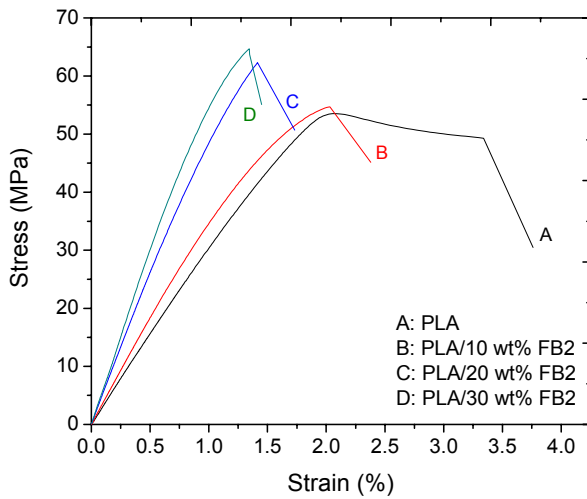


Figure 5.23: Schematic cross-section of composites showing the orientation of fibres in the surface layers (S) and core layer (C) with respect to the melt flow direction (MFD) (X → width, Y → thickness, Z → length).

5.6 Mechanical properties of short hemp fibre reinforced PLA composites

5.6.1 Tensile properties

Typical stress versus strain records of the PLA and composites are presented in Figure 5.24(a). It may be observed that the curves initially show linear deformation, followed by a small non-linear deformation prior to the attainment of the maximum strength. It can also be seen that the curves became steeper with increased fibre content. In Figure 5.24(b), it can be seen that the two sample halves were completely separated at a very high fracture speed, typical of an unstable fracture. All the samples showed similar fracture behaviour.



(a)



(b)

Figure 5.24: (a) Typical stress versus strain curves for tensile testing of PLA and composites (PLA/FB2), (b) photograph of the specimens after testing.

Figure 5.25 shows the average tensile strength, Young's modulus and failure strain of the untreated fibre (FB1 and FB2) reinforced PLA composites as a function of fibre content. As expected, the inclusion of hemp fibres in PLA increased the tensile strength and the Young's modulus of the composites. It is apparent that the tensile strength and Young's modulus of the PLA/FB2 composites were higher than those of the PLA/FB1 composites at all the fibre contents. The superior tensile strength and Young's modulus of the PLA/FB2 composites can be attributed to the greater tensile strength and Young's modulus of the FB2 fibres. It can be seen that the tensile strength of the PLA/FB2 composites

increased gradually from 51 to 68 MPa, as the fibre in the composites increased from 0 to 30 wt%, which was approximately 33% higher than that of the PLA. In the same way, the Young's modulus of the PLA/FB2 composites increased steadily from 3.5 to 7.6 GPa, as the fibre in the composites increased from 0 to 30 wt%, which was about 117% higher than that of the PLA.

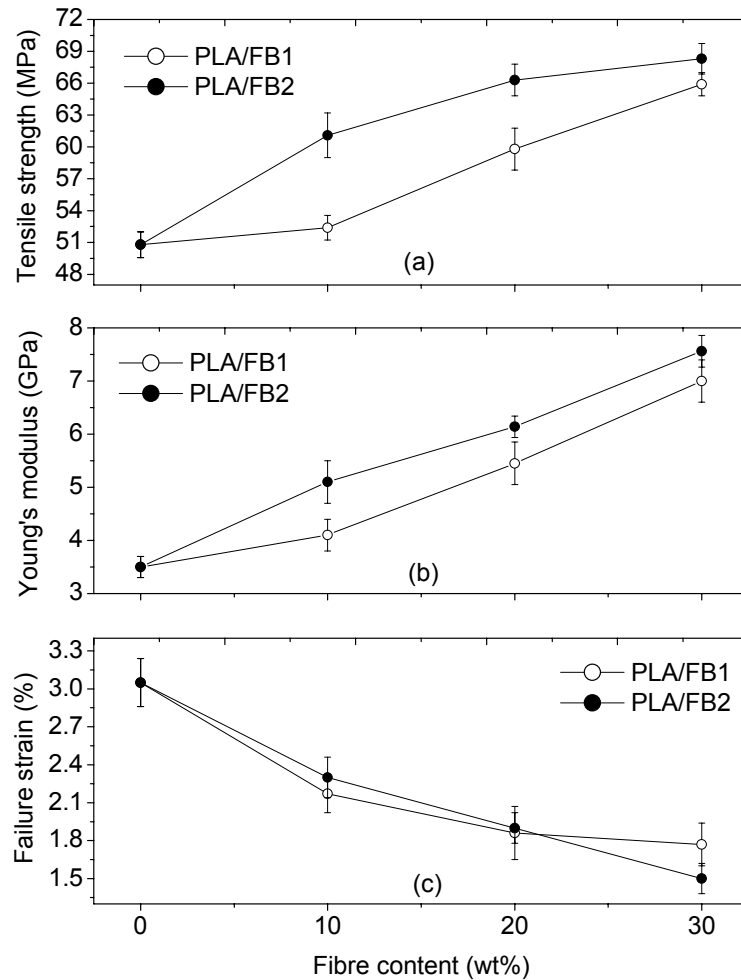


Figure 5.25: Tensile properties of untreated hemp fibre reinforced PLA composites as a function of fibre content.

On the other hand, the failure strain of the PLA/FB1 and PLA/FB2 composites both decreased gradually from 3.1% to 1.8 and 1.5%, respectively, as the fibre in the composites increased from 0 to 30 wt%. This behaviour could be explained by the differing failure strains of fibre and matrix. The hemp fibres fail at relatively low strain, leaving the matrix un-reinforced (fibre failure strain < matrix failure strain); changes of the stress

concentrations at the broken fibre ends may then promote fracture of the matrix, leading to overall failure of the composites at strains below that of the unreinforced PLA itself.

The average tensile strength and Young's modulus of the treated hemp fibre/PLA composites are depicted in Figures 5.26 and 5.27, respectively. The tensile strength and Young's modulus of the PLA/ALK, PLA/ALKSIL and PLA/SIL composites increased compared with those of the PLA/FB2 composites. This could be attributed to the greater interfacial strength and PLA crystallinity in the PLA/ALK, PLA/ALKSIL and PLA/SIL composites. On the other hand, the tensile strength and Young's modulus of the PLA/ACY and PLA/MA composites decreased compared with those of the PLA/FB2 composites. The decrease in tensile strength and Young's modulus of the PLA/MA composites could be due to the lower interfacial strength and PLA crystallinity in the PLA/MA composites. In the case of the PLA/ACY composites, the tensile strength and Young's modulus decreased compared with those of the PLA/FB2 composites, although the average interfacial strength of the PLA/ACY composites was slightly greater than that of the PLA/FB2 composites. It was thought that the lower degree of PLA crystallinity in the PLA/ACY composites could be the reason for decreasing the tensile strength. Cunha *et al.* [183] also found that the tensile strength of the acetylated pine wood fibre/PLA composites decreased compared to the untreated pine wood fibre/PLA composites. Among all the samples, the tensile strength and Young's modulus of the PLA/ALK composites were found to be the highest, a result similar to that for interfacial strength. The tensile strength and Young's modulus of the PLA/ALK composites were 75.5 MPa and 8.2 GPa, respectively, about 10.5 and 8.2% higher than those of the PLA/FB2 composites. These results were better than any reported tensile properties for the short natural fibre/PLA composites [82, 89, 95]. It was also found that Young's modulus of the PLA/ALK composites was greater than that of the PLA/glass fibre composites (6.7 GPa); however, tensile strength of the PLA/glass fibre composites was slightly higher (80.2 MPa) than that of the PLA/ALK composites [184].

As can be noted in Figure 5.26, the relationship between tensile strength and fibre content was not linear, which indicated that at higher fibre content, the benefit to composite strength by adding fibre was somewhat decreased. Taking into account the fibre length distribution, this non-linear relationship at higher fibre content could be explained by the increase of population of the shorter fibres below the critical length in composites (see Table 5.2).

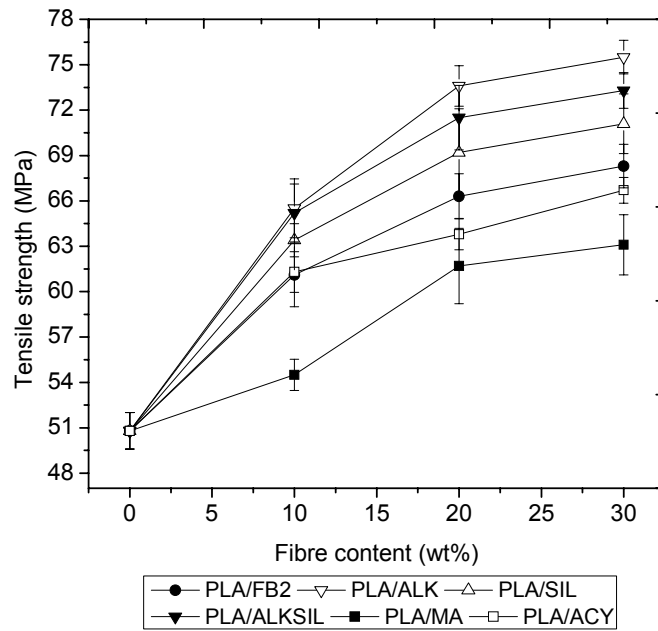


Figure 5.26: Tensile strength of treated hemp fibre reinforced PLA composites as a function of fibre content.

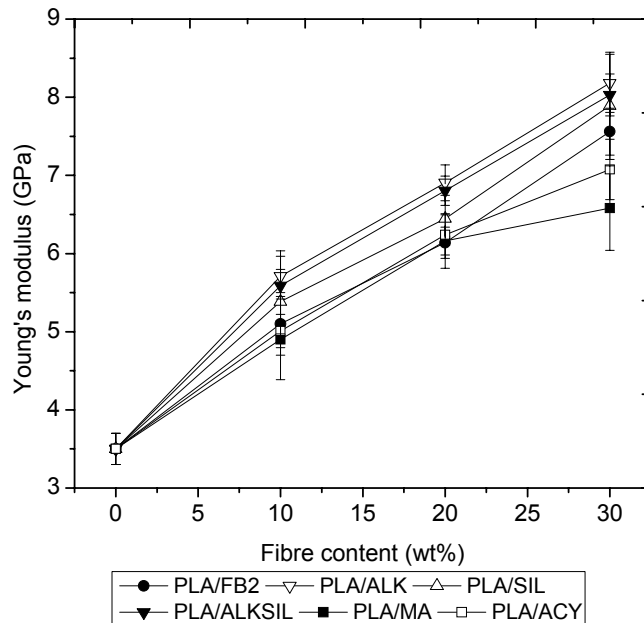


Figure 5.27: Young's modulus of treated hemp fibre reinforced PLA composites as a function of fibre content.

Like the untreated fibre/PLA composites, the failure strain of the treated fibre/PLA composites also decreased with increased fibre content as can be seen in Figure 5.28. As

noted earlier, this behaviour could be due to the lower failure strain of the fibres compared to that of PLA. It is evident that the variation of failure strain for different composites did not follow a similar order as the fibre content increased from 10 to 30 wt%. This was probably due to the variability of short fibre dispersion in composites at high fibre content. Nevertheless, the failure strain of all the samples was found to vary less than 1% for 10 to 30 wt% reinforcements.

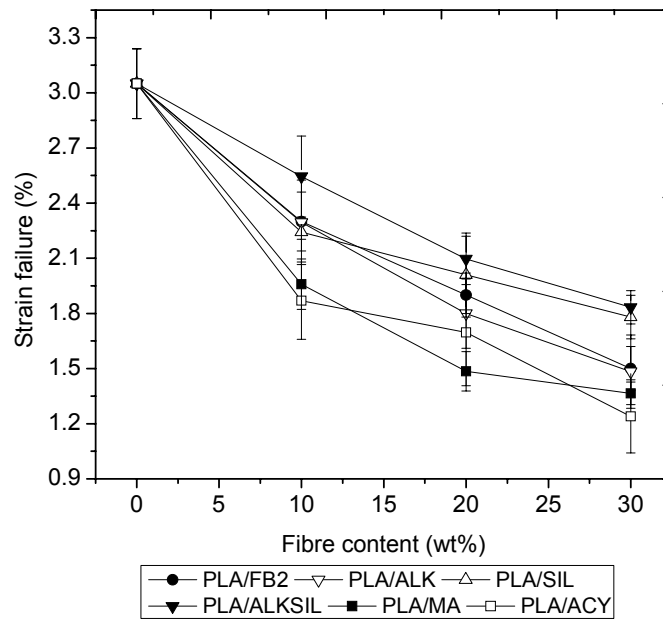


Figure 5.28: Failure strain of treated hemp fibre reinforced PLA composites as a function of fibre content.

The relationship between the tensile strength of composites and fibre strength (untreated and treated) is presented in Figure 5.29. The solid lines in this graph indicate the trend, and do not represent any data fitting. Similar type of relationship for wood fibre and wood fibre/polypropylene composites has been shown by Nyström *et al.* [185]. It can be seen that the data are slightly scattered, which could be due to (i) the variation of fibre properties, e.g. diameter and crystallinity, and (ii) the variability of fibre dispersion in the composites. However, a general trend was that the tensile strength of PLA/hemp fibre composites increased with increased fibre strength. This behaviour revealed that the strength of hemp fibre is one of the important factors which defines the tensile strength of PLA/hemp fibre composites.

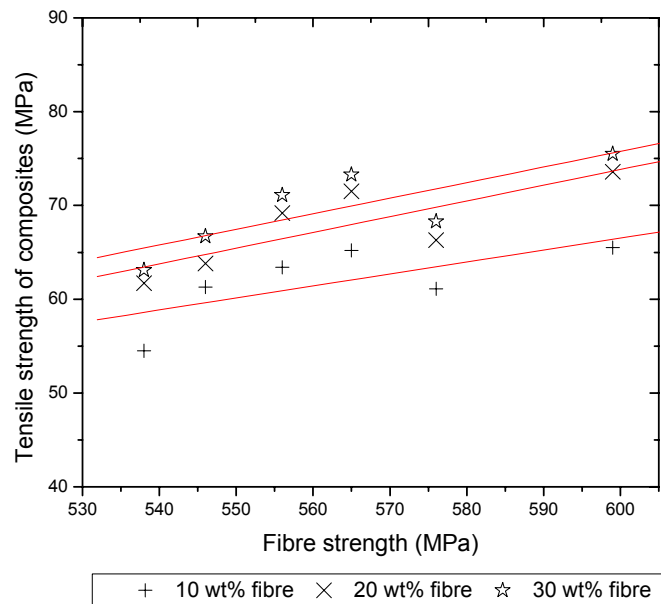


Figure 5.29: Relationship between tensile strength of composites and fibre strength.

5.6.2. Comparison between theoretical and experimental tensile properties

Mechanical performance of composite materials can be predicted on the basis of mathematical modelling. The advantage of a comprehensive mathematical model is it reduces costly and time-consuming experiments. In this study, it is hoped that the combined experiment–modelling effect will allow for a better and deeper understanding of the structure–property relationship in the quest for a guided design for the hemp fibre composites with the desired, optimized properties.

5.6.2.1 Prediction of tensile properties by Hirsch model

Table 5.3 presents the stress transfer factor (x) of the PLA/hemp fibre composites which was obtained using Equation 2.9 to achieve the best fit for theoretical and experimental tensile strength and Young's modulus of the composites. As can be observed, the value of x depends on the reinforcement type (particular treatment applied to fibres) of the composites, and increased in an order similar to IFSS results (see section 5.3). It can also be noted that the values of x for the tensile strength prediction were somewhat lower than those of the Young's modulus. This was because the x values for the Young's modulus prediction define the stress transfer for the elastic deformation part only.

Figures 5.30 and 5.31 show the calculated tensile strength and Young's modulus, respectively, for different composites as a function of fibre volume fraction, along with the experimentally obtained tensile strength and Young's modulus. The experimental values showed a negative deviation from the model as the fibre content increased which could be explained by the fact that the populations of the short fibres (fibres below the critical fibre length) increased with increased fibre content as seen earlier (see section 5.5.1). Another reason could be due to agglomeration of fibres at higher fibre content (see section 5.6.3).

Table 5.3: List of stress transfer factor used to fit Hirsh model.

Sample	Stress transfer factor (x)	
	For tensile strength	For Young's modulus
PLA/FB2	0.13	0.63
PLA/ALK	0.22	0.72
PLA/ACY	0.12	0.61
PLA/MA	0.01	0.55
PLA/SIL	0.16	0.68
PLA/ALKSIL	0.19	0.70

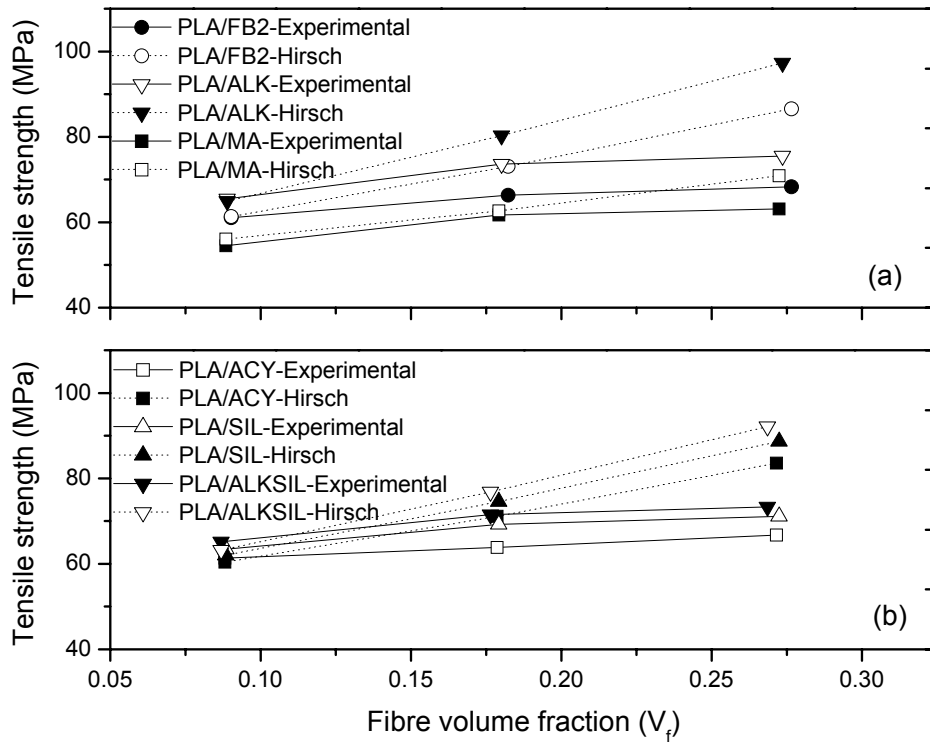


Figure 5.30: Comparison between experimental and predicted tensile strength of the PLA/hemp fibre composites (results presented in two different graphs for clarity).

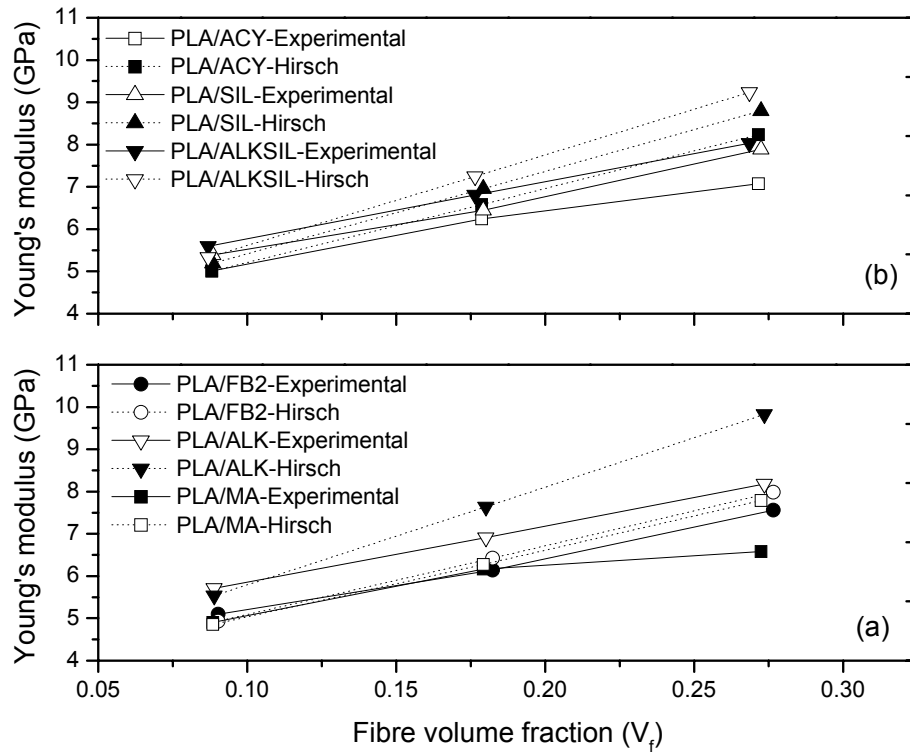


Figure 5.31: Comparison between experimental and predicted (by Hirsch model) Young's modulus of the PLA/hemp fibre composites (results presented in two different graphs for clarity).

5.6.2.2 Prediction of tensile strength by modified rule of mixtures (MROM) model

Figure 5.32 shows the calculated tensile strength of the PLA/hemp fibre (untreated and treated) composites using the MROM model (see Equation 2.10) as a function of fibre volume fraction, along with the experimentally obtained tensile strength. According to the literature [186], the fibre orientation factor (K_1) has a value of unity for the axially aligned arrangement, and yields a value of 0.34 for the injection moulded natural fibre composites. In this study, K_1 was assumed to be equal to 0.34, because short fibre/PLA composites were fabricated by injection moulding. Different values of stress transfer factor (K_2) were obtained to fit the experimental and theoretical tensile strength as presented in Table 5.4.

As can be seen in Figure 5.32, the calculated tensile strength showed a good agreement with the experimental results when the fibre content was low. However, the experimental results showed a negative deviation from the theoretical results as the fibre volume fraction

increased. The above observations are consistent with the Hirsch model as seen previously. Thus, a reasonably good agreement between the theoretical and experimental tensile properties of the PLA/hemp fibre composites can be obtained by the Hirsch and MROM models when the fibre content is low. A similar finding has also been reported by other researchers [24].

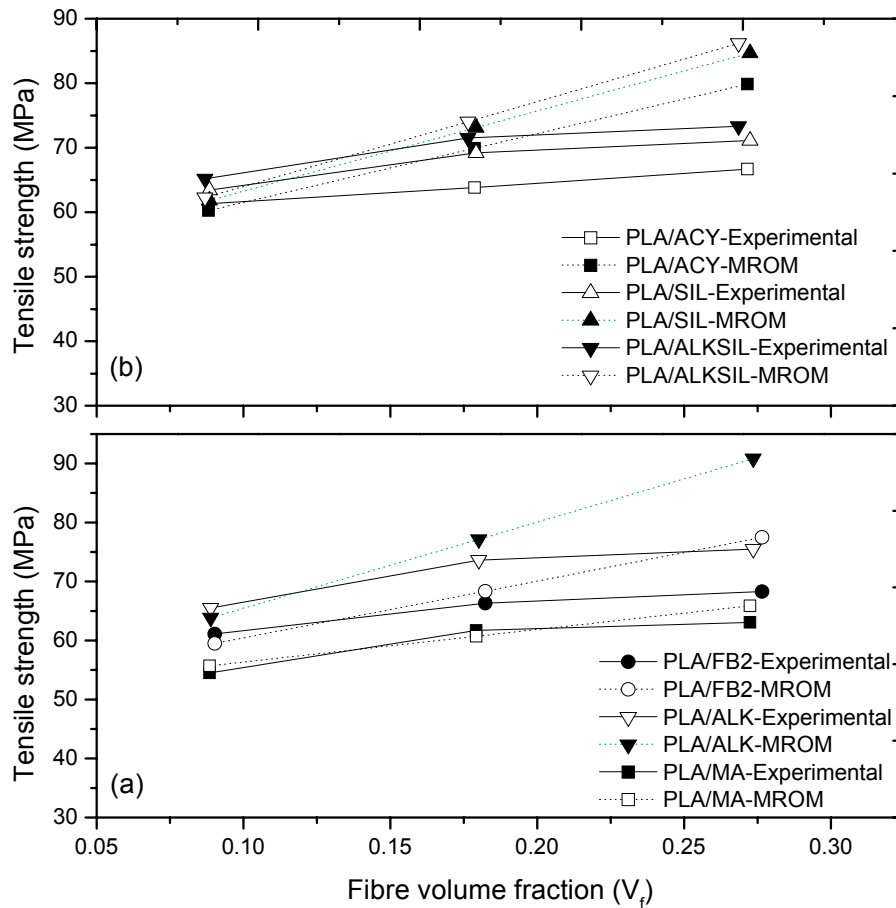


Figure 5.32: Comparison between experimental and predicted (by MROM) tensile strength of the PLA/hemp fibre (untreated and treated) composites (results presented in two different graphs for clarity).

Table 5.4: List of K_2 values used to fit the MROM model.

Sample	K_2
PLA/FB2	0.75
PLA/ALK	0.97
PLA/ACY	0.85
PLA/MA	0.58
PLA/SIL	0.93
PLA/ALKSIL	0.95

5.6.3 Microscopic analysis of the tensile fracture surface of PLA and composites

The tensile fracture surfaces of PLA and composites were analysed using a scanning electron microscope (SEM). The morphology of PLA fracture surface is shown in Figure 5.33. It can be seen that the fracture surface was moderately flat and smooth (A), however, matrix tearing and/or roughness (B) was also noticed to some extent. Thus, tensile failure of the PLA was neither completely brittle nor completely ductile, but rather mixed. This was also supported by the stress versus strain graph [see Figure 5.24(a)].

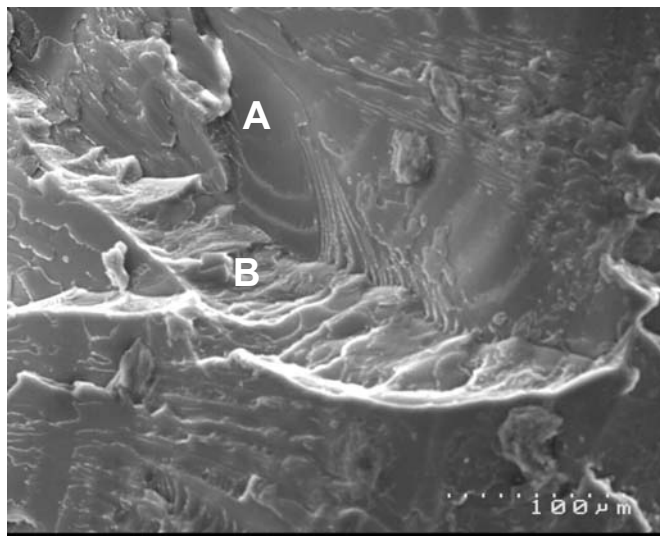


Figure 5.33: SEM micrograph of the tensile fracture surface of PLA.

The fracture surface morphology of the untreated fibre (FB2) and PLA composites containing 10 to 30 wt% fibre is presented in Figure 5.34(a-c). In these figures, some gaps between the fibres and the PLA can be seen, which could be due to either debonding during tensile testing or poor adhesion. Poor adhesion could be due to the presence of wax, pectin and other impurities in the surface of untreated fibres. Fibre fracture, which could be the results of good stress transfer from the matrix to the fibres, was evident in all the micrographs. Fibre pull-out and the corresponding holes were visible in all the micrographs. However, it is evident that the concentration of fibre pull-out increased as the fibre content increased. This should be due to the increase of short fibres (fibres below the critical length) at higher fibre content. The fibre length distribution of the composites also supported this observation, where it was seen that a significant number of fibres were below the critical length at higher fibre content. Fibre agglomeration was another feature

identified in the composites at high fibre content as can be seen in Figure 5.35. The decrease in fibre length and agglomeration of fibres could be the reasons why the higher fibre content in PLA did not increase the tensile strength linearly with respect to the fibre content as seen in Figure 5.26.

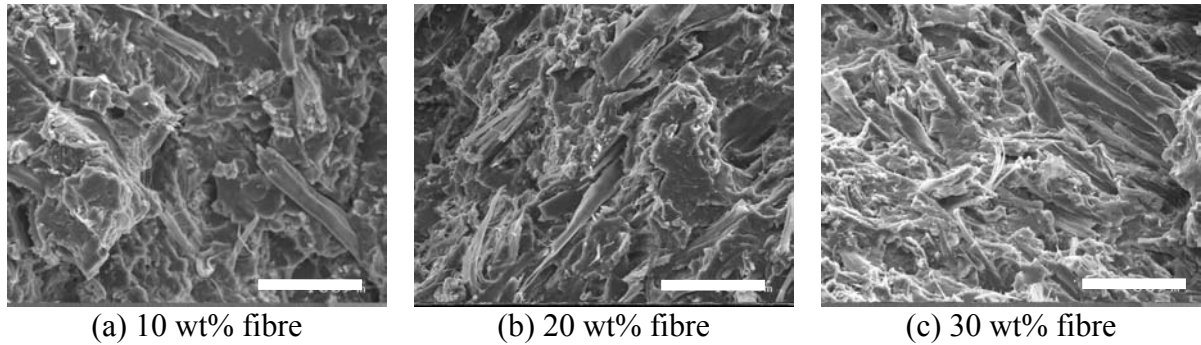


Figure 5.34: SEM micrograph of the tensile fracture surface of PLA/FB2 composites at different fibre contents (scale bar = 100 µm).

Fracture surface morphology of the PLA/ALK composites is presented in Figure 5.36. It can be observed that the fibres are tightly connected with the matrix. It can also be seen that some fibres were broken and/or torn. The fibrillation of fibre was another feature, which was most probably caused by regions of the fibre, well bonded to the matrix, being ‘torn’ from underlying layers of the fibres. All these observations supported strong bonding in the PLA/ALK composites.

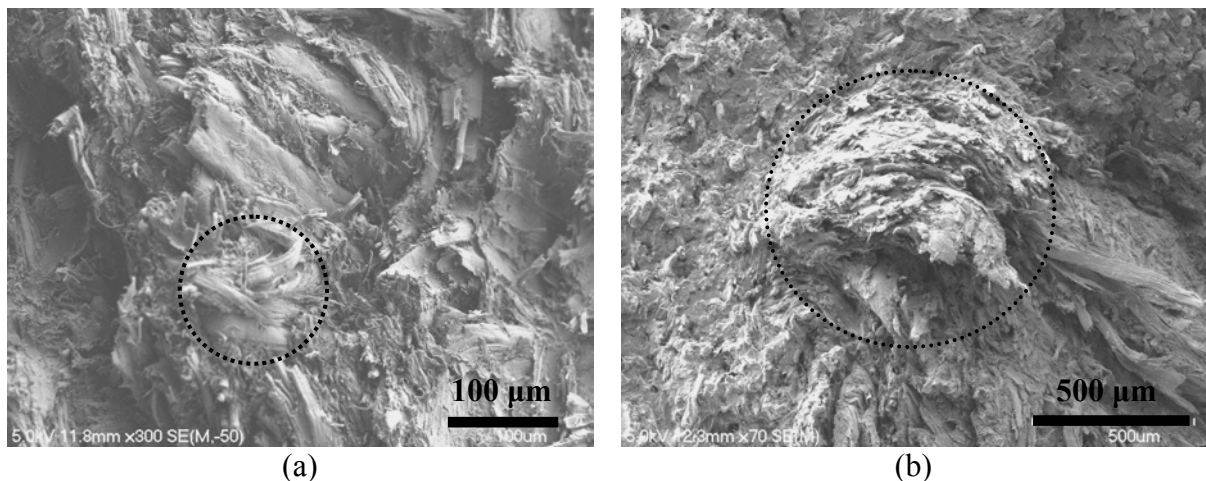


Figure 5.35: SEM micrographs of the tensile fracture surface of PLA/FB2 (30 wt% fibre) composite showing fibre agglomeration (indicated by circle).

The fracture surfaces of PLA/SIL and PLA/ALKSIL composites are shown in Figure 5.37. The general features (e.g. fibre fracture and fibre pull-out) of these composites are similar to that of PLA/ALK composites. As can be seen, SIL and ALKSIL fibres are enclosed by the PLA suggesting good adhesion in between fibre and matrix. Thus, the stress was transformed from the matrix to fibres efficiently when the load was applied. In Figure 5.38(a), there is apparently little adhesion between ACY fibres and PLA in the fracture surface of PLA/ACY composites as evidenced by the extensive fibre pull-out. In the case of PLA/MA composites [see Figure 5.38(b)], a larger number of holes appeared in the fracture surface due to the pull-out of fibres. All these observations suggest relatively poor interfacial adhesion in the PLA/ACY and PLA/MA composites when compared with the other treated fibre/PLA composites. The above fractographic evidences support the tensile strength results of the composites as presented before.

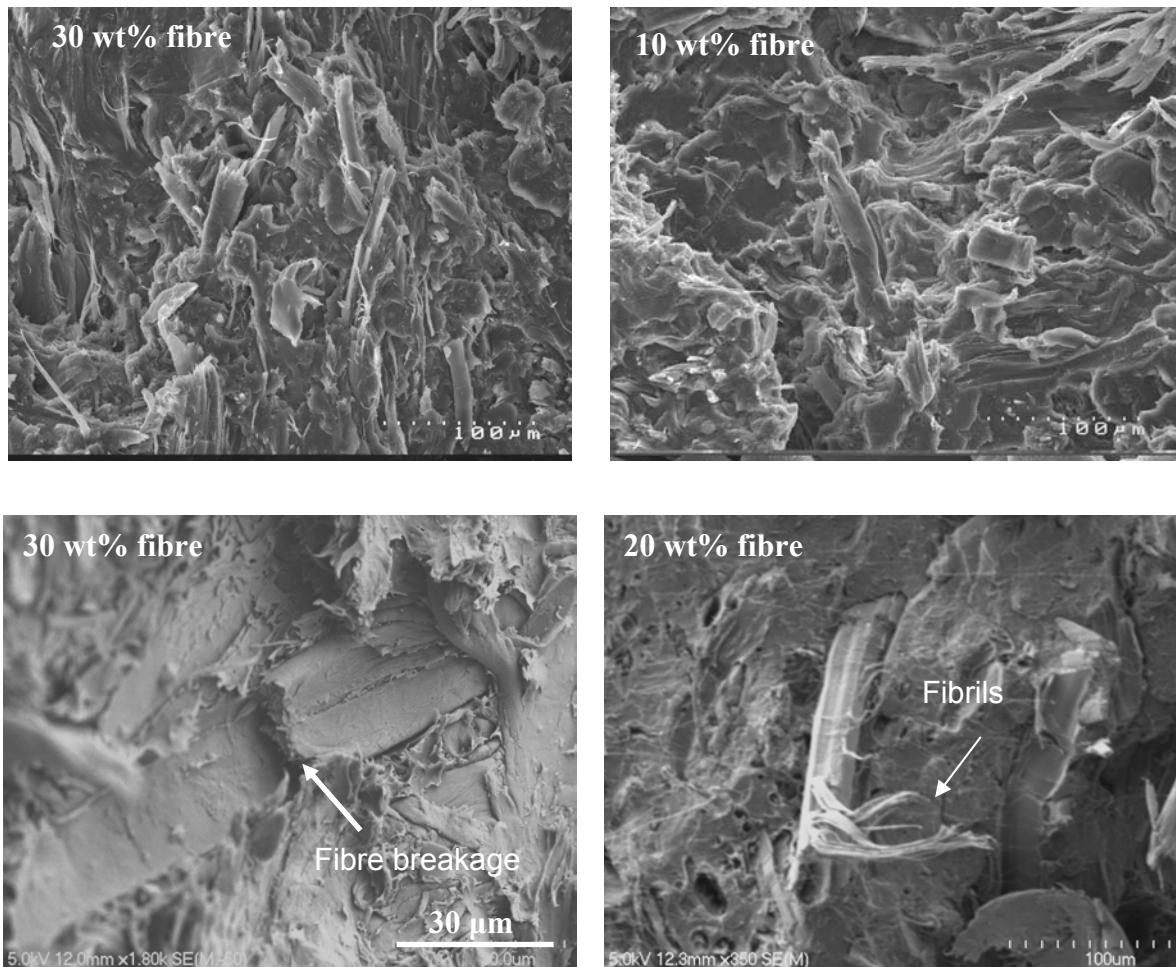


Figure 5.36: SEM micrographs of tensile fracture surface of PLA/ALK composites.

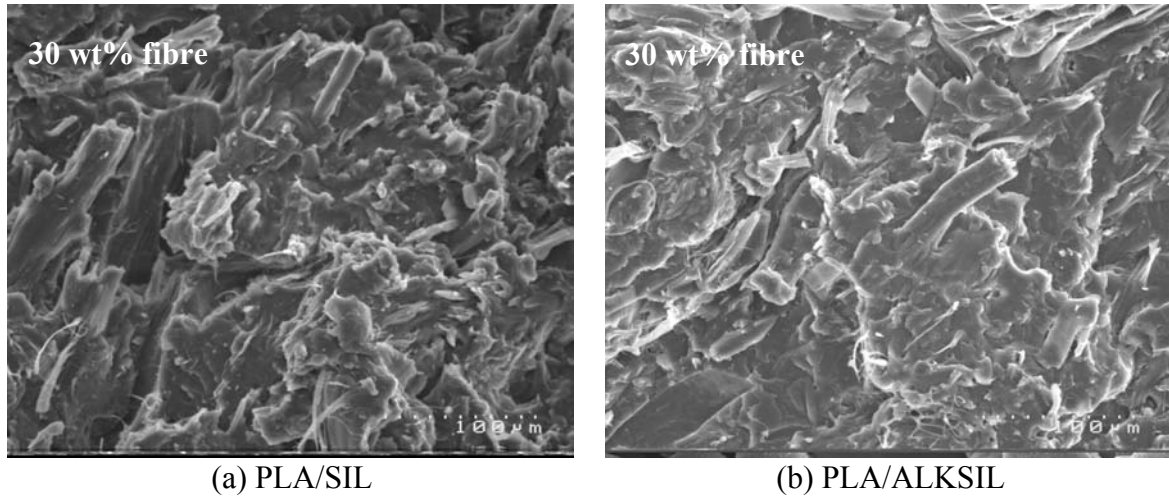


Figure 5.37: SEM micrographs of tensile fracture surface of PLA/SIL and PLA/ALKSIL composites.

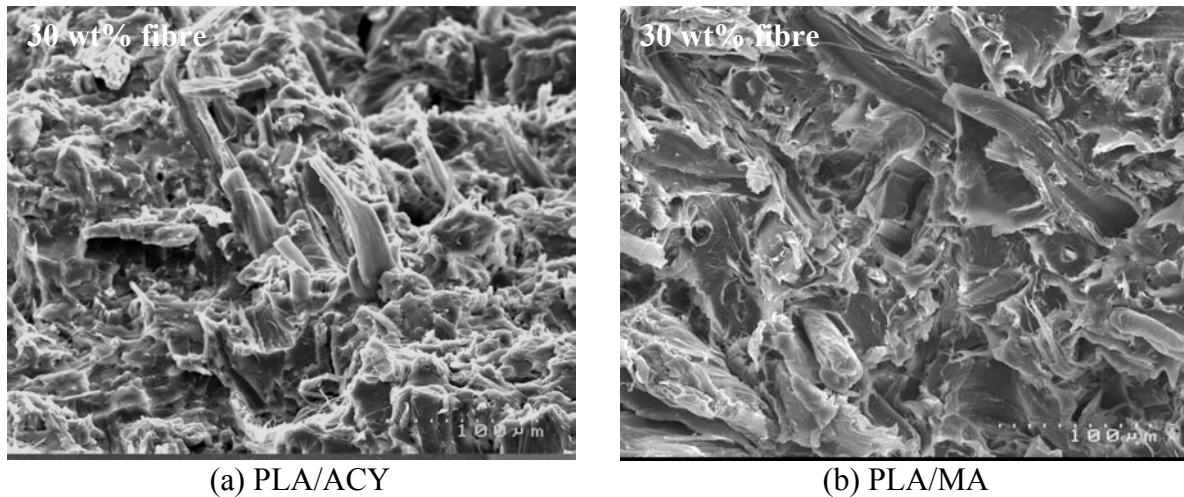


Figure 5.38: SEM micrographs of tensile fracture surface of PLA/ACY and PLA/MA composites.

5.6.4 Flexural properties

Typical flexural stress-deflection records for PLA and composites are presented in Figure 5.39. It may be observed that, as with the tensile tests, the traces show an initially linear portion, followed by a non-linear region prior to the attainment of maximum flexural stress. Once the maximum stress is attained, the recorded stress diminishes abruptly. The transformation to this form of post maximum stress behaviour demonstrates that the brittleness of samples predominate the fracture mode.

The average flexural strength and flexural modulus of the PLA/untreated hemp fibre (FB1 and FB2) composites as a function of fibre content are presented in Figure 5.40. As can be

seen, the flexural strength decreased with increased fibre content. In contrast, the flexural modulus of the composites increased as the fibre content increased. Similar to tensile strength and Young's modulus findings, the flexural strength and flexural modulus of the PLA/FB2 composites are higher than those of the PLA/FB1 composites. The decrease in flexural strength with respect to the fibre content is consistent with other work on natural fibre/PLA composites [164, 187]. However, there is no explanation in the literature for this behaviour. This behaviour could be explained as follows. In a flexural test, there is a combination of tensile and compressive stress. In Figure 5.41, compressive fracture is characterised by the stress whitening (C), whereas, at the tension site (T) smooth brittle-like fracture is evident. The compression of fibres in a matrix can be subjected to "kinking" [188]. Instead of having a compression wave form in the fibres, a weak spot in the fibres (i.e. defects in fibres) can be the source of a bend, or a kink [132, 141]. In turn, the kinks will induce stress concentration points in the matrix which could act as sites of potential crack initiation, fibre/matrix debonding and the overall source of failure [135, 138]. As the fibre content increases, the stress concentration points increase simultaneously; consequently, the flexural strength decreases. The SEM micrographs of the fracture surface also support this explanation (see Figure 5.42), where it can be seen that the debonding occurred in the vicinity of the PLA and hemp fibre interface due to the kink. In addition, as the fibre content increases the number of fibre ends (stress concentration points) increases, accordingly the flexural strength decreases.

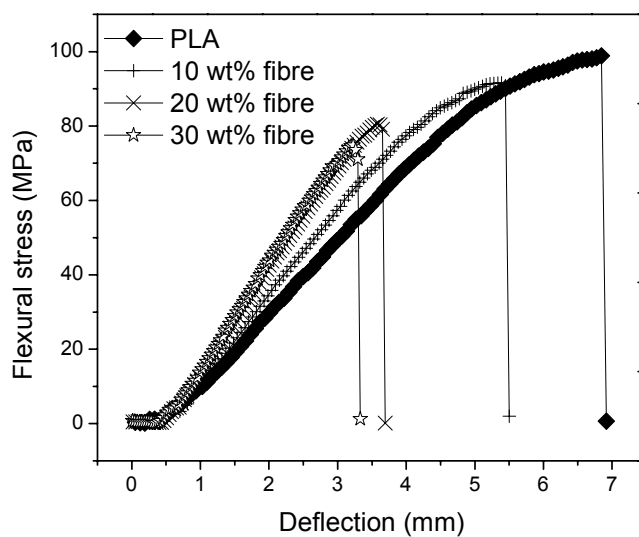


Figure 5.39: Flexural stress-deflection records for PLA/FB2 composites in three point flexure.

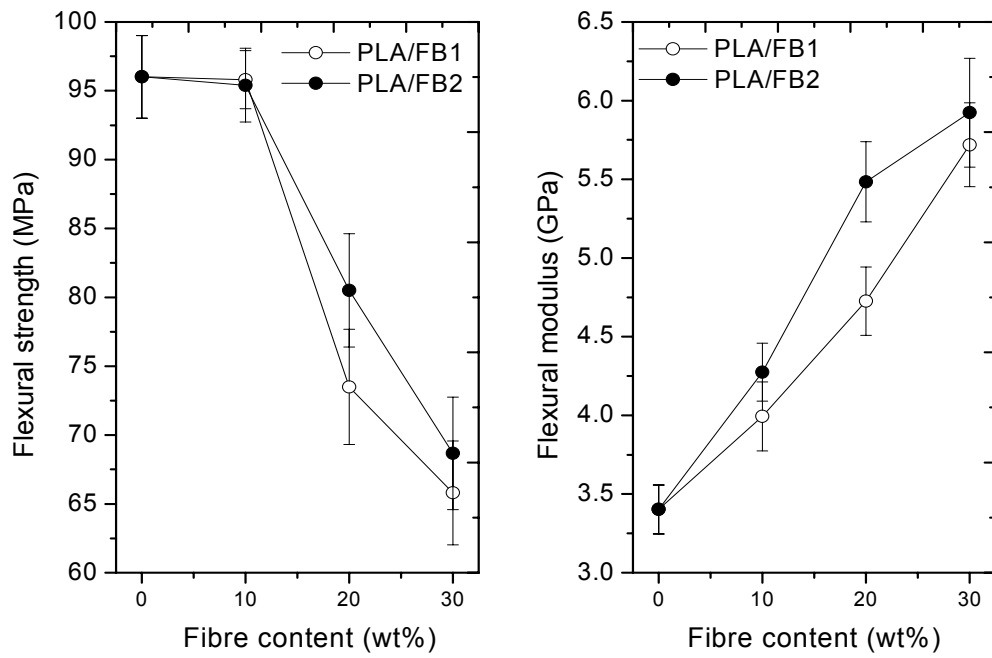


Figure 5.40: Flexural properties of untreated hemp fibre reinforced PLA composites as a function of fibre content.

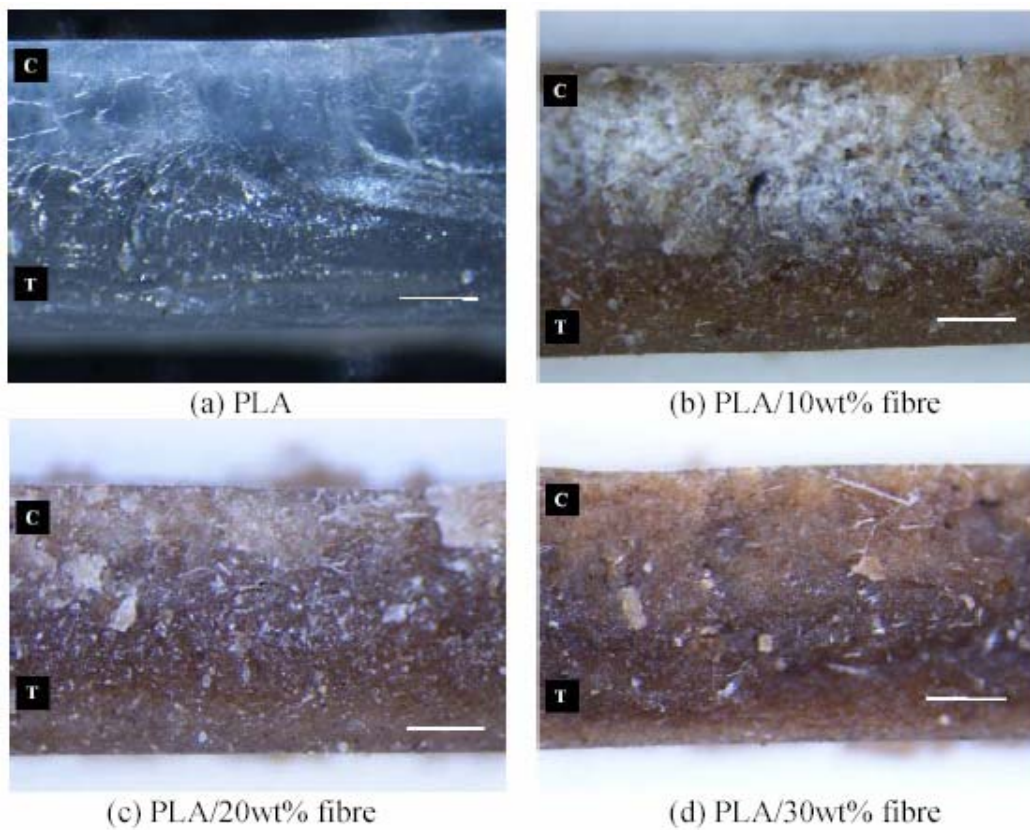


Figure 5.41: Fracture surfaces of flexural tested PLA and composites. The labelled regions are compressive (C) and tension (T) fracture in specimen (scale bar = 1 mm).

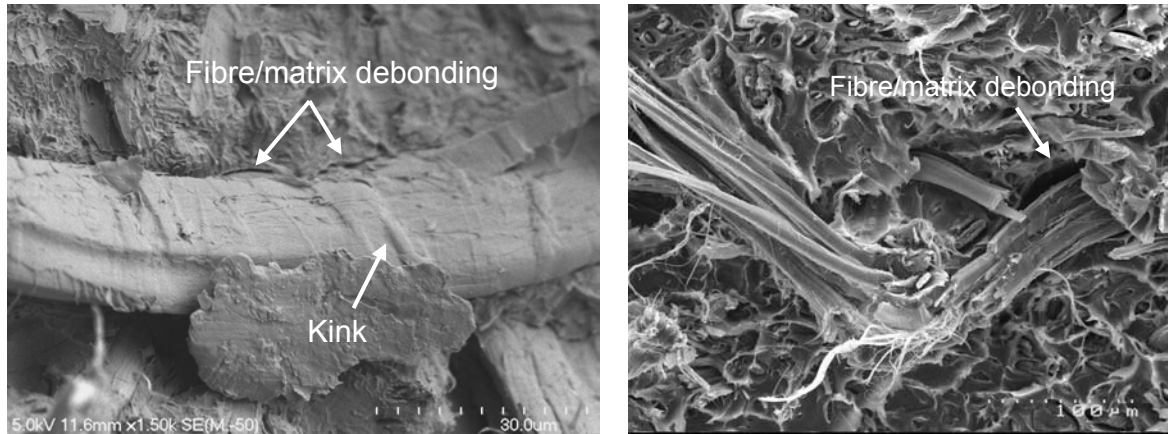


Figure 5.42: SEM micrographs of the flexural tested fracture surface of PLA/FB2 composites (30 wt% fibre) showing fibre/matrix debonding.

The average flexural strength and flexural modulus of the treated hemp fibre/PLA composites as a function of fibre content are depicted in Figures 5.43 and 5.44, respectively. Like the untreated fibre/PLA composites, the flexural strength of the treated hemp fibre/PLA composites decreased with increased fibre content, and the flexural modulus of the composites increased with increased fibre content. In general, alkali and silane treatments enhanced the flexural strength and flexural modulus of the composites, which is consistent with other studies [163, 164, 171]. The PLA/ALK composites with 30 wt% fibres had the highest flexural modulus of 6.33 GPa.

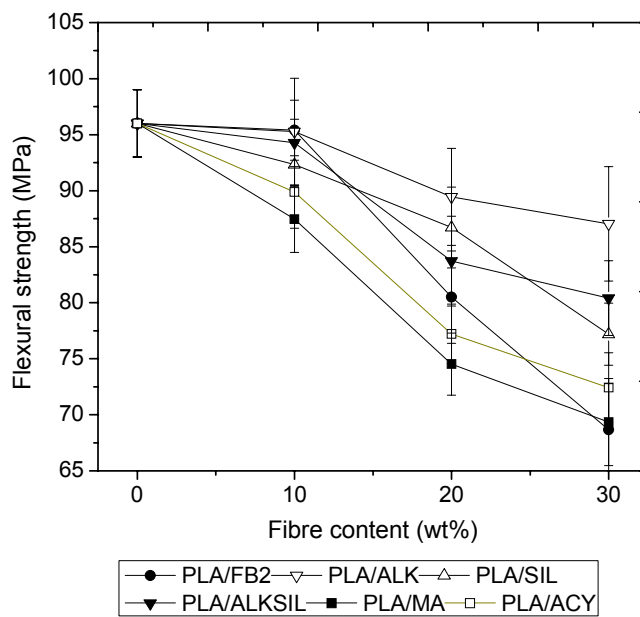


Figure 5.43: Flexural strength of the treated hemp fibre reinforced PLA composites as a function of fibre content.

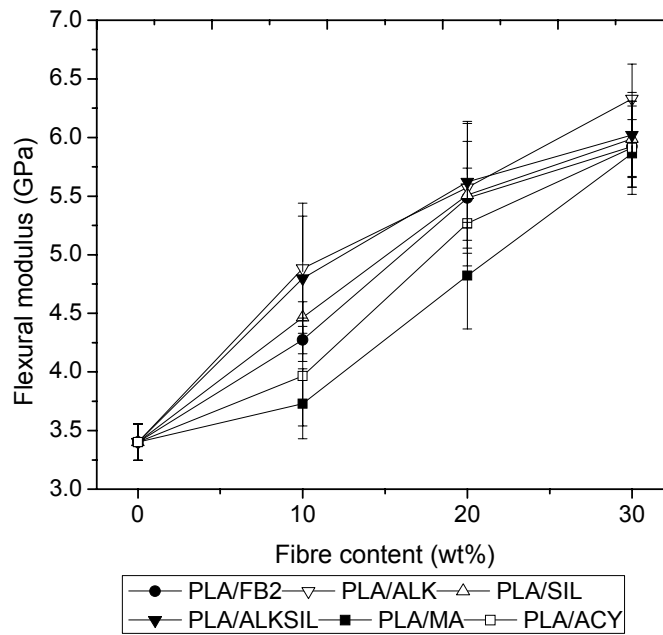


Figure 5.44: Flexural modulus of treated hemp fibre reinforced PLA composites as a function of fibre content.

5.6.5 Impact strength

Figure 5.45 shows the average impact strength for un-notched and notched composites (PLA/FB1 and PLA/FB2) as a function of fibre content. It may be observed that the impact strength increased with increased fibre content, except the PLA/FB1 composites at 30 wt% fibre content. It is noted before that the FB1 fibres were degraded somewhat during storage, thus the discrepancy in the impact behaviour of the PLA/FB1 compared to PLA/FB2 composites at 30 wt% fibre content may be due to the presence of large amounts of degraded FB1 fibres. It is also evident that impact strength of unnotched samples was greater than that of notched samples. This higher impact strength of unnotched samples could be due to the additional energy required for the crack initiation in the unnotched specimens compared to the notched specimens [189].

The average impact strength of unnotched and notched samples of treated hemp fibre/PLA composites as a function of fibre content are depicted in Figures 5.46 and 5.47, respectively. As can be seen, impact strength of all composites increased with increased fibre content. This was because as the fibre content increased, more interfaces exist on the crack path, and more energy was consumed. In fact, concentration of short fibres (fibres

below the critical length) increased with increased fibre content (see section 5.5.1), which lead to increased pull-out and appears to have increased impact strength. Similar to the tensile and flexural properties, it can be observed that the alkali and silane treatments enhanced the impact strength of composites. This finding is in agreement with other studies [163, 164, 171]. The PLA/ALK composites with 30 wt% fibres had the highest unnotched and notched impact strength. Impact strength of the unnotched PLA/ALK composite samples was about 13% higher (28.1 kJ/m^2) than that of the PLA/FB2 composites (24.7 kJ/m^2) at 30 wt% fibre content. For the same composites, impact strength of the notched samples was approximately 12% higher (2.64 kJ/m^2) than that of the PLA/FB2 composites (2.34 kJ/m^2).

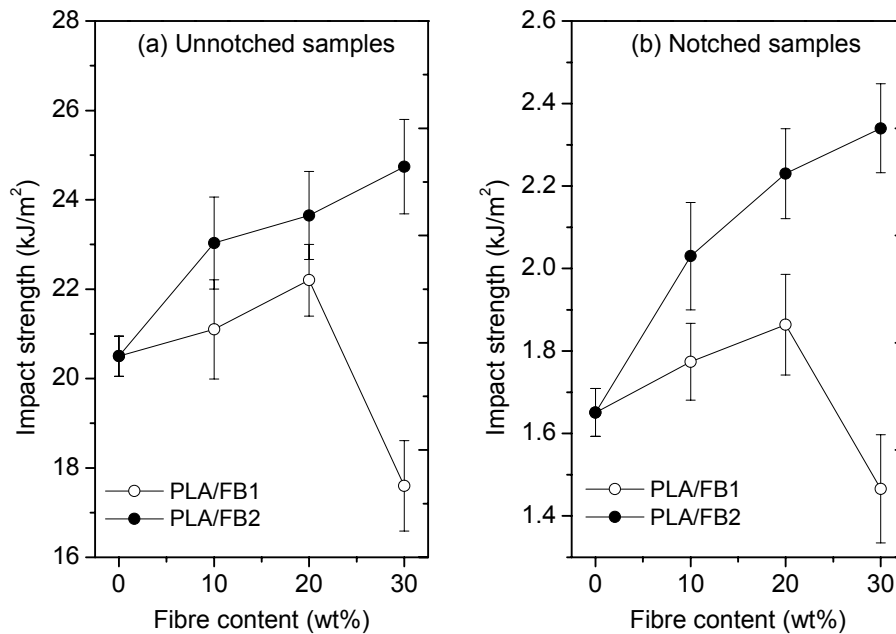


Figure 5.45: Impact strength of untreated hemp fibre reinforced PLA composites as a function of fibre content.

Fibrillation of fibres, which is associated with high energy absorption [105], can be observed in the impact tested fracture surfaces of alkali and silane treated fibre reinforced PLA composites (PLA/ALK, PLA/SIL and PLA/ALKSIL) (see Figure 5.48). The increased PLA crystallinity of the alkali and silane treated fibre composites compared to untreated fibre composites (see section 5.4.3) could be the other factor which leads to increase the impact strength. Indeed, impact strength of the composites increased in the following order: PLA/MA < PLA/ACY < PLA/FB2 < PLA/SIL < PLA/ALKSIL <

PLA/ALK which is consistent with the order of PLA crystallinity in composites (see section 5.4.3). Perego *et al.* [190] and Todo *et al.* [191] also showed that the impact strength of PLA increased with increased crystallinity of PLA.

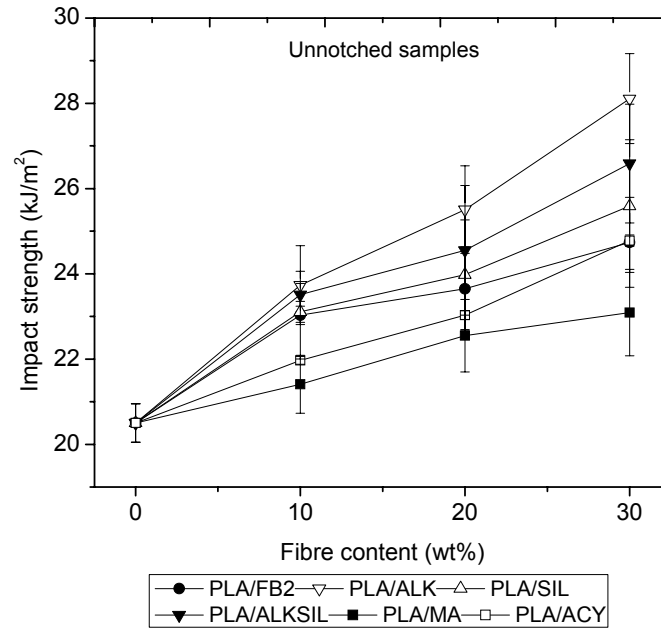


Figure 5.46: Impact strength of the treated hemp fibre reinforced PLA composites for the un-notched samples at different fibre contents.

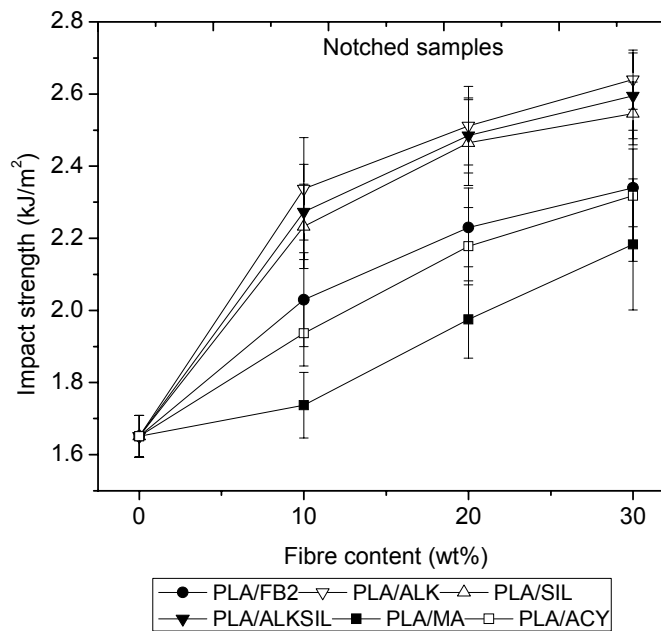


Figure 5.47: Impact strength of the treated hemp fibre reinforced PLA composites (notched samples) as a function of fibre content.

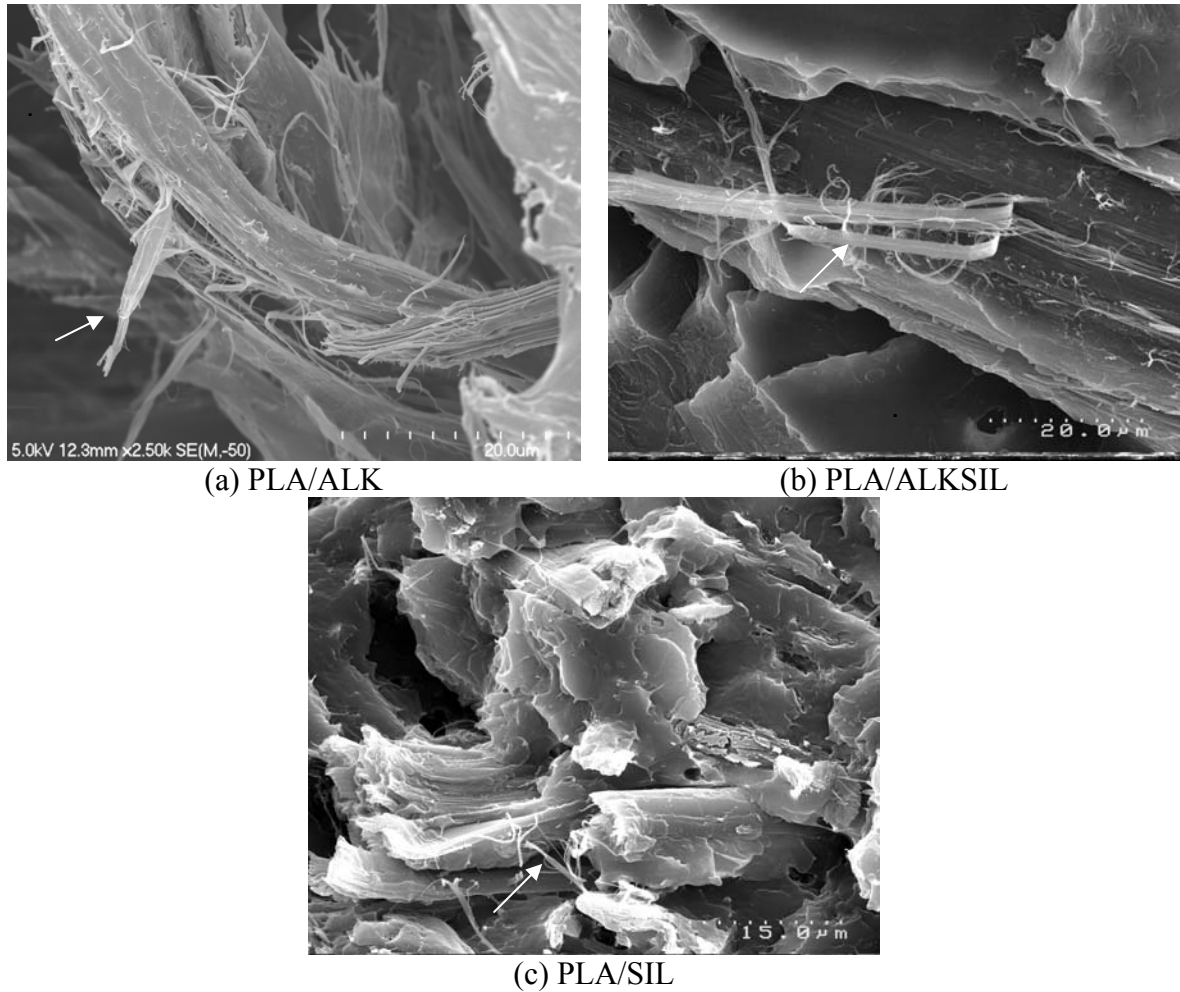


Figure 5.48: SEM micrographs showing fibrils (indicated by arrow) in the impact fracture surface of notched PLA composite samples (30 wt% fibre).

5.6.6 Fracture toughness

5.6.6.1. Effect of loading rate

Typical load-displacement records for the PLA and composites (PLA/FB1) under various loading rates are depicted in Figure 5.49. It may be observed that these showed initially linear deformation, followed by an amount of non-linear deformation prior to the attainment of the maximum load. Once the maximum load was attained, the recorded load diminished gradually which was most probably a result of cracking along with limited plastic deformation. It can be easily seen that the curves became steeper with increased fibre content. This behaviour was expected because the Young's modulus of the hemp fibre is superior to that of PLA as mentioned earlier. It is also evident that the area under the curves decreased with increased loading rate. This observation is attributed to decrease of plastic deformation at higher loading rates.

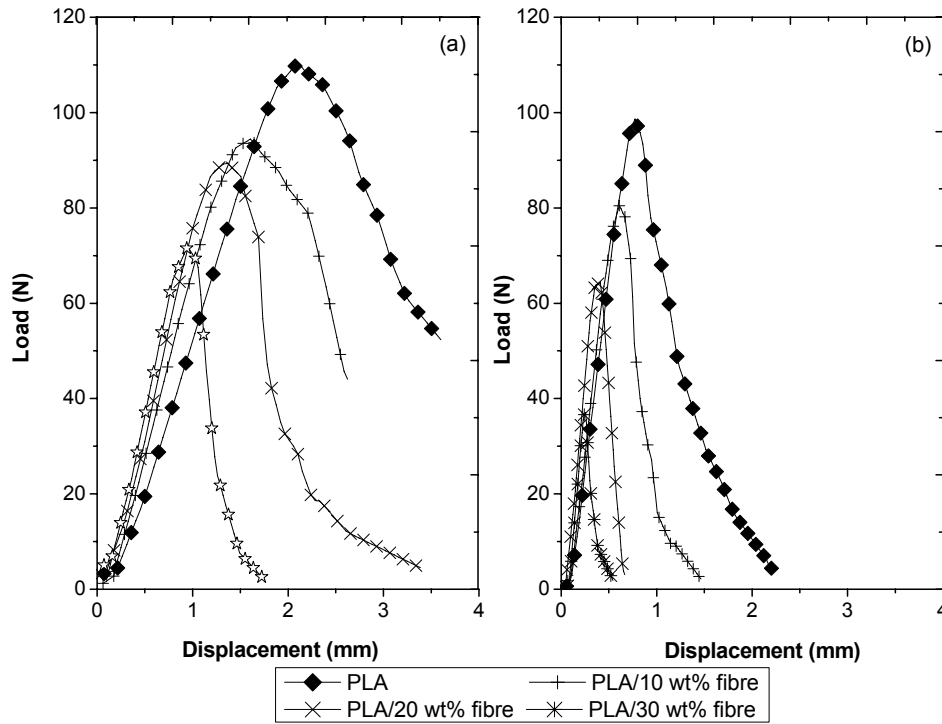


Figure 5.49: Typical load-displacement curves of PLA and composites (PLA/FB1) at (a) 5 mm/min, and (b) 10 mm/min.

As can be seen clearly in Figure 5.50, if a line (AC) is drawn with a gradient of 5% less than that of the tangent (AB) to the original loading line, the recorded maximum load ($P_{\max}$) lies between these two lines, which meet the requirement of the standard [128] for the allowance of $P_{\max}$ to be used as P_Q for the calculations of K_{Ic} (see Equation 3.4). This form of load-displacement behaviour was observed for all the samples tested.

Figure 5.51 illustrates the average K_Q of PLA and composites as a function of loading rate. It can be seen that the K_Q for all fibre contents decreased with increased loading rate up to 10 mm/min above which it stabilised at a constant value. It was also observed that (using Equation 3.6 and data from Table 5.5) at a loading rate of 5 mm/min, K_Q of the matrix and composites did not satisfy the plane strain conditions. Accordingly, it can be assumed that at this loading rate (and lower loading rates where yield strength would be expected to be lower) the deformation mechanism has been strongly influenced by plane stress conditions. On the other hand, K_Q at a loading speed of 10 mm/min was found to

fulfil the required criteria given in Equation 3.6 and therefore be equivalent to K_{Ic} . Since the magnitude of K_Q from 10 mm/min to higher loading rates was approximately constant, and given the general expectation of increased yield strength with increased loading rate, it is likely that the criterion of Equation 3.6 was also met for the higher loading rates above 10 mm/min.

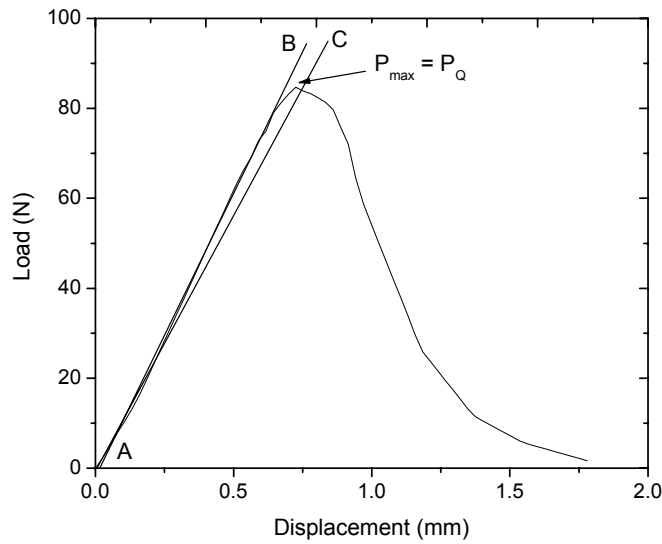


Figure 5.50: Measurement method of P_Q from a load-displacement curve.

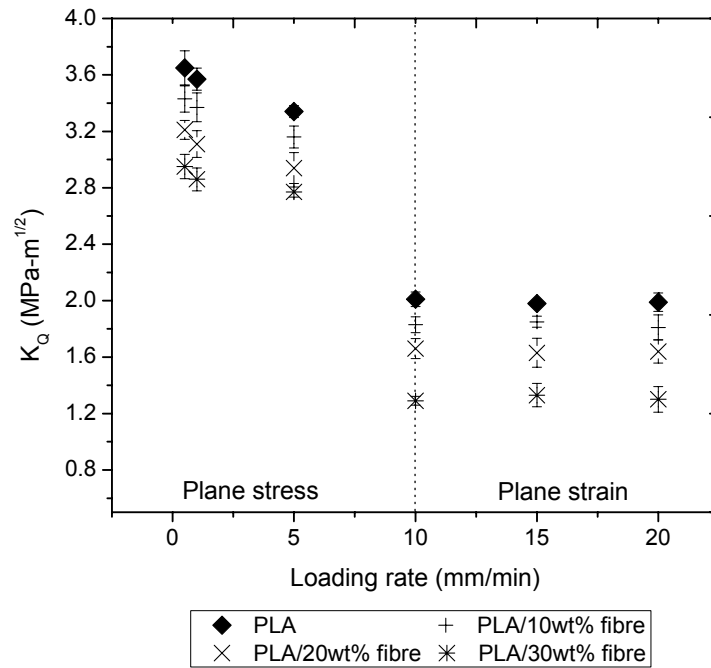


Figure 5.51: K_Q as a function of loading rates.

Table 5.5: Tensile yield strength and fracture toughness of composites at two different testing speeds.

Test speed (mm/min)	Fibre content (wt%)	Tensile yield strength, σ_y (MPa)	Fracture toughness, K_Q (MPa-m ^{1/2})
5	0	50.7	3.34
	10	52.4	3.16
	20	59.8	2.91
	30	65.9	2.79
10	0	53.9	2.01
	10	55.7	1.83
	20	60.4	1.66
	30	67.2	1.29

Several observations of the strain rate dependency of fracture toughness for different materials have been reported. For instance, Gensler *et al.* [192] worked on the influence of loading rate on the fracture toughness of isotactic polypropylene. They observed a similar drop in K_Q at higher loading rates. In another report, Kanchanomai *et al.* [193] found similar behaviour with epoxy resin. They showed that at lower loading rates there was significant plastic deformation formed in the vicinity of crack tip resulting in the increase of the crack tip radius or blunting which increased crack growth resistance. Karger-Kocsis *et al.* [194] also observed increasingly brittle behaviour of short glass fibre reinforced poly(ether ether ketone) composites at higher loading rates.

Also from Figure 5.51, it is evident that the K_Q of the PLA/hemp composites decreased with increased fibre content. One likely influence is the stress concentration due to the presence of fibres. However, research elsewhere on PLA, has shown the influence of degree of crystallinity on fracture toughness, which could be affected by fibre content, such that toughness decreased as crystallinity increased [191]. This is because crack can propagate easily through the crystalline phase.

5.6.6.2 Fractography analysis (effect of loading rate)

Optical light micrographs of cracks (side view) of the PLA samples tested under different loading rates are shown in Figure 5.52. As can be clearly seen, extensive crazing was generated in the crack-tip region for samples tested at lower loading rates (1 and 5 mm/min). On the other hand, crazing was not so apparent at higher loading rates (10

mm/min). Similar behaviour has also been observed for isotactic polypropylene [192] and PLA [191] such that the reduction of crazing at higher loading rates corresponds to the reduction of energy dissipation in the crack tip region compared to the samples tested at lower loading rate.

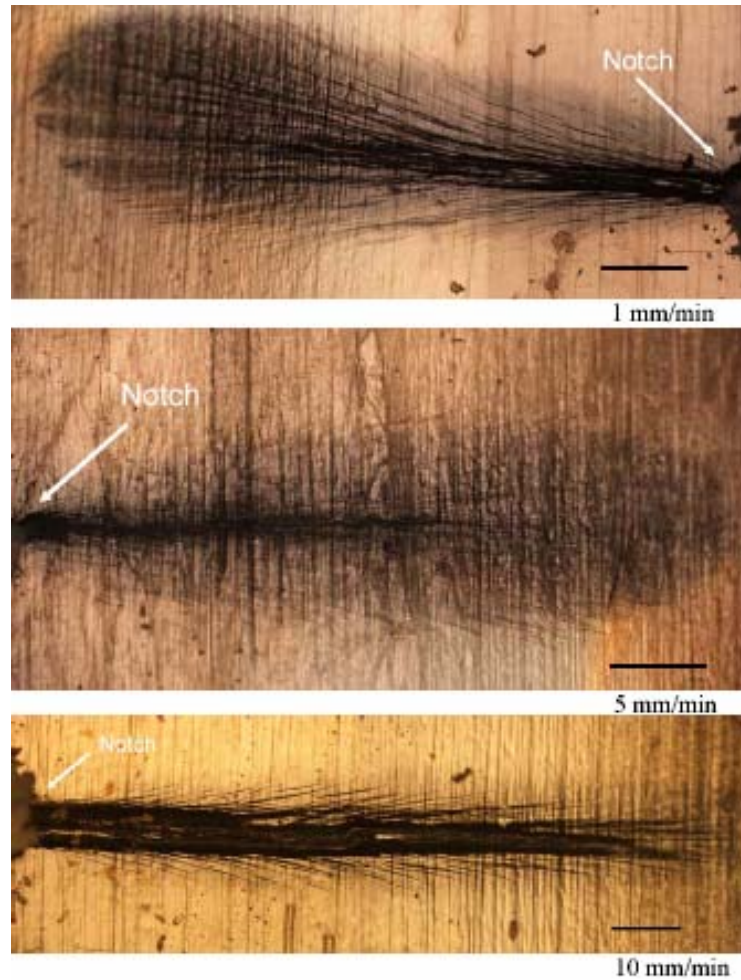


Figure 5.52: Light microscope images of crazing in PLA during fracture toughness testing at different loading rates (scale bar = 500 μ m).

Typical fracture surfaces of PLA investigated for lower (<10 mm/min) and higher (>10 mm/min) loading rates are presented in Figure 5.53. The fracture surfaces showed two distinct zones, namely a smooth zone suggesting brittle-like fracture next to the initial starter notch and a stress-whitened zone associated with crazing which is considered characteristic of plane-stress conditions [192]. An increase in size of the smooth brittle-like region with reduction in the stress-whitened region occurred when the loading rate was increased. It appears that, at higher loading rates, crack propagation involves less crazing resulting in lower fracture toughness [195].

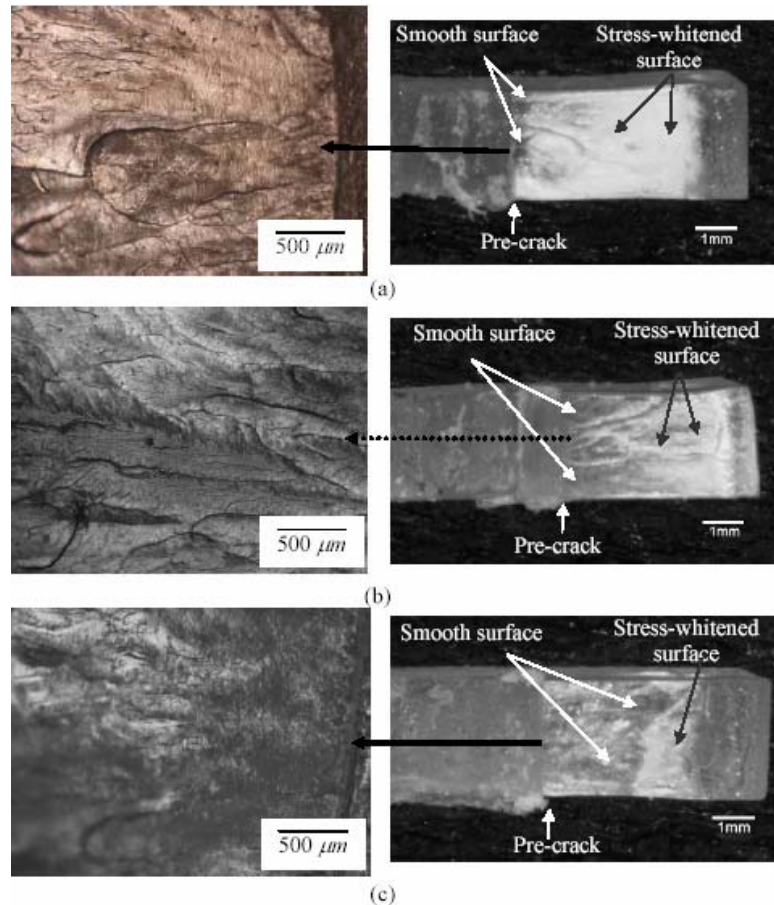


Figure 5.53: Light microscope images of PLA fracture surfaces tested in different loading rates (a) 1 mm/min, (b) 5 mm/min, and (c) 10 mm/min.

Typical crack paths of PLA/hemp fibre composites (side view) tested at 5 mm/min and 10 mm/min) are presented in Figures 5.54 and 5.55, respectively. As can be seen, the cracks were initiated from the tip of the pre-existing crack, but did not propagate directly across the sample and appear to have been influenced by the presence of fibres such that increased fibre content resulted in a more irregular crack path. Within the composites tested at 5 mm/min (see Figure 5.54), evidence of localised matrix is present suggesting limited plastic deformation. A closer examination of the crack propagation path indicates that the two fracture surfaces were not completely separated, but rather connected by the deformed matrix. For lower loading rates, this behaviour was commonly observed for all the samples irrespective of the amounts of fibre content. There was a significant reduction in the plastic flow and/or matrix tearing when the samples were tested at 10 mm/min loading rates (see Figure 5.55) which could explain the reduction of K_Q at higher loading rates. In contrast to lower loading rates, two fracture surfaces were completely separated ahead of the starter defect.

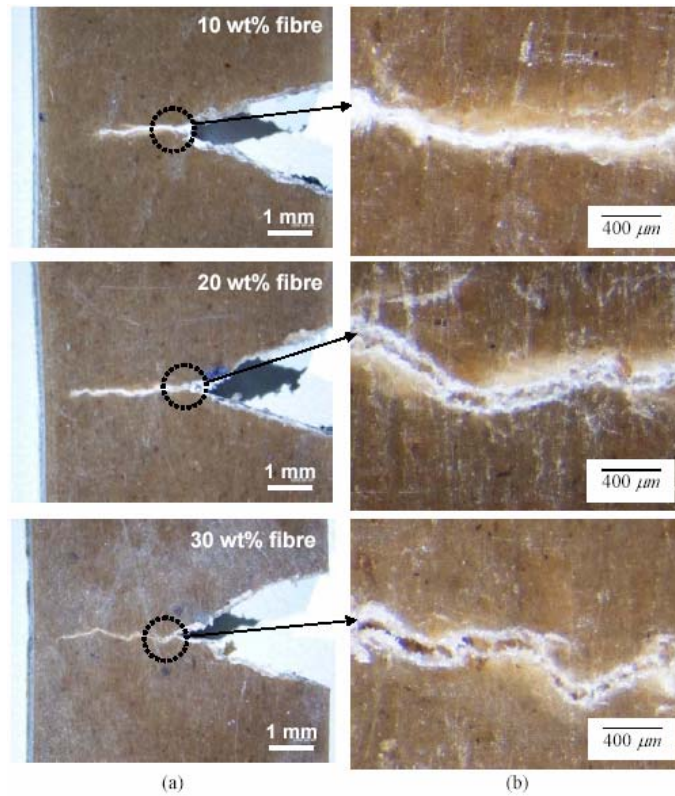


Figure 5.54: Fracture behaviour of PLA/hemp fibre composites tested at the loading speed of 5 mm/min; (a) low magnification and (b) high magnification.

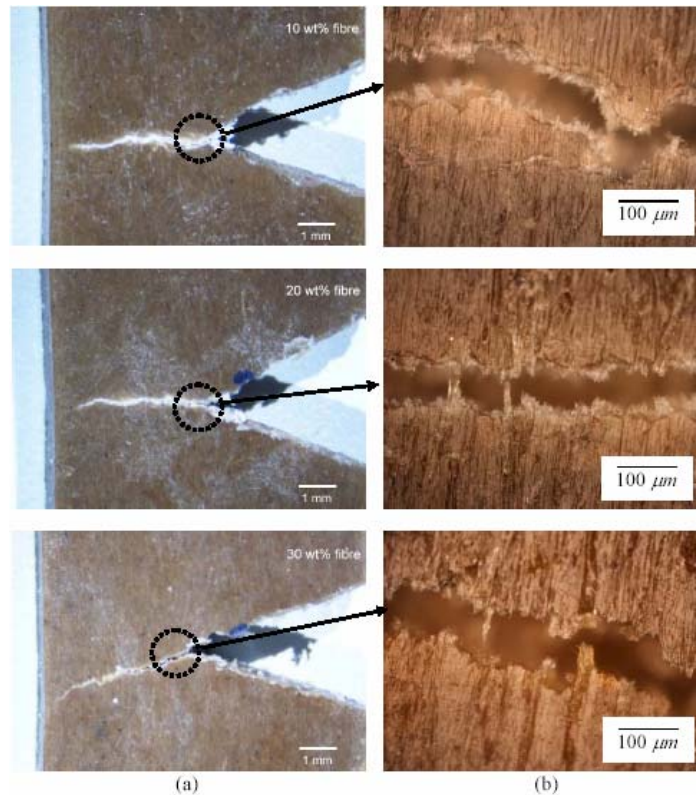


Figure 5.55: Fracture behaviour of PLA/hemp fibre composites tested at the loading speed of 10 mm/min; (a) low magnification and (b) at high magnification.

5.6.6.3 Effect of fibre treatment

Figures 5.56 and 5.57 present the average K_{Ic} and G_{Ic} of hemp fibre (untreated and treated) reinforced PLA composites as a function of fibre content, respectively. As can be seen, K_{Ic} and G_{Ic} of all the composites decreased with increased fibre content. This could again be due to increased stress concentration points (number of fibre ends) and PLA crystallinity of the composites compared to PLA only samples. In general, ACY and MA fibres were found to increase the K_{Ic} and G_{Ic} of the composites compared to untreated fibre (FB2) composites. This could be due to the lower degree of PLA crystallinity in the PLA/ACY and PLA/MA composites compared with that of the PLA/FB2 composites. On the other hand, ALK, SIL and ALKSIL fibres were found to decrease the K_{Ic} and G_{Ic} of the composites compared to the untreated fibre composites. This could be attributed to the greater PLA crystallinity in the PLA/ALK, PLA/SIL and PLA/ALKSIL composites compared with that of the PLA/FB2 composites. Among all the composite samples, PLA/MA composites with 10 wt% fibres had the highest K_{Ic} and G_{Ic} of 1.92 MPa-m^{1/2} and 5.79 kJ/m², respectively.

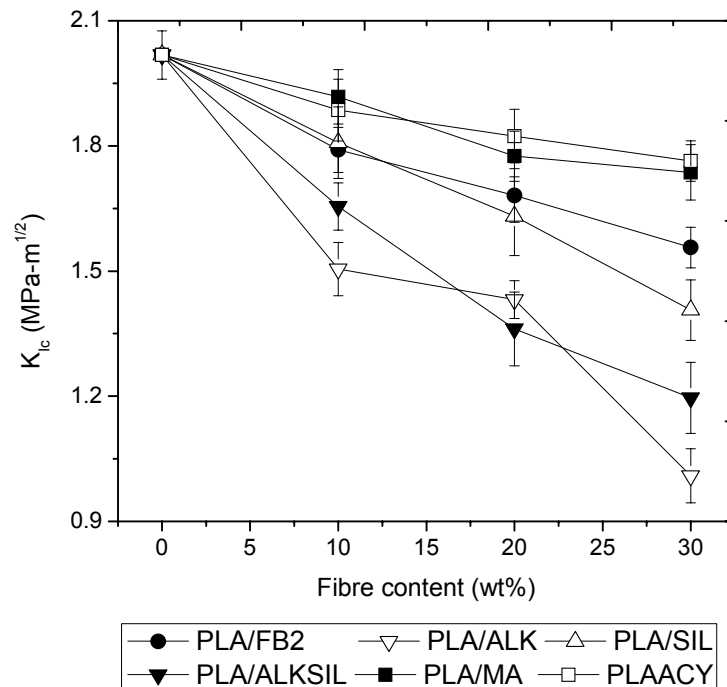


Figure 5.56: K_{Ic} for treated hemp fibre/PLA composites as a function of fibre content.

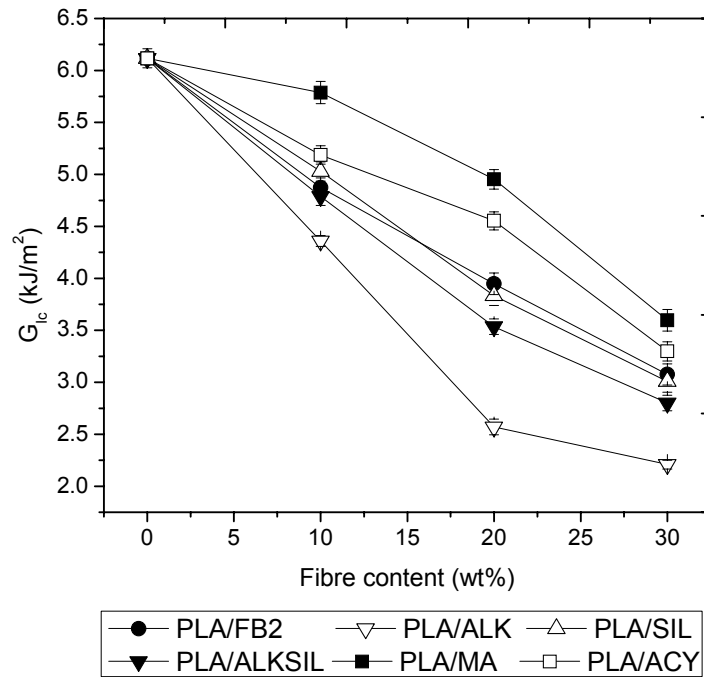


Figure 5.57: G_{ic} for treated hemp fibre/PLA composites as a function of fibre content.

5.6.7 Relationships between IFSS with tensile strength, flexural strength, impact strength and plane strain fracture toughness of short hemp fibre/PLA composites

In Figure 5.58, it can be seen that the tensile strength of the PLA/hemp fibre (untreated and treated) composites increased approximately linearly with increased IFSS. This behaviour was expected because a strong interface is favourable to transfer the applied load from the matrix to the fibres, which in turn enhances the composite strength.

The impact and flexural strength of the PLA/hemp fibre (untreated and treated) composites as a function of IFSS are presented in Figures 5.59 and 5.60, respectively. Like the tensile strength, the impact strength of the composites increased with increased IFSS. Tokoro *et al.* [171] observed similar relationship, where the impact strength of PLA/bamboo fibre composites increased with increased IFSS. Like the tensile and impact strength, the flexural strength of composites also increased with increased IFSS. However, the addition of fibres had a negative effect on the flexural strength of the composites as can be seen in Figure 5.60. The reasons for this behaviour are already explained in section 5.6.4. In

Figure 5.61, it can be observed that K_{Ic} of the composites decreased with increased IFSS. This was because a strong interface with a high value of IFSS could promote crack propagation [196], accordingly K_{Ic} decreased.

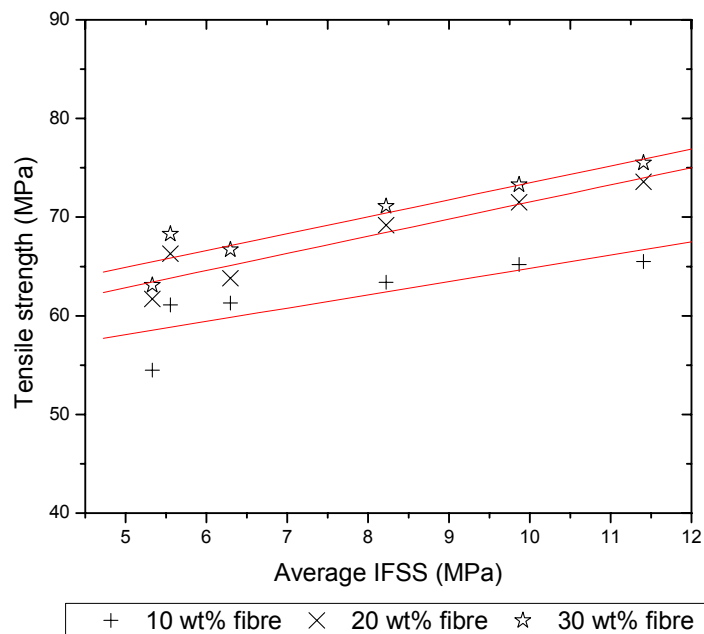


Figure 5.58: Relationship between tensile strength and IFSS for the PLA/hemp fibre composites with different treated fibres.

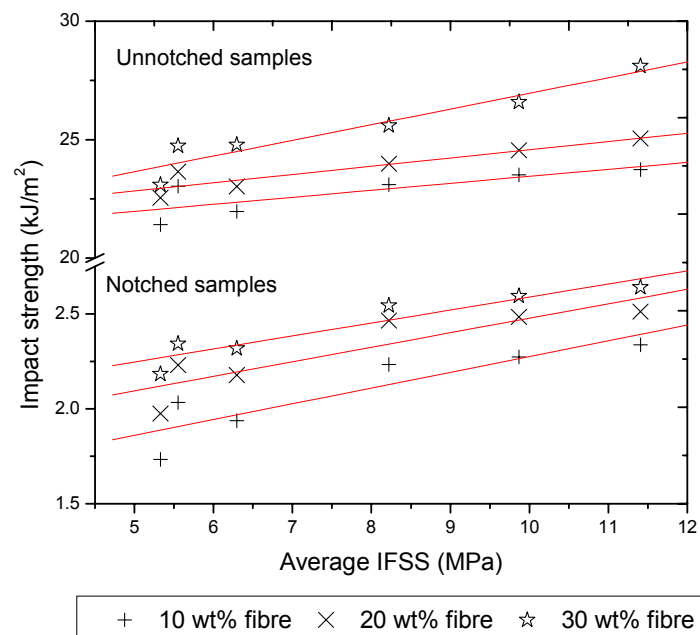


Figure 5.59: Relationship between impact strength and IFSS for the PLA/hemp fibre composites with different treated fibres.

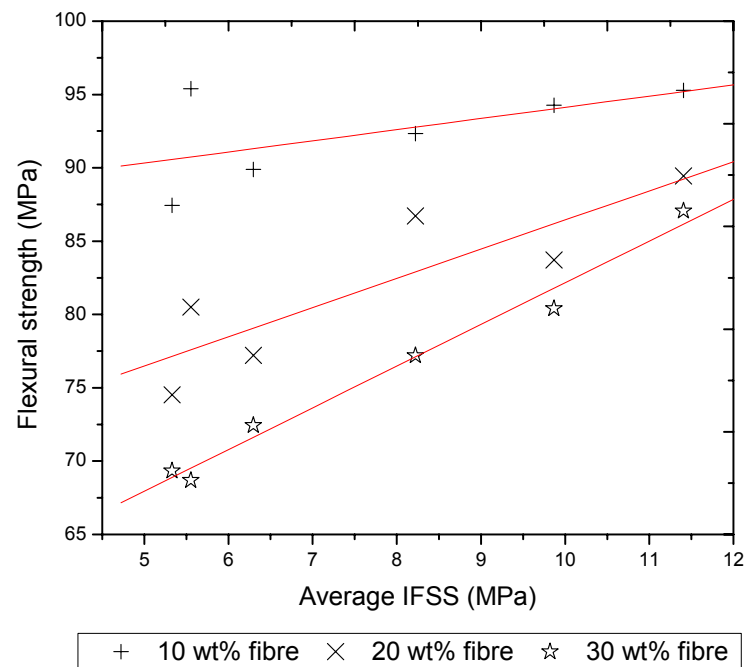


Figure 5.60: Relationship between flexural strength and IFSS for the PLA/hemp fibre composites with different treated fibres.

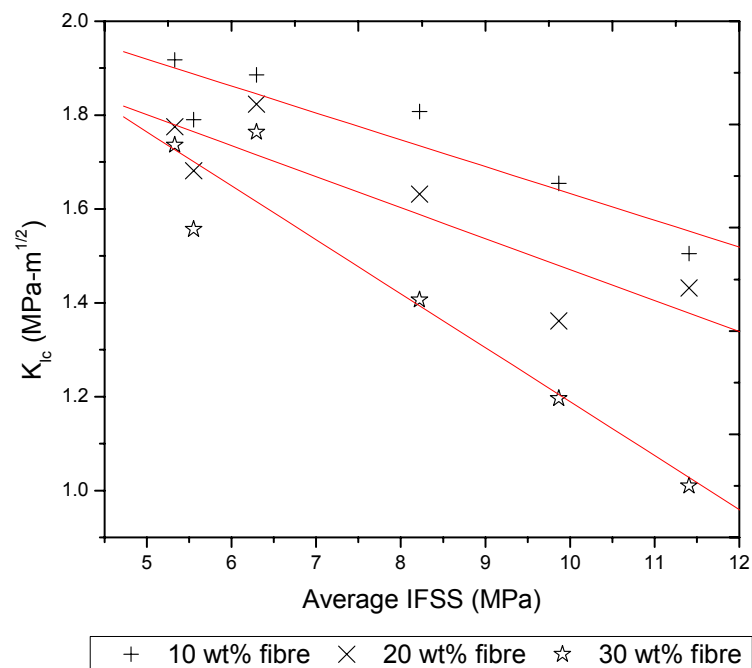


Figure 5.61: Relationship between K_{Ic} and IFSS for the PLA/hemp fibre composites with different treated fibres.

5.6.8 Relationships between PLA crystallinity with tensile strength, flexural strength, impact strength and plane strain fracture toughness of short hemp fibre/PLA composites

From Figure 5.62 to 5.64, it can be observed that the tensile, impact and flexural strength of the PLA/hemp fibre (untreated and treated) composites increased with increased PLA crystallinity. This observation can be explained based on the individual behaviour of crystalline phase of PLA and hemp fibres. It is seen earlier (see section 5.4.1) that the hemp fibres act as a nucleating agent for PLA to crystallise at the fibre/matrix interface, in addition to its role as in reinforcement. This crystalline interface improves the interfacial strength [35, 197, 198], which in turn leads to better transfer of applied load from the matrix to fibres. In addition, the nucleating agent (i.e. fibre) impels the degree of orientation of the polymer chains and increases the crystallization rate. This improves the molecular entanglement between the crystal grains. Consequently, the boundary strength between the crystals increases, which is beneficial to increase the tensile, impact and flexural strength of the composites [199].

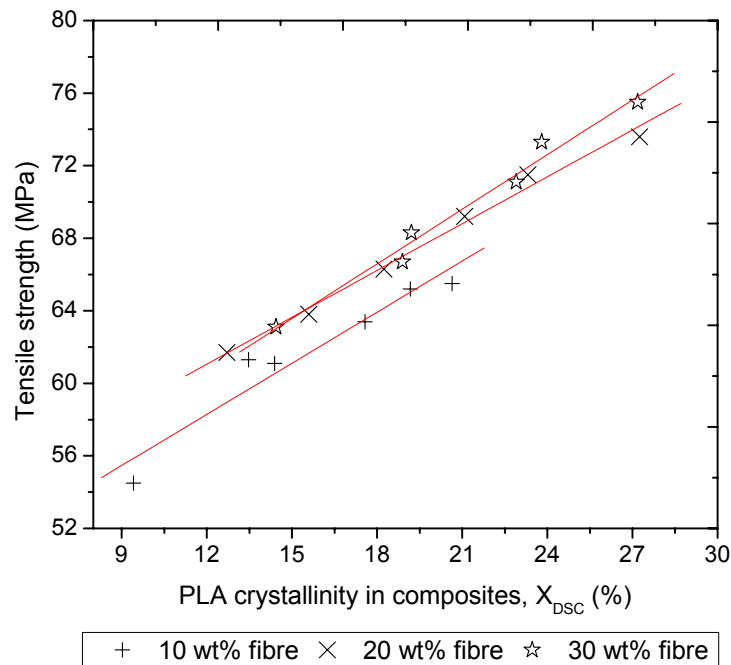


Figure 5.62: Relationship between tensile strength and PLA crystallinity for the PLA/hemp fibre composites with different treated fibres.

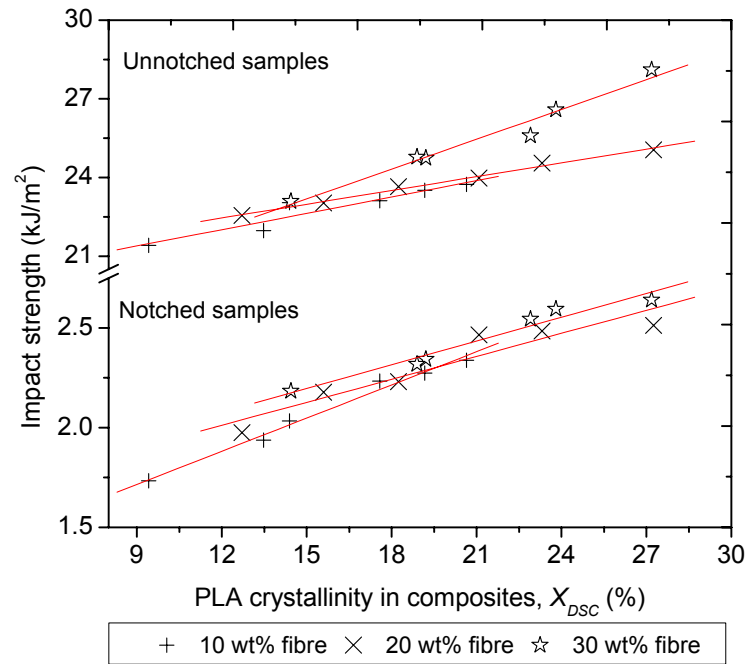


Figure 5.63: Relationship between impact strength and PLA crystallinity for the PLA/hemp fibre composites with different treated fibres.

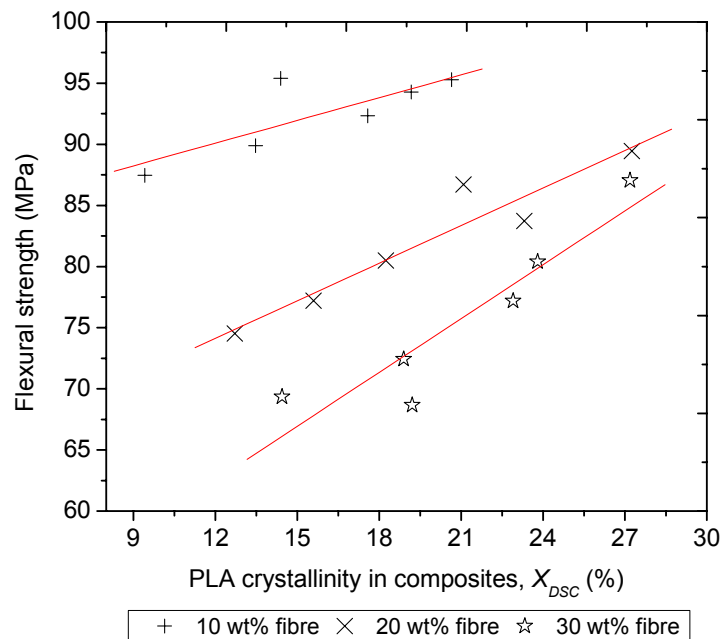


Figure 5.64: Relationship between flexural strength and PLA crystallinity for the PLA/hemp fibre composites with different treated fibres.

Figure 5.65 shows that K_{Ic} of the composites decreased as the PLA crystallinity increased. This was because cracks can easily propagate through the crystalline phase

[198]. Ye *et al.* [200] have also reported similar relationship for the glass fibre (GF) reinforced polypropylene (PP) composites (GF/PP), where they found that the fracture toughness of the GF/PP composites decreased with increased crystallinity of PP in the composites.

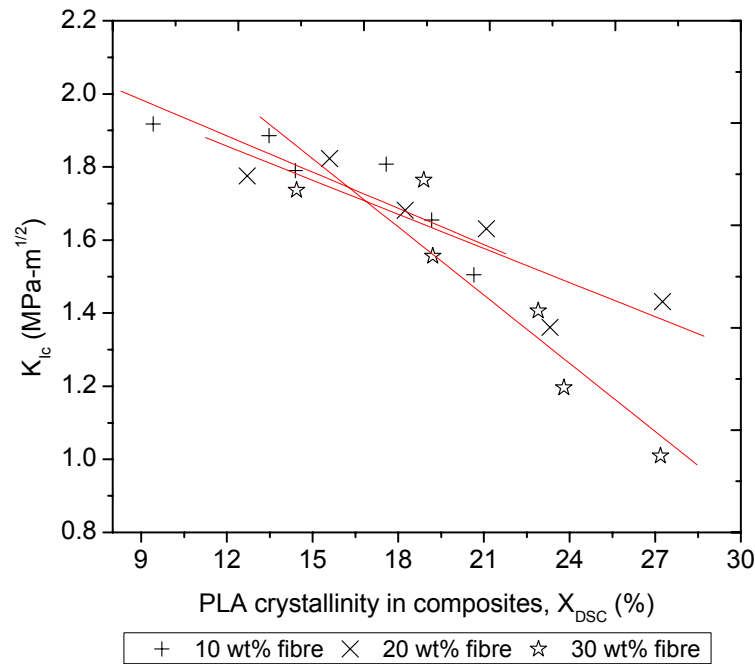


Figure 5.65: Relationship between K_{Ic} and PLA crystallinity for the PLA/hemp fibre composites with different treated fibres.

5.6.9 Dynamic mechanical thermal analysis (DMTA)

The effect of fibre content on the storage modulus (E'), loss modulus (E'') and mechanical damping factor ($\tan \delta$) of hemp fibre reinforced PLA composites (PLA/ALK) are presented in Figures 5.66, 5.67 and 5.68, respectively. The variation of E' with temperature at different fibre content is illustrated in Figure 5.66. As can be observed, E' of the composites increased with increased fibre content at all temperatures. This was because the distribution of load transfer in the composites improved (i.e. load was more evenly distributed) as the fibre content increased [201]. At 25°C, E' of the composites at 10, 20 and 30 wt% fibre content increased by 37, 63 and 70%, respectively, compared with that of the unreinforced PLA. This trend was consistent with the Young's modulus of composites (see section 5.6.1).

Also from Figure 5.66, a general declining trend in the E' of PLA and composites was observed when the specimens went through higher temperatures. The most rapid reduction occurring in the region between 48 to 52°C corresponding to the glass transition temperature (T_g) of PLA. It is also evident that E' of the samples started to increase above T_g region, which could be explained as follows. During injection moulding, the samples were quickly cooled from the processing temperature (185°C) to the mould temperature (25-30°C), which restricted the mobility of PLA chains, and thus prevented the formation of extensive amounts of crystallinity. However, when these samples were reheated above the T_g during testing, the molecular motion of the PLA chains increased and they tended to rearrange themselves to form crystallites. This phenomenon is referred to as cold crystallisation [80, 187, 202]. Thus, the degree of crystallinity of the samples increased through this process, consequently E' increased.

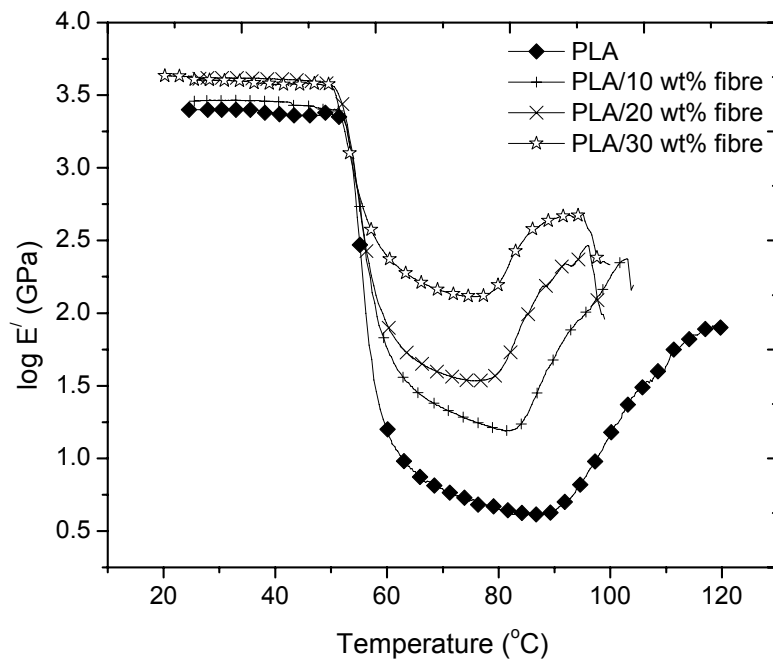


Figure 5.66: Influence of fibre content on the storage modulus of hemp fibre reinforced PLA composites (PLA/ALK).

Like the storage modulus, the loss modulus (E'') of the composites increased with increased fibre content at all temperatures as shown in Figure 5.67. It is also evident that E'' around the T_g region was broadened slightly with increased fibre content. This could be due to the increase in energy absorption and greater resistance to flow with increased

fibre content [130, 203]. The loss modulus peak represents the glass transition temperature (T_g) of polymers [130, 204]. As can be seen in Table 5.6, T_g of the PLA did not change significantly by the addition of fibres, a finding consistent with other literature [187].

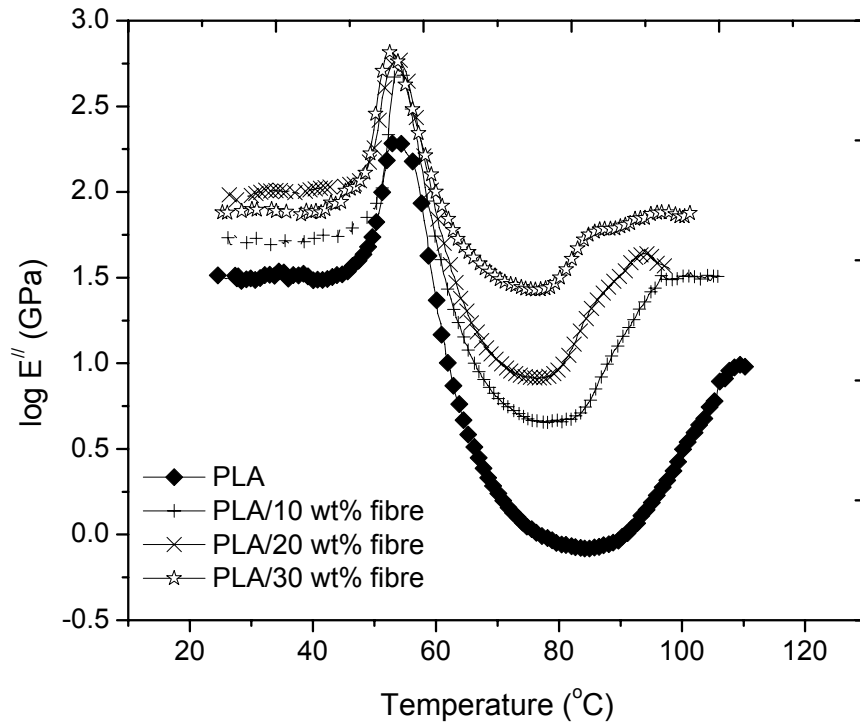


Figure 5.67: Influence of fibre content on the loss modulus of hemp fibre reinforced PLA composites (PLA/ALK).

Table 5.6: E' , T_g and $\tan \delta_{\max}$ of hemp fibre reinforced PLA composites (PLA/ALK) at different fibre content.

Fibre content	E' (GPa) at 25°C	T_g (°C)	$\tan \delta_{\max}$
0	2.51	53.5	2.01
10	2.88	53.8	1.15
20	4.10	53.6	0.98
30	4.28	53.7	0.55

The variation of mechanical damping factor ($\tan \delta$) of the composites as a function of temperature is depicted in Figure 5.68. As can be observed, the maximum height of $\tan \delta$ ($\tan \delta_{\max}$) decreased with increased fibre content (see Table 5.6). This was because the added fibres restricted the chain mobility of PLA, leads to lower flexibility and lower degrees of molecular motion [130, 187].

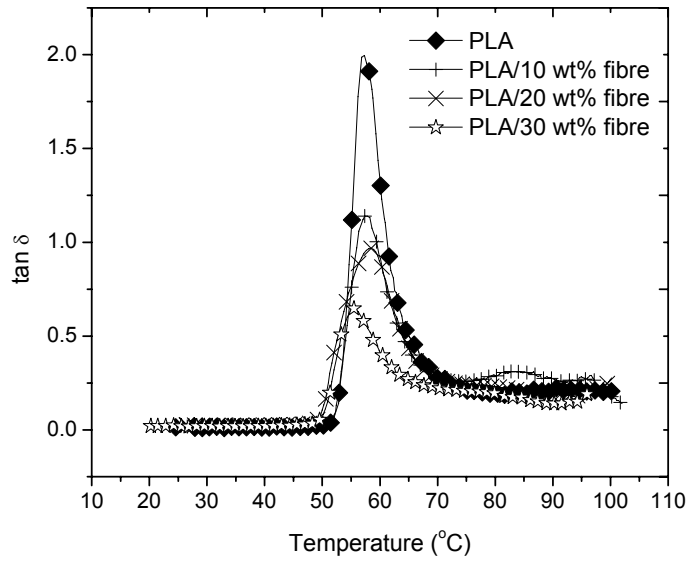


Figure 5.68: Influence of fibre content on the $\tan \delta$ of hemp fibre reinforced PLA composites (PLA/ALK).

Figure 5.69 presents the storage modulus (E') of PLA/hemp fibre composites of different treated fibres (30 wt%). The E' at 25°C of the PLA/ACY, PLA/SIL, PLA/ALKSIL and PLA/ALK composites improved by 12, 18, 23 and 40% respectively, when compared with that of the PLA/FB2 composites. These results again suggested that the interfacial strength between PLA and hemp fibres improved after the treatment (e.g. alkali, silane and acetylation) of fibres. This observation agrees with the work of Huda *et al.* [163, 164] and Pilla *et al.* [89]. The E' of PLA/MA composites did not increase compared to the PLA/FB2 composites, which was consistent with the fibre/matrix interfacial strength results.

Figure 5.70 shows the temperature dependencies of the loss modulus (E'') spectra for PLA/hemp fibre composites of different treated fibres (30 wt%). It can be seen that the loss modulus peak (i.e. T_g) of the composites changed from 1 to 3°C irrespective of the type of treatment given to the hemp fibres (see Table 5.7). This was consistent with other work on pine wood fibre/PLA composites [89]. In addition, it is evident that the area under the peak of the composites depends on reinforcement type (the particular treatment applied to fibres). This was likely the result of disruption of the movement of polymer chains by the surface properties of added fibres. Another reason could be the coexistence of PLA crystalline domains (i.e. spherulites and transcrystals) with amorphous chains which

constrict molecular motions of the amorphous macromolecules in the vicinity of the interface between both components [205].

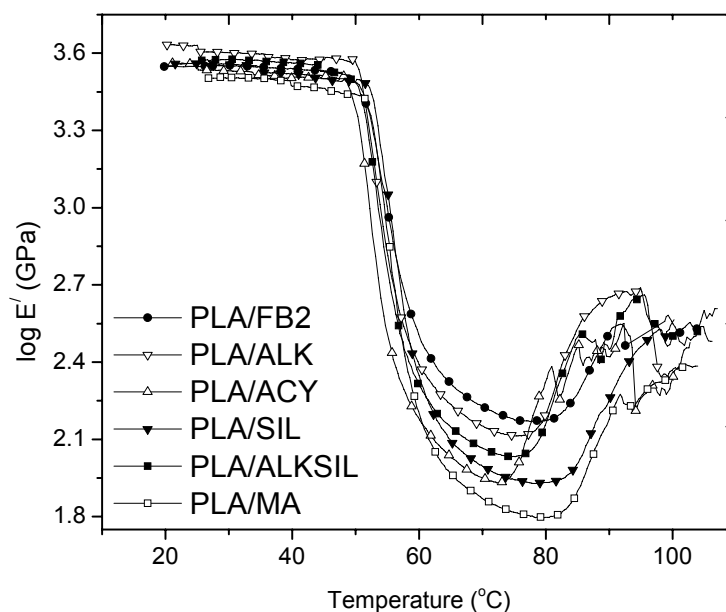


Figure 5.69: Effect of fibre treatment on the storage modulus hemp fibre reinforced PLA composites (30 wt% fibre).

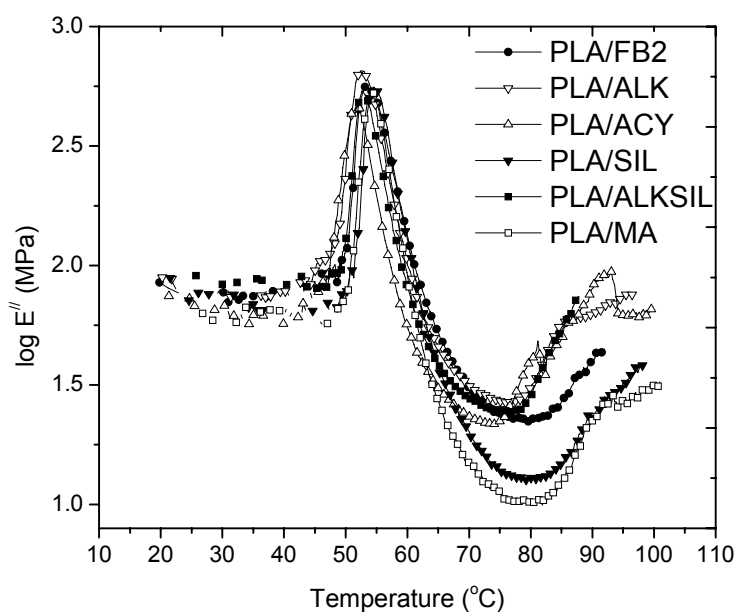


Figure 5.70: Effect of fibre treatment on the loss modulus of hemp fibre reinforced PLA composites (30 wt% fibre).

For the composites with an equal amount of fibres, the mechanical damping factor ($\tan \delta$) can be used to characterise the effect of fibre treatment on the fibre/matrix interfacial

adhesion [130]. Strong adhesion between the fibre and matrix tends to reduce the mobility of the molecular chains at the interface and therefore reduces the damping (i.e. $\tan \delta_{\max}$) [204]. The effect of fibre treatment on the variation of $\tan \delta$ with respect to the temperature is depicted in Figure 5.71 and the $\tan \delta_{\max}$ is presented in Table 5.7. Among the treated fibre composite samples, the PLA/ALK composites had the lowest $\tan \delta_{\max}$ which reflects the strong interaction between the alkali treated fibre and the PLA. It was observed that $\tan \delta_{\max}$ for the untreated and treated fibre composites were in general agreement with the IFSS findings (see section 5.3).

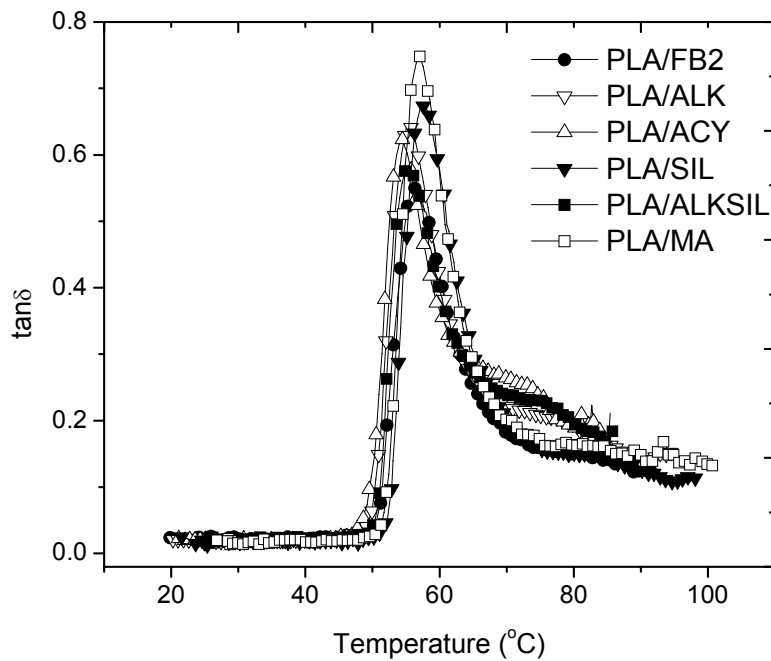


Figure 5.71: Effect of fibre treatment on the $\tan \delta$ of hemp fibre reinforced PLA composites (30 wt% fibre).

Table 5.7: E' , T_g and $\tan \delta_{\max}$ of untreated and treated hemp fibre reinforced PLA composites (30 wt% fibre).

Sample	E' (GPa) at 25°C	T_g (°C)	$\tan \delta_{\max}$
PLA	2.51	53.5	2.01
PLA/FB2	3.04	52.7	0.67
PLA/ALK	4.28	53.7	0.55
PLA/ACY	3.42	51.9	0.65
PLA/SIL	3.61	54.5	0.63
PLA/ALKSIL	3.74	54.2	0.58
PLA/MA	3.00	52.7	0.75

5.7 Aligned long hemp fibre reinforced PLA composites

As the alkali treated short hemp fibre/PLA composites had the best mechanical properties, the investigation was expanded to produce high strength alkali treated hemp fibre/PLA composites using aligned long fibres. The composites were fabricated according to the method described in section 3.3.2.2.

5.7.1 Tensile properties

The average tensile strength, Young's modulus and failure strain of the alkali treated aligned long fibre/PLA composites as a function of fibre content are shown in Figure 5.72. Tensile properties of alkali treated short fibre/PLA composites are presented for comparison. As can be seen, the average tensile strength and Young's modulus of the long fibre composites (30 wt% fibre) were higher than those of the short composites, which would be expected due to higher reinforcement efficiency for the aligned long fibres. In short fibre composites, a high amount of composite fracture near the fibre-end positions of the short fibres might occur which could reduce the effective fibre length and hence the tensile strength and Young's modulus [206].

It is apparent that the tensile strength and Young's modulus of the long fibre PLA composites increased with increased fibre content up to 35 wt% and further increment of fibres (40 wt%) caused a decrease in the tensile strength and Young's modulus. At 35 wt% fibre content, the average tensile strength and Young's modulus of the long fibre/PLA composites was 85.4 MPa and 12.6 GPa, respectively. This tensile strength of the long hemp fibre/PLA composites was found to be lower (about 14 MPa) than the reported tensile strength of aligned jute fibre mat/PLA composites [96]. This could be due to somewhat misalignment of hemp fibres in the composites. The hemp fibres used in this work were in bales of tangled and twisted strips. Despite the fact that the fibres were carded, they appeared to somewhat crimped due to spring-back during composite processing. However, Young's modulus of the long hemp fibre/PLA composites found to be better than any reported long fibre/PLA composites [96].

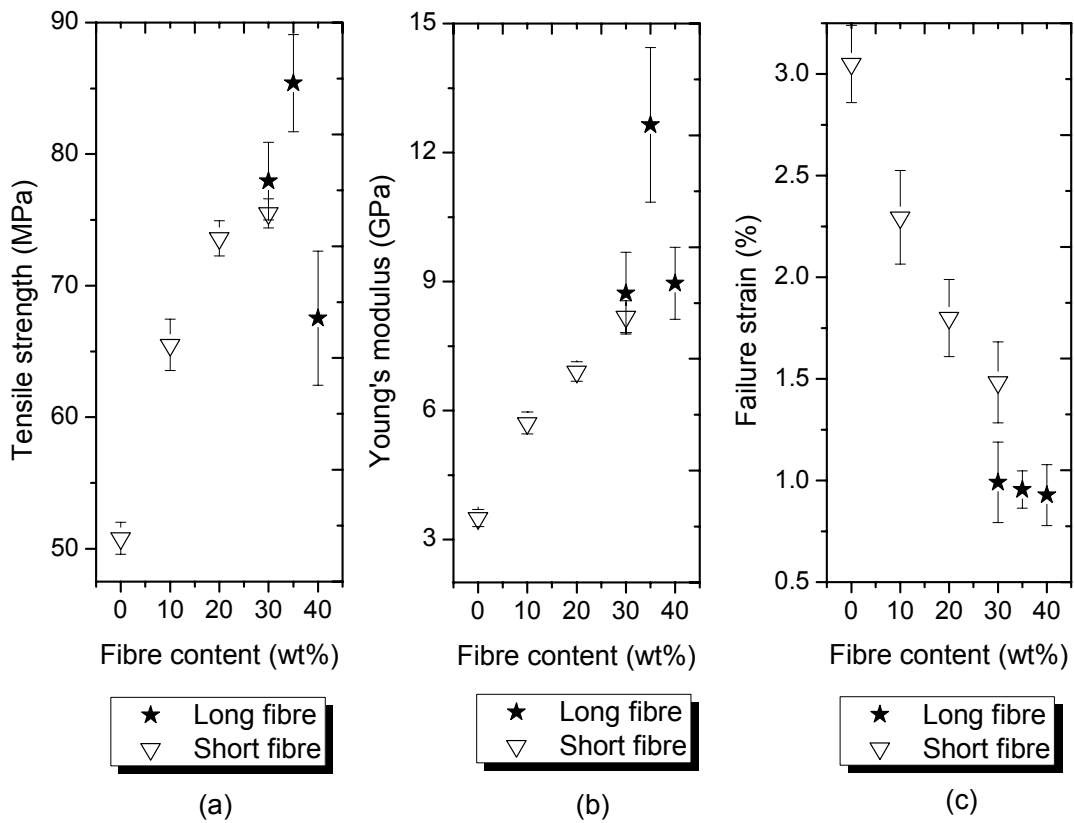


Figure 5.72: Tensile properties of alkali treated long and short fibre/PLA composites.

A photograph of a tensile tested long fibre/PLA composite is presented in Figure 5.73, where it can be seen that the two sample halves were completely separated, typical of an unstable fracture. The fracture surface of the composites reinforced with 35 wt% fibres [see Figure 5.74(a)] showed that the fibres were well bonded with the matrix which leads to good stress transfer from the matrix to the fibres. Fibrillation of fibres in the fracture surface was evident too, most probably caused by regions of the fibres, well bonded to the matrix, being ‘torn’ from underlying layers of the fibres. This fibrillation phenomenon was consistent with the alkali treated short fibre/PLA reinforced composites as seen earlier (see section 5.6.3).

In the case of 40 wt% fibre content [see Figure 5.74(b)], fibres were not thoroughly wetted due to the insufficient amounts of matrix being available to cover the fibres. As a result, fibres were not well connected with the matrix, and some gaps between the fibres and matrix were evident. In this situation, load on the composites was not distributed evenly

from the fibre to fibre through the matrix, and catastrophic failure of the composites was observed because of poor wetting of the fibres.



Figure 5.73: Photograph of a tensile tested aligned long hemp fibre (35 wt% fibre) reinforced PLA composite (PLA/ALK).

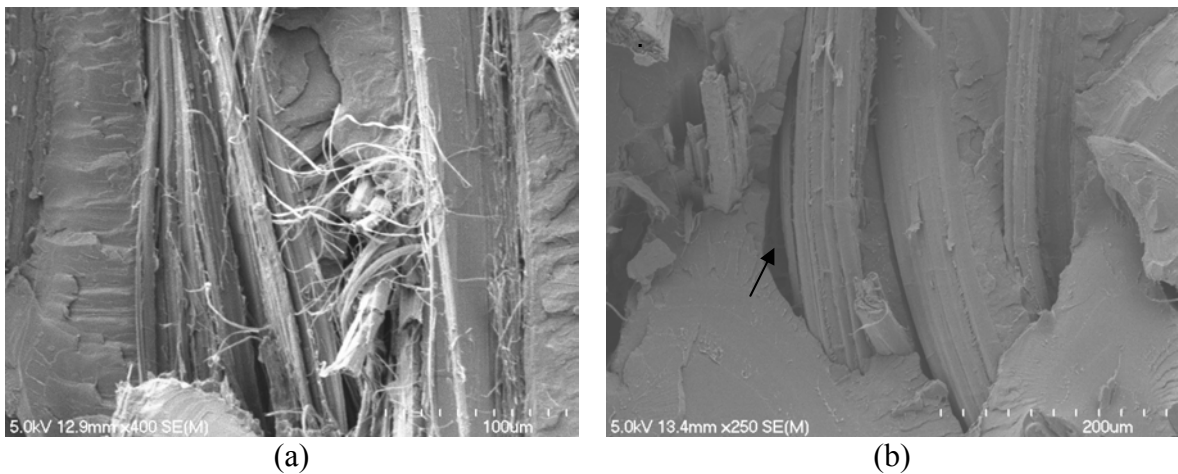


Figure 5.74: SEM micrograph of the tensile fracture surface of long fibre ALK/PLA composites; (a) 35 wt% fibre and (b) 40 wt% fibre.

Again from Figure 5.72, it can be observed that failure strain of the long fibre composites was lower than short fibre composites. This was because long fibre composites were stiffer than the short fibre composites due to fibre alignment. It was found that failure strain of the long fibre composites decreased from 2.8 to 0.93% as the fibre content increased from 0 to 40 wt%. Plackett *et al.* [96] reported similar decrease in failure strain for the aligned jute fibre mat/PLA composites.

5.7.2 Flexural properties

Figure 5.75 shows the average flexural strength and flexural modulus of the alkali treated long fibre/PLA composites as a function of fibre content. The flexural strength and flexural modulus of the alkali treated short fibre/PLA composites are presented for comparison. As can be seen, similar to short fibre composites, flexural strength of the long fibre composites decreased (from 95.3 to 67.5 MPa) with increased fibre content. The reason for this decrease in flexural strength has been explained earlier (see section 5.6.4), where it was seen that the fibre defects (i.e. kinks) could induce stress concentration points in the composites during flexural testing, accordingly flexural strength decreased. SEM micrograph as shown in Figure 5.76 for the long fibre reinforced PLA composites again supported this explanation.

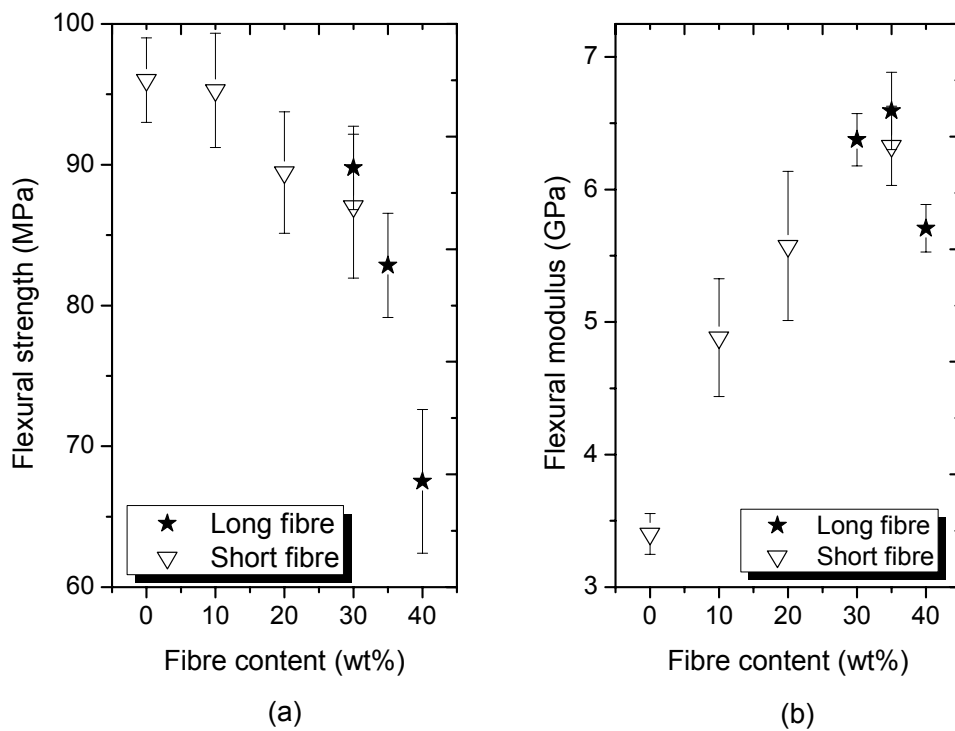


Figure 5.75: Flexural strength and flexural modulus of long and short hemp fibre reinforced PLA composites (PLA/ALK).

Flexural modulus of the composites increased from 3.84 to 6.59 GPa as the fibre content increased from 0 to 35 wt%, however, further increment of fibres (40 wt%) caused a reduction in flexural modulus, which was consistent with the Young's modulus of long

fibre composites. At 30 wt% reinforcements, flexural strength and flexural modulus of long fibre composites were 3.1 and 6.5% higher, respectively, compared with those of short fibre composites, which again suggests higher reinforcement efficiency for the aligned long fibres.

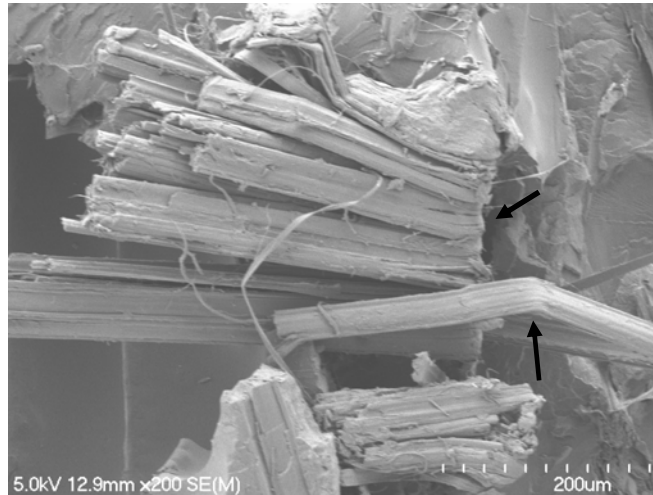


Figure 5.76: SEM micrograph of the flexural tested fracture surface of long hemp fibre reinforced PLA composites (PLA/ALK) showing the kinks (indicated by arrows).

5.7.3 Impact strength

Figure 5.77 presents the average impact strength as a function of fibre content, for alkali treated long fibre/PLA composites. Impact strength of the alkali treated short fibre/PLA composites are presented for comparison. Similar to tensile strength of the long fibre composites, it may be observed that the impact strength for both the unnotched and notched long fibre composites increased as the fibre content increased and attained the maximum value at 35 wt% fibre content. Further increment of fibres caused a decrease in impact strength of the composites. At 35 wt% fibre content, the impact strength of the unnotched and notched samples were 32.8 and 7.4 kJ/m², respectively. For an equivalent amount of fibres (30 wt%), the impact strength of the notched samples of the long fibre composites was 101% higher than that of the short fibre composites. For the same composites, the impact strength of the unnotched samples was 6.6% higher than that of the short fibre composites.

A photograph of impact tested long fibre PLA composites is presented in Figure 5.78. As can be seen, samples were not completely separated into two pieces but fibres bridged the

gap to hold the sample together. This mode of failure was associated with high energy absorption [207]. In addition, examination of the impact fracture surfaces showed fibre pullout due to the fracture of long fibre during impact loading [see Figure 5.79(a)]. Fibrillation was also evident in the impact fracture surface [see Figure 5.79(b)], which was consistent with the short fibre composites.

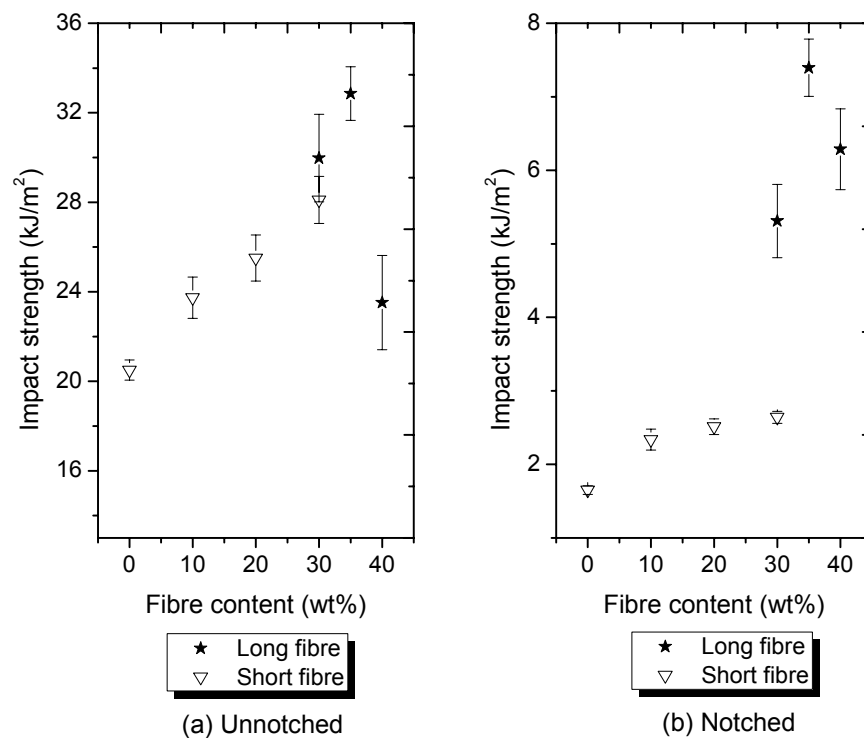


Figure 5.77: Impact strength of long and short fibre reinforced PLA composites (PLA/ALK) as a function of fibre content.

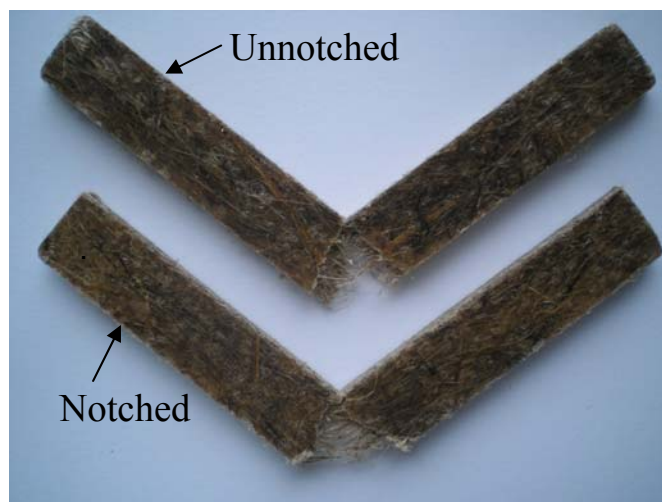


Figure 5.78: Photograph of the impact tested long hemp fibre reinforced PLA composites (35 wt% fibre).

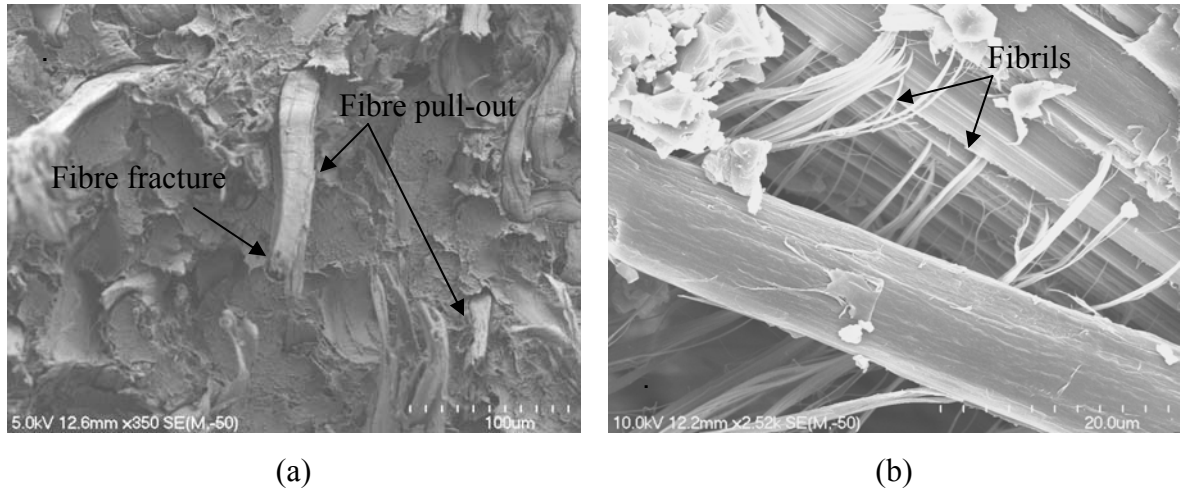


Figure 5.79: SEM micrographs of the impact fracture surface of long fibre PLA/ALK composites (35 wt% fibre).

5.7.4 Fracture toughness

Figure 5.80 shows the average K_{Ic} and G_{Ic} of the alkali treated long and short fibre composites as a function of fibre content. As can be observed, K_{Ic} and G_{Ic} of the long fibre composites was higher than those of the short fibre composites. This was because in the long fibre composites the fibres were oriented perpendicular to the loading direction thus had greater resistance to crack propagation. Figure 5.81 indicated that crack propagation was suppressed somewhat due to the fibre bridging. Like short fibre composites, K_{Ic} and G_{Ic} of the long fibre composites decreased with increased fibre content. This could again be due to the crystalline interface of PLA/hemp fibre composites through which cracks can propagate easily. At 30 wt% reinforcement, K_{Ic} and G_{Ic} of the long fibre composites were 36.4 and 25.1%, respectively, higher than those of the short fibre composites.

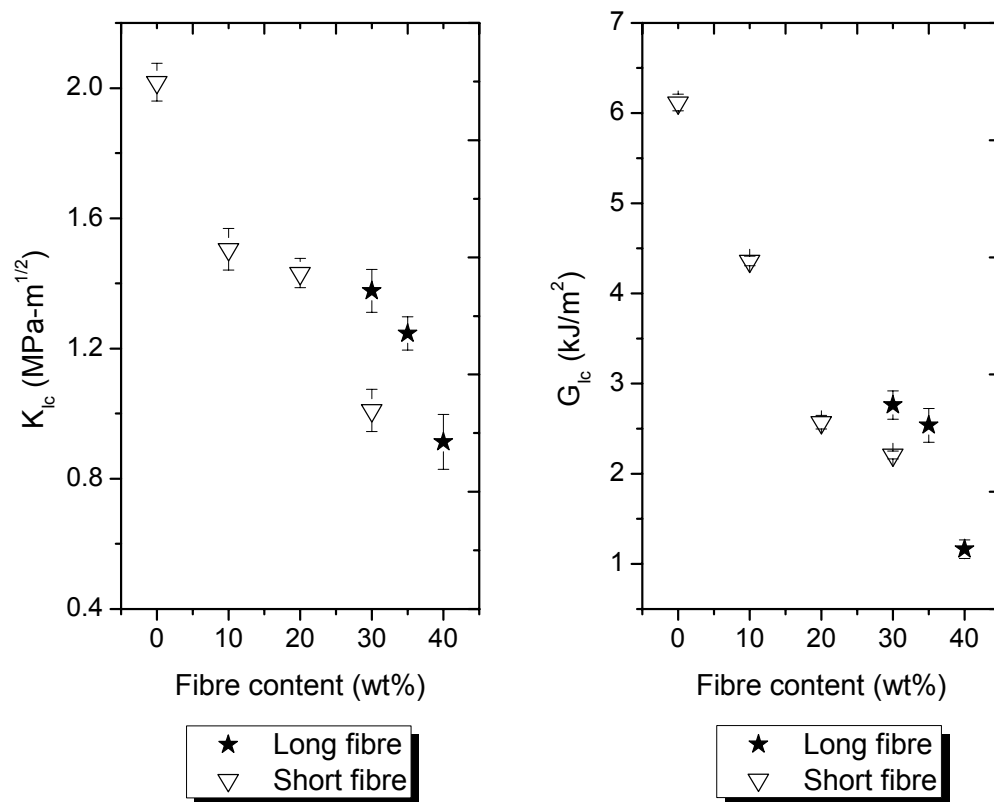


Figure 5.80: K_{Ic} and G_{Ic} of long and short hemp fibre reinforced PLA composites (PLA/ALK) as a function of fibre content.

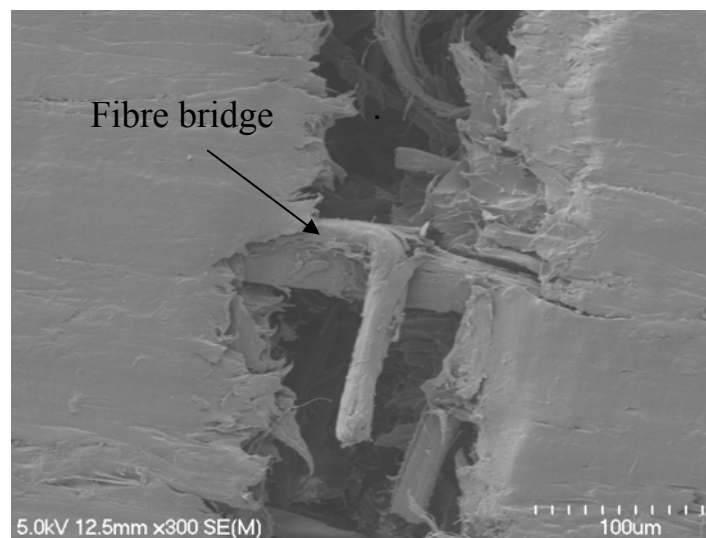


Figure 5.81: SEM micrograph of the long fibre PLA/ALK composites showing the fibre bridging in SENB tested sample (30 wt% fibre).

5.7.5 Dynamic mechanical thermal analysis (DMTA)

Figure 5.82 shows the DMTA results (storage modulus, loss modulus and damping factor) of the alkali treated long and short fibre composites (30 wt% fibre) as a function of temperature. As can be seen, storage modulus (E') of long fibre composites was significantly higher than that of short fibre composites throughout temperature range. This behaviour suggests that the long fibre PLA composites were very stiff compared to short fibre composites even at high temperature. E' at 25°C of the long fibre composites was 5.8% higher than that of the short fibre composites. This trend was consistent with the composite Young's modulus (see section 5.7.1).

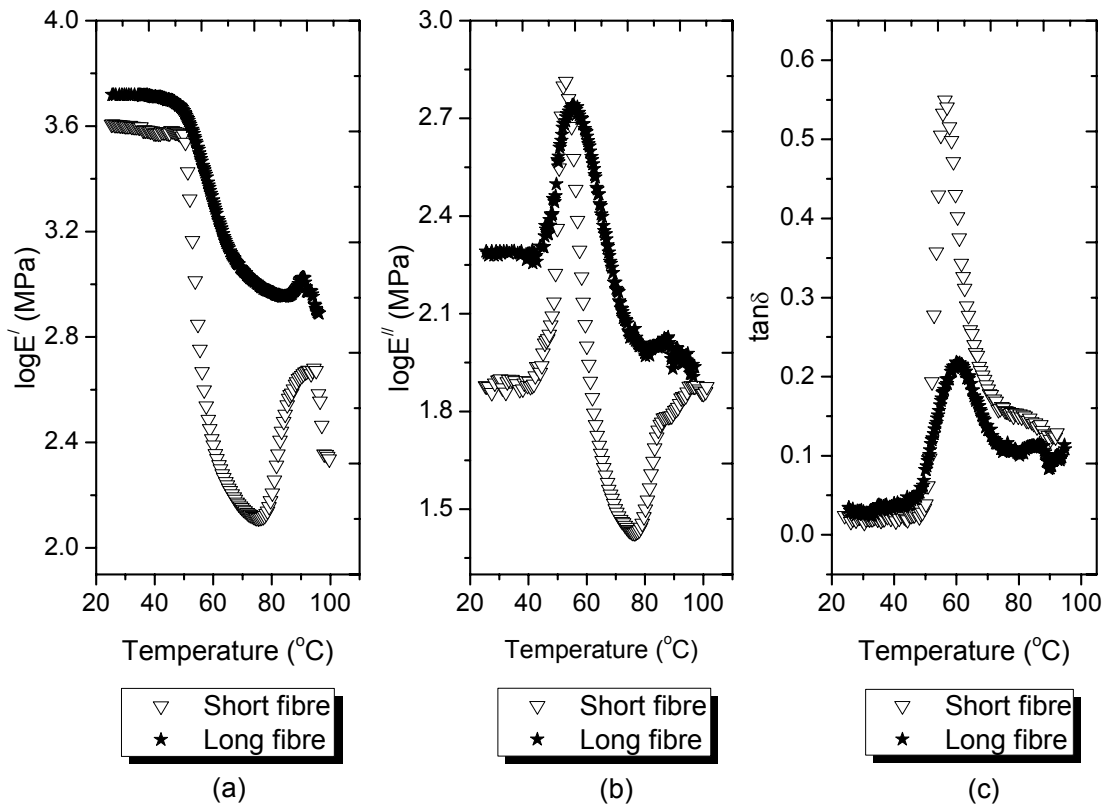


Figure 5.82: Dynamic mechanical thermal properties of long and short hemp fibre (30 wt% fibre) reinforced PLA composites (PLA/ALK).

A small difference in glass transition temperature (less than 2°C) was noticed between the short and long fibre composites [see Figure 5.82(b)]. However, considerable broadening of the loss modulus peak suggests greater hindrance to any large scale motion of polymer chains in long fibre composites which, in contrast, was pronounced in short fibre

composites. Fibre length and alignment also affected the damping behaviour of the composites as can be seen in Figure 5.82(c). As can be observed, $\tan \delta_{\max}$ of long fibre composites was significantly lower than that of short fibre composites (see Table 5.8), again suggesting a reduction of PLA chain mobility in the long fibre composites.

The storage modulus (E'), glass transition temperature (T_g) and damping factor ($\tan \delta_{\max}$) for long fibre composites at 30 and 35 wt% fibre contents are presented in Table 5.8. At 35 wt% fibre, E' of the composites was 5.59 GPa, about 23.4% higher than the composites reinforced with 30 wt% fibres. Similar to short fibre composites, T_g of long fibre composites did not change significantly with increased fibre content. $\tan \delta_{\max}$ of long fibre composites decreased slightly with increased fibre content, a finding similar to that for short fibre composites.

Table 5.8: E' , T_g and $\tan \delta_{\max}$ of long and short fibre reinforced PLA composites (PLA/ALK).

Composite type	Fibre content (wt%)	E' (GPa) at 25°C	T_g (°C)	$\tan \delta_{\max}$
Long fibre	30	4.53	55.4	0.22
	35	5.59	54.9	0.19
Short fibre	30	4.28	53.7	0.55

5.7.6 Differential scanning calorimetry (DSC) analysis

Thermal properties of long fibre composites at different fibre contents (30, 35 and 40 wt%) was measured by DSC are presented in Table 5.9. In Figure 5.83, it can be seen that crystallinity of long fibre composites increased with increased fibre content up to 35 wt%. A further increment in fibre content (40 wt%) caused a reduction in crystallinity due to the (i) space limitation for the crystal growth and (ii) decrease in the amounts of matrix.

It is well known that the crystallinity of semi-crystalline polymers depends on the processing conditions and/or thermal history [208]. Thus, the variation of PLA crystallinity in the short and long fibre composites (30 wt% fibre) (see Figure 5.83) was due to the different processing methods applied for composite fabrication.

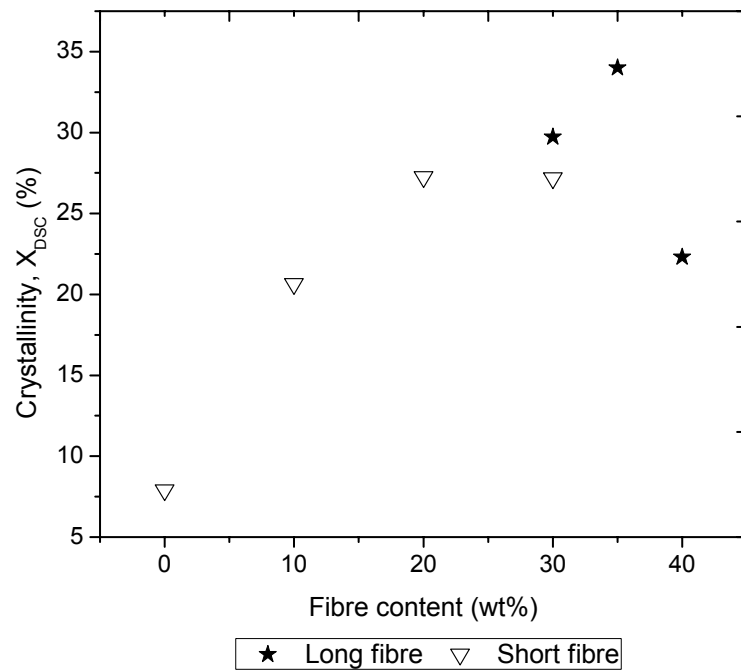


Figure 5.83: PLA crystallinity of long and short hemp fibre reinforced PLA composites (PLA/ALK).

Table 5.9: Thermal properties (DSC) of long hemp fibre reinforced PLA composites (PLA/ALK).

Composite type	Fibre content (wt%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)
Long fibre	30	56.9	98.9	151.2-155.4	22.35
	35	57.3	103.1	151.9-156.2	31.56
	40	57.5	103.6	149.6-154.1	26.45

CHAPTER SIX

Results and Discussion: Part III – Unsaturated Polyester/Hemp Fibre Composites

6.1 Introduction

This chapter covers results of:

- FT-IR analysis for unsaturated polyester resin (UPE) and hemp fibre (untreated and treated) reinforced UPE composites;
- interfacial shear strength (IFSS) between hemp fibres (untreated and treated) and UPE;
- influence of fibre content (short and long fibre) and fibre treatment on the tensile properties, impact strength, flexural properties, plane strain fracture toughness, strain energy release rate and dynamic mechanical thermal properties of hemp fibre/UPE composites;
- relationships between the tensile strength, impact strength, flexural strength and plane strain fracture toughness of the hemp fibre UPE composites with IFSS; and
- comparison between mechanical properties of hemp fibre/UPE composites and hemp fibre/PLA composites.

6.2 FT-IR analysis of UPE and UPE/hemp fibre composites

A typical FT-IR spectrum for UPE is presented in Figure 6.1. The principal absorption peaks obtained for the UPE are as follows:

- a peak around 3436 cm^{-1} which can be attributed to the stretching vibrations of hydroxyl (OH) groups;
- strong peaks at 3083, 3060, 3027 and 2922, assigned to C-H stretching;
- a peak at 2854 cm^{-1} assigned to the symmetric stretching vibrations of the methylene group (CH_2);
- a very intense peak observed at 1727 cm^{-1} due to the carbonyl (C=O) stretching from the ester linkage;

- peaks at 1585 and 1493 cm^{-1} attributed to the C=C stretching vibrations within the aromatic ring;
- a strong peak at 1238 cm^{-1} due to the twisting vibration of CH_2 groups; and
- peaks at 1160 and 1129 cm^{-1} assigned to the C-O stretching vibration [209-212].

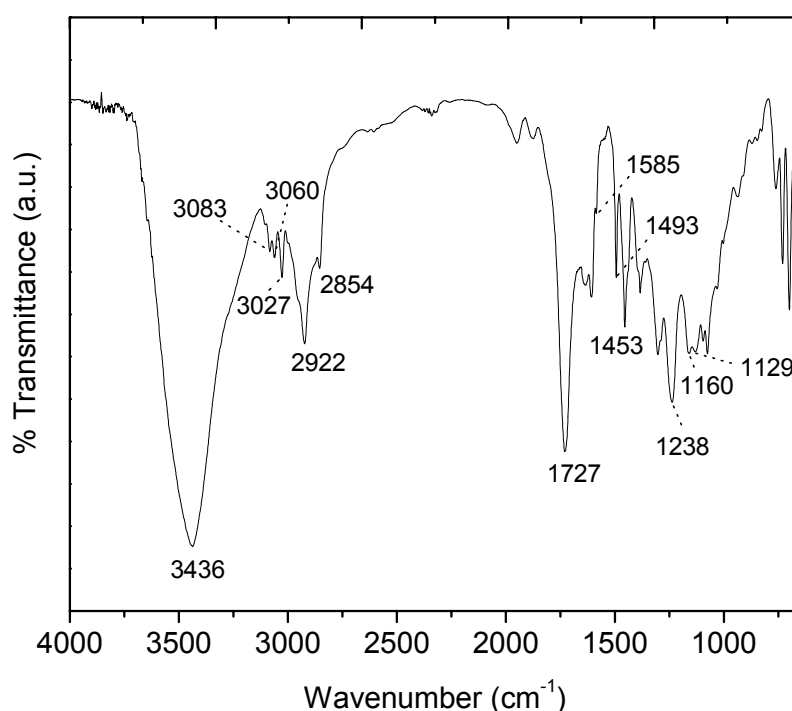


Figure 6.1: FT-IR spectrum of cured UPE sample.

In Figure 6.2, an FT-IR spectrum for UPE/FB2 composites is compared with those for UPE and FB2 fibres. As can be observed, the stretching vibration peak for OH group of the UPE/FB2 composites (3440 cm^{-1}) was much broader than that of the UPE (3436 cm^{-1}) and FB2 fibres (3410 cm^{-1}). This suggests that hydrogen bonding could have occurred between UPE and FB2 fibres. Other researchers have also reported similar observations for the polyester/glass fibre and polyester/carbon fibre composites [209]. For UPE, the peak intensity of the C=O group at 1727 cm^{-1} was relatively lower than that of the OH group at 3436 cm^{-1} . For the composites, the peak intensity of the C=O group at 1727 cm^{-1} was observed to be significantly higher than that of the OH group at 3440 cm^{-1} . This indicates that covalent bonding has taken place through an esterification reaction between the fibre OH groups and polyester COOH groups.

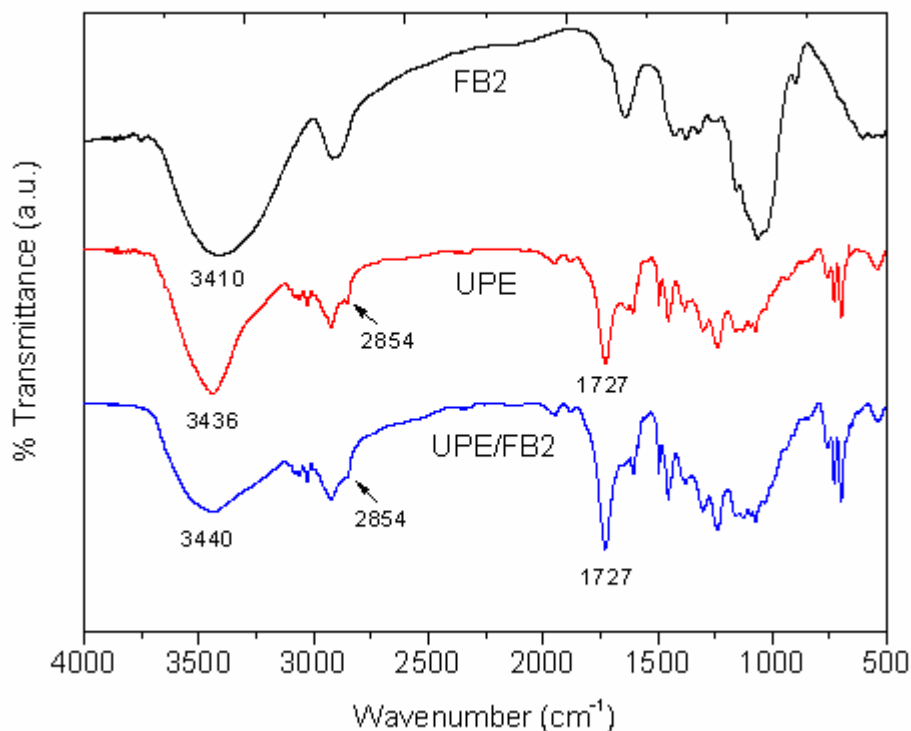


Figure 6.2: FT-IR spectrum of untreated fibre and UPE composite (UPE/FB2). Spectra of FB2 and UPE are shown for comparison.

The FT-IR spectra for various treated hemp fibre reinforced UPE composites are presented in Figure 6.3. In general, the spectra of all the treated hemp fibre reinforced UPE composites were fairly similar to that for untreated fibre reinforced composites. However, in the treated fibre composites, the peak for C=O groups at 1727 cm^{-1} was more intense than the untreated fibre composites suggesting more esterification reactions, increasing in the order: UPE/FB2 < UPE/ALK < UPE/ACY < UPE/MA < UPE/SIL < UPE/ALKSIL. It appears that due to the removal of impurities (wax, pectin and dirt) from the surface of untreated fibres, for alkali treated fibres, the number of available OH groups increased for greater esterification with UPE. As discussed in section 4.4, disruption of hydrogen-bonding in the crystalline region of hemp fibres during treatment with acetic anhydride, maleic anhydride and silane led to increased free OH groups enabling increased esterification with UPE. It is also possible that esterification has occurred between (i) maleated fibre COOH groups (see Figure 4.14) and polyester OH groups, and (ii) silane treated fibre OH groups (see Figure 4.15) and polyester COOH groups.

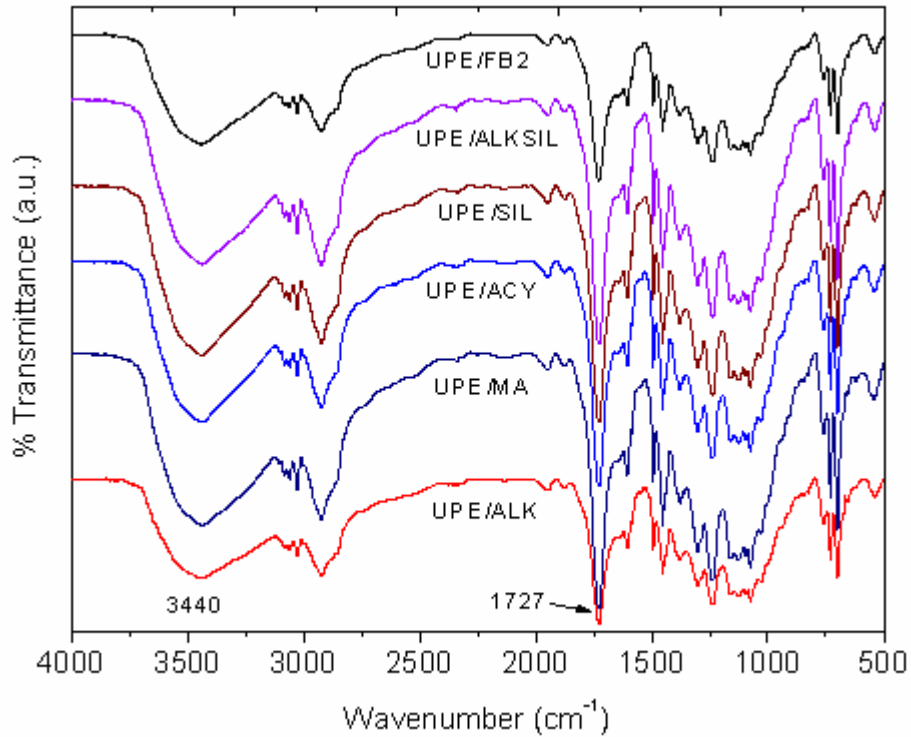


Figure 6.3: FT-IR spectra of various treated hemp fibre reinforced UPE composites. Spectrum of UPE/FB2 is shown for comparison.

6.3 Interfacial shear strength (IFSS) of UPE/hemp fibre samples

A representative graph of load versus displacement obtained from the pull-out tests for the UPE/hemp fibre samples is presented in Figure 6.4. Similar curves have been observed for glass fibre/polyester samples elsewhere [196]. Initial debonding is believed to have taken place at point A, when the stress field around the embedded fibre was sufficient to initiate cracking. Debonding is expected to have continued (crack propagation) until the debonding force reached a maximum at point B, after which a sudden drop of load was observed. Finally, in the pull-out process (C-D) load decreased gradually.

Figure 6.5 shows the debonding force for UPE/hemp fibre (untreated and treated) samples as a function of fibre embedded length. As can be seen, the debonding force showed a reasonably linear relationship with the embedded fibre length for all samples, though with different slopes. The higher slopes obtained for the treated samples compared to the untreated samples suggest stronger interfaces for treated fibres than untreated fibres.

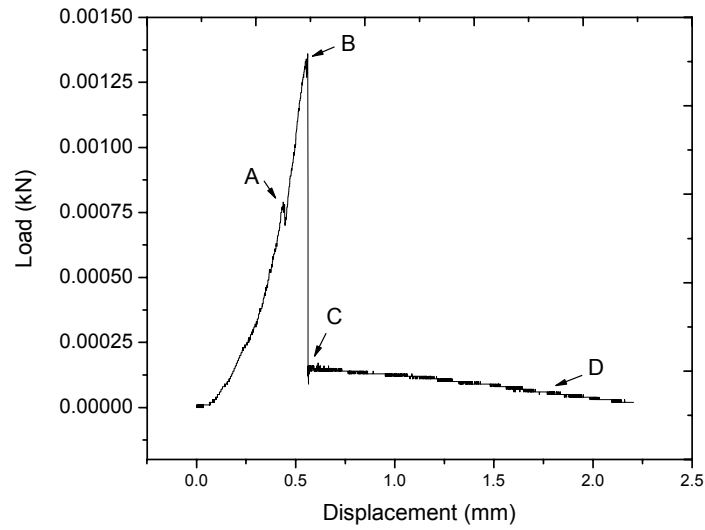


Figure 6.4: Typical load versus displacement curve for pull-out tests of UPE and hemp fibre sample.

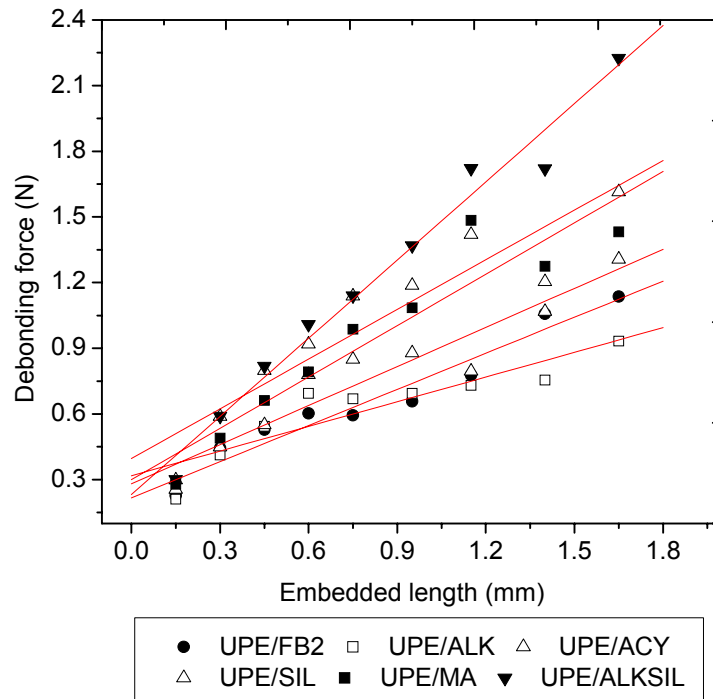


Figure 6.5: Debonding force versus embedded fibre length for UPE/hemp fibre (untreated and treated) samples.

IFSS as a function of fibre embedded length for the UPE/hemp fibre (untreated and treated) samples is depicted in Figure 6.6. As can be observed, IFSS showed a non-linear relationship with the embedded fibre length, indicating a brittle interfacial fracture as

reported in literature [169]. This was consistent with the PLA/hemp fibre samples as seen in Figure 5.11. Similar observation has also been reported by other researchers for glass fibre/polyester composites [196].

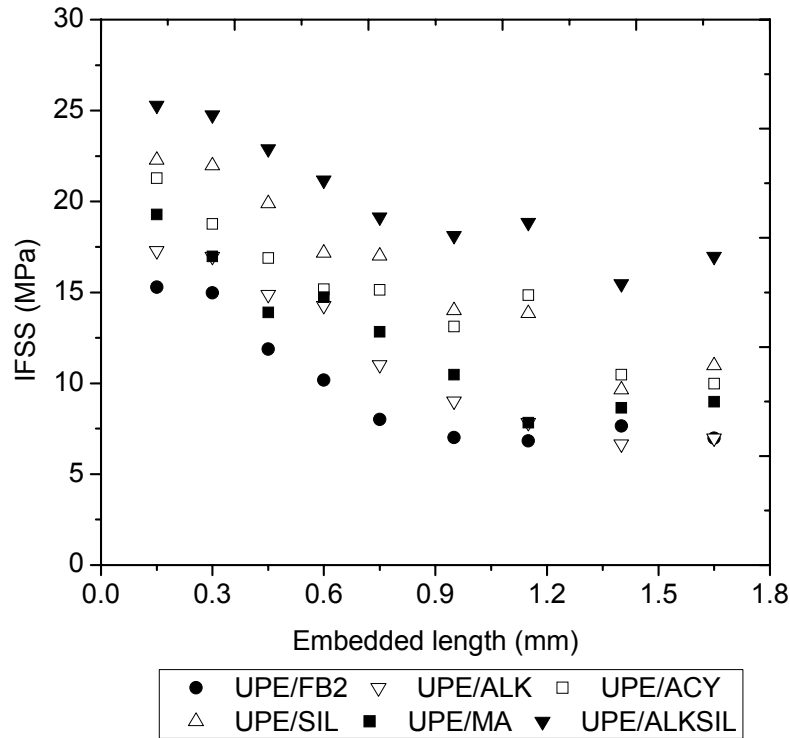


Figure 6.6: IFSS as a function of embedded length for UPE/hemp fibre (untreated and treated) samples.

The average IFSS of UPE/hemp fibre (untreated and treated) samples is shown in Figure 6.7. As can be seen, IFSS increased in the order: UPE/FB2 (9.9 MPa) < UPE/ALK (11.7 MPa) < UPE/ACY (12.6 MPa) < UPE/MA (15.1 MPa) < UPE/SIL (16.3 MPa) < UPE/ALKSIL (20.3 MPa). This trend was consistent with the level of esterification between the treated fibres and the UPE as seen in the FT-IR results (see section 6.2).

The IFSS results of UPE/hemp fibre samples are reasonable when compared with other studies on natural fibre/polyester samples. For instance, the IFSS of untreated flax fibre/UPE and alkali-acetic anhydride treated flax fibre/UPE samples was found to be 14.2 and 16.1 MPa (measured by microbond test), respectively, as reported by Baley *et al.* [99]. In another work, Joffe *et al.* [213] found that the IFSS (measured by single fibre

fragmentation test) of the silane treated flax fibre/polyester samples (22 MPa) improved by 22.2% compared with that for the untreated flax fibre/polyester samples (18 MPa).

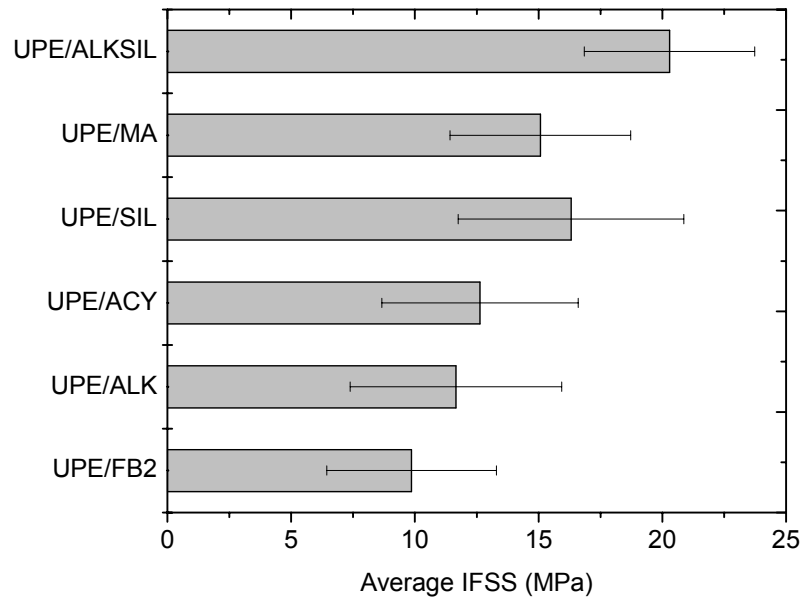


Figure 6.7: Average IFSS of UPE/hemp fibre (untreated and treated) sample.

6.4 Short hemp fibre reinforced unsaturated polyester (UPE) composites

6.4.1 Tensile properties

Typical tensile stress versus strain records for UPE and composites are presented in Figure 6.8. The matrix only sample initially showed linear behaviour, followed by nonlinear deformation. Once the stress reached maximum, the recorded stress dropped suddenly. The stress-strain curves of the composites showed knees (indicated by arrow) at relatively lower stress levels, which indicated the onset of microcracking [25] due to stress concentration from fibre ends [214] as observed on the fracture surfaces of composites (see Figure 6.9). The failure strain of the composites for all the fibre types (untreated and treated) was found to be lower than that of the matrix itself.

Figure 6.10 presents the average tensile strength as a function of fibre content for the random short fibre (untreated and treated) UPE composites. In the case of untreated hemp fibre/UPE composites (UPE/FB2), it can be observed that the tensile strength reached a minimum value at 20 wt% fibre content, thereafter increased with fibre content (20 to 50 wt%), except at the highest fibre content (60 wt%) where another decrease in the tensile

strength occurred. This trend of strength reduction at low fibre contents is well documented [215]. The minimum fibre volume fraction ($V_{f \min}$) to reinforce the matrix (i.e. strength higher than that of matrix) can be calculated using Equation 6.1 [215]:

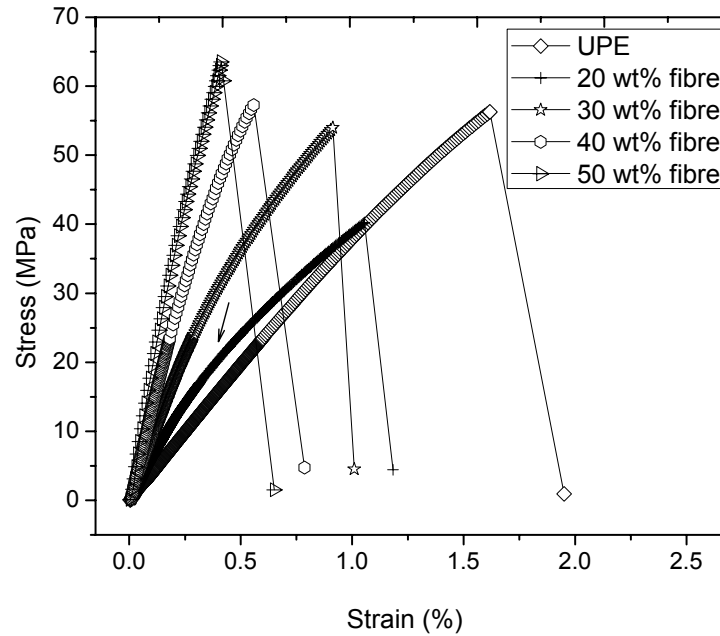


Figure 6.8: Typical tensile stress versus strain records for UPE/hemp fibre (ALKSIL) composites.

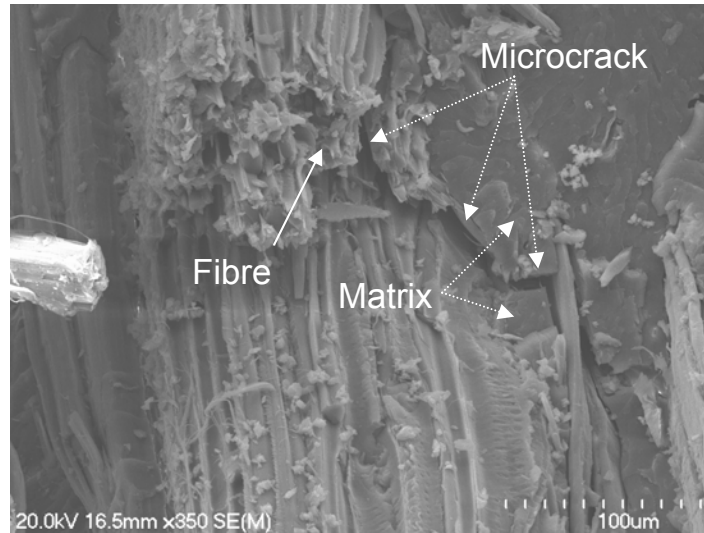


Figure 6.9 SEM micrograph of UPE/ALKSIL composite at 50 wt% fibres, showing the microcrack.

$$V_{f \min} = \frac{\sigma_m - \sigma_m^*}{K_1 K_2 \sigma_f - \sigma_m^*} \quad (6.1)$$

where σ_m is the tensile strength of matrix, σ_m^* is the strength of matrix at the failure strain of fibre, σ_f is the strength of fibre, K_1 is the fibre orientation and K_2 is the fibre length or stress transfer factor.

$$K_2 = l / (2l_c) \quad \text{for } l < l_c \quad (6.2)$$

$$K_2 = 1 - [l_c / (2l)] \quad \text{for } l \geq l_c \quad (6.3)$$

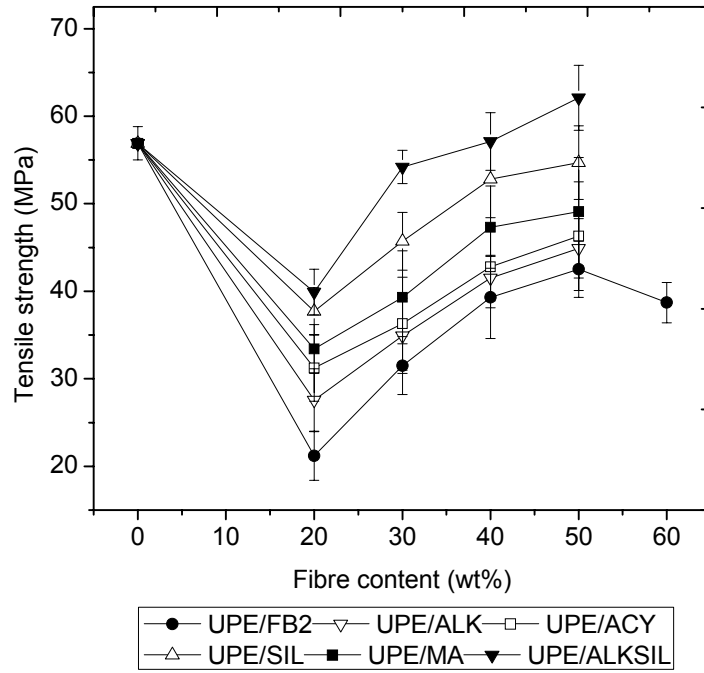


Figure 6.10: Tensile strength of UPE/hemp fibre (treated and untreated) composites as function of fibre content.

It has already been reported that for random short fibre composites the value of K_1 is 0.2 [22, 24, 133]. K_2 was obtained using Equations 2.6 and 6.3, and found to be approximately 0.96. By substituting these values for K_1 , K_2 and the average tensile strengths of UPE ($\sigma_m = 56.9$ MPa) and hemp fibres (from Figure 4.24) into Equation 6.1 (where σ_m^* was 51.1 MPa at the average fibre failure strain of 1.5%), $V_{f \min}$ was calculated to be approximately 10%, which would suggest that the strength should be higher than the matrix for all composites tested (16 to 42% by volume of fibre). However, of all the composites tested, the strength only exceeded that of the matrix for UPE/ALKSIL composites with highest IFSS at 33% by volume (40 wt%) fibre content. Stress

concentration due to the presence of fibre in conjunction with a brittle matrix could explain the reduction of tensile strength for composites compared to the unreinforced samples as seen in Figure 6.10. Since the failure strain of the hemp fibres (1-2%) was somewhat close or less than that of the UPE (about 1.95%), this would lead to UPE less effectively reinforced at relatively low strains, but riddled with stress concentrators (added to by the broken fibres) as can be seen in Figure 6.11. The decrease in tensile strength at the highest fibre content (60 wt% fibres) is believed to be due to insufficient matrix to wet the fibres as observed by SEM (see Figure 6.12).

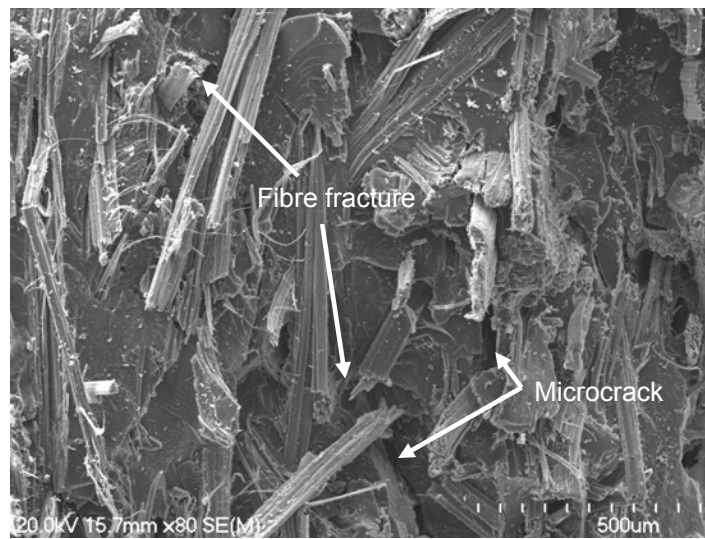


Figure 6.11: SEM micrograph of the tensile fracture surface of UPE/FB2 composites at 30 wt% fibres, showing fibre fracture.

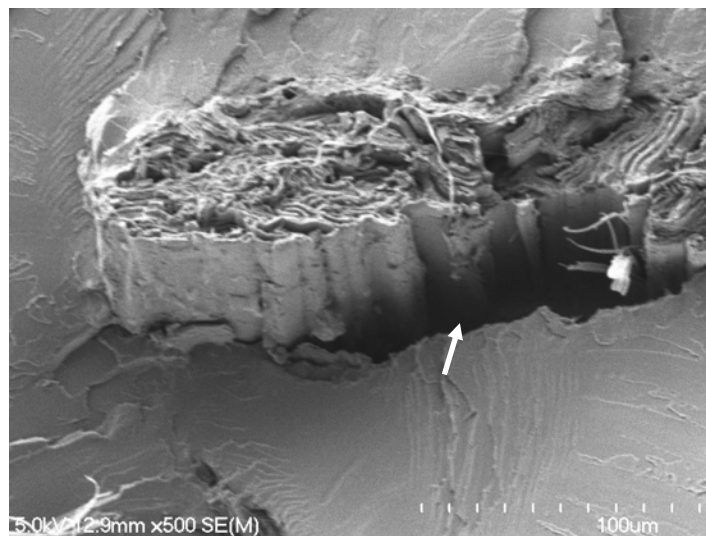


Figure 6.12: SEM micrograph of UPE/FB2 composites at 60 wt% fibres, showing poor wetting of fibre (indicated by arrow).

It is also evident (Figure 6.10) that tensile strength of UPE/hemp fibre composites (fibre content 20 to 50 wt%) improved after the treatment of fibres and increased in a similar order as seen for IFSS (see section 6.3). Of the various treatments, the alkali-silane treated fibre composites (UPE/ALKSIL) with 50 wt% fibres had the highest tensile strength of 62.1 MPa. Fracture surfaces of the UPE/ALKSIL composites (see Figure 6.13) showed that the fibre was well bonded to the matrix; fibre breakage and fibrillation took place during the fracture of specimens.

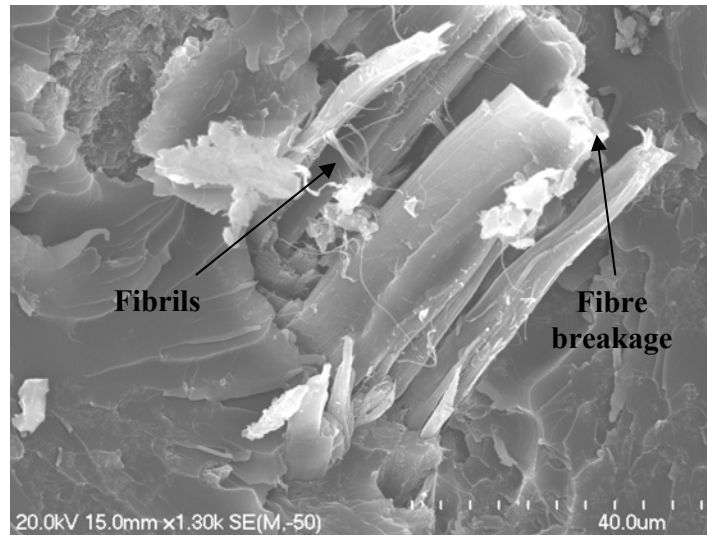


Figure 6.13: SEM micrograph of UPE/ALKSIL composite at 50 wt% fibres, showing strong bonding between fibre and matrix, fibrils and fibre breakage.

Figure 6.14 shows the average Young's modulus of hemp fibre/UPE composites as a function of fibre content. In the case of untreated fibre/UPE composites, Young's modulus increased with increased fibre content until it reached a maximum value at 50 wt% fibre content, and thereafter decreased at the highest fibre content (60 wt%). The decrease in Young's modulus at the highest fibre content could again be explained by the inefficient stress transfer from matrix to fibres due to the insufficient amounts of resin to wet the fibres thoroughly. It can also be seen that the Young's modulus of hemp fibre/UPE composites improved after the treatment of the fibres. This could be explained again by the better bonding between the treated fibres and UPE, which caused effective stress transfer from the matrix to the fibres. Like tensile strength, the highest improvement in Young's modulus was found for the UPE/ALKSIL composites. The UPE/ALKSIL composites with 50 wt% fibres had the highest Young's modulus of 13.35 GPa. This result was better than

any reported Young's modulus for short natural fibre reinforced polyester composites [64, 105, 107, 216].

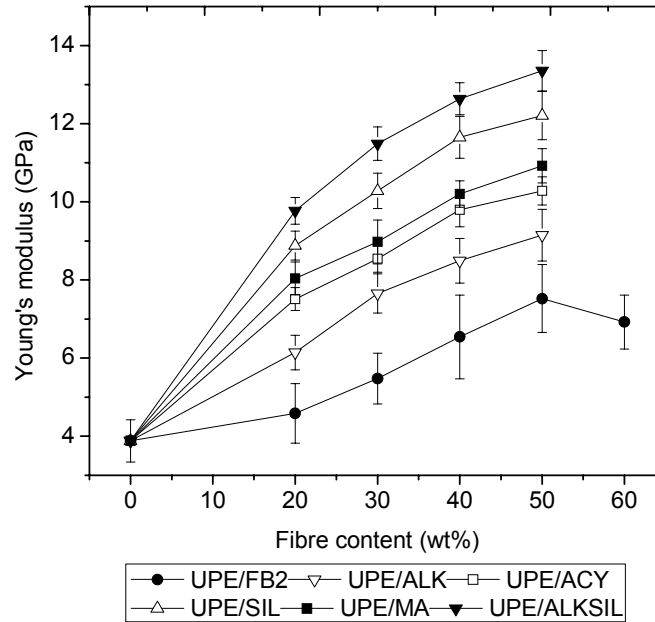


Figure 6.14: Young's modulus of different treated and untreated hemp fibre/UPE composites as function of fibre content.

The average failure strain of UPE/hemp fibre composites as a function of fibre content is depicted in Figure 6.15. It can be seen that failure strain for both untreated and treated fibre composites (between 0.45 and 0.83%) decreased dramatically compared to unreinforced UPE (1.95%), a finding similar to that for PLA/hemp fibre composites (see section 5.6.1). The reduction in failure strain of the composites could be due matrix cracking due to stress concentrations caused by reinforcing fibres as discussed in section 5.6.1. No general trend was apparent for the failure strain with respect to fibre content, which could be due to variability of fibre dispersion.

Plotting tensile strength of UPE/hemp fibre composites versus fibre (untreated and treated) strength demonstrated no obvious trend (see Figure 6.16). This indicates that, including fibre strength, the other major factor, namely IFSS of composites, has influenced composite strength. This observation justifies the use of fibre treatment for improvement of IFSS in order to produce strong and stiff UPE/hemp fibre composites.

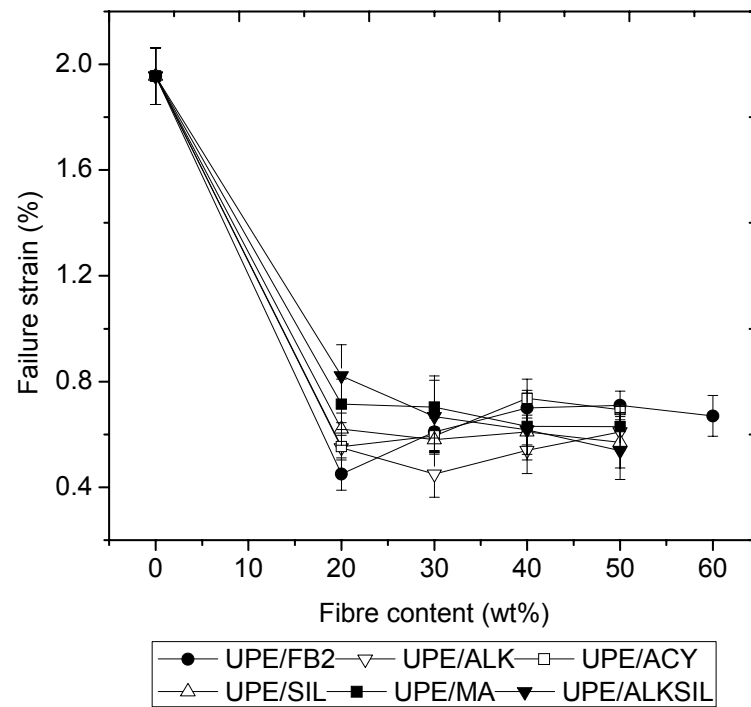


Figure 6.15: Failure strain of different treated and untreated hemp fibre/UPE composites as function of fibre content.

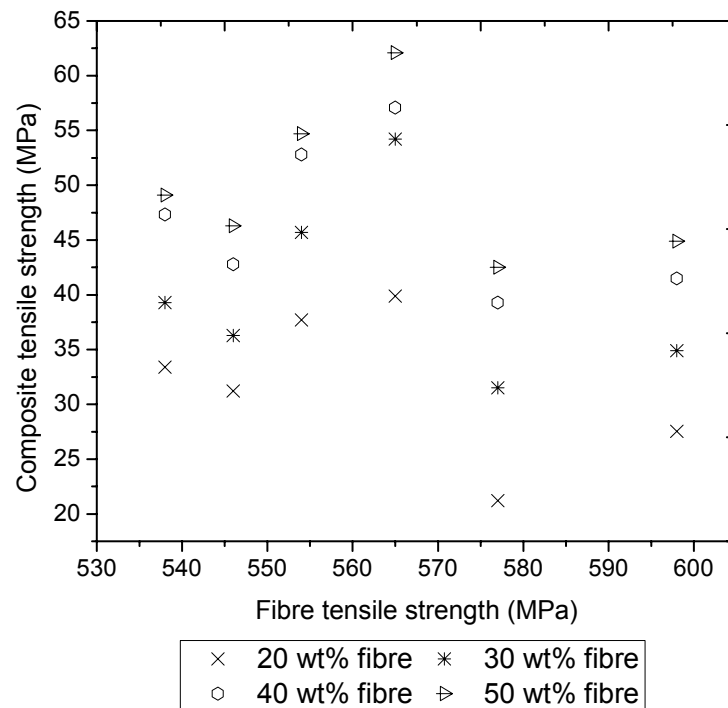


Figure 6.16: Tensile strength of UPE/hemp fibre composites versus fibre (untreated and treated) strength.

6.4.2 Flexural properties

Typical flexural stress versus deflection graphs for the UPE/hemp fibre composites are presented in Figure 6.17. Both the unreinforced UPE and composite samples showed initially linear deformation followed by non-linear deformation before reaching maximum stress. Once the maximum stress was attained, the recorded stress diminished gradually for composites but more dramatically for unreinforced UPE.

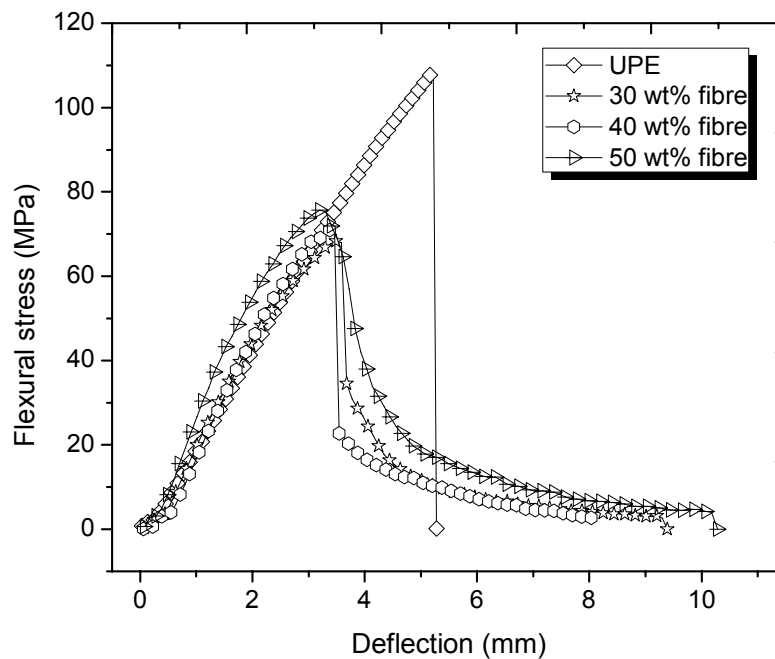


Figure 6.17: Typical flexural stress-deflection records of UPE/hemp fibre composites (UPE/ALKSIL) in three point flexure.

The average flexural strength of UPE/hemp fibre (untreated and treated) composites as a function of fibre content is presented in Figure 6.18. The flexural strength decreased with increased fibre content (0 to 50 wt%) as observed for the PLA/hemp fibre composites. The reason for this may again be attributed to the increase of a population of fibre defects with increased fibre content. These fibre defects (e.g. kinks) could act as a source of stress concentration in composites, as supported by the SEM micrograph (see Figure 6.19). Flexural strength of the treated fibre composites was higher than that of the untreated fibre composites. Among all the treated fibre composites, the ALKSIL fibre reinforced composites had the highest flexural strength at all fibre contents as for tensile strength.

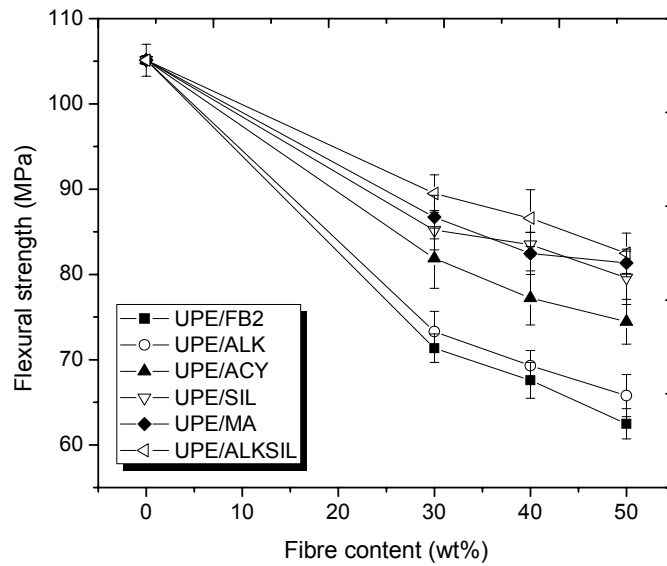


Figure 6.18: Flexural strength of untreated and treated hemp fibre/UPE composites as a function of fibre content.



Figure 6.19: SEM micrograph for flexural tested fracture surface of UPE/FB2 composites showing kinks (indicated by arrows).

The relationship between average flexural modulus and fibre content is shown in Figure 6.20. As expected, flexural modulus of the composites increased with increased fibre content. It can also be seen that the flexural modulus of hemp fibre/UPE composites improved after the treatment of fibres. In general, the flexural modulus of the composites with different treated fibres increased in a similar order as seen for the IFSS such that the ALKSIL fibre reinforced composites with 50 wt% fibres had the highest flexural modulus

of 6.1 GPa. This result was better than any reported flexural modulus for the short natural fibre reinforced polyester composites [64, 104, 105, 107].

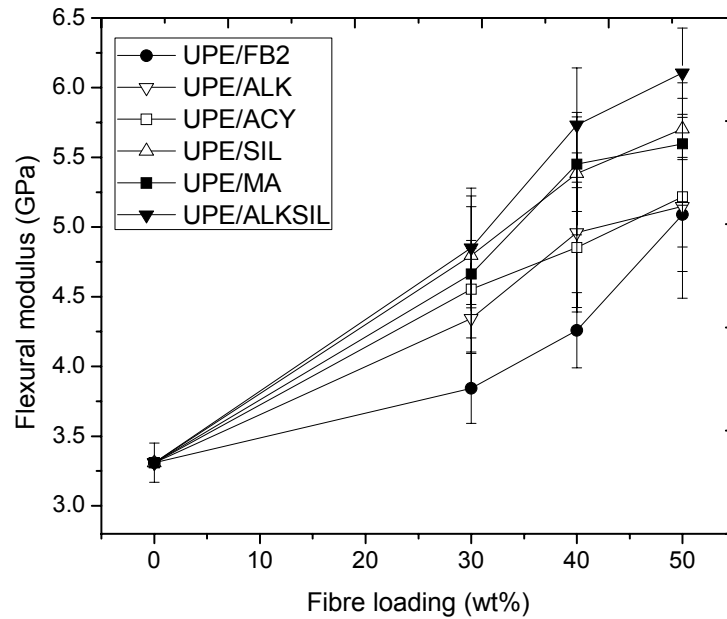


Figure 6.20: Flexural modulus of untreated and treated hemp fibre reinforced UPE composites as a function of fibre content.

6.4.3 Impact strength

The average impact strength of UPE/hemp fibre composites (notched samples) as a function of fibre content is presented in Figure 6.21. As can be observed, the impact strength of composites gradually increased with increased fibre content, a finding similar to that for PLA/hemp fibre composites (see section 5.6.5). It is also evident that impact strength of all the treated fibre composites was higher than that of the untreated fibre composites at all fibre contents. These findings were in general agreement with other researchers [105]. Similar to tensile and flexural properties, the UPE/ALKSIL composites with 50 wt% fibres had the highest impact strength of 7.1 kJ/m².

Figure 6.22 presents SEM micrographs of the fracture surfaces of impact tested silane treated fibre composites (UPE/SIL and UPE/ALKSIL). Fibre fibrillation occurred for all treated fibre reinforced UPE composites similar to strongly bonded PLA/ALK composites (see section 5.6.5), which corroborates the above improvements in impact strength of the treated fibre UPE composites compared to the untreated fibre UPE composites.

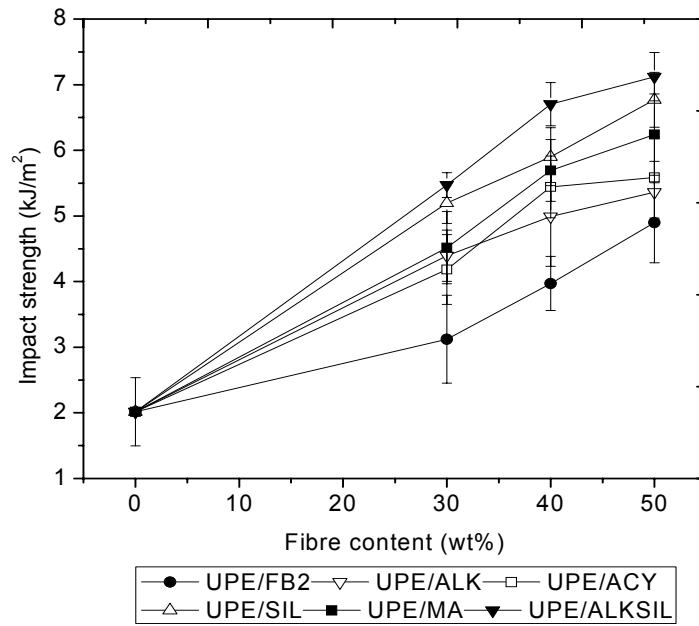


Figure 6.21: Impact strength of untreated and treated hemp fibre/UPE composites (notched samples) as a function of fibre content.

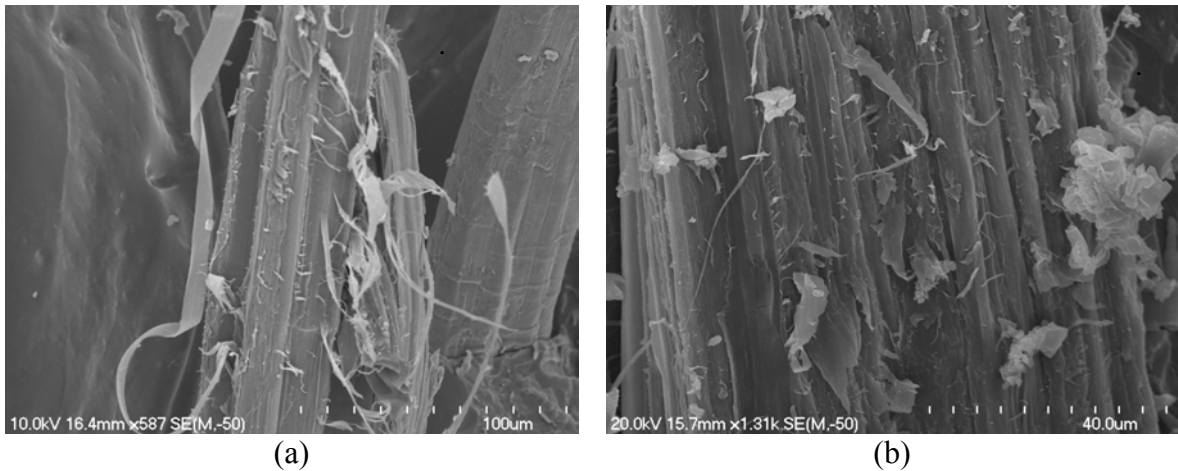


Figure 6.22: SEM micrographs of the impact fracture surface of (a) UPE/SIL and (b) UPE/ALKSIL composites showing the fibrillation of fibres due to fracture.

6.4.4 Fracture toughness

Typical load-displacement records of single-edge-notch bend (SENB) tests for the UPE and UPE/hemp fibre composites are presented in Figure 6.23(a). It may be observed that, as for the flexural tests, initially the samples deformed linearly, followed by nonlinear deformation prior to the attainment of maximum load. Once the maximum load was attained, the recorded load diminished gradually for composites but more dramatically for

unreinforced UPE. When a line (AC) was drawn with a gradient of 5% less than that of the tangent (AB) to the original loading line [see Figure 6.23(b)], the recorded maximum load was found to lie between two lines which met the requirement of standard [217] to allow maximum load to be used for the calculation of K_{Ic} and G_{Ic} (see section 3.4.7.4).

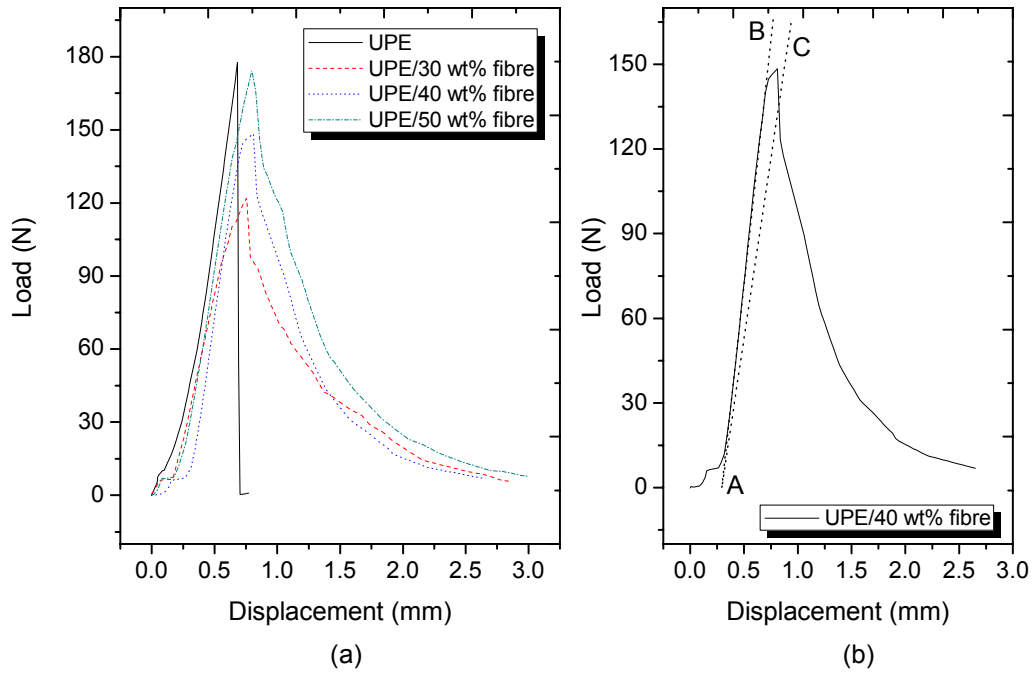


Figure 6.23: Typical load-displacement curves for SENB tests of UPE/FB2 samples.

The average plane strain fracture toughness (K_{Ic}) and the strain energy release rate (G_{Ic}) of the UPE/hemp fibre composites as a function of fibre content are presented in Figures 6.24 and 6.25, respectively. The average K_{Ic} and G_{Ic} of the UPE only samples was determined to be $1.76 \text{ MPa}\cdot\text{m}^{1/2}$ and 3.21 kJ/m^2 , respectively. K_{Ic} of the UPE only samples was found to be very close to the value reported by other researchers for thermoset polyester ($1.92 \text{ MPa}\cdot\text{m}^{1/2}$) [218]. As can be seen, K_{Ic} and G_{Ic} of the composites appeared to reach a minimum value at 30 wt% fibre content, and thereafter increased with increased fibre content. When compared with the UPE only samples, the initial decrease in K_{Ic} and G_{Ic} of the composites (at 30 wt% fibre content) could be due to increase in stress concentration points (number of fibres) in the samples. For higher fibre loads (40 and 50 wt%), the increase in K_{Ic} and G_{Ic} could be due to increased debonding (i.e. energy absorption) as the fibre content increased because more and more fibres being available to

pull out as the crack surfaces separated. Hence, the total energy absorption increased with increased fibre content [181]. Friedrich [130] also found a similar trend in fracture toughness (K_{Ic}) of glass fibre reinforced polyethylene terephthalate composites.

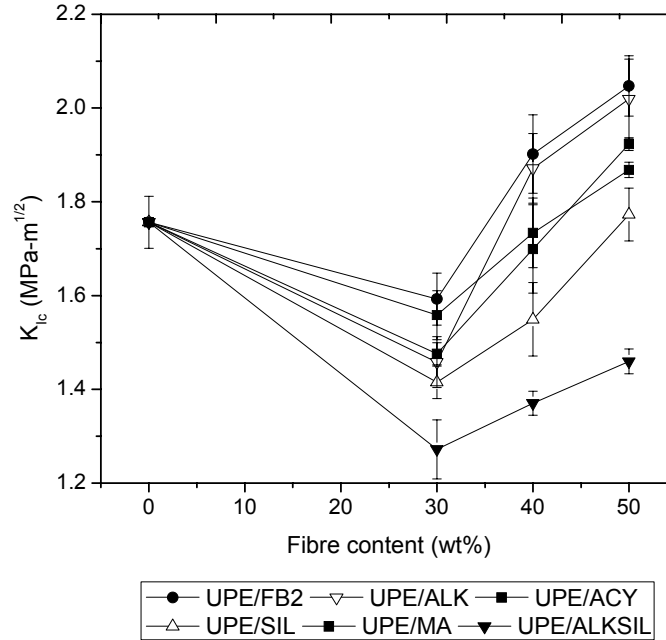


Figure 6.24: K_{Ic} of untreated and treated hemp fibre reinforced UPE composites as a function of fibre content.

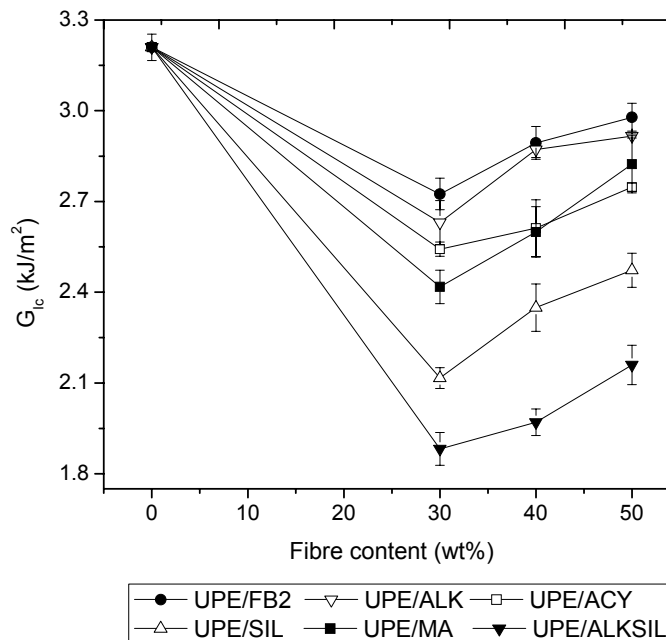
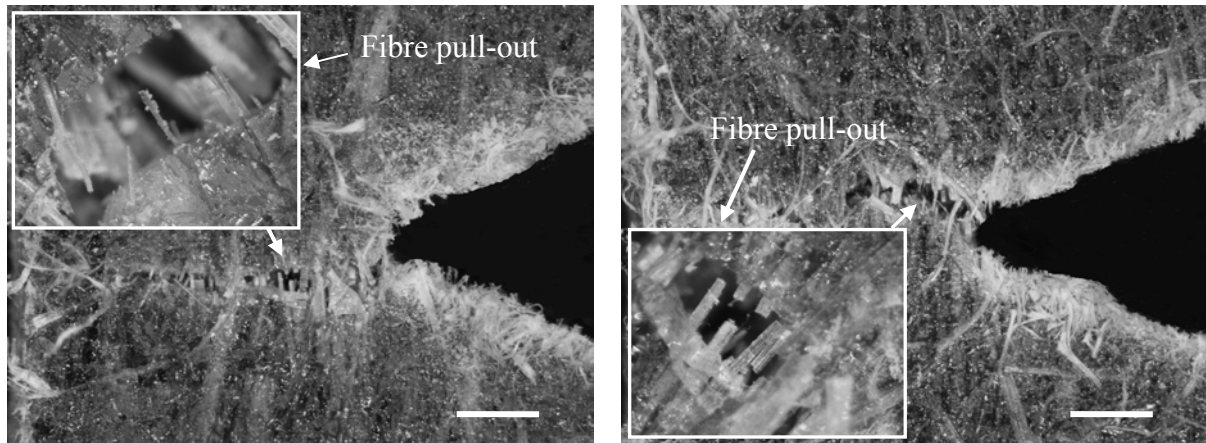


Figure 6.25: G_{Ic} of untreated and treated hemp fibre reinforced UPE composites as a function of fibre content.

It can also be observed that the average K_{Ic} and G_{Ic} of the treated hemp fibre/UPE composites were lower than those of the untreated fibre/UPE composites at all fibre contents. This is likely to be because the interfacial strength between hemp fibre and UPE matrix increased due to the treatment of fibres (see section 6.3), which promoted crack propagation in the composites during testing. Indeed more fibre pull-out was observed for the untreated fibre composites compared to those of the treated fibre composites (see Figure 6.26).



(a) UPE/ALKSIL composites (50 wt% fibre)

(b) UPE/FB2 composites (50 wt% fibre)

Figure 6.26: Optical light micrographs of hemp fibre/UPE composites showing the fracture behaviour of SENB test samples (scale bar = 1 mm).

6.4.5 Relationships between IFSS with tensile strength, flexural strength, impact strength and plane strain fracture toughness of short hemp fibre/UPE composites

In Figures 6.27 to 6.29, the tensile, impact and flexural strength of the untreated and treated short fibre reinforced UPE composites can be seen to increase, approximately, linearly with increased IFSS. In fact this behaviour was expected because a strong interface is favourable for transmitting the applied load effectively from the matrix to fibres, which in turn enhances the composite strength. Figure 6.30 shows that the plane strain fracture toughness (K_{Ic}) of the composites decreased with increased IFSS. This can be explained due to a strong interface with a high value of IFSS encouraging crack propagation as mentioned earlier (see section 5.6.7). The above trends in tensile strength, flexural strength, impact strength and plane strain fracture toughness with respect to IFSS for the

short fibre UPE composites were consistent with the short fibre reinforced PLA composites (see section 5.6.7).

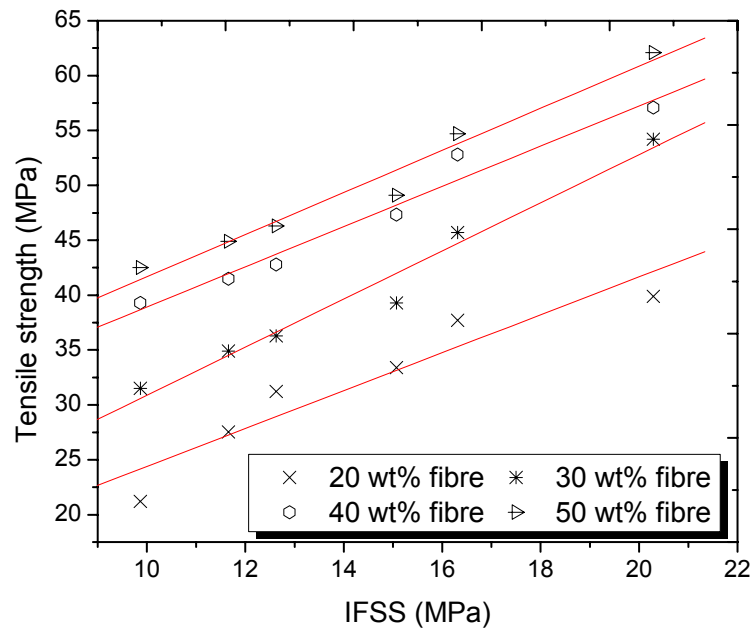


Figure 6.27: Relationship between tensile strength and IFSS of untreated and treated short fibre reinforced UPE composites.

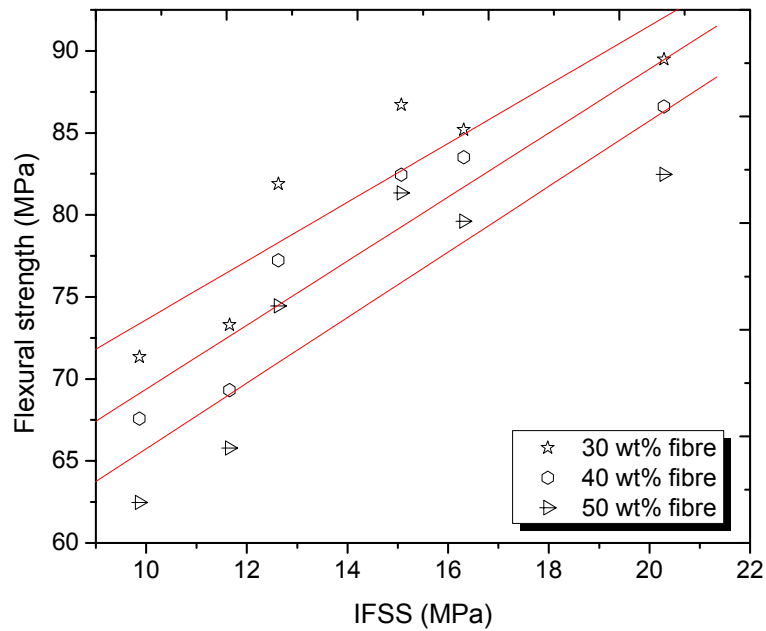


Figure 6.28: Relationship between flexural strength and IFSS of untreated and treated short fibre reinforced UPE composites.

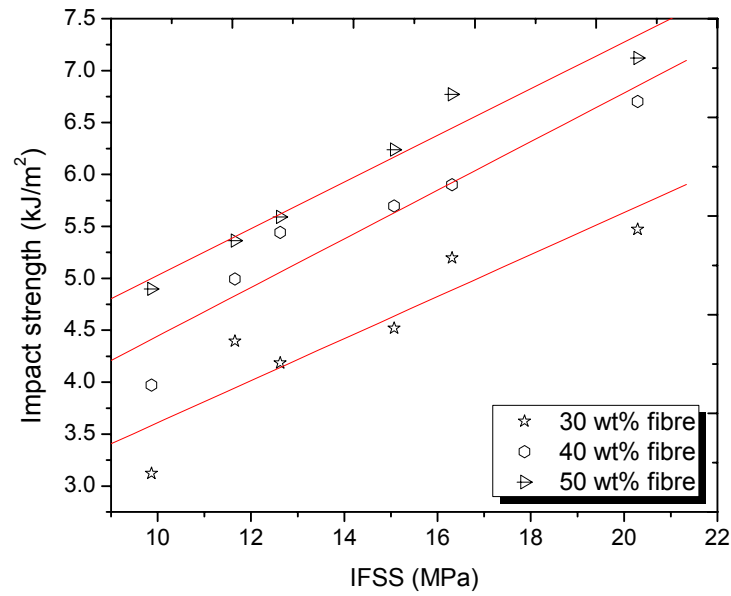


Figure 6.29: Relationship between impact strength and IFSS of untreated and treated short fibre reinforced UPE composites.

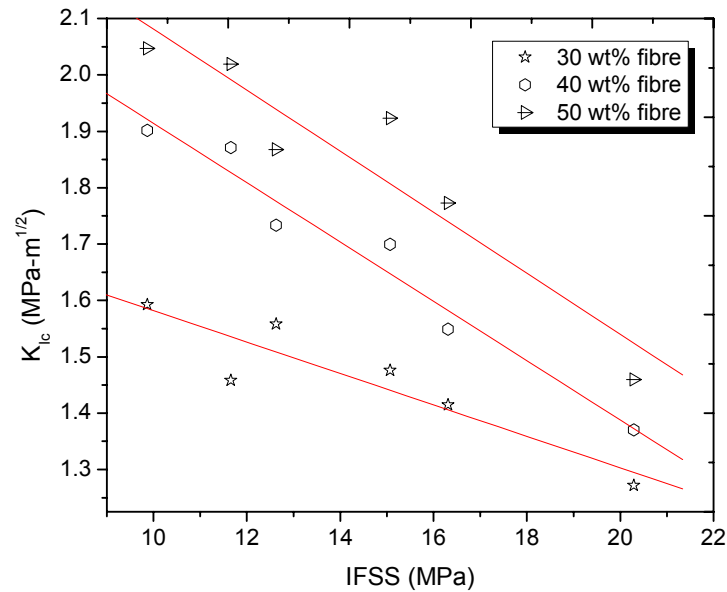


Figure 6.30: Relationship between K_{Ic} and IFSS of untreated and treated short fibre reinforced UPE composites.

6.4.6 Dynamic mechanical thermal analysis (DMTA)

The effect of fibre content on the storage modulus (E'), loss modulus (E'') and damping factor ($\tan \delta$) of the combined alkali and silane treated fibre reinforced UPE composites

(UPE/ALKSIL) is presented in Figures 6.31, 6.32 and 6.33, respectively. In Figure 6.31, as expected, the E' of the composites was greater at all temperatures compared with that of the UPE only samples. E' for all samples decreased gradually with increased temperature. This trend was more prominent above the glass transition region, T_g (around 95°C) which is likely to be due to increased mobility of polymer networks. In composite samples, the mobility of polymer networks was restricted at higher temperatures due to the presence of fibres, so the E' of the composites was higher than that of the unreinforced UPE at high temperatures. It can also be observed that the E' of the composites increased with increased fibre content (see Table 6.1), a trend similar to that for Young's modulus (see section 6.4.1). This finding was also consistent with the PLA/hemp fibre composites (see section 5.6.9).

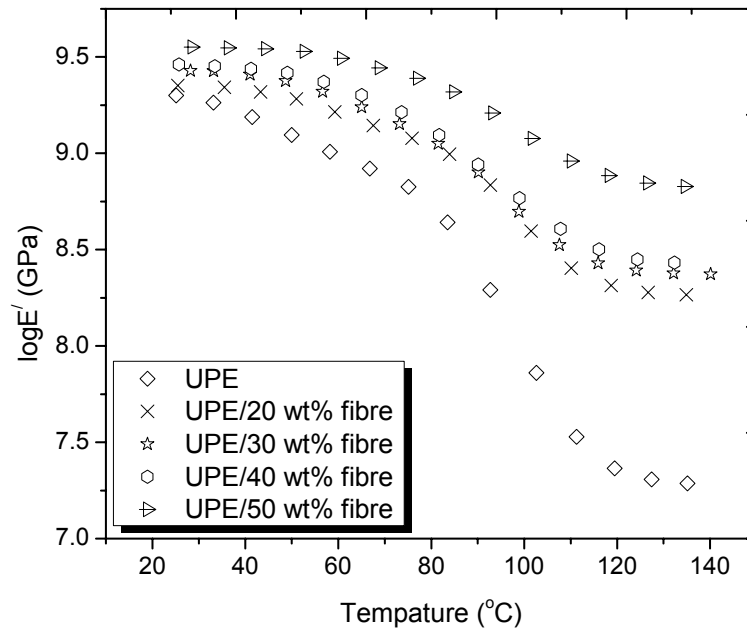


Figure 6.31: Effect of fibre content on the storage modulus of UPE/ALKSIL composites as a function of temperature.

The variation of loss modulus (E'') with temperature at different fibre content is presented in Figure 6.32. It can be observed that the E'' of the samples did not change significantly with respect to the temperature until it reached the T_g region (around 95°C). Further increase in temperature caused a gradual decrease in the E'' . This could again be explained by the increased flexibility of polymer networks above T_g . T_g of the unreinforced and reinforced samples did not change markedly with increased fibre content,

a finding similar to that for PLA/hemp fibre composites. It can also be seen that E'' around the T_g region broadened with increased fibre content which was consistent with the PLA/hemp fibre composites (see section 5.6.9).

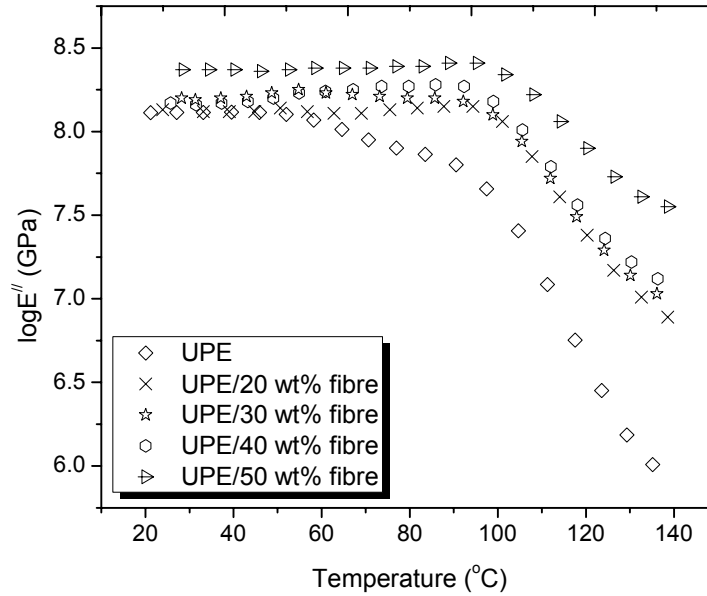


Figure 6.32: Effect of fibre content on the loss modulus of UPE/ALKSIL composites as a function of temperature.

The variation of $\tan \delta$ of the composites as a function of temperature is presented in Figure 6.33. As can be seen, the maximum height of $\tan \delta$ ($\tan \delta_{\max}$) decreased with increased fibre content (see Table 6.1), which could again be due to the restricted molecular mobility of polymer networks in the presence of fibres as mentioned earlier (see section 5.6.9). It can also be seen that the position of $\tan \delta$ peak with respect to temperature did not change significantly with increased fibre content, a finding consistent with other research work [207].

Table 6.1: E' and $\tan \delta$ for UPE/ALKSIL composites at different fibre contents.

Fibre content	E' (GPa) at 27°C	$\tan \delta_{\max}$
0	2.10	0.532
20	2.23	0.281
30	2.50	0.246
40	2.59	0.228
50	3.50	0.223

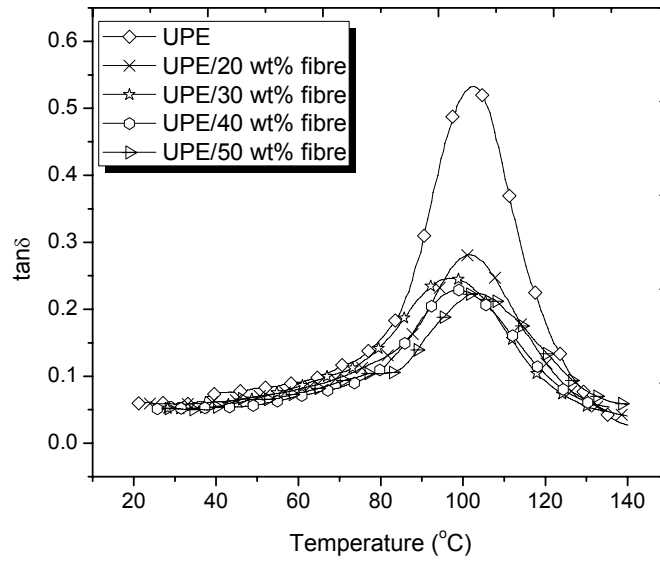


Figure 6.33: Effect of fibre content on the damping factor of UPE/ALKSIL composites as a function of temperature.

Figure 6.34 shows the E' as a function of temperature for the treated fibre/UPE composites at 50 wt% fibre content. The general declining trend of the E' with respect to temperature for the treated fibre composites was fairly similar to that of the untreated fibre composites. As can be observed, E' of the composites improved after the treatment of fibres (see Table 6.2), which was consistent with the interfacial strength results (see section 6.3).

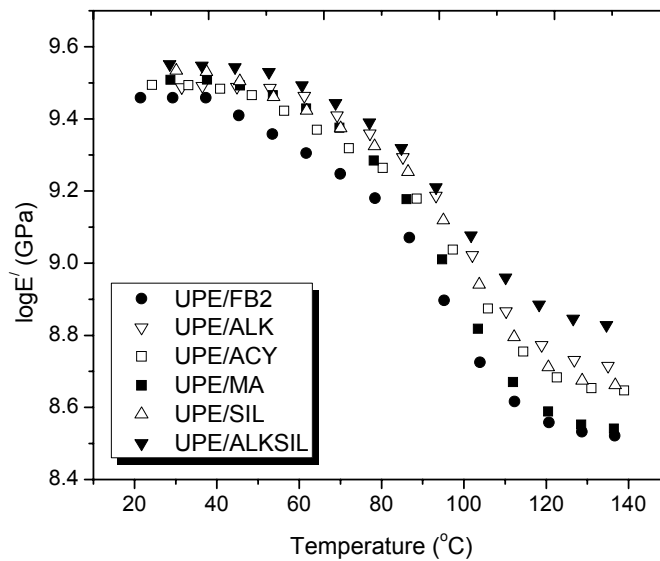


Figure 6.34: Effect of fibre treatment on the storage modulus of UPE/hemp fibre composites as a function of temperature (50 wt% fibre).

Figure 6.35 illustrates the E'' as a function of temperature for the treated fibre/UPE composites at 50 wt% fibre content. Similar to the E' , the E'' of different treated fibre composites did not change significantly with respect to the temperature until they reached the T_g region (around 95°C), then decreased abruptly. No significant change in T_g was noticed for the treated fibre composites when compared with those of the untreated fibre composites.

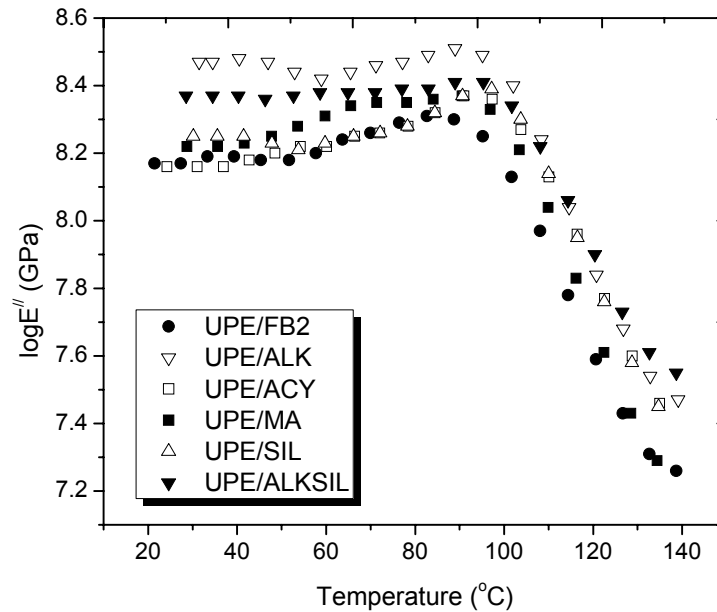


Figure 6.35: Effect of fibre treatment on the loss modulus of UPE/hemp fibre composites as a function of temperature (50 wt% fibre).

Figure 6.36 presents the $\tan \delta$ curves of the treated fibre composites as a function of temperature. It shows that the change in temperature and variation of fibre treatment affected the damping nature of the composites. The $\tan \delta$ peak of the treated fibre composites was found to be shifted to some extent when compared to the untreated fibre composites (UPE/FB2). This shift indicates better fibre/matrix interfacial strength in the treated fibre composites [219]. The maximum $\tan \delta$ value ($\tan \delta_{\max}$) of the composites was also found to depend on fibre treatment (see Table 6.2) and highest for untreated fibre composites, which again indicated that the interfacial strength between hemp fibres and UPE improved due to the treatment of the fibres; strong fibre/matrix interfacial adhesion tends to reduce the molecular motions at the interface, therefore reduces the damping, as mentioned previously (see section 5.6.9).

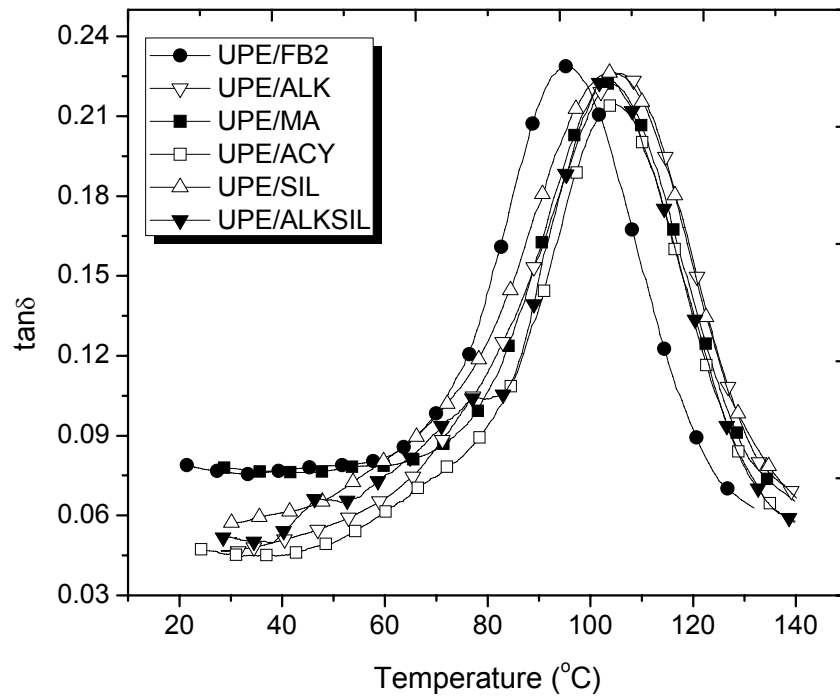


Figure 6.36: Effect of fibre treatment on the damping factor ($\tan \delta$) of UPE/hemp fibre composites as a function of temperature (50 wt% fibre).

Table 6.2: E' and $\tan \delta_{\max}$ for untreated and treated hemp fibre/UPE composites.

Sample	E' (GPa) at 27°C	$\tan \delta_{\max}$
UPE	2.10	0.532
UPE/FB2	3.03	0.227
UPE/ALK	3.10	0.226
UPE/ACY	3.13	0.214
UPE/MA	3.22	0.221
UPE/SIL	3.40	0.225
UPE/ALKSIL	3.50	0.223

6.5 Aligned long hemp fibre reinforced UPE composites

Combined alkali and silane treated random short fibre composites (UPE/ALKSIL) had the best mechanical properties as discussed so far. Similar to PLA/hemp fibre composites, aligned long fibres (ALKSIL) were used to further improve the mechanical properties of UPE/ALKSIL composites. The composites were fabricated according to the method described in section 3.3.2.4.

6.5.1 Tensile properties

Figure 6.37 shows the average tensile strength, Young's modulus and failure strain of aligned long fibre composites (UPE/ALKSIL) as a function of fibre content. Tensile properties of the random short fibre composites (UPE/ALKSIL) are shown for comparison. It can be seen that the tensile strength increased from 56.9 to 83 MPa for long fibre composites as the fibre content increased from 0 to 50 wt%. Similarly, the Young's modulus of the long fibre composites increased from 3.9 to 14.4 GPa as the fibre content increased from 0 to 50 wt%. It can be seen that composites with long fibres had better tensile strength and Young's modulus compared to the short fibre composites at all fibre contents. This superior tensile strength and Young's modulus of long fibre composites compared to short fibre composites would be expected as a result of fibre alignment in the loading direction and better load bearing efficiency (less fibre ends). It was found that failure strain of the long fibre composites decreased from 1.95 to 1.01% as the fibre content increased from 0 to 50 wt% and was higher than that of short fibre composites at all fibre contents.

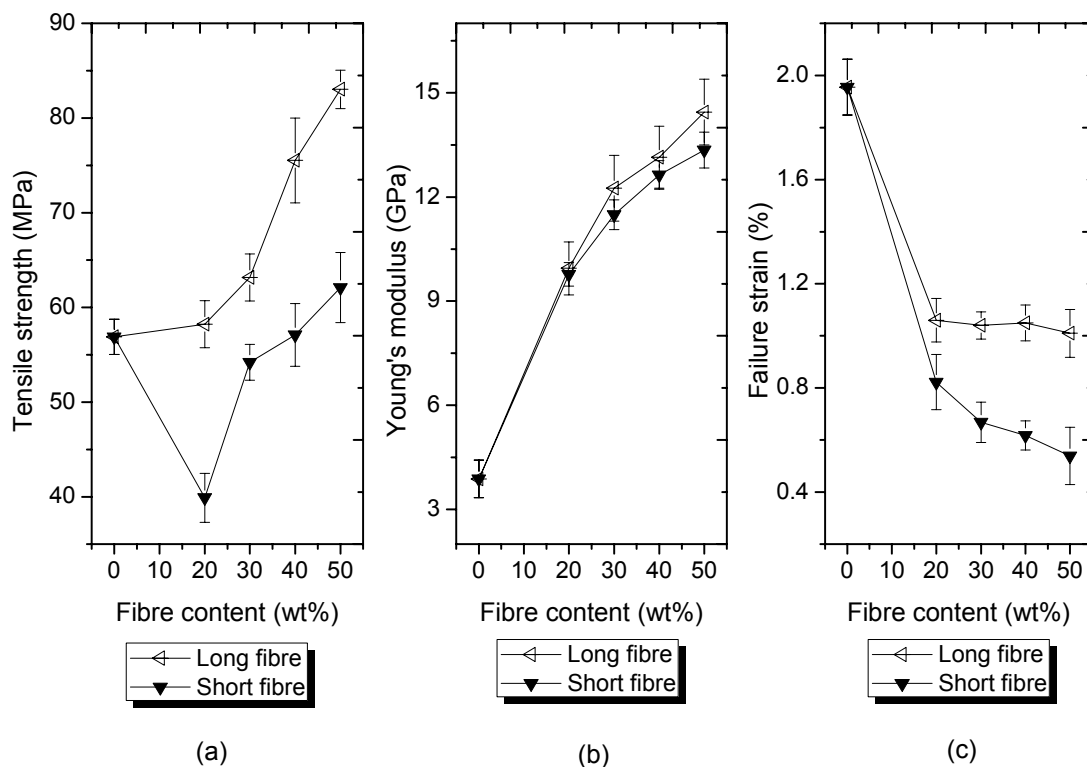


Figure 6.37: Tensile strength, Young's modulus and failure strain of the long fibre composites (UPE/ALKSIL) as a function of fibre content.

6.5.1.1 Comparison between the theoretical and experimental tensile strength

Figure 6.38 shows the tensile strength of the aligned long fibre composites (UPE/ALKSIL) obtained using the MROM model (see Equation 2.10) as a function of fibre volume fraction (V_f), along with the experimentally obtained values. The stress transfer factor $K_2 = 0.21$ (assuming orientation factor, $K_1 = 1$) gave the best fit with experimentally obtained tensile strength. As can be seen, there was a negative deviation of the experimental tensile strength from the theoretical tensile strength at lower V_f (0.155 to 0.329). This behaviour could again be explained by the misalignment of fibres due to tangling of long fibres, even though the fibre was carded. At higher V_f , higher alignment would be expected due to constraint by neighbouring fibres giving better reinforcement efficiency.

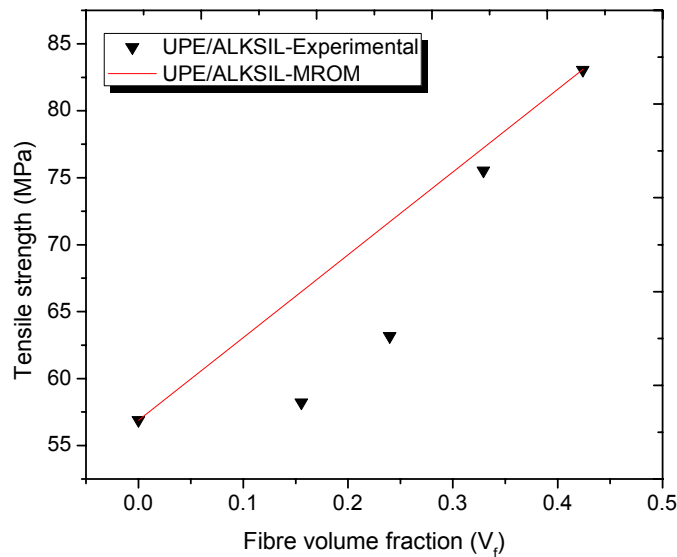


Figure 6.38: Comparison of between predicted (by MROM) and experimental tensile strength of long fibre composites (UPE/ALKSIL).

6.5.2 Flexural properties

Figure 6.39 shows the average flexural strength and flexural modulus of the aligned long fibre composites (UPE/ALKSIL) as a function of fibre content. Flexural strength and flexural modulus of the random short fibre composites (UPE/ALKSIL) are shown for comparison. As can be seen, flexural strength of the aligned long fibre composites decreased from 105.1 to 87.5 MPa as the fibre content increased from 0 to 50 wt%. On the

other hand, flexural modulus of the long fibre composites increased from 3.3 to 6.7 GPa as the fibre content increased from 0 to 50 wt%. The above trends in flexural strength and flexural modulus of the long fibre composites were consistent with the random short fibre UPE composites. Flexural strength and flexural modulus of the long fibre composites was higher than those of the short fibre composites at all fibre contents. This flexural behaviour of the UPE/hemp fibre composites was consistent with the PLA/hemp fibre composites (see section 5.6.4 and 5.7.2).

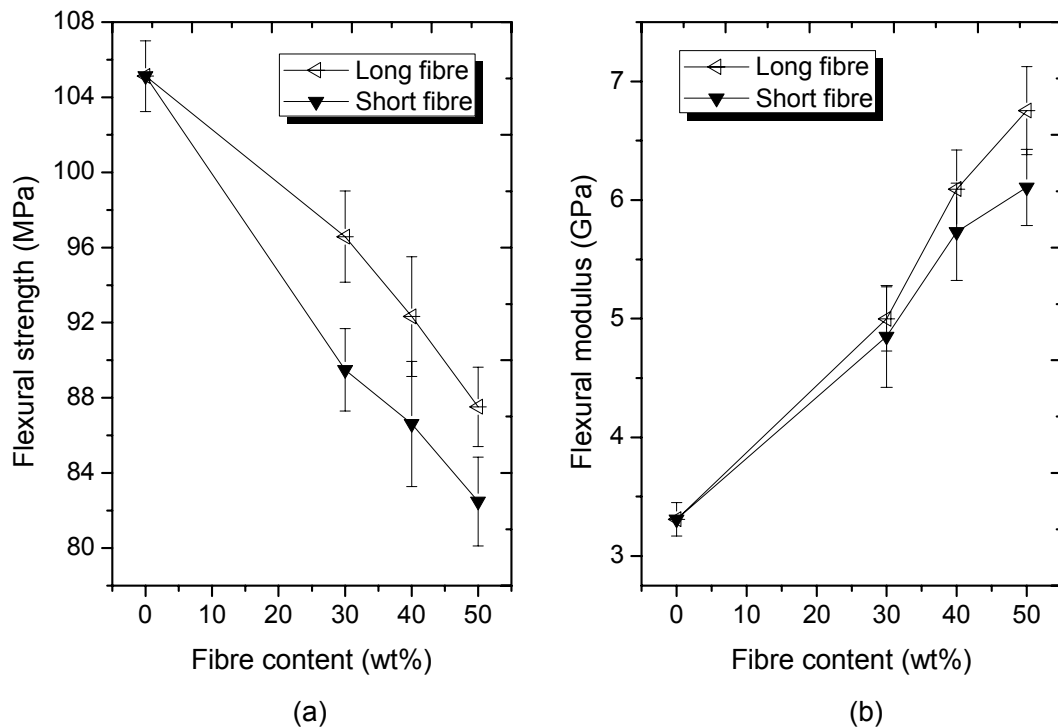


Figure 6.39: Flexural strength and flexural modulus of the long fibre composites (UPE/ALKSIL) as a function of fibre content.

The fracture surfaces of aligned long fibre UPE composites (see Figure 6.40) as for short fibre UPE composites, and short and long fibre PLA composites supported the possibility that defects (i.e. kinks) in the fibre induce stress concentration points during flexural loading.



Figure 6.40: SEM micrograph of flexural tested long fibre composites (UPE/ALKSIL) showing kinks (indicated by arrow).

6.5.3 Impact strength

Figure 6.41 presents impact strength of the long fibre composites (UPE/ALKSIL) as a function of fibre content. Impact strength of the random short fibre composites (UPE/ALKSIL) composites are shown for comparison. As can be seen, impact strength of the long fibre composites (UPE/ALKSIL) increased with increased fibre content similar to that of short fibre composites. Examination of composite fracture surfaces (see Figure 6.42) indicated that fibrillation occurred during impact loading, a finding similar to short fibre UPE (see section 6.4.3) and, short and long fibre PLA composites (see sections 5.6.5 and 5.7.3). The highest impact strength was found to be 15.85 kJ/m^2 for composites reinforced with 50 wt% fibre. It is also evident that the impact strength of long fibre composites was higher than that of short fibre composites, which was similar to the PLA/hemp fibre composites. This could be explained by the greater resistance to crack propagation in the composites due to the alignment of long fibres perpendicular to the direction of impact loading [207].

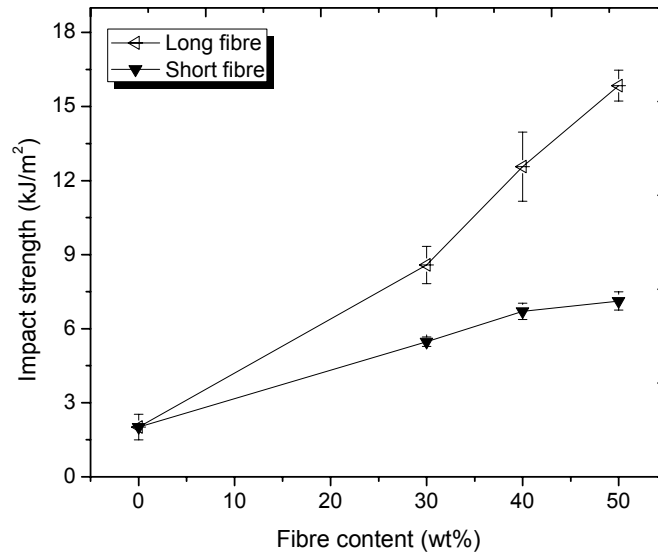


Figure 6.41: Impact strength of the long fibre composites (UPE/ALKSIL) as a function of fibre content.

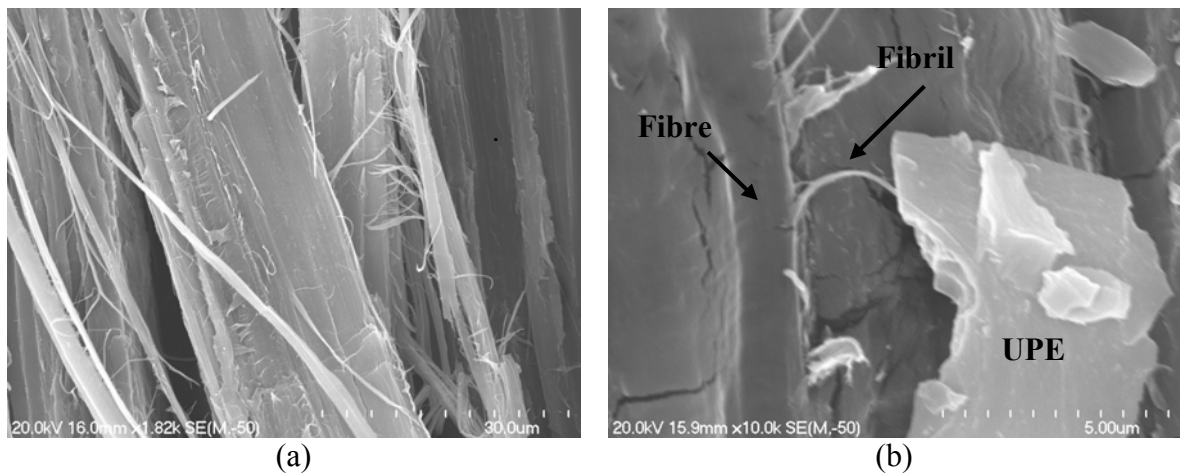


Figure 6.42: SEM micrographs of the impact fracture surface of long fibre UPE/ALKSIL composites (50 wt% fibre).

6.5.4 Fracture toughness

Figure 6.43 shows K_{Ic} and G_{Ic} of the long fibre composites (UPE/ALKSIL) as a function of fibre content. K_{Ic} and G_{Ic} of the random short fibre composites (UPE/ALKSIL) composites are shown for comparison. K_{Ic} of long fibre composites increased from 1.75 to 2.87 MPa-m^{1/2} as the fibre content increased from 0 to 50 wt%. Similarly, G_{Ic} of the long composites increased from 3.21 to 4.25 kJ/m² as the fibre content increased from 0 to 50 wt%. This could be explained by the increase in resistance to crack propagation with

increased fibre content due to the alignment of fibres. Indeed, fibre bridging (see Figure 6.44) was seen to increase with increased fibre content. This was consistent with the long fibre/PLA composites (see section 5.7.4). It is also apparent that K_{Ic} and G_{Ic} of the long fibre composites were significantly higher than those of the short fibre composites. This could be due to fewer stress concentration points (number of fibre ends) in the long fibre composites compared to the short fibre composites.

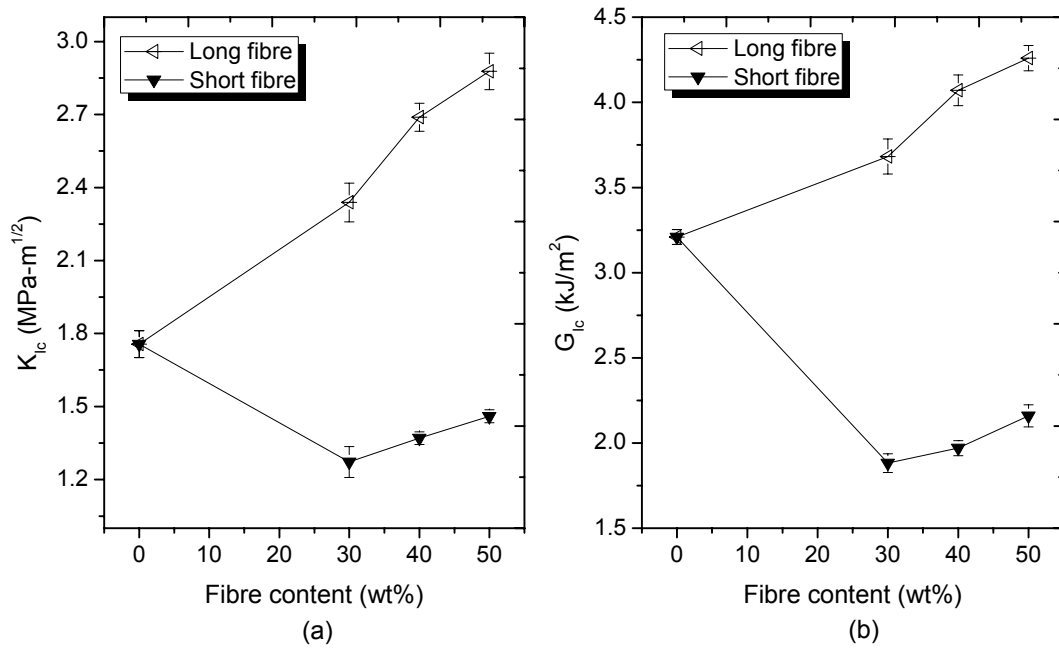


Figure 6.43: K_{Ic} and G_{Ic} of the long fibre composites (UPE/ALKSIL) as a function of fibre content.

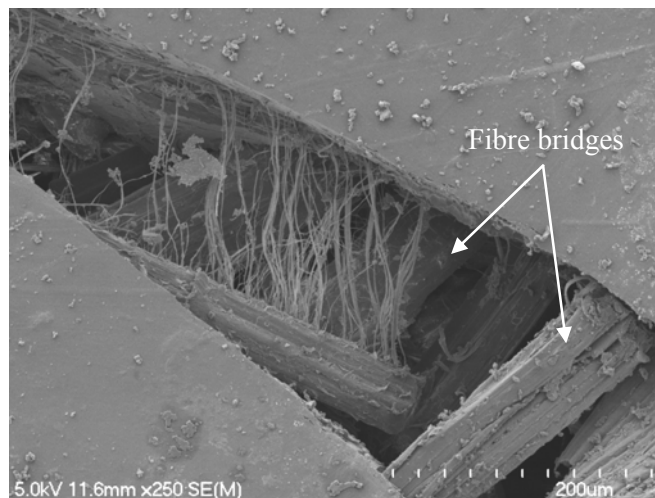


Figure 6.44: SEM micrograph of the long fibre UPE/ALKSIL composites showing the fibre bridging in SENB tested sample (50 wt% fibre).

6.5.5 Dynamic mechanical thermal analysis

Figure 6.45(a) shows the storage modulus (E') of long fibre composites (UPE/ALKSIL) as a function of temperature at different fibre contents. It can be seen that E' versus temperature curves of the long fibre composites were quite similar to those of the short fibre composites (see Figure 6.31). However, E' of the long fibre composites was significantly higher compared to that of the short fibre composites across the whole temperature range, which again suggests better stress transfer in the aligned long fibre composites compared to short fibre composites. This behaviour was consistent with the long fibre/PLA composites (see section 5.7.5).

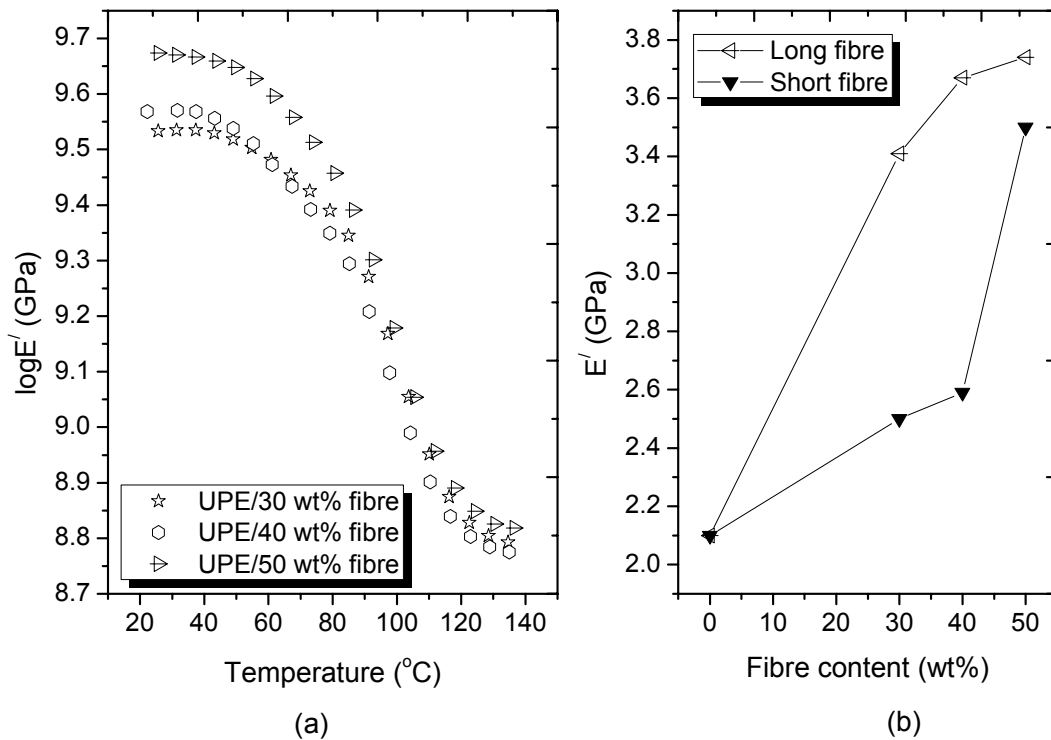


Figure 6.45: (a) Storage modulus of the long fibre UPE/ALKSIL composites as a function of temperature, and (b) comparison of the storage modulus of long and short fibre UPE/ALKSIL composites at 27°C as a function of fibre content.

A comparison of E' at 27°C between the short and long fibre composites as a function of fibre content is presented in Figure 6.45(b). It is evident that the E' of both the short and long fibre composites increased with increased fibre content, a finding similar to that for PLA/hemp fibre composites (see section 5.7.5). E' of the long fibre composites was found

to be about 36.4 and 41.7 and 6.8%, respectively, higher than that of the short fibre composites at 30, 40 and 50 wt% fibre contents. This trend was consistent with the composite Young's modulus as seen in section 6.5.1.

Figure 6.46 presents the loss modulus (E'') of the long fibre UPE/ALKSIL composites as a function of temperature at different fibre loads. As can be seen, the E'' versus temperature curves of the long fibre composites were quite similar to those of the short fibre composites (see Figure 6.32). T_g of long and short fibre composites appeared similar.

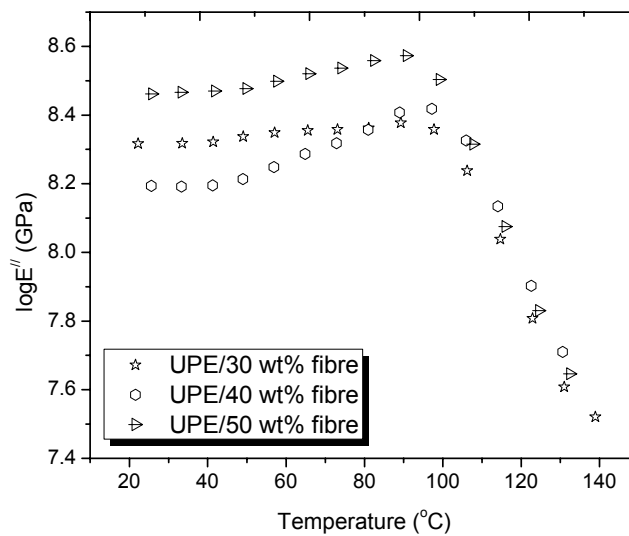


Figure 6.46: Loss modulus of long fibre UPE/ALKSIL composites as a function of temperature.

The mechanical damping factor ($\tan \delta$) of long fibre UPE/ALKSIL composites as a function of temperature is shown in Figure 6.47(a). It can be seen that $\tan \delta_{\max}$ of composites decreased with increased fibre content, which could be due to the decrease in the molecular mobility of polymer chains at higher fibre content as mentioned earlier (see section 6.4.6). A comparison of the $\tan \delta$ between short and long fibre composites as a function of fibre content is presented in Figure 6.47(b). It is evident that the $\tan \delta_{\max}$ of both the short and long fibre composites decreased with increased fibre content. However, $\tan \delta_{\max}$ of the short fibre composites was slightly greater than the long fibre composites which again indicated greater molecular mobility of polymer chains in the short fibre composites compared to the long fibre composites as mentioned in section 5.7.5.

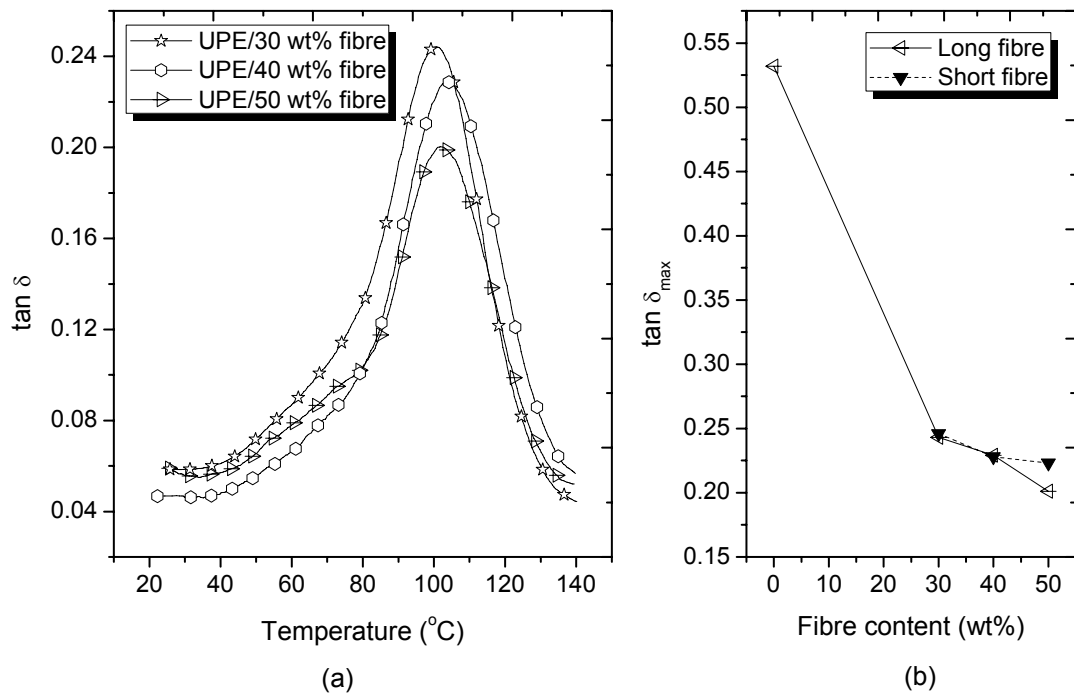


Figure 6.47: (a) Mechanical damping factor ($\tan \delta$) of long fibre UPE/ALKSIL composites as a function of temperature, and (b) $\tan \delta$ peak height ($\tan \delta_{\max}$) of the short and long fibre UPE/ALKSIL composites as a function of fibre content.

6.6 Comparison between hemp fibre reinforced UPE and PLA composite properties

IFSS of the UPE/hemp fibre (untreated and treated) and PLA/hemp fibre (untreated and treated) composites are compared in Figure 6.48. The IFSS of all the UPE/hemp fibre samples appeared higher than that of the PLA/hemp fibre samples. This indicates that the number of functional groups in the UPE resin to bond with the fibres may be higher than the PLA matrix. In addition, viscosity of the UPE resin was possibly lower than the PLA matrix during sample preparation, which facilitated UPE resin for better bonding with fibres.

The average tensile properties, flexural properties, impact strength (notched samples), and K_{Ic} and G_{Ic} of the untreated and treated short hemp fibre/UPE composites with 30 wt% fibre were compared with those of the untreated and treated short hemp fibre/PLA composites (see Figures 6.49 to 6.52). This was because in this study 30 wt% short fibres

was common to both the UPE and PLA composites to compare their mechanical properties.

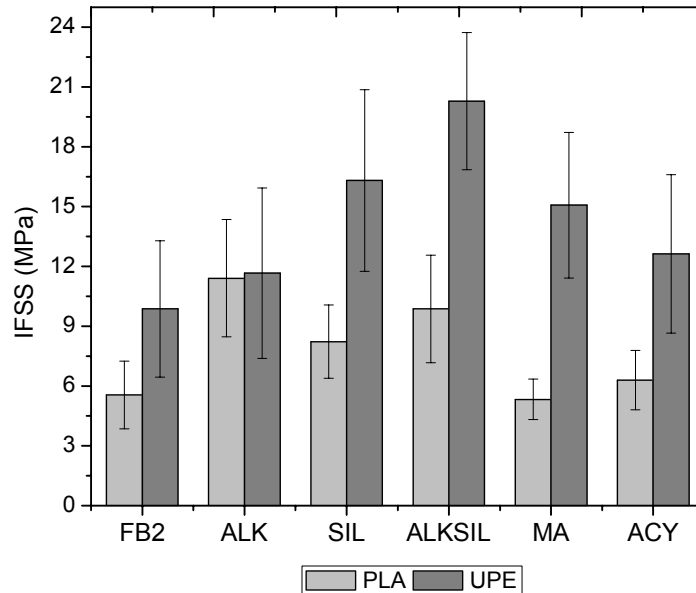


Figure 6.48: IFSS of UPE/hemp fibre and PLA/hemp fibre samples.

Figure 6.49(a) shows that tensile strength of UPE was about 12% higher than that of PLA. However, a comparison with the PLA/hemp fibre composites reveals a large difference in the tensile strength of the UPE/hemp fibre composites, the former being significantly greater than the latter. This could be explained by the fact that failure strain of UPE was comparatively lower than that of PLA [see Figure 6.49(c)]. Thus, a small applied strain could cause microcracking in the UPE composites at a relatively lower stress level due to stress concentration (see section 6.5.1). The consequence of this was that composite (i.e. UPE composites) failure occurred at a much lower stress. Figure 6.49(b) shows that Young's modulus of UPE matrix was about 11% higher than that of PLA matrix. Similarly, Young's modulus of UPE/hemp fibre composites was significantly higher than that of PLA/hemp fibre composites, except for the UPE/FB2 and UPE/ALK composites. The superior Young's modulus of UPE/SIL, UPE/ALKSIL, UPE/ACY and UPE/MA composites could be due to greater interfacial strength between the treated fibres (SIL, ALKSIL, ACY and MA) and UPE as seen in Figure 6.48. The decrease in Young's modulus of FB2 and ALK fibre reinforced UPE composites compared to that of PLA composites (PLA/FB2 and UPE/ALK) could be due to relatively small difference in

interfacial strength between UPE (UPE/FB2 and UPE/ALK) and PLA (PLA/FB2 and PLA/ALK) composites (see Figure 6.48). A comparison between the failure strain of UPE and PLA composites is presented in Figure 6.49(c). The failure strain of UPE matrix was approximately 36% lower than that of PLA matrix. Failure strain of UPE/hemp fibre composites was also lower than that of PLA/hemp fibre composites for all fibre types (untreated and treated).

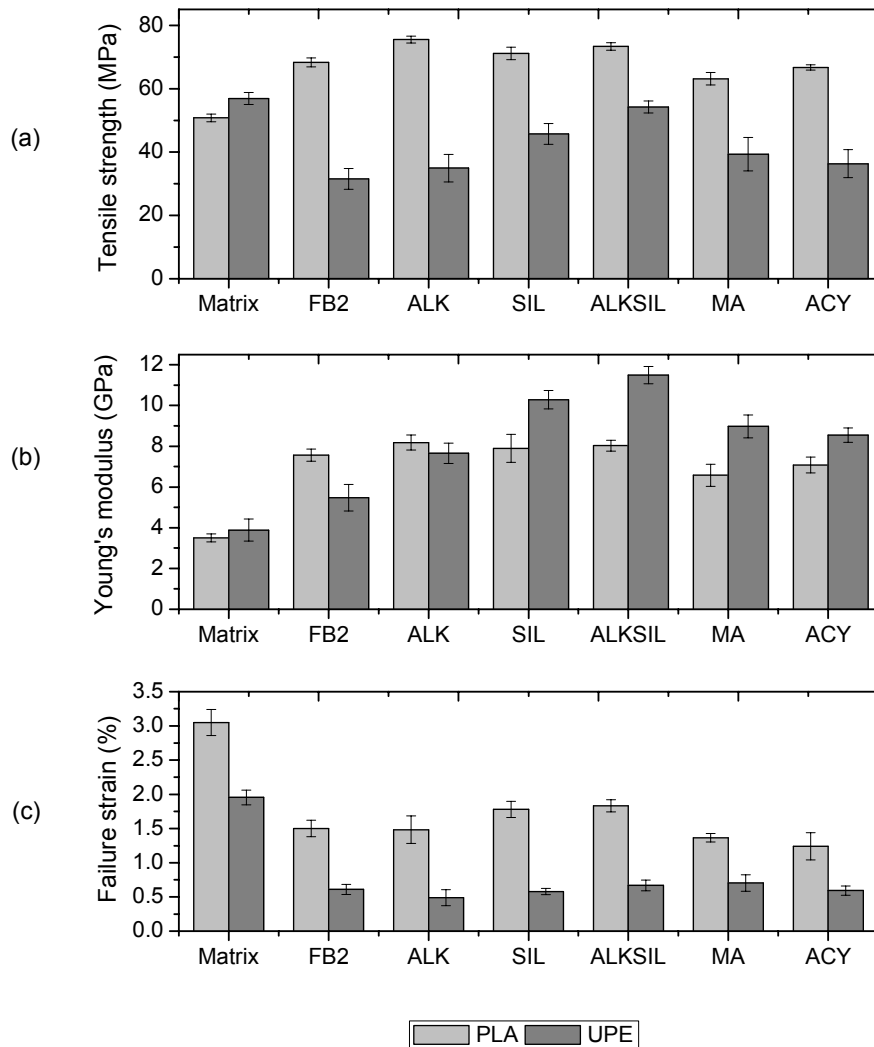


Figure 6.49: Tensile strength (a), Young's modulus (b) and failure strain (c) of untreated and treated short hemp fibre reinforced UPE and PLA composites at 30 wt% fibre content.

A comparison between the average flexural strength and flexural modulus of UPE/hemp fibre and PLA/hemp fibre composites is presented in Figure 6.50. Flexural strength of UPE matrix was found to be about 9.5% higher than that of PLA matrix [see Figure 6.50(a)].

Similarly, flexural strength of UPE/hemp fibre composites appeared to be significantly higher than that of PLA/hemp fibre composites, except the UPE/ALK composites. Unlike flexural strength, flexural modulus of UPE matrix was found to be approximately 2.8% lower than PLA matrix [Figure 6.50(b)] and in the same way, flexural modulus of UPE/hemp fibre composites were significantly lower than that of PLA/hemp fibre composites for all reinforcement types (untreated and treated).

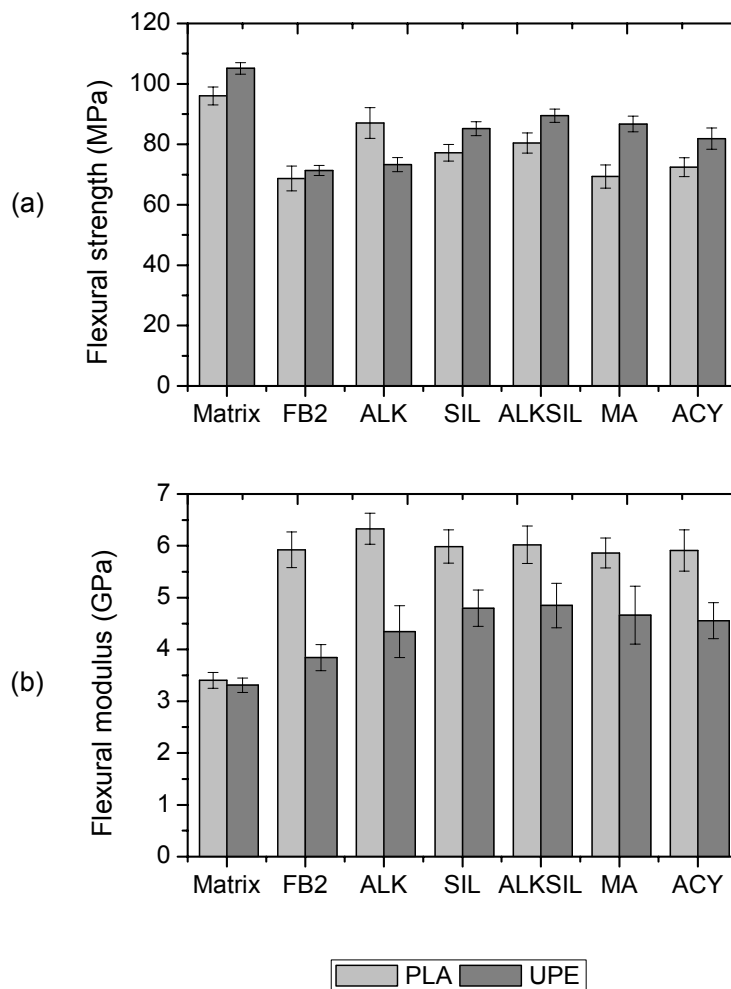


Figure 6.50: Flexural strength (a) and flexural modulus (b) of untreated and treated short hemp fibre reinforced UPE and PLA composites at 30 wt% fibre content.

In Figure 6.51, the average impact strength of UPE/hemp fibre composites is compared with that of PLA/hemp fibre composites. Impact strength of UPE matrix was about 22% higher than that of PLA matrix. Similarly, impact strength of the UPE/hemp fibre

composites was significantly higher than that of PLA/hemp fibre composites, which could again be due to better bonding between hemp fibre (untreated and treated) and UPE.

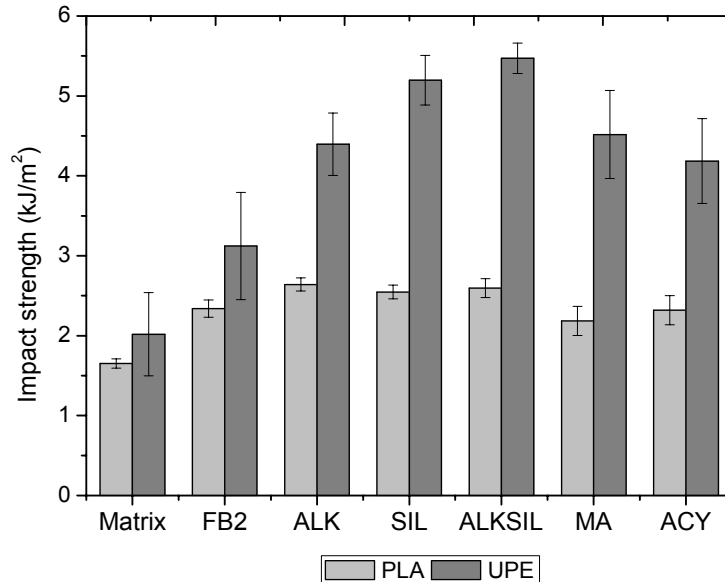


Figure 6.51: Impact strength of untreated and treated short hemp fibre reinforced UPE and PLA composites (notched samples) at 30 wt% fibre content.

K_{Ic} and G_{Ic} of UPE/hemp fibre composites are compared with those of PLA/hemp fibre composites in Figure 6.52. K_{Ic} of the unreinforced PLA was about 14.9% higher than that of the unreinforced UPE [see Figure 6.52(a)]. However, PLA composites were found to have lower K_{Ic} than that of UPE composites, except the PLA/MA composites. This decrease in K_{Ic} of PLA/hemp fibre composites compared to UPE/hemp fibre composites could be due to increased PLA crystallinity in the composites which facilitated crack propagation (see sections 5.6.8). G_{Ic} of the unreinforced PLA was about 90% higher than that of unreinforced UPE. Similarly, G_{Ic} of the PLA/hemp fibre composites was significantly higher than that of the UPE/hemp fibre composites, except the PLA/ALK composites [see Figure 6.52(b)].

The above studies demonstrate that mechanical properties of hemp fibre reinforced UPE and PLA composites at the same fibre content strongly influenced by the fibre/matrix interfacial strength and matrix (UPE and PLA) properties.

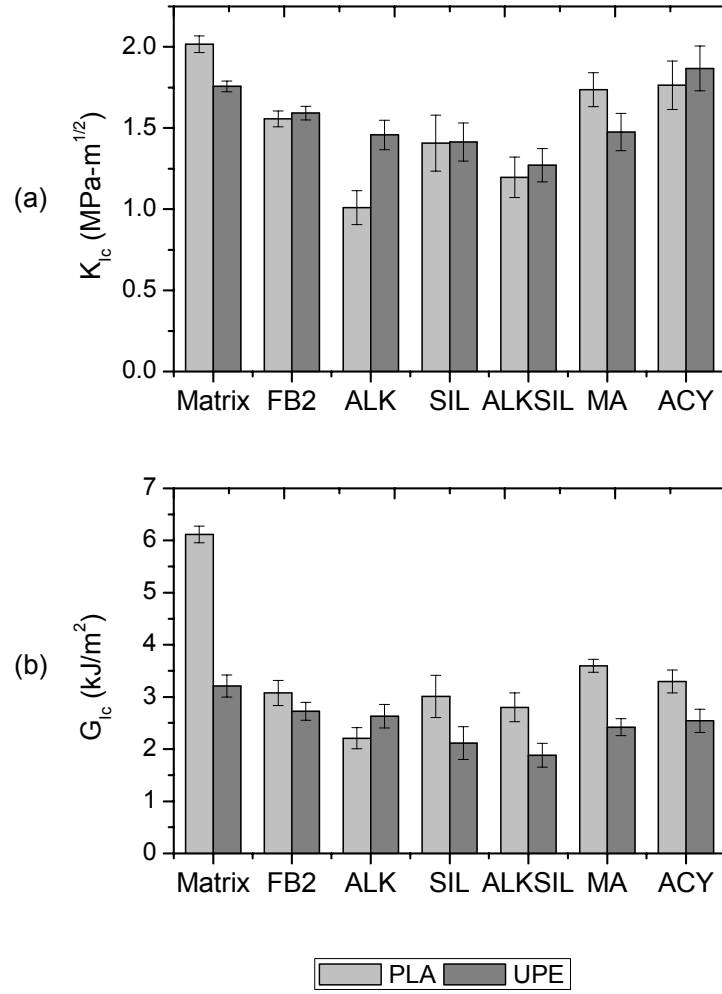


Figure 6.52: K_{Ic} (a) and G_{Ic} (b) of untreated and treated short hemp fibre reinforced UPE and PLA composites at 30 wt% fibre content.

CHAPTER SEVEN

Conclusions

7.1 Fibre treatment and characterisation

In this study, industrial hemp fibres were subjected to different chemical treatments, namely alkali, silane, acetic anhydride and maleic anhydride, in an attempt to improve the interfacial strength and mechanical properties of PLA and UPE matrix composites.

It was observed that the average tensile strength of alkali treated fibres slightly increased compared with that of untreated fibres. This was thought to be due to the removal of non-cellulosic materials facilitating closer packing and alignment of cellulose chains. This was supported by the fact that alkali treatment increased the crystallinity index of hemp fibres. On the other hand, the average tensile strength of acetic anhydride, maleic anhydride and silane treated fibres slightly decreased compared with that of untreated fibres. This was thought to be due to the reduction of hydrogen bonding leading to disruption in crystalline cellulose during treatment as supported by decreased crystallinity index. The average Young's modulus of all the treated fibres increased slightly compared with that of the untreated fibres. This was considered to be due to densification of fibre cell walls as a result of removal of non-cellulosic materials during treatment as supported by SEM.

Thermal stability of hemp fibres increased after all treatments which could again be due to densification of fibre cell wall. In addition, it was thought that the grafted molecules of treated fibres (except the alkali treated fibres) had enhanced resistance to thermal degradation. Defects observed along the length of fibres, including surface cracks, kink bands and miscellaneous irregularities, were seen to act as stress concentration points in composites.

7.2 Polylactide/hemp fibre composites

IFSS of PLA/hemp fibre samples improved after the treatment of fibres, except for the maleic anhydride treated fibre/PLA samples. The improvement in IFSS was considered to be due to enhanced bonding as supported by FT-IR results and transcrystallinity of PLA at

the fibre/matrix interface. Crystallinity of PLA in all composites increased with fibre content which could be due to increased availability of nucleation sites leading to the formation of increased transcrystallinity; although the increase was smaller as the fibre content increased from 20 to 30 wt%. This was probably due to the (i) decrease of matrix content or (ii) space limitation. It was also observed that the nucleating effect of fibres in PLA depends on fibre treatment as supported by degree of PLA crystallinity measured using DSC.

It was found that PLA could be reinforced with a maximum of 30 wt% fibres using conventional injection moulding, but could not be processed at higher fibre contents due to poor melt flow of the compounded materials. It was also observed that the population of short fibres (below the critical length) in the composites significantly increased with increased fibre content. This was thought to be due to the fibre/fibre, fibre/matrix and fibre/equipment interactions leading to decrease in fibre length. Tensile strength, Young's modulus and storage modulus of the short fibre/PLA composites increased with increased fibre content (10 to 30 wt%). Impact strength of the composites also increased with increased fibre content. Flexural modulus of the composites increased although flexural strength decreased with increased fibre content which was likely to be due to the increase of stress concentration (number of fibre ends and fibre defects). K_{Ic} and G_{Ic} of composites decreased with increased fibre content which could again be due to the increase of stress concentration (number of fibre ends) and crystallinity of PLA in composites. It was observed that the K_Q (trial K_{Ic}) of short fibre/PLA composites decreased as loading rate increased, until stabilising at a loading rate of 10 mm/min and higher. Tensile properties, flexural properties, impact strength and storage modulus of the composites were improved with fibre treatment (except for maleic anhydride treated fibre/PLA composites), which was consistent with the IFSS results.

Alignment of long fibres was found to be an effective technique to improve the mechanical and dynamic mechanical properties of PLA/hemp fibre composites compared to those of short hemp fibre/PLA composites. The highest mechanical and dynamic mechanical properties were obtained with a 35 wt% aligned long alkali treated fibre composites with tensile strength of 85.4 MPa, Young's modulus of 12.6 GPa, flexural modulus of 6.59 GPa,

impact strength of 7.4 kJ/m² (notched) and 32.8 kJ/m² (un-notched), and a storage modulus of 5.59 GPa.

7.3 Unsaturated polyester/hemp fibre composites

IFSS of UPE/hemp fibre samples increased after treatment of fibres which is believed to be due to enhanced bonding between fibre and matrix as supported by FT-IR results. Tensile strength of all short hemp fibre/UPE composites decreased at initial loading (20 wt% fibre), but thereafter increased with increased fibre content (30 to 50 wt%). However, tensile strength of the composites exceeded that of the UPE matrix only for the combined alkali and silane treated fibre composites (UPE/ALKSIL) at 40 wt% fibre content. The decrease in tensile strength of the composites could be due stress concentrations caused by the fibres in conjunction with brittle matrix. At the highest fibre content (60 wt%) tensile strength of untreated fibre/UPE composites decreased again, which could be attributed to the ineffective stress transfer from fibre to matrix due to the lack of sufficient matrix as observed by SEM. Young's modulus of the composites increased with increased fibre content (20 to 50 wt%), however, decreased at the highest fibre content (60 wt%), similar to tensile strength. Storage modulus of the composites increased with increased fibre content (20 to 50 wt%), similar to Young's modulus. Flexural modulus of the composites increased with increased fibre content (30 to 50 wt%), however, flexural strength decreased, a trend similar to the hemp fibre/PLA composites. It was found that the impact strength of the hemp fibre/UPE composites increased with increased fibre content (30 to 50 wt%) which could be due to increased pull-out of fibres. K_{Ic} and G_{Ic} of the 30 wt% fibre composites decreased compared to PLA only samples. However, additional increases in fibre content (40 and 50 wt%) resulted in improved K_{Ic} and G_{Ic} . The initial decrease in K_{Ic} and G_{Ic} is likely to be due to the influence of stress concentration by the fibres; in contrast, further increase in fibre content in composites lead to increased pull-out which appears to have increased K_{Ic} and G_{Ic} . Tensile properties, flexural properties, impact strength and storage modulus of the UPE/hemp fibre composites were improved after the treatment of fibres which was consistent with the IFSS results.

The use of aligned long fibres improved the mechanical and dynamic mechanical properties of UPE/hemp fibre composites similar to PLA/hemp fibre composites. A UPE composite consisting of 50 wt% aligned long alkali-silane treated fibres had the highest

tensile strength of 83 MPa, a Young's modulus of 14.4 GPa, flexural modulus of 6.7 GPa, impact strength (notched) of 15.85 kJ/m² and storage modulus of 3.74 GPa.

Overall, alkali treatment appears to be the best to produce high strength hemp fibre reinforced PLA composites due to the enhanced fibre/matrix interfacial strength. Combined alkali and silane treatment would be the best to produce high strength hemp fibre reinforced UPE composites due to the enhanced fibre/matrix interfacial strength. Alternatively, maleic anhydride treated hemp fibre reinforced PLA composites and untreated hemp fibre reinforced UPE composites appear to be the best for high fracture toughness due to the enhanced energy dissipation during fracture. It also appears that aligned long hemp fibres enhanced composite strength and fracture toughness. Therefore, for large scale production of hemp fibre composites, treated hemp fibre should be available in the form of mat. 35 wt% alkali treated aligned long fibre would be suitable for the production of high strength structural material of PLA composites. 50 wt% alkali/silane treated aligned long fibre would be suitable for the production of high strength large structural material of UPE composites.

The research conducted and presented herein accomplished what was set out to be achieved, namely, to provide a greater understanding of the controlling parameters (fibre content, fibre treatment and interfacial strength) which influence the mechanical properties of the industrial hemp fibre reinforced PLA and UPE composites.

CHAPTER EIGHT

Recommendations and Future Work

The study findings led to the following recommendations:

- In this study, it was observed that the industrial hemp fibres contain defects along their length. It was not clear at what stage the fibre became damaged; however, it seems likely that some damage probably increased during extraction/processing of fibres from plants. This damage leads to reduction in fibre strength as shown by other studies. Therefore, in order to be able to produce high strength hemp fibres and their composites, it is important to develop new technology for fibre separation from the plants.
- In this research, it was found that up to 30 wt% fibres can be used to produce injection moulded PLA composites. It was also seen that the fibre length decreased significantly after processing (extrusion and injection moulding). Thus, an investigation could be carried out to produce higher amounts of short fibre content PLA composites by one step processing method (extruder equipped with a sheet die); this process would also help to increase the population of fibres above the critical length.
- In this investigation, fibres were treated as a means of improving fibre/matrix interfacial strength. Further investigation could be carried out using coupling agents along with reactive extrusion to improve the compatibility between the fibres and the PLA.
- PLA and UPE are very brittle, thus plasticisers could be used to improve the toughness of the PLA and UPE composites.
- Aligned long fibres were found to improve the mechanical properties of composites. Thus, mats made out of hemp fibre yarns could be used to produce high strength PLA and UPE composites.

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