The Processing, Production and Improvement of Hemp-Fibre Reinforced Polypropylene Composite Materials
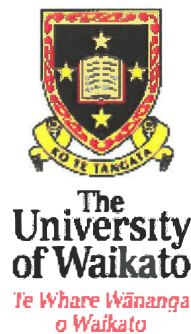
A thesis submitted in partial fulfilment
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by

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Wisdom rests in the heart of one who has understanding

Proverbs 14:33

Abstract

Increasing worldwide environmental awareness is encouraging scientific research into the development of cheaper, more environmentally friendly and more sustainable construction and packaging materials. Natural fibre reinforced thermoplastic composites are strong, stiff, lightweight and recyclable, and have the potential to meet this need. Industrial hemp fibre is amongst the strongest of the natural fibres, and possesses a similar specific strength and stiffness to E-glass, but with additional benefits such as low cost and low production energy requirements.

The favourable mechanical properties of hemp, however, have yet to be transferred successfully to thermoplastic-matrix based composite materials. The main objective of this research was to produce an improved hemp-fibre reinforced polypropylene composite material by optimising the fibre strength, fibre-processing methods, composite-processing methods and fibre-matrix interfacial bonding.

To obtain the strongest and stiffest fibres for use in composites, an investigation was performed on a crop of New Zealand grown hemp to determine the effects of plant growth duration on fibre strength and stiffness. By conducting single fibre tensile tests on retted hemp fibre, it was discovered that the optimum cultivation time was 114 days, producing fibres with an average tensile strength of 671 MPa, and a Young's modulus of 40 GPa. It was also found that the retting process considerably reduced the tensile strength and stiffness of the hemp fibres.

Biological fibre-treatments using 3 varieties of fungi were then used to modify the surface morphology of hemp fibres, so that the adhesion between the fibres and a polypropylene matrix could be improved. It was found, however, that these treatments severely degraded the fibres, and reduced their tensile properties to such an extent that they were deemed unsuitable for use as composite reinforcements.

An investigation was then conducted to determine a suitable fibre treatment method to remove lignin and other non-structural constituents from the fibre wall, to separate the fibres from their fibre bundles, and to retain the fibre strength. Various alkali treatments were used, and a treatment consisting of fibre digestion in a 10% NaOH solution with a maximum processing temperature of 160^0C and a hold time of 45 minutes, was found to provide the best combination of fibre strength retention, lignin removal and fibre separation.

Finally, the alkali treated fibres, polypropylene and a maleated polypropylene (MAPP) coupling agent were compounded using a twin-screw extruder, before being injection moulded into composite tensile test specimens. A range of composites with differing fibre and MAPP weight contents were then produced and tensile tested. It was found that the addition of 2% MAPP greatly improved the tensile strength and interfacial bonding of the 30% fibre composites, while only moderate improvements were observed for the 40% fibre composites. An increase in the fibre content from 0% to 40% greatly improved the stiffness of the composites. The most successful composite produced consisted of 40% long alkali treated fibres with 2% MAPP, and had a tensile strength and Young's modulus of 39 MPa and 4.4 GPa respectively.

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Introduction

1.1 Overview of Composite Materials

Fibre-reinforced composites are strong, stiff and lightweight materials that incorporate strong, stiff, but commonly brittle fibres into a softer, more ductile matrix. The matrix material transmits applied forces to the reinforcing fibres within the composite, resulting in a material with improved mechanical properties compared to the un-reinforced matrix material.

Many composites used today are at the leading edge of materials technology, enabling their use in advanced applications such as aircraft and aerospace vehicles. The idea of using composite materials, however, is not a new or recent one but has been around for thousands of years. The Israelites used chopped straw to reinforce mud bricks; and Mongol warriors used a composite consisting of bullock tendon, horn, bamboo strips, silk and pine resin to produce high-performance archery bows.

Since the early 1960s, there has been an increase in the demand for stronger, stiffer and more lightweight materials for use in the aerospace, transportation and construction industries. High performance demands on engineering materials have led to extensive research and development into new and improved materials such as composites. Composite materials used for structural purposes often have low densities, resulting in high stiffness to weight and high strength to weight ratios compared to traditional engineering materials. In addition, the high fatigue strength to weight ratio and fatigue damage tolerance of many composites also makes them an attractive option.

As a result, these materials are rapidly being utilised in industries that have traditionally used metals, and are now at the forefront of research and development in many related areas.

Composite materials can be grouped into five major categories, which include ceramic matrix composites, metal matrix composites, intermetallic matrix composites, carbon-carbon composites and polymer matrix composites (PMCs). The focus of this research is on the development of PMCs.

A PMC can consist of either a thermoplastic or thermoset matrix, which is used to bind and transfer applied stresses from the composite to the reinforcing fibres. Thermosets are plastics that cannot be melted once cured, and include resins such as epoxies and phenolics. Thermoplastics, on the other hand, are plastics that can be repeatedly melted, thus enabling them to be recycled. Commonly used thermoplastics include polyethylene, polypropylene and polyvinyl chloride (PVC). Both thermoset and thermoplastic matrices have advantages and disadvantages when compared to each other, and these can be seen in Table 1.1.

Table 1.1 Comparison of thermoplastic and thermoset matrices.

Thermoplastic Advantages	Thermoplastic Disadvantages
• Unlimited shelf life	• Prone to creep
• Easy to handle (no tackiness)	• Poor melt flow characteristics
• Recyclable	• Thermoplastics need to be heated above the melting point to sufficiently wet the fibres
• Easy to repair be welding and solvent bonding	
• Post formable	
• Tough	

Thermoset Advantages	Thermoset Disadvantages
• Low resin viscosity	• Brittle
• Good fibre wet-out	• Non-recyclable via standard techniques
• Excellent thermal stability once polymerised	• Not post formable
• Chemically resistant	
• Creep resistant	

The reinforcing fibres in PMCs can be either short or continuous, with continuous-fibre reinforcement providing the best mechanical properties in the direction of fibre alignment. Continuous fibre composites are primarily reinforced with high performance carbon or aramid (eg. Kevlar) fibres. These composites are often utilised in applications such as aircraft components, where the exceptional fibre properties can be fully exploited. Some commonly used continuous-fibre composite processing methods include compression moulding, hand lay-up, filament winding and pultrusion. Such materials, however, cannot always be adapted to mass production and are often limited to simple shapes.

Short-fibre composites, on the other hand, are primarily reinforced with chopped fibres such as glass, graphite and cellulose fibres. These types of composites are cheaper and easier to fabricate, and are well established in many applications where a medium to low strength and stiffness are required. Compared to continuous fibre composites, short fibre composites can easily be processed in a similar manner to the matrix. For short fibre composites with a thermoplastic matrix, it is thereby possible to mass-produce complex-shaped moulded products by extrusion, injection moulding and compression moulding.

Composite properties are strongly influenced by the properties and distribution of the fibres and matrix, as well as the degree of stress transfer between the two components. The mechanical properties such as strength and stiffness are of great importance when designing composite products, and can be predicted for short-fibre composites by using various prediction methods. The Modified Rule of Mixtures [1] is one such method, and can be used to calculate the tensile strength of a composite material:

$$\sigma_c = V_m \sigma_m{}^* + V_f \sigma_f K_1 K_2 \tag{1}$$

where

σ_c = the tensile strength of the composite

σ_f = the tensile strength of the fibres

V_m = the matrix volume fraction

V_f = the fibre volume fraction

K_1 = orientation factor

K_2 = a factor dependant on the stress transfer between the matrix and the fibres

σ_m* = the tensile contribution of the polymer matrix at the failure strain of the composite

The mechanical properties of short fibre composites are more difficult to predict than continuous-fibre composites. This is due to the complexity of determining parameters such as fibre dispersion, orientation and geometry (aspect ratio) of the fibres within the composite, fibre and matrix volume fractions and the interfacial shear strength between the fibres and matrix.

1.2 Natural Fibre Reinforced Thermoplastic Composites

High performance composites reinforced with carbon or aramid (such as Kevlar) fibres are the most commonly used composites in applications where exceptional strength, stiffness and low density are required. They are, however, prohibitively expensive for use in more general applications. As a result of this, glass fibres are the most commonly used reinforcing fibres in the composites industry to date. Glass fibres have many benefits including low cost and relative ease of manufacture, as well as maintaining a moderate strength and stiffness to weight ratio. However, they also have many disadvantages. They tend to be abrasive, thus making them dangerous to work with as well as increasing the wear on processing machinery. More importantly, glass fibres could present a health risk to those working with them. The biggest problem with glass and other synthetic fibres is that they are difficult to dispose of at the end of their lifetimes.

The fibres cannot be incinerated, as the residue can cause considerable damage to a furnace. Glass fibre reinforced thermoplastics cannot be recycled, as the fibres break during the reprocessing operations. The only method of disposal is to discard the waste in landfills, which is becoming more costly as countries apply landfill taxes.

Government regulations and a growing environmental awareness throughout the world have encouraged the development and utilisation of materials compatible with the environment. Natural fibres, especially hemp and flax, have become increasingly suitable alternatives to glass fibre and have the potential to be used in cheaper, more sustainable and more environmentally friendly composite materials. The properties of natural fibres in relation to those of E-glass can be seen in Table 1.2.

Table 1.2 Properties of natural fibres in relation to those of E-glass [2] [3].

Properties	Fibres								
	E-glass	Hemp	Jute	Ramie	Coir	Sisal	Flax	Cotton	Kenaf
Density, g/cm^3	2.55	1.48	1.46	1.5	1.25	1.33	1.4	1.51	-
Tensile strength, MPa	2400	550-900	600-1100	500	220	600-700	800-1500	400	930
E-modulus, GPa	69	50-70	10-30	44	6	38	60-80	12	-
Specific stiffness, E/d	27	34-47	7-21	29	5	29	43-57	8	-
Elongation at failure, (%)	3	1.6	1.8	2	15-25	2-3	1.2-1.6	3-10	-
Moisture absorption, (%)	-	8	12	12-17	10	11	7	8-25	-

Natural fibres are cheap, abundant and renewable, and can be produced at low cost in many parts of the developing world. They are strong and stiff, and due to their low densities, have the potential to produce composites with similar specific properties to those of E-glass. Table 1.3 shows a comparison between glass fibre, recycled newspaper and kenaf fibre reinforced polypropylene composites. Hemp fibre is generally stronger than kenaf fibre, so the use of hemp in a polypropylene matrix instead of kenaf would result in a stronger composite material.

Table 1.3 Comparison of polypropylene (PP) composites [4].

Property	Fibre Type			
	None	**Kenaf**	**Recycled Newspaper fibre**	**Glass**
Fibre content, %	0	50	40	40
Tensile Modulus, GPa	1.7	8.3	4.4	9
Tensile strength, MPa	33	65	53	110
Elongation at break, %	>10	2.2		32.5
Flexural strength, GPa	41	98	80	131
Flexural modulus, GPa	1.4	7.3	3.9	6.2
Notched Izod impact, J/m	24	32	21	107
Specific gravity, (g/cm^3)	0.9	1.07	0.98	1.23
Water absorption, % in 24h	0.02	1.05	0.95	0.06
Mould (linear) shrinkage, cm/cm	0.028	0.003		0.004

Unlike synthetic fibres, natural fibres require very little energy to produce, and because they possess high calorific values, can be incinerated at the end of their lifetime for energy recovery. It has been estimated that natural fibre reinforced polypropylene composites consisting of 65% fibre (by weight) would consume only 30,800 MJ/ton of composite in processing energy, as opposed to 81,890 MJ/ton for glass fibre reinforced polypropylene composites consisting of 30% fibre (Table 1.4) [5]. It can also be seen in Table 1.4 far less energy is required for hemp fibre cultivation than for glass fibre production, and that the hemp fibre composites mentioned produce more energy during incineration than the glass fibre composites.

All plant-derived fibres utilise carbon dioxide when they are grown and can be considered CO_2 neutral, meaning that they can be burned at the end of their lifetime and no additional CO_2 is released into the atmosphere. Glass fibres, on the other hand, are not CO_2 neutral and require the burning of fossil fuels to provide the energy needed for production. The burning of fossil fuel based products releases enormous amounts of CO_2 into the atmosphere, and this phenomenon is believed to be the main cause of the greenhouse effect and the world's climatic changes [2].

Table 1.4 Overall energy schedule for natural fibre mat thermoplastic (NMT) composites and glass fibre mat thermoplastic (GMT) composites [5]

Quantity (1 metric ton)	NMT (65% fibre)	Energy (MJ)	GMT (30% fibre)	Energy (MJ)
(a) Materials				
	Hemp cultivation	1340	Glass fibre production	14 500
	PP production	35 350	PP production	70 700
	Total	36 690	Total	85 200
(b) Production				
	Composite	11 200	Composite	11 200
(c) Incineration				
PP *incineration*				
	Energy required	117	Energy required	234
	Energy released	-7630	Energy released	-15 260
Hemp fibre incineration			*Glass Fibre incineration*	
	Energy required	1108	Energy required	516
	Energy released	-10 650		
	Net	-17 055	Net	-14 510
(d) Balance				
	Gross energy required	49 115	Gross energy required	97 150
	Energy released	-18 222	Energy released	-15 260
	Net energy required	30 800	Net energy required	81 890

* The average fibre content in glass fibre plastics (auto sector) is taken as 30%, although in commercial grades it varies from 22 to 40%.

Natural fibre thermoplastic composites, unlike their glass counterparts, do not splinter during fracture therefore making them suitable for crash-absorbing applications where safety is of concern. One of the most distinct advantages of using natural fibres in reinforced thermoplastic composites is the fact that the fibres are incredibly durable, and can be recycled several times with little reduction in strength and stiffness [1]. Synthetic fibres on the other hand, tend to fracture with further processing and recycling, resulting in significant fibre length reductions (Table 1.5).

Table 1.5 Length of fibres after processing [6].

Fibre	Fibre diameter (µm)	Before processing		After processing	
		Length (mm)	L/D	Length (mm)	L/D
Glass	13	6.35	488	0.22	17
Carbon	8	6.35	794	0.18	22
Cellulose	12	2.0	167	1.20	100
Aramid	12	6.35	529	1.33	111
Nylon	25	6.35	254	4.51	180

* All fibres except cellulose fibres were chopped to 6.35mm before being dispersed in an elastomer (NR or NBR) on a mill, then separated by solvent extraction.

Natural fibres, however, display large amounts of variation in fibre properties from plant to plant, such as strength, stiffness, fibre length and cross sectional area. These variations can ultimately lead to difficulties in composite design and performance predictions. Natural fibres are also thermally unstable compared to most synthetic fibres, and are limited to processing and working temperatures of 180 ^{0}C. Another major drawback when using natural fibres is the fact that they are hydrophilic (absorb water) and polar in nature, whereas common thermoplastic matrices such as polypropylene are hydrophobic (do not absorb water) and non-polar. Natural fibres used in thermoplastic matrices are therefore dimensionally unstable and display poor fibre-matrix interfacial bonding, which leads to a reduction in mechanical properties of the composite. It is therefore necessary to modify the fibres, the matrix or both to produce a composite with improved mechanical properties. Much work still needs to be done in this area to enable natural fibre reinforced thermoplastic composites to compete with glass fibre composites in terms of strength and stiffness.

1.3 Opportunities for Natural Fibre Composites

Several billion tons of fillers and reinforcements are used annually in the plastics industry, and there is a huge potential market for recyclable, energy efficient and more environmentally friendly composite materials.

One of the largest potential users of natural fibre composites is the automotive industry. Faced with the pressures of producing fuel-efficient and low polluting vehicles, the automotive industry has used fibre reinforced plastic composites to reduce the weight of its products. Unfortunately, the production and use of composites is energy intensive and polluting, and glass, carbon, and aramid fibre reinforced thermoset composites are difficult to dispose of and cannot be recycled. The use of a thermoplastic matrix presents an opportunity to produce recyclable composites but these recyclable composites require the use of durable natural fibres for reinforcement, as synthetic fibres become damaged during reprocessing. Natural fibre composites also have distinct environmental advantages over competing materials. They can be incinerated to recycle thermal energy, and because natural fibres are carbon dioxide neutral, the only additional CO_2 emitted into the atmosphere from incineration would come from the combustion of the thermoplastic matrix.

Recent government regulations are encouraging the development and use of natural fibres in the automotive industry. In July 2002, The European Union Council of Ministers approved the EU end-of-life vehicle directive, which will have a huge impact on the materials and processing methods used to produce motor vehicles in the future. The directive states that from 2015 onwards, all new vehicles should be 85% reusable and recyclable by weight, 10% can be used for energy recovery and only 5% can be disposed of in landfills [7]. However, the automotive industry may be compelled to use other lightweight and recyclable materials such as foamed aluminium or composites made of only one petrochemical plastic (matrix and fibres made of the same plastic).

Many countries around the world have committed themselves to the Kyoto protocol, whereby a reduction in greenhouse gas emissions (mostly CO_2) must be reduced to levels below that of 1990 between the years 2008 and 2012. Pervaiz et al [5] showed that, by converting the net energy consumed during composite production into CO_2 emissions, 3 tons CO_2 per ton of product could be saved by utilising hemp fibre instead of glass fibre in composite materials (Figure 1.1).

It is also stated that the projected automotive consumption of natural fibres (excluding wood) by 2005 is 45 million kg per annum, and that an annual CO_2 reduction of 135,000 tons could be achieved (assuming that thermoplastic composites containing 65% wt fibre are used).
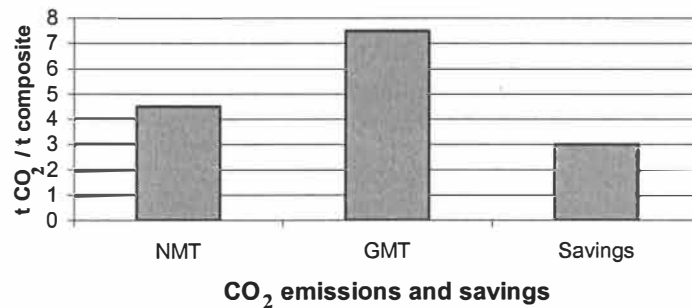
Figure 1.1 CO_2 emissions per ton of composite, and reduction in emissions by substituting glass fibres with hemp fibres [5].

At present, approximately 30,000 tons of natural fibre is used annually in the European Union automotive industry. Most major European motor vehicle manufacturers are now incorporating natural fibre composite components into their vehicles. The use of natural fibre composites for serial parts in the automotive industry can be seen in Table 1.6. The currently used natural fibre composites are mainly press-moulded parts, consisting of non-woven natural fibres in a thermoset or thermoplastic matrix. Typical applications include door inserts, hat racks, pillar cover panels and boot linings.

The use of natural fibre composites is not, however, limited only to the automotive industry. At least 20 manufacturers are currently producing wood-fibre reinforced thermoplastic decking for the American markets. Window and door profile manufacturers form another large industrial segment that uses wood-fibre reinforced polymers. Other natural fibre composite applications that have been reported include walls, flooring, louvres, and indoor and outdoor furniture [8].

Table 1.6 Use of natural fibres for serial parts in the automotive industry (1997-2001) [7].

Manufacturers/Customers	Model/ Application (dependant on model)
Audi	TT, A2, A3, A4 Avant (1997), A4 Variant (1997), A6, A8 (1997), Roadster, Coupe Seat back, side and back door panels, parcel tray, boot lining, rear flap lining, rear storage panel, spare tyre lining
BMW	3,5 and 7 Series and others Door inserts/door panels, headliner panel, boot lining, seat back
Citroen	C4 (2001) Door inserts
DaimlerChrysler	A-Klasse, C-Klasse, E-Klasse, S-Klasse Door inserts, Windshield/dashboard, business table, column cover
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156, Sportwagon
Ford	Mondeo CD 162 (1997), Cougar (1998), Mondeo (2000), Focus Door inserts, B-column cover, Parcel tray, in the future also motor protection (cover undershield)
MAN	Bus (1997) Headliner panel
Mitsubishi	Miscellaneous models (since 1997)
Nissan	Miscellaneous models
Opel	Astra, Vectra, Zafira Headliner panel, door inserts, column cover, instrument panel, rear shelf panel
Peugeot	New model 406
Renault	Clio, Twingo
Rover	Rover 2000 and others Insulation, rear storage panel
Saab	Coupe (1998) Door inserts
SEAT	Door inserts, seat backs
Toyota	Miscellaneous models
Volkswagen	Golf A4, Golf 4 Variant (1998), Passat Variant, BoraDoor inserts, seat backs, rear flap lining, parcel tray
Volvo	C70, V70, Coupe (1998) Door inserts, Parcel tray

Unfortunately, the current generation of natural fibre reinforced thermoplastic composites does not offer sufficient mechanical properties to warrant their use in more demanding structural and load bearing applications. It is thereby necessary to improve the strength and stiffness of the composites as well as confronting issues such water absorption and thermal instability before they can be used to their full extent in industry.

1.4 Research Objectives

The purpose of this research was to produce an improved hemp-fibre reinforced polypropylene composite material using New Zealand grown hemp fibre. Improvements were made by:

- optimising the single fibre mechanical properties by investigating the effect of cultivation time on hemp fibre strength and stiffness;
- optimising the fibre treatment methods to improve fibre separation and lignin removal, whilst retaining fibre strength and stiffness;
- utilising a coupling agent to improve the fibre-matrix interfacial bonding of the composites;
- improving fibre-matrix compounding by use of a twin-screw extruder.

Chapter 2:
Literature Review

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Literature Review

2.1 Natural Fibres

Natural organic fibres can be derived either from animal or plant sources. The majority of useful natural textile fibres are plant derived, with the exceptions of wool and silk. All plant fibres are composed of cellulose, whereas fibres of animal origin consist of proteins. Depending on the origin of the fibre, cellulose fibres can be classified into the following categories:

- Grasses and reeds: These fibres are found in the stems of monocotyledonous plants such as bamboo and sugar cane.
- Leaf fibres: These fibres run lengthwise through the leaves of most monocotyledonous plants such as sisal, henequen and abaca.
- Bast Fibres: These fibres are situated in the inner bark (phloem) of the stems of dicotyledonous plants. Common examples are jute, flax, hemp and kenaf.
- Seed and fruit hairs: These are fibres that come from seed-hairs and flosses, which are primarily represented by cotton and coconut.
- Wood fibres: These fibres are found in the xylem of angiosperm (hardwood) and gymnosperm (softwood) trees. Examples are pine, maple and spruce.

Natural cellulose fibres tend to be stronger and stiffer than their animal counterparts, and are therefore more suitable for use in composite materials.

2.2 Comparison of Cellulose Fibres

For centuries, cellulose fibres have been used extensively in the manufacture of various products such as rope, string, clothing, carpets and other decorative products. Wood fibres are the most abundantly used cellulose fibres due to their extensive use in the pulp and paper industries, although other fibre types are becoming increasingly important (Table 2.1).

<p align="center">**Table 2.1 Commercially important fibre sources [9]**</p>

Fibre Source	Species	World Production (10^3 tonnes)	Origin
Wood	(>10,000 species)	1,750,000	Stem
Bamboo	(>1250 species)	10,000	Stem
Cotton lint	Gossypium sp.	18,450	Fruit
Jute	Corchorus sp.	2,300	Stem
Kenaf	Hibiscus cannabinus	970	Stem
Flax	Linum usitatissimum	830	Stem
Sisal	Agave sisilana	378	Leaf
Roselle	Hibiscus sabdariffa	250	Stem
Hemp	Cannabis sativa	214	Stem
Coir	Cocos nucifera	100	Fruit
Ramie	Boehmeria nivea	100	Stem
Abaca	Musa textiles	70	Leaf
Sunn hemp	Crorolaria juncea	70	Stem

There are several physical properties that are important in selecting suitable cellulose fibres for use in composites. Fibre dimensions, defects, variability, crystallinity and structure are some of the most important properties that must be considered [10]. Mechanical properties are even more important when selecting a suitable fibre for composite reinforcement. To produce a strong composite material, it is important to start off with strong reinforcing fibres. However, fibre strength alone is not sufficient to obtain strong composites, as good bonding to the matrix and good fibre orientation are also needed.

The cost of the cellulose fibres is also a factor that could influence fibre selection. Fibre prices tend to fluctuate considerably and are dependent on a number of factors, such as supply, demand, quality and exchange rates [11]. A comparison of the relative costs of a number of fibres can be seen in Table 2.2. The costs of cellulose fibres are considerably lower than that of glass and carbon, but significant additional costs would be incurred in processing the material to form fibres for use in composites. Despite this, cellulose fibres still appear to be a cheaper option when compared to synthetic fibres.

Table 2.2 Natural plant fibre costs

Fibre Type	Price $US/Kg
Jute	0.4 - 0.7
Hemp	0.5 - 1.5
Flax	0.4 - 0.8
Sisal	0.6 - 1
Wood	0.2 - 0.4
Glass	1.5 - 2.5
Carbon	10 - 100

From the information provided in Table 1.3 in Chapter 1, it can be seen that the strongest cellulose fibres are hemp, jute and flax, with hemp and flax having the highest Young's modulus values. Hemp and flax fibres have high aspect ratios (length/width), and this is important in composites as it gives an indication of possible strength properties [10].

The most suitable cellulose fibres for use in composite materials are therefore hemp and flax. Flax is more widely accessible and slightly cheaper than hemp due to its widespread use in the textiles industry. Hemp, however, has the potential for much higher fibre yields that could result in lower costs with improvements in cultivation techniques [12]. Hemp, compared to flax, also has the advantage of being extremely disease and pest resistant, and can be planted at high densities to prevent weeds from growing between the plants.

Pesticides and herbicides are therefore not required to grow hemp, and this provides a distinct advantage over flax in many countries where restrictions on herbicide use is present [13].

2.3 Industrial Hemp Fibre

Industrial hemp fibres (*Cannabis sativa* L) have been widely used in many civilizations, and it is estimated that the earliest use of hemp was over 6000 years ago. Hemp fibres have long been valued for their high strength and long fibre lengths, and have been used extensively in the fabrication of ship ropes and sails, as well as for paper and textiles. In the middle of the 19th century, hemp cultivation decreased with competition from other natural fibres (cotton, sisal, jute) and synthetic fibres, as well as with the disappearance of the sailing navy. Due to its relationship with marijuana, industrial hemp was banned in many countries with the introduction of stricter drug laws [14]. In New Zealand, it was illegal to grow hemp between the late 1930's and 2001. Regulations are now easing in many countries, and in October 2001, nine growers were issued licenses to trial a crop of hemp in New Zealand for industrial purposes.

The essential difference between industrial hemp and marijuana is the amount of THC (Tetrahydrocannabinols) present within the plant. THC is a psychoactive chemical thought to have a range of detrimental effects of human beings, including low blood pressure, induced euphoria and long term degeneration of brain activity. There is ongoing debate as to whether the narcotic hemp plant is actually a different variety of plant, or actually the industrial variety bred to produce high levels of THC. An industrial hemp plant will naturally attain a THC content of 0.6%, and it is generally accepted that a content of 2% is required to have a noticeable effect on the human body.

2.3.1 Hemp Plant Morphology

Industrial hemp is part of the Mulberry genus and is a fast growing annual plant. It can grow up to five metres in height, and can reach between six and sixty millimetres in diameter depending on the plantation density. Hemp plants have a well-developed primary root with numerous branched secondary roots. Industrial hemp is naturally dioecious, meaning that it has separate male and female plants with different growth characteristics. The male plants tend to be taller and slenderer with few leaves surrounding the flowers, while female plants are shorter and stockier with many leaves at each terminal inflorescence (Figure 2.1)

The hemp stalk consists of a woody core, surrounded by an outer layer (bark) containing strong bast fibres (Figure 2.2). The hollow woody core, called the hurd, is responsible for providing the stiffness of the hemp plant stem. Surrounding the hurd is the vascular cambium (growing tissue) which is an outer ring of phloem and cortex bundles (bast fibres) that provides tensile strength for the plant. An epidermis situated on the outside of the stem prevents parasites from attacking the stalk. The bast section of the stem represents about one third of the total stem volume, while the hurd represents about two thirds. The cross-sectional structure of a hemp stalk can be seen in Figure 2.3.

The bast fibres are the long, strong fibres used in textiles, ropes and composites. They are found in the inner and outer bark layers of the stem, and can be further categorised as being either primary or secondary bast fibres. Both are virtually solid in cross section, although a small lumen (void) is sometimes present. The larger primary bast fibres are mostly found nearer the epidermis, while the secondary fibres dominate the inner regions of the bark. A comparison between the primary and secondary bast fibres can be seen in Table 2.3.
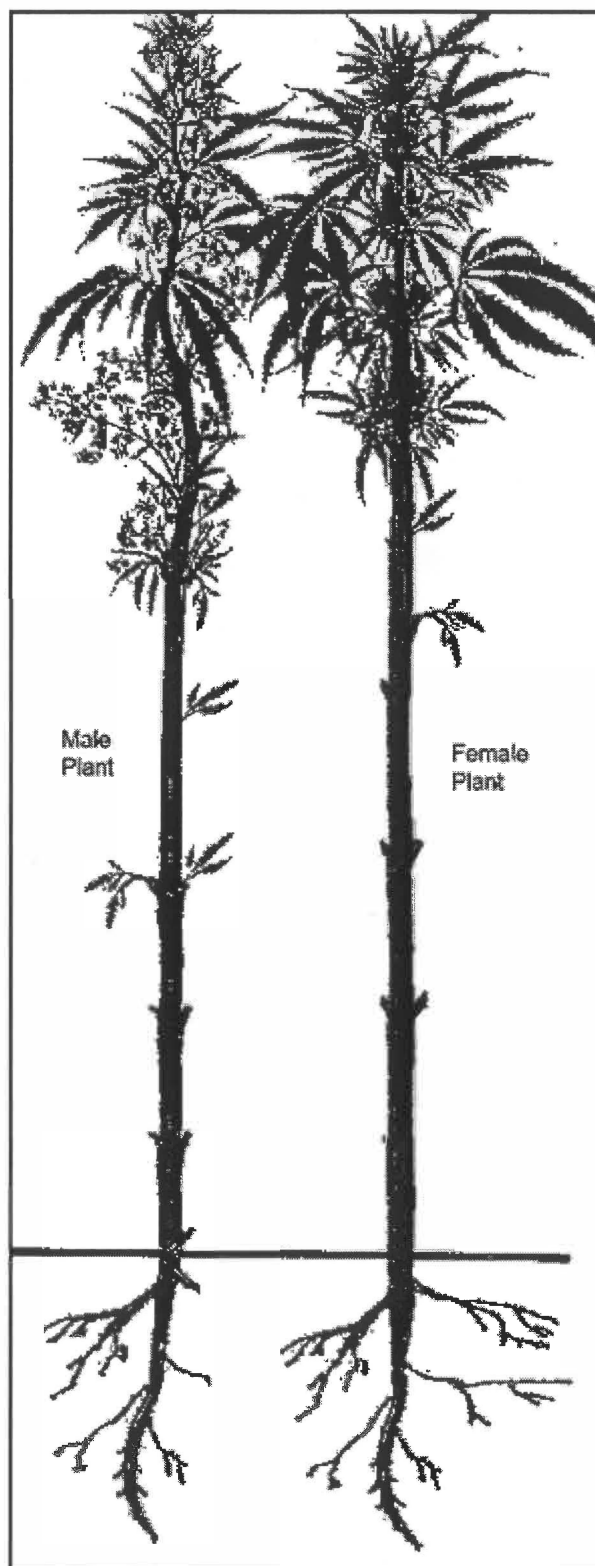
Figure 2.1 Male and female industrial hemp plants
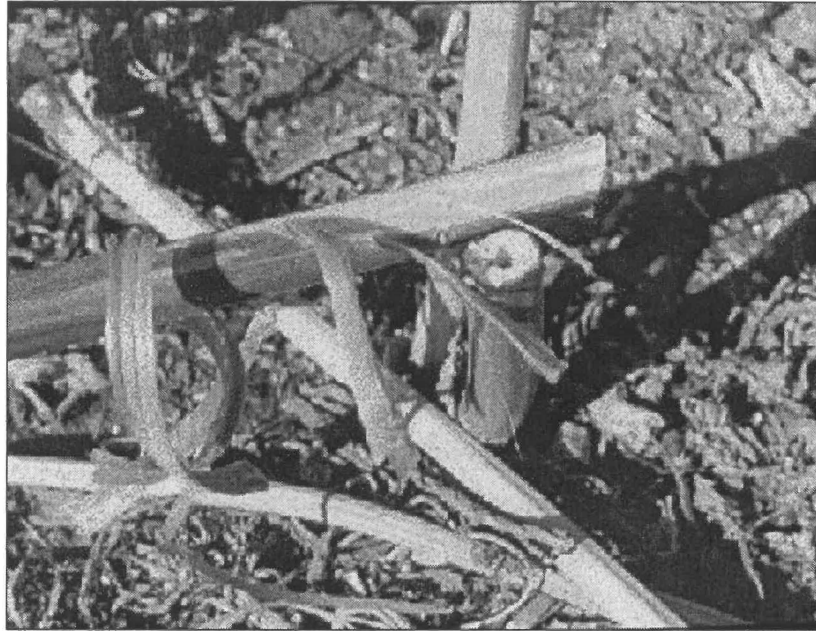
Figure 2.2 Cut hemp stalk
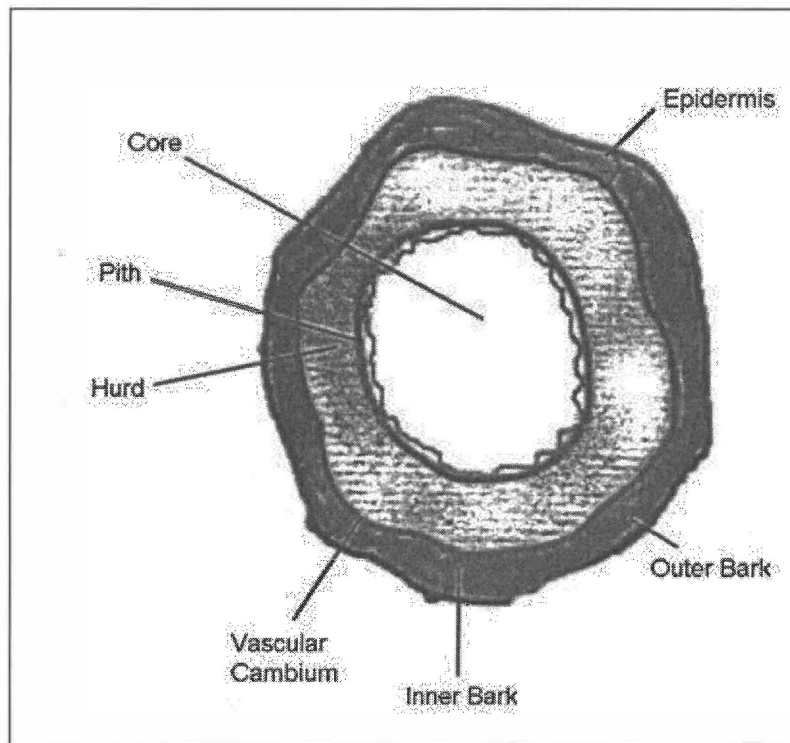
Figure 2.3 Hemp stem cross-section

Table 2.3 Bast fibre comparisons

	Secondary Bast Fibre	Primary Bast Fibre
Diameter (μm)	18-20	28-38
Length (mm)	18-25	25-40
Tensile Strength (MPa)	< 300	< 1000
Cellulose (%w/w)	32-50	55-85

Elementary bast fibres overlap over a considerable length and are glued together by an interface known as the middle lamella, which consists mainly of pectin and hemicellulose. These groups of joined fibres are known collectively as fibre bundles, and are responsible for making up the bark tissue.

The hurd fibres are situated in the woody core of the hemp stalk, and are very thin-walled and short compared to bast fibres. They have large lumens, high lignin and low cellulose contents compared to bast fibres, and they are weak and brittle. As a result, they are not suitable for use in composite materials, but can be used in the papermaking industry as a filler material. A comparison between the bast and hurd fibres can be seen in Table 2.4.

Table 2.4 Summary of hemp stalk composition

Type Of Fibre	Fibre Length (mm)	Fibre Width (μm)
Bast	5-55 (ave 25)	18-25 (ave 22)
Hurd	0.5	25

2.3.2 Bast Fibre Morphology

Elementary bast fibres, along with all lignocellulosic fibres, can actually be considered as composites because they consist of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicellulose. Each fibre (Figure 2.4) consists of many microfibrils that run along the length of the fibre. The fibre wall, or cell wall, is divided into two distinct parts, namely the primary cell wall and the secondary cell wall. The primary cell wall is relatively thin, about 0.2 μm and consists of pectin, some lignin and cellulose. The secondary cell wall makes up most of the fibre diameter, and consists of oriented, highly crystalline microfibrils and amorphous hemicellulose. The microfibrils are packed together in a fibrillar structure, the mesofibrils, with the fibrils oriented spirally at approximately 10^0 to the fibre axis. The fibrils are presumably glued together by a hemicellulose rich phase [3].
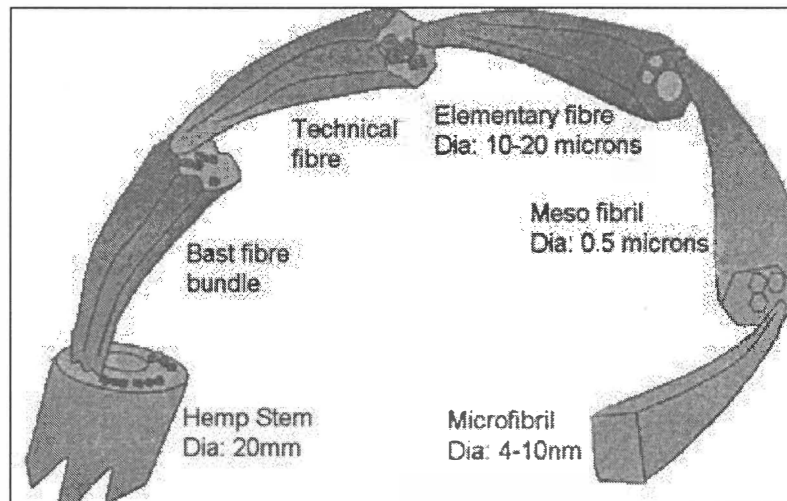
Figure 2.4 Composition of hemp stem

2.3.3 Factors Affecting Fibre Properties

The mechanical properties of single fibres are strongly influenced by many factors, particularly chemical composition and internal fibre structure, which differ between different parts of a plant as well as different plants. The most efficient cellulose fibres are those with a high cellulose content coupled with a low microfibril angle in the range of $7\text{-}12^0$ to the fibre axis. Other factors that may affect the fibre properties are maturity, separating processes, microscopic and molecular defects such as pits and nodes, soil type and weather conditions under which they were grown. The highly oriented crystalline structure of cellulose makes the fibres stiff and strong in tension, but also sensitive towards kink band formation under compressive loading. The presence of kink bands significantly reduces fibre strength in compression and in tension [3].

2.3.4 Hemp Growing Conditions

Hemp is a hardy plant, and grows well in a moderately cool climate. The plant prefers well-drained soils that are high in organic matter, with a neutral or slightly alkaline pH. Clay soils are not suitable, as they restrict the rate of nutrient uptake. Hemp plants are not considered drought tolerant, and will attain an optimum growth rate with an annual rainfall of 750mm. The plant is fast growing, sometimes exceeding a growth rate of one inch per day, and therefore an abundance of water is crucial over the first 30-40 growth days. To achieve maximum fibre production, industrial hemp should be planted in a tight formation ($\sim$180 per m^2).

2.3.5 Hemp Harvesting

Hemp is an annual plant, and has five stages in its lifecycle: germination, growth, flowering, seed formation and death. As the plant goes through these growth stages, the chemical composition and fibre properties of the plant tissues change [10]. Harvesting of hemp for high quality fibre is normally done when 50% of the seeds resist compression [15], or when one third of the anthers on the male plants are shedding pollen. If harvested earlier, the fibre is softer and finer, but also weaker and less dense.

2.4 Hemp Fibre Constituents

The chemical composition of hemp varies according to the variety, the area of production and the maturation of the plant. Hemp fibres are mainly composed of cellulose, hemicellulose, lignin and pectin, although the quantities of each are different in bast and hurd fibres (Table 2.5). Bast fibres contain higher cellulose contents, and are therefore stronger than hurd fibres. Hurd fibres also contain high levels of lignin, which is an undesirable component for cellulose fibres used in composite manufacture

Table 2.5 Chemical analysis of hemp (% w/w) [16]

	Cellulose	Hemicellulose	Pectins	Lignin	Wax + fat	Ash	Proteins
Bast fibre	55	16	18	4	1	4	2
Woody core	48	12	6	28	1	2	3

2.4.1 Cellulose

The long, thin crystalline microfibrils that dominate the secondary cell wall are made of cellulose, and are responsible for providing a high tensile strength to the fibres. Cellulose is a linear polymer consisting of D-anhydroglucose units joined together by β-1,4-glycosidic linkages [9] (Figure 2.5).
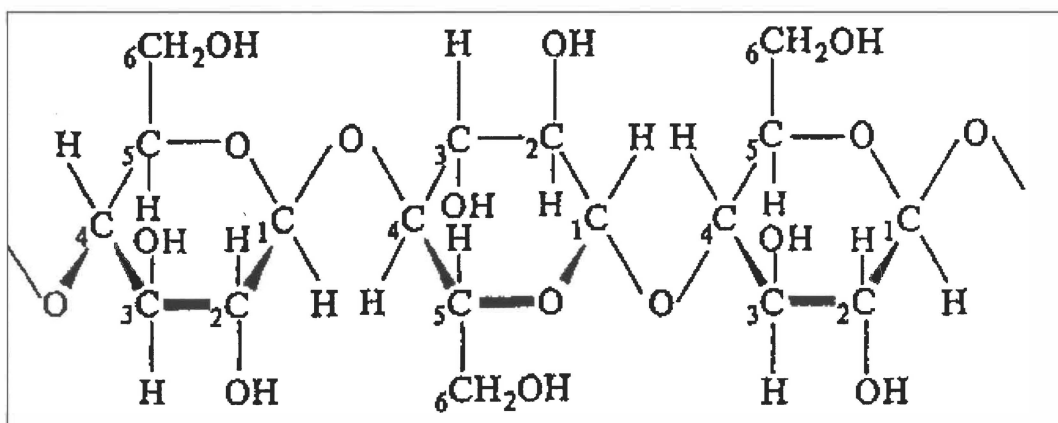
Figure 2.5 The structure of cellulose

The anhydroglucose units do not lie exactly in plane, but assume a chair conformation, with successive glucose residues rotated through an angle of 180^0. Cellulose may either be crystalline or amorphous (non-crystalline), and native cellulose is usually composed of crystalline segments alternating with regions of amorphous cellulose. Most plant-derived cellulose is highly crystalline and may contain as much as 80% crystalline cellulose [10]. The rigidity and strength of cellulose and lignocellulose based materials is a result of hydrogen bonding, both between chains and within chains [17].

The amorphous cellulose regions have a lower frequency of inter-chain hydrogen bonding, thus exposing reactive inter-chain hydroxyl groups (OH) to bonding with water molecules. Amorphous cellulose can therefore be considered hydrophilic due to its tendency to bond with water. Crystalline cellulose on the other hand is highly packed, and very few accessible inter-chain OH groups are available for bonding with water. As a result, crystalline cellulose is far less hydrophilic than amorphous cellulose. Crystalline microfibrils have tightly packed cellulose chains within the fibril, with accessible hydroxyl groups present on the surface of the structure (Figure 2.6). Only the very strongest acids and alkalis can penetrate and modify the crystalline lattice of cellulose.
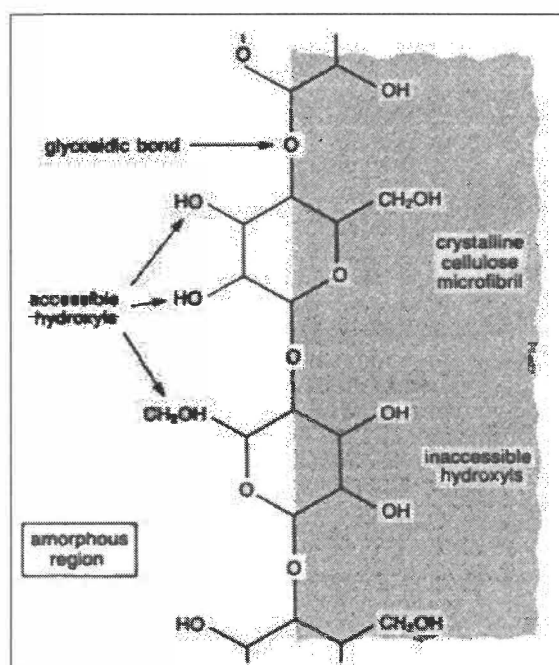
Figure 2.6 Microfibril surface [18]

2.4.2 Lignin

Lignin is a little understood hydrocarbon polymer with a highly complex structure consisting of aliphatic and aromatic constituents, which form a matrix sheath around the cellulose microfibrils and fibres [9]. Lignin provides compressive strength to the slender microfibrils, and prevents them from buckling under compressive loads. No regular structure for lignin has been demonstrated, and it is totally amorphous as opposed to the ordered structure of crystalline cellulose. Lignin is distributed throughout the primary and secondary cell walls, with the highest concentration being found at the middle lamella. The dissolution of lignin in the middle lamella using chemicals aids fibre separation, as is commonly done in the pulp and paper industries. When exposed to ultraviolet light, lignin undergoes photochemical degradation [19].

2.4.3 Hemicellulose

The hemicellulose fraction of the fibre contains a collection of polysaccharide polymers containing mainly the sugars D-xylopyranose, D-glocopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amounts of other sugars [10]. Hemicellulose appears to form a link between cellulose and lignin, thus permitting the effective transfer of shear stresses between the cellulose microfibrils and the lignin [20]. Unlike cellulose, the hemicellulose polymer chains are rarely crystalline and are mainly responsible for the water absorption in the fibre wall. They are also heavily branched and have short side chains, whereas cellulose is a long unbranched polymer. Hemicellulose chains align themselves to the cellulose microfibrils, but lack good lateral bonding as bulky side-chains and substitution prevent regular close packing [10]. Hemicellulose has a greater solubility in solvents compared to cellulose, and can be broken down in high temperature environments.

2.4.4 Pectins

Pectins are a collective name for the heteropolysaccharides found in the primary cell walls of most non-wood plant fibres, and they consist of α-1, 4-linked galacturonic acid units, sugar units of various compositions, and their respective methyl esters [9]. Pectin, along with lignin and hemicellulose, are used to connect the elementary fibres together and can easily be hydrolysed at elevated temperatures. A summary of the cell wall polymers responsible for the properties of cellulose fibres can be seen in Figure 2.7.

| **Biological Degradation** |
| Hemicellulose |
| Accessible Cellulose |
| Non-Crystalline Cellulose |

| **Moisture Sorption** |
| Hemicellulose |
| Accessible Cellulose |
| Non-Crystalline Cellulose |
| Lignin |
| Crystalline Cellulose |

| **Ultraviolet Degradation** |
| Lignin |
| Hemicellulose |
| Accessible Cellulose |
| Non-Crystalline Cellulose |
| Crystalline Cellulose |

| **Thermal Degradation** |
| Hemicellulose |
| Cellulose |
| Lignin |

| **Strength** |
| Crystalline Cellulose |
| Amorphous Constituents |
| Lignin |

Figure 2.7 Cell wall polymers responsible for the properties of lignocellulosics in order of importance [21]

2.5 Thermoplastic Matrices

The primary drawback when using cellulose fibres is the lower processing temperature permissible due to the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures of natural fibre composites are therefore limited to about 200 ^{0}C, although it is possible to use higher temperatures for short periods of time [4]. The first criterion for selecting a suitable composite matrix is a polymer melting temperature below 200^{0}C. Lower temperature processing also reduces processing costs and is more environmentally friendly. Low temperature processing therefore limits the type of thermoplastic that can be used in natural fibre composites to polypropylene (PP), high-density polyethylene (HDPE) low-density polyethylene (LDPE) and polyvinylchloride (PVC) (Table 2.6). These plastics are all commonly used in the plastics industry, they are not expensive and are recyclable.

Table 2.6 Physical properties of various polymers [22]

Properties	Limits	Type of Polymer		
		PP	**LD-PE**	**HD-PE**
ρ (g/cm^3)	Upper	0.920	0.925	1.000
	Lower	0.899	0.910	0.941
W_{24h} (%)	Upper	0.02	<0.015	0.2
	Lower	<0.01		<0.01

Natural fibre composites need to be lightweight, and therefore require a thermoplastic matrix with a low density. Density is often used for the calculation of specific properties, and these specific properties consequently give a better indication of benefits achievable with the material. In the case of hemp fibre reinforcement, PP and LDPE have the lowest densities and are therefore the most suitable in this respect.

Water absorption in the matrix is a great disadvantage in composites, as water can migrate through the polymer to the fibre/matrix interface, resulting in a reduction in the strength of the composite. A matrix with a low level of moisture absorption is thereby desirable, and PP and LDPE are suitable as they have the lowest levels of moisture absorption.

The mechanical properties of the matrix material do not significantly affect the strength of composites containing 50% or more fibre volume fraction. Only a 5 - 10% difference in mechanical properties can be expected when using different thermoplastic matrices in 50% volume fraction reinforced composites. Only in composites with low reinforcing levels do the mechanical properties of the matrix become important [22]. PP happens to have the best combination of tensile strength and stiffness compared to LDPE and HDPE.

It can therefore be concluded that polypropylene is the most suitable thermoplastic for use in natural fibre composites as it has the lowest density, absorbs a low amount of water, has the best mechanical properties and is the cheapest of the 3 polymers [23].

2.6 Issues Regarding the Use of Natural Fibres in Composites

Natural fibres present many advantages compared to synthetic fibres, thus making them attractive reinforcements for composite materials. They are cheap, abundant and renewable, and have good specific properties such as tensile strength and stiffness. Unlike brittle synthetic fibres, natural fibres are flexible and will not fracture when processed over sharp curvatures. This enables the fibres to maintain the desired aspect ratio for good composite performance.

Despite these fibre advantages, untreated natural fibre composites have performed well below their potential capabilities, and therefore have not been extensively used in the thermoplastics industry.

The main reasons for this are as follows:

- Poor interfacial bonding between the cellulose fibres and the thermoplastic matrix
- Limited thermal stability of the composite
- High moisture absorption of the cellulose fibres
- Poor fibre dispersion within the composite
- Biodegradability of the fibres

Other factors that govern the properties of short fibre reinforced composites are:

- The fibre aspect ratio
- Fibre orientation
- Fibre volume fraction

These factors are explained in detail in the following text.

2.6.1 Interfacial Bonding

Almost all plant derived cellulose fibres are polar and hydrophilic in nature, mainly as a consequence of their chemical structure. Plant fibres contain non-cellulosic components such as hemicellulose, lignin and pectin, of which the hemicelluloses and pectins are the most hydrophilic. These components have many accessible hydroxyl (OH) and carboxylic acid groups, which are active sites for the sorption of water [24]. The cellulose component also contains many OH groups, but little water can be accommodated within the highly linear and highly crystalline microfibrils. As a result, only free OH groups on the microfibril surface are available for sorption.

Polyolefins such as polypropylene, however, are largely non-polar and hydrophobic in nature. This incompatibility of the polar cellulose fibres and non-polar thermoplastic matrix leads to poor adhesion, which then results in a composite material with poor mechanical properties [25]. To fully utilise the mechanical properties of the reinforcing fibres and thereby improve the composite properties, it is necessary to improve the bond between the fibre and matrix. This can be achieved by either modifying the surface of the fibre to make it more compatible with the matrix, or by modifying the matrix with the addition of a coupling agent that bonds well to both fibre and matrix.

When the fibre and matrix have been brought into close proximity with one another, the following interfacial bonding mechanisms may occur:
- Mechanical interlocking
- Electrostatic bonding
- Chemical bonding
- Interdiffusion bonding

It should be noted that it is possible for multiple bonding mechanisms to occur at the same interface at the same time.

2.6.1.1 Mechanical Interlocking

Mechanical interlocking on the fibre/matrix interface occurs when the fibre surface is rough and jagged. This mainly increases the interfacial shear strength, and makes the phenomenon of fibre pullout less likely.

2.6.1.2 Electrostatic Bonding

When the fibre or matrix is positively charged and the other is negatively charged, electrostatic bonding occurs. This electrostatic attraction only occurs when there is a difference in charge and intimate contact between the composite components.

2.6.1.3 Chemical Bonding

This type of bonding occurs when a reaction takes place between reactive chemical groups on the fibre surface and compatible groups in the matrix. The strength of the bond depends on and the type of bond and the number of bonds per unit area. The most common chemical bonds and relative bond strengths are as follows [18]:

- Covalent Bond: $200 - 800$ kJ mol^{-1}
- Hydrogen Bond: $10 - 40$ kJ mol^{-1}
- Van der Waals: $1 - 10$ kJ mol^{-1}

2.6.1.4 Interdiffusion Bonding

Atoms or molecules of the fibre and matrix may interdiffuse at the interface to give interdiffusion bonding. For interfaces involving polymers, this type of bonding may take place when polymer chains from each component entangle and intertwine together. The strength of this bonding mechanism depends on the distance over which the chains are intertwined, the degree of entanglement and the number of chains per unit of area.

2.6.2 Thermal Stability

Cellulose fibres are thermally unstable, and cellulose degradation starts to occur at temperatures exceeding 200^0C. This results in the exclusion of some manufacturing processes, and also limits the use of the composite to low temperature applications. Joseph et al [26], however, found that in the case of chemically modified sisal/PP composites, the extent of degradation at a given temperature was less than that of an untreated sisal/PP composite. This improvement in thermal stability was attributed to the improvement in fibre/matrix adhesion with the use of a coupling agent.

2.6.3 Moisture Absorption

A further problem associated with using cellulose fibres in composite materials is high moisture absorption [4]. A moisture build up in the fibre cell wall can lead to fibre swelling and dimensional changes in the composite, particularly in the direction of the fibre thickness [21]. Another problem associated with fibre swelling is a reduction in the adhesion between the fibre and the matrix, leading to a reduction in the mechanical properties of the composite. The debonding between the fibre and matrix may be initiated by the development of osmotic pressure pockets at the surface of the fibre, which is a result of the leaching of water-soluble substances from the fibre surface [27].

Besides dimensional stability, the hydrophilic nature of cellulose fibres also influences the processability of the composite. The tendency of cellulose fibres to absorb moisture causes off gassing (void formation) during compounding with the thermoplastic matrix, leading to the formation of a highly porous material. These pores can act as stress concentration points, and can lead to premature failure of the composite during loading.

Joseph et al [27] showed that the water uptake of natural fibre composites can be reduced considerably by chemically treating the composite, and therefore improving the interfacial bonding.

2.6.4 Fibre Separation and Dispersion

The incorporation of cellulose fibres into a thermoplastic polymer is often associated with poor fibre dispersion due to the wide differences in polarity and strong intermolecular hydrogen bonds between the fibres [4]. To obtain a satisfactory performance from the composite, it is necessary to have a good fibre distribution within the matrix. A good distribution implies that the fibres are fully separated from each other, and each fibre is fully surrounded by the matrix. Insufficient fibre dispersion can lead to clumping and agglomeration of the fibres, resulting in an inhomogeneous mixture of resin-rich and fibre rich areas.

This segregation is undesirable, as the resin rich areas are weak, while the fibre rich areas (clumps) are susceptible to microcracking. Microcracks contribute to inferior mechanical properties of the composite. It is therefore necessary to ensure a homogeneous fibre distribution in order to achieve maximum strength and performance of the composite material.

There are two major factors that affect the extent of fibre distribution and dispersion within a composite. They are: (a) strong hydrogen bonding between the fibres, and (b) fibre length.

To separate the fibres from their fibre bundles, it is necessary to dissolve the pectins and lignin joining the individual fibres together. Fibre separation can easily be performed by treating the fibres with a strong alkali [28]. Fibre separation also occurs during compounding with the thermoplastic matrix. Several factors contribute to this fibre attrition, such as the shearing forces generated in the compounding equipment, residence time, temperature and viscosity of the mix [4].

Cellulose fibres and polypropylene generally do not mix well due to their polar and non-polar characteristics. It is therefore possible to improve compatibility by modifying the fibre surface using dispersing agents such as stearic acid, or by pre-treating the fibre with acetic anhydride [29] [9]. Fibre clumping is not as severe a problem with the treated fibre as it is with untreated fibre [30].

The length of fibres used in the composite is a critical factor. They should not be too long, otherwise they may get entangled with each other resulting in clumping and reduced composite efficiency. If the fibres are too short, the stress transfer area will be too small for them to offer effective reinforcement. As fibre lengths are reduced during composite processing, the ultimate fibre lengths present in the composite are dependent on the type of compounding and moulding equipment used.

To produce efficient composites with well-dispersed fibres, it is therefore necessary to make a careful selection of the initial fibre lengths, processing aids, processing techniques and processing conditions.

2.6.5 Biodegradability

Natural cellulose fibres degrade easily when exposed to nature. Some of these methods of degradation include biological, thermal, aqueous, photochemical, chemical and mechanical degradation processes [21]. In order to produce cellulose fibre-based composites with a long service life, it is necessary to retard this natural degradation. One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry. Undesirable natural fibre properties such as dimensional instability, flammability, biodegradability, and chemical degradation can be eliminated or slowed down in this manner [21]. Chemical treatments can reduce the water uptake in the fibres, and can therefore reduce the amount of fibre swelling and biological degradation by blocking the available OH groups on the fibre surface [31].

2.6.6 Fibre Aspect Ratio

The fibre aspect ratio (length/diameter) is a critical parameter in a composite material. For each short-fibre composite system, there is a critical fibre aspect ratio, which may be defined as the minimum fibre aspect ratio in which the maximum allowable fibre stress can be achieved for a given load [32]. The critical fibre aspect ratio can be calculated using the following equation [1]:

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

Where

l_c = critical fibre length

d = diameter of fibre

σ_f = the tensile strength of the fibres

τ_i = interfacial shear stress

The critical fibre length is not only determined by fibre and matrix properties, but also by the quality of the fibre/matrix interface. Load is transferred from the fibre to the matrix by shear along the interface. For maximum reinforcement, the fibre aspect ratio of any composite system should be above its critical value. This will ensure maximum stress transfer to the fibres before the composite fails. If the fibre aspect ratio is lower than its critical value, insufficient stress will be transferred and reinforcement of the fibres will be insufficient [32] (ie. the fibres are not loaded to their maximum stress value). By contrast, if the fibre aspect ratio is too high, the fibres may get entangled during mixing resulting in poor fibre dispersion. An aspect ratio in the range of 100 – 200 after composite processing is recommended for high performance short-fibre composites [32].

2.6.7 Fibre Orientation

Fibre orientation is an important parameter that influences the mechanical behaviour of short-fibre composites. The maximum composite strength occurs when the reinforcing fibres are aligned, and are oriented parallel to the direction of the applied load. Short-fibre composites, however, rarely consist of fibres oriented in a single direction. During extrusion compounding and injection moulding processes, progressive and continuous changes in fibre orientation throughout the moulded components take place. These changes are complex, and are related to the size and concentration of the fibres, the viscoelastic properties of the melted polymer matrix, the mould cavity and the processing conditions [33]. During extrusion and injection moulding, the polymer melt will undergo both extensional and shear flow, the effects of which can be seen in Figure 2.8. Thus, it is possible to achieve some degree of fibre alignment using extrusion and injection moulding. A further technique for improving the alignment of fibres in short fibre thermoplastic composites is compression moulding.
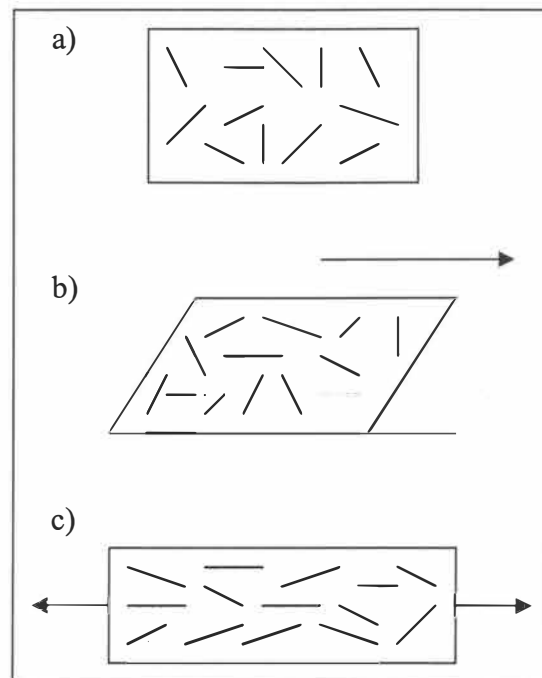
Figure 2.8 Changes in fibre orientation during processing:
a) Initial random distribution
b) Rotation during shear flow
c) Alignment during elongational flow

2.6.8 Fibre Volume Fraction

One of the most significant factors determining the mechanical properties of composite materials is the reinforcing fibre content. Changes in composite properties with variations in fibre content, particularly tensile strength and Young's modulus, can be predicted using failure prediction models such as the 'Modified Rule of Mixtures' (Equation 1, Chapter1) [1].

At low fibre fractions, a decrease in tensile strength is usually observed. This is due to the introduction of flaws created by the fibre ends. These flaws act as stress concentrators, and cause the bonds between the fibre and matrix to break. At higher volume fractions, the matrix is sufficiently restrained and the stress is more evenly distributed. This results in the reinforcement effect outweighing the effects of the stress concentrations.

As the fibre volume fraction is further increased, the tensile properties gradually improve until they surpass those of the matrix. The corresponding fibre volume fraction at which the strength properties of the composite cease to decline and start to increase is known as the critical fibre volume fraction, V_{crit} (Figure 2.9). At very high fibre volume fractions, the strength of the composite starts to decrease due to insufficient filling of the matrix material. Nishino et al [34] produced a kenaf fibre reinforced poly-L-lactic acid composite, and found that the strength increase with an increase in fibre volume fraction was linear up until 70% fibre (by volume), after which there was a reduction in strength.
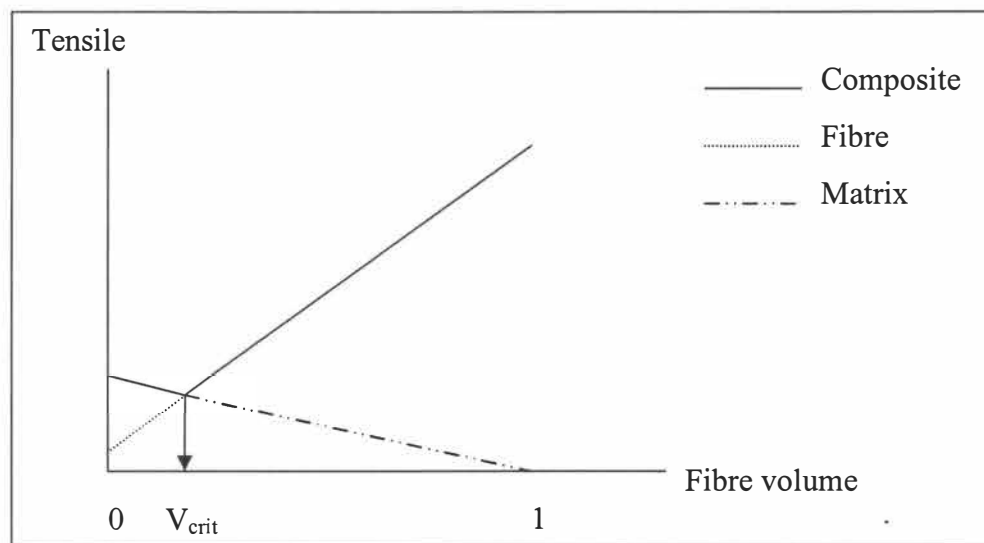
Figure 2.9 The relationship between tensile strength and fibre volume fraction for short-fibre reinforced composites

Another explanation for the decrease in composite mechanical properties at high fibre volume fractions has been mentioned by Fu et al [35]. During the injection moulding of short-fibre reinforced polymers, fibre breakage takes place as a result of fibre-polymer interaction, fibre-fibre interaction, and fibre contact with the surfaces of the processing equipment. At high fibre volume fractions, there is an increase in fibre-fibre interaction and fibre-equipment contact, resulting in a reduction in fibre length and fibre efficiency. A high fibre content therefore leads to a reduction in the mean fibre length, and if the mean fibre length is very different to the critical fibre length, the reinforcement efficiency is reduced.

2.7 Fibre and Matrix Treatments

Natural fibre reinforced thermoplastic composites have poor mechanical properties due to poor adhesion between the fibre and matrix. To improve interfacial bonding, modifications can be made to the fibres, the matrix or both the fibres and the matrix.

Matrix modifications generally consist of the addition of chemical coupling agents and compatiblizers to the unformed thermoplastic matrix, with the purpose of improving the chemical bonding and wettability of the polar cellulose fibres and non-polar matrix.

Fibre treatments may be biological or chemical, and are performed to achieve one or more of the following objectives:

- Removal of undesirable fibre constituents
- Roughening up of the fibre surface
- Separation of individual fibres from their fibre bundles
- Modification of the chemical nature of the fibre surface
- Reduction in the water uptake of the fibre

2.7.1 Biological Treatments

One method of fibre treatment involves the use of naturally occurring micro-organisms, namely bacteria and fungi. These treatments occur in aqueous environments and are relatively cheap to perform, but tend to be time consuming and water polluting. Two methods of biological fibre treatment are retting and fungal treatments

2.7.1.1 Retting

Retting is the controlled degradation of plant stems to free the bast fibres from their fibre bundles, as well as to separate them from the woody core and epidermis. During the retting process, bacteria (predominantly *Clostridia* species) and fungi, release enzymes to degrade pectic and hemicellulosic compounds in the middle lamella between the individual fibre cells [36]. This results in the separation of the bast fibres from the woody core, and leaves the fibres soft and clean (Figure 2.10). The retting duration is an important parameter, as under-retting can result in partially separated fibres, while over-retting can weaken the fibre and cause higher losses in subsequent processing.
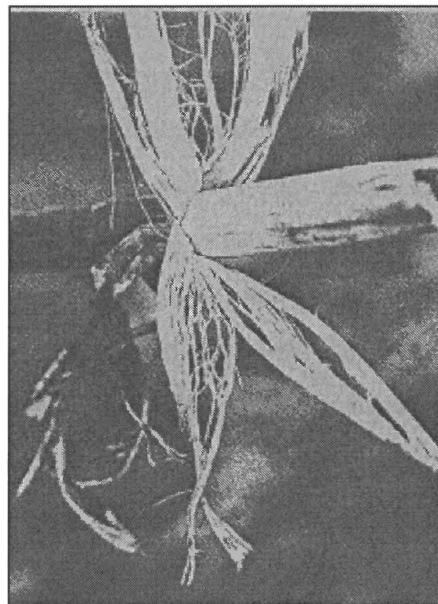
Figure 2.10 Retted hemp stem

Retting may take the form of water retting, where the plant stems are submerged in water, or dew retting, where plant stems are left in the field to partially degrade. Water retting requires abundant supplies of water and produces a more uniform and high quality fibre [37], but is not generally practiced because of environmental pollution problems. Dew retting, on the other hand, is a much slower process [38] and can only be performed in regions where sufficient dew is released at night.

Traditionally, retting has yielded high quality fibre, but fibre quality is also dependent on the weather [39] and on each farmer's skill and judgement. If hemp is grown from seed, harvest does not occur until later on in the season when the weather is cool, and this can negatively affect the retting process and therefore fibre quality.

2.7.1.2 Fungal Treatments

Natural cellulose fibres are prone to fungal attacks in damp and humid conditions. Fungal infestations of wood, especially by sapstain and white-rot fungi, have long caused serious wood quality problems such as decay and discolouration. These disadvantages, however, can be used for a positive effect in assisting the selective removal of plant fibre components (ie. cellulose, hemicellulose, and lignin), and physically modifying the fibre wall for improved fibre/matrix interfacial bonding.

Sapstain fungi grow in wood, and can cause severe wood discolouration due to the presence of pigmented hyphae (intertwined threads that bore into the wood). These fungi derive their nourishment from the plant cell contents, and can spread rapidly throughout a suitable growing medium. Sapstain fungi are significant because their hyphae can break into the plant fibres, and make fine holes as they pass through the cell wall. This leads to an increase in the permeability of the fibre, thus making it more susceptible to water absorption [40]. The sapstain activity has potential benefits for fibre treatment, as the holes in the cell wall created by the fungal hyphae increase the fibre surface area, and expose additional reactive OH groups for bonding with the matrix. These holes also roughen up the cell wall, and may lead to an improvement in mechanical interlocking with the matrix.

White-rot fungi (*Basidiomycotina*) are responsible for some of the most destructive forms of wood degradation. They usually remove cell wall constituents (lignin, hemicellulose and cellulose) simultaneously at approximately equal rates. However, a few varieties of white-rot fungi have the ability to degrade lignin and hemicellulose at a faster rate than cellulose [41].

White-rot fungi form extensive hyphae that penetrate the wood tissues, forming large boreholes in the cell walls. As these fungi degrade the wood cell walls to derive nourishment, they quickly weaken the infected areas [40]. Wood under decay by white rot fungi maintains its fibrous nature and loses strength gradually until it is completely degraded. The wood appears stringy or lamellate in later stages of decay due to the degradation of lignin [42]. White-rot fungi may also have the potential to assist fibre treatment, based on their ability to preferentially degrade lignin and hemicellulose, they can assist with fibre separation and can also roughen the fibre surfaces to improve interfacial bonding

2.7.2 Chemical Treatments

Fibre treatments involving the use of chemicals play an important role in improving the reinforcing capabilities of the fibres. These treatments can either be classified as fibre pre-treatments, coupling agents, compatibilizers or dispersing agents. Pre-treatments include the use of chemicals that remove undesirable and non-strength contributing fibre constituents such as lignin, pectin and hemicellulose. Compatibilizers are chemicals that lower the surface energy of the fibre to make it more non-polar and therefore compatible with the thermoplastic matrix. Dispersing agents are used to improve the dispersibility of the fibres in the matrix. Coupling agents are mainly responsible for improving the adhesion between the reinforcing fibres and the matrix material, but can sometimes reduce the water uptake of the fibres and assist with fibre dispersion as well. Due to this overlap in functions and to simplify matters, all bonding agents and surfactants have been grouped together as chemical treatments.

So far, over forty coupling agents have been used in the production and research of natural fibre composites [43]. The most popular treatments include the use of alkalis, anhydrides and anhydride-modified copolymers, silanes and isocyanates.

2.7.2.1 Alkali Treatments

Alkali fibre treatments using sodium hydroxide (NaOH) have been used extensively in the pulping of wood fibre for paper use. The alkali treatment of lignocellulose fibres, especially when performed at elevated temperatures, is an effective method of removing lignin and hemicellulose in the fibre wall [18], as well as producing a cleaner and rougher fibre surface [44].

Some alkali treatments can result in the selective degradation of lignin, pectin and hemicellulose in the fibre wall, whilst having little effect on the cellulose components. This lignin, pectin and hemicellulose removal assists in the separation of the elementary fibres, as well as the exposure of more active OH sites for interfacial bonding [28]. Furthermore, it has been reported that the removal of cementing materials (lignin and hemicellulose) within the fibre wall leads to better packing of the cellulose chains, thus increasing the crystallinity index of the fibre. In addition, treatments with NaOH lead to a decrease in the spiral angle and an increase in the molecular orientation of the cellulose chains [45]. Alkali treatment also results in a rougher fibre topography, which improves interfacial bonding by giving rise to additional sites for mechanical interlocking [44].

Alkali fibre treatment is therefore a suitable pre-treatment process for natural fibres that are to be used in thermoplastic composites.

2.7.2.2 MAPP Treatments

Maleic anhydride (MA) grafted polypropylene (MAPP) is a coupling agent that also acts as a compatibilizer. It consists of long polymer chains with a MA functional group grafted onto one end. MAPP acts as a bridge between the non-polar polypropylene matrix and the polar fibres by chemically bonding with the cellulose fibres through the MA groups, and bonding to the matrix by means of chain entanglement.

The MA functional group interacts strongly with the fibre surface through covalent and hydrogen bonding with the reactive OH groups on the surface of the cellulose and lignin (Figure 2.11). The polymer chains of MAPP then form a bond with the unreactive polypropylene matrix by means of chain entanglement. These entanglements function as physical cross-links that provide some mechanical integrity up to and above the glass transition temperature of the matrix [4]. The length of polymer chain is an important characteristic regarding the level of chain entanglement. When polymer chains are very short, there is little chance of entanglement between coupling agent and matrix chains as they can easily slide past one another (Figure 2.12). When the polymer chains are longer, entanglement can then occur, but the viscosity of the coupling agent also becomes high resulting in poor fibre wetting. If the MAPP chains are extremely long, they may then entangle with the polypropylene molecules so that the MA groups on the MAPP have difficulty migrating to the OH groups on the fibre surface. An optimum chain length or a critical molecular weight is therefore necessary to develop sufficient entanglement with the matrix polymer.
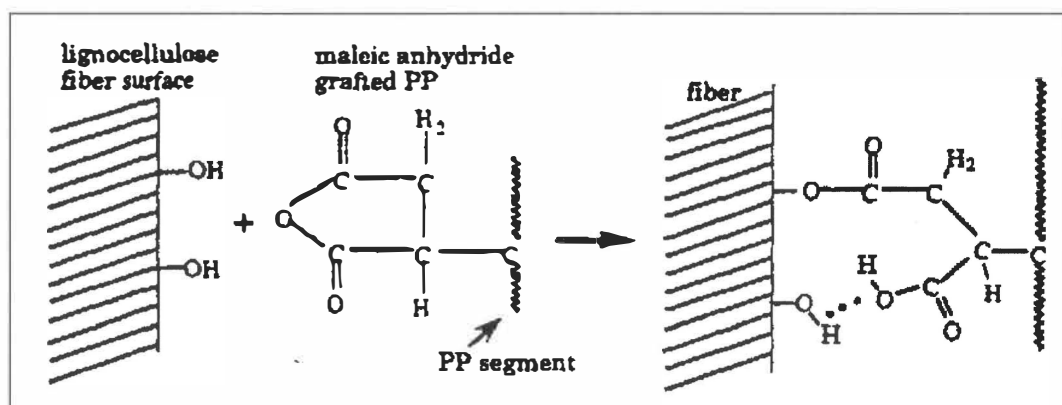
Figure 2.11 Reaction mechanisms of maleated PP with the surface of the lignocellulosic fibre. Note potential for both covalent and H-bonding [4].
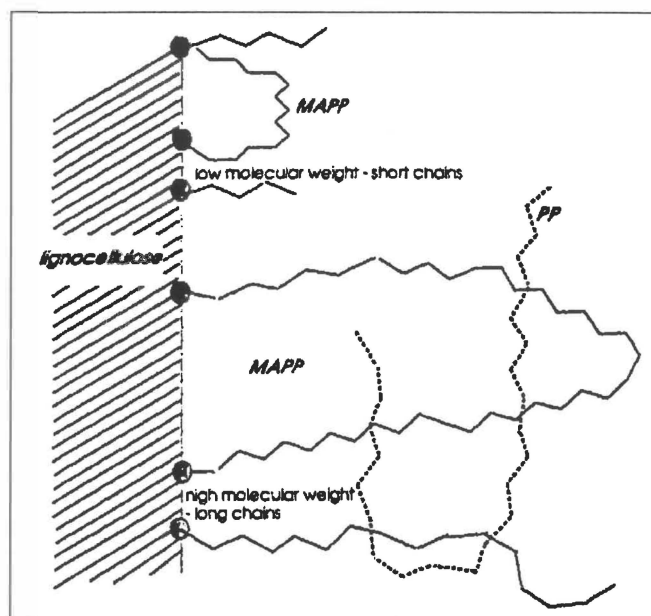
Figure 2.12 Schematic of possible PP molecular entanglements with the longer chains of MAPP. Shorter chains of MAPP have less opportunity to entangle with the PP molecules [4].

Sanadi et al. [46] used MAPP (Eastman Chemical Epolene G-3002) with kenaf fibre reinforced polypropylene composites. The resulting composites with 50wt% kenaf fibre and 3% MAPP displayed a tensile strength increase of 88% and a Young's modulus increase of 350%. Pickering and Ji [47] used MAPP (Aldrich A-C 950P) to couple radiata pine fibres with polypropylene, and achieved increases in tensile strength and Young's modulus of 123% and 177% respectively with fibre weight fraction of 50% and a MAPP weight fraction of 2%.

2.7.2.3 Acetic Anhydride Treatment

Fibre treatment with acetic anhydride (acetylation) is an effective method of reducing the hydrophilic characteristics of cellulose fibres [48], as well as improving fibre dispersion within a thermoplastic composite. Acetic anhydride is a compatibilizer that lowers the surface energy of the fibre to make it non-polar and more similar to the thermoplastic matrix [43]. This is achieved by the formation of stable acetate bonds with the reactive OH groups on the fibre surface.

Once the acetic anhydride has bonded with the OH groups of the fibre, they are no longer reactive and are therefore no longer free to bond with other OH groups, water or other chemicals. Chemical modification of cellulose fibres with acetic anhydride is a good method of providing dimensional stability and decay resistance [49].

Baillie and Zafeiropoulos [9] treated dew-retted and green flax fibres with acetic anhydride. They found that acetylation did not significantly affect the single fibre tensile strength of dew retted flax fibres, and that a slight increase in strength was observed for green flax fibres (11.8% increase in strength). The strength increase in green flax was thought to be due to the removal of some of the more amorphous components of the fibre such as pectin. It was also reported that acetylation slightly improved the interfacial bonding of dew retted flax reinforced isostatic polypropylene composites, and caused a significant improvement for the green flax composites. A shear strength increase of 2.3% was observed for the acetylated dew-retted flax composites, and a shear strength increase of 83% was observed for the acetylated green flax composites.

2.7.2.4 Silane Treatments

Organic-inorganic silane coupling agents have been used for over 50 years to couple glass fibres with polymeric matrices. They have, however, been more recently used to couple cellulose fibres to thermoplastics such as polystyrene and polypropylene [50] and polyethylene [51]. Silane-based coupling agents are hydrophilic compounds based on a silicon molecule with different organic groups attached. One group interacts with the hydrophilic cellulose fibres, while another group reacts with the hydrophobic thermoplastic matrix material [52]. The reaction between cellulosic materials and silanes is not simple. It is known that silane coupling agents react with cellulose water (or additional water) to form silanol (Si-OH) groups. After hydrolysis, the coupling agent can develop either covalent or hydrogen bonds with the free OH groups on the fibre surface, but the degree of conversion of such OH groups is not well known [50].

Valadez-Gonzalez et al. [51] showed that the partial removal of lignin and other alkali soluble compounds from the fibre surface greatly increases the adsorption of the silane coupling agent onto the fibre wall.

Bataille et al. [53] produced a highly bleached hardwood pulp-fibre reinforced polypropylene composite using the silane coupling agent γ-metacryloxy-propyltrimethoxysilane (A-174). By including the silane coupling agent and processing the composite at 140 ^{0}C, they achieved a tensile strength increase of 50%.

2.7.2.5 Isocyanate Treatments

Polymeric isocyanates have been used as coupling agents to improve the interfacial bonding in natural fibre reinforced thermoplastic composites. Isocyanates contain a reactive isocyanate group (-N=C=O) which is able to react with the hydroxyl groups of cellulose. As a result, the hydrophilic nature of wood is reduced [27]. A number of isocyanates are available, but the most reactive isocyanate that can be used with cellulose fibres and a PVC (thermoplastic) matrix is Polymethylenepolyphenyl isocyanate (PMPPIC) [43]. Raj et al. [54] also showed that PMPPIC was the most reactive isocyanate when coupling chemithermomechanical pulp with polyethylene. The tensile strength and Young's modulus improvements of the chemithermomechanical pulp reinforced polyethylene composite using a PMPPIC coupling agent were 60% and 90% respectively.

2.8 Processing of Short-Fibre Reinforced Composites

The processing methods used to fabricate thermoplastics reinforced with short cellulose fibres are generally the same as those used for short fibre synthetic composites. The most widely used techniques for mixing fibres with a thermoplastic matrix are melt mixing and extrusion. Injection moulding and compression moulding are two of the most commonly used composite forming techniques, although extrusion is also sometimes used.

2.8.1 Melt Mixing

Melt mixing using a radial flow (turbulent) mixer is a commonly used method for combining short reinforcing fibres and thermoplastic materials. The thermoplastic material is initially heated up to its melting temperature before the fibres are added to the mix [55]. After the mixing has taken place, the composite mix can be rolled or formed into the desired shape. Various mixer settings such as the mixing duration, rotor speed and melt-chamber temperature can affect the composite properties. Joseph et al. [56] combined sisal fibres with polypropylene using a Haake Rheocord mixer. They showed that ineffective mixing and poor fibre dispersion occurred at short mixing times (<10 min) and low mixing speeds (<50 rpm), while low mixing temperatures (<170^0C) resulted in extensive fibre breakages. Composite strength loss due to fibre breakage also occurred at high mixing times (>10 min) and high mixing speeds (>50 rpm), with high mixing temperatures resulting in fibre degradation and poor fibre dispersion.

2.8.2 Extrusion

Extrusion is one of the most effective methods of compounding natural fibres and thermoplastic materials. The extruder creates a homogenous melt from the thermoplastic (usually pellets or powder) and fibres fed into it. This composite melt is drawn forward through the extruder barrel by counter-rotating screws where it is melted further, mixed and compressed. The homogenous extruder melt then exits the barrel through a shaped die that determines the shape of the extrudate [55] (Figure 2.13).
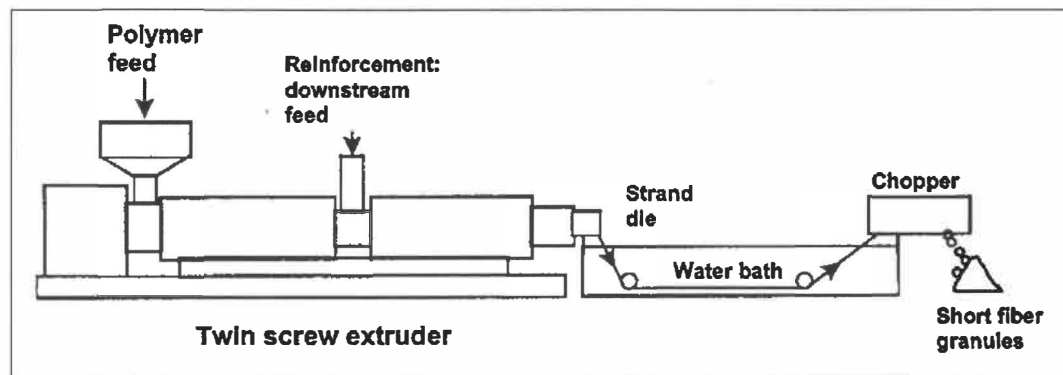
Figure 2.13 The extrusion compounding process for the manufacture of short fibre reinforced thermoplastic injection moulding granules [57].

Extrusion using a twin-screw extruder is often carried out prior to injection moulding because a good fibre distribution within the matrix is achievable [58], and the extruded composite is easily chopped into injection mouldable pellets. In producing fibre reinforced composites using extrusion techniques, it is necessary to optimise the extent of compounding. Inadequate compounding causes poor dispersion and poor wetting of the fibres, while excessive compounding causes severe fibre damage and fibre shortening, all of which lead to a reduction in mechanical strength.

Most fibre damage is caused by friction between fibres, or between fibres and the thermoplastic melt. One method of minimising fibre breakage is to feed the thermoplastic into the main in-feed port and to feed the fibres into a second port further down the barrel [59]. This enables the thermoplastic to melt before coming into contact with the fibres, thus reducing the shear forces acting on the fibres. A second method preserving the fibres during compounding is to keep the compounding distance as short as possible, and also to exclude kneading elements on the extruder screws [60].

Another variable that can affect the composite strength is processing temperature. If the temperature is too low, insufficient wetting of the fibres can occur, resulting in a weaker composite. If the temperature is too high fibre degradation occurs, also resulting in a weaker composite.

2.8.3 Injection Moulding

Injection moulding is one of the most widely used processes for manufacturing moulded parts from thermoplastic and reinforced thermoplastic materials. It is one of the few manufacturing processes capable of producing net shape composite parts in high volumes and high production rates [61].

Short fibre reinforced composites can be processed into complex shaped components with standard injection moulding machines as used for common thermoplastics. Composite materials for injection moulding must be capable of flow under pressure and are therefore usually short fibre reinforced thermoplastics with a relatively low fibre fraction (typically <50wt% or 30vol%). However, too low a fibre fraction does not give sufficient property improvements to the moulded composite. At high volume fractions, difficulties in processing can compromise properties such as impact performance [61].

The injection moulder performs the function of melting the pre-formed (usually by extrusion) composite pellets, delivering a homogeneous melt to the machine nozzle, and injecting the melt into the closed mould. The mould unit, which comprises of a fixed half and a moving half, contains the cavity into which the composite is injected and cooled, thus forming the part shape [62] (Figure 2.14).
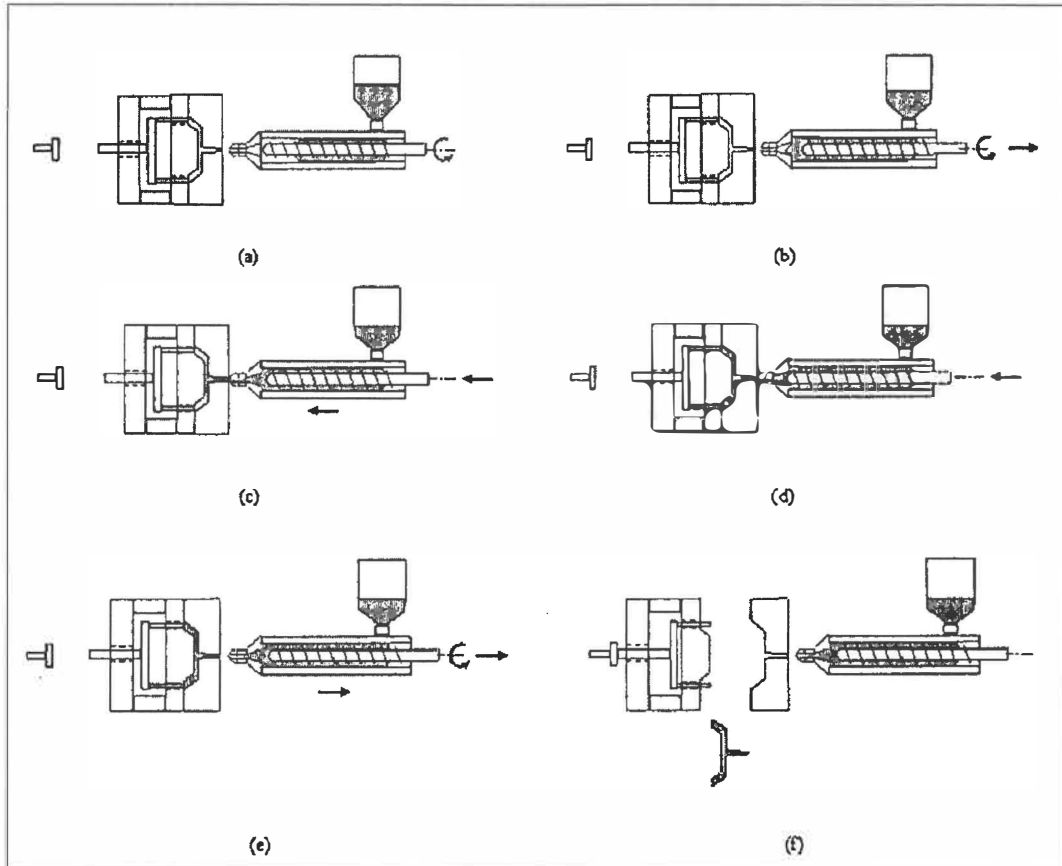
Figure 2.14 Basic operations of the injection moulding cycle: (a) start up; (b) screw back 1; (c) injection; (d) hold-on; (e) screw back 2 ; (f) cooling and ejection [61].

Unlike extrusion and melt mixing, it has been found that injection moulding does not significantly damage cellulose reinforcing fibres. Keller [60] compared the fibre length distribution of an extruded hemp fibre reinforced thermoplastic composite with the same composite that had been extruded and then injection moulded. The results showed that average hemp fibre length after extrusion was 0.53mm (reduced from 8mm average length), and that there was no significant reduction in fibre length with the addition of the injection moulding process.

2.8.4 Compression Moulding

Compression moulding is a commonly used processing technique for producing large, relatively flat composite parts with good mechanical properties. The compression moulding of glass mat thermoplastics is widely used for the production of complex semi-structural components, notably for the automotive industry [63]. Compression moulding basically involves the hot pressing of randomly orientated or aligned fibre mats, either chopped or in continuous form, with a thermoplastic material.

The compression moulding operation begins with the placement of a stack of alternating fibre-mat and thermoplastic sheets onto the bottom half of a preheated mould cavity [55]. The top half of the mould is lowered at a constant rate until the desired process pressure is reached, thus causing the melting and consolidation of the composite. Once the composite has been consolidated, it is cooled and removed from the mould.

Chapter 3:
Materials and
Methods

Chapter 3:
Materials and Methods

3.1 Introduction

The purpose of this research was to produce an improved hemp-fibre reinforced polypropylene composite by optimising the fibre strength, fibre processing, composite processing and fibre-matrix interfacial bonding. The first step to achieving this objective was to optimise the strength of the reinforcing fibres by investigating the effects of cultivation time on the hemp fibre strength and stiffness. Once the optimum growing time had been established, biological and alkali treatments were performed on the hemp fibres to either improve fibre separation, remove lignin, or to roughen the fibre surface to improve bonding with a polypropylene matrix. The fibre strength and stiffness were then determined for each treatment, and Kappa tests were performed to determine the amount of residual lignin in the alkali treated fibres.

Once the best fibre treatment process had been determined, treated fibres could then be used in the fabrication of composite materials. Composites were produced by compounding the chopped fibres and polypropylene powder in a twin-screw extruder, before being pelletised and injection moulded into tensile test specimens. A maleated polypropylene (MAPP) coupling agent was added to some composites, and a range of composites were produced by varying the hemp fibre and MAPP contents of each. All composites were then tensile tested to determine their strength and stiffness.

In this research, two crops of raw industrial hemp (*Cannabis sativa* L) were used:

(a) Hawkes-Bay hemp: This hemp was grown for experimental purposes in the Hawkes Bay region of New Zealand, and was harvested in the summer of 2001/2002. The seeds were planted late in the growing season, and as a result the crop size and yield were well below what was expected. This hemp was harvested after seed production, and partial retting had occurred due to delays stalk baling. The average stalk height was 1.72 metres, and stalk diameters varied from 8mm to 14mm.

(b) Waikato hemp: This hemp was grown by Hemptech NZ Ltd in the Waikato Region of New Zealand, and was planted in mid October 2002. Harvesting was done at 5-day intervals starting at the end of January 2003. After harvesting, stalks were baled and stored under cover to prevent retting. The average stalk height was 3.15m, and stalk diameters varied from 14mm to 25mm (Figure 3.1).

Figure 3.1 Waikato hemp crop

3.2 The Effects of Cultivation Time on Fibre Strength and Stiffness

As the chemical constituents and physiology of hemp bast fibre change throughout the growing season, the fibre properties vary accordingly. Fibre characteristics such as strength, length, diameter, chemistry and homogeneity are influenced considerably by the time of harvest [64]. The purpose of this experiment was to investigate the effects of cultivation time on the strength and stiffness of hemp bast fibre.

3.2.1 Crop Harvesting and Retting

For this experiment Waikato hemp was harvested at 5-day intervals, starting at 99 days after planting (when pollen was just about to be released by the male plants). Further harvests were performed at 104, 109, 114, 119 and 124 days after planting. For each harvest 20 plants were cut down, and special care was made to collect a mixed selection of male and female plants, as well as to select plants from the outer and inner regions of the plantation.

Once the hemp stalks had been harvested, samples from each growing period were water retted to separate the strong bast fibres from the woody core, and to enable individual fibres to be separated from their fibre bundles. To speed up the water retting process, a retting mixture containing all the necessary micro-organisms was prepared prior to the retting process by immersing some partially retted Hawkes-Bay hemp stalks in water for 10 days. The retting mixture was then diluted with water, and distributed evenly into buckets containing hemp samples. The hemp samples were then retted for a period of 6 days under lab conditions. The bast fibre was then removed from the woody core, washed using a pulp and paper fibre-washer (Figure 3.2), and dried in a drying oven at 80^0C for 48 hours.
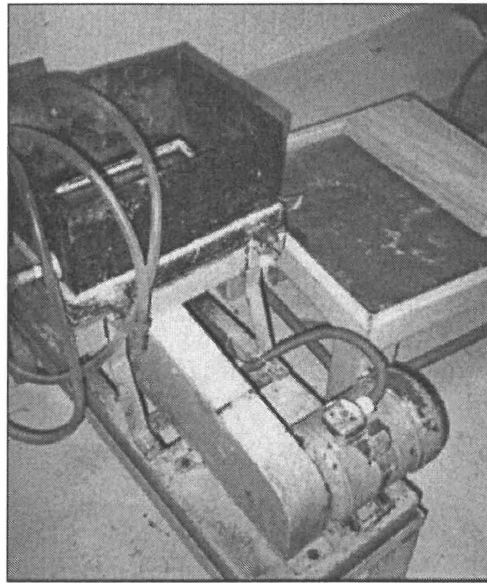
Figure 3.2 Pulp and paper fibre-washer

3.2.2 Single Fibre Tensile Testing

After retting, washing and drying, single hemp fibres from each harvest were tensile tested in accordance with the ASTM D3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials.   Retted and unretted control fibres were separated by hand and mounted on cardboard mounting-cards with 10mm holes punched into them to provide a 10mm gauge length. A small amount of PVA glue was applied to the two edges on either side of the hole along the length of the card, and the fibres were carefully put into place (Figure 3.3).
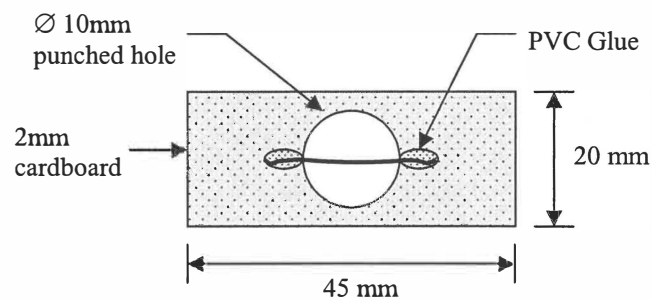
Figure 3.3 Single fibre mounting

The fibres were then inspected, using an optical microscope with a calibrated eyepiece at 200x magnification in order to measure the average diameter of each fibre, and to ensure that only a single fibre was present on each card. The mounted single fibres were then individually placed in the grips of an Instron-4204 tensile testing machine (Figure 3.4), and the supporting sides of the mounting cards were carefully cut using a hot-wire. The fibres were then tensile tested to failure at a rate of 0.5mm/min using a 10N-load cell. Average strengths were obtained using results from thirty specimens.
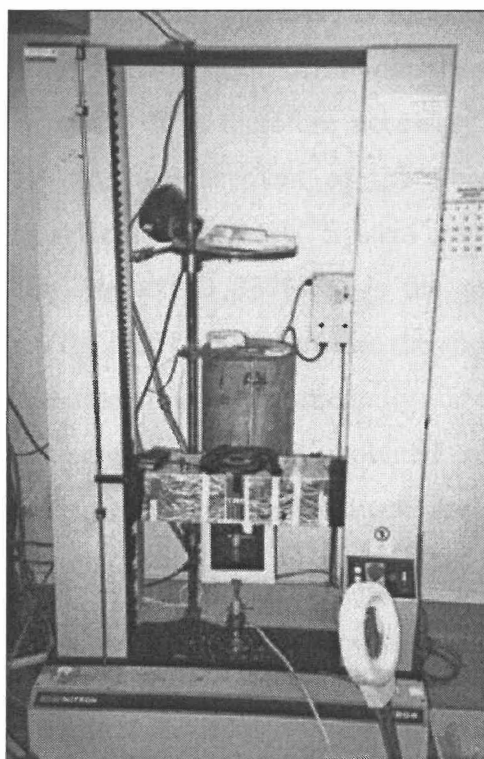
Figure 3.4 Instron-4204 tensile testing machine

3.2.3 Compliance

To calculate the Young's modulus of a test specimen using tensile test data, it is necessary to obtain accurate values for tensile load and displacement (elongation). The load cell of the Instron tensile tester measures load values, but an extensometer or strain gauge attached to the sample would be required to accurately measure the displacement. Unfortunately, the use of a standard extensometer or strain gauge on hemp fibres is not possible due to their small diameters. The displacement of the fibre during the tensile test can therefore only be measured individually through the displacement of the testing machine cross-head. The cross-head displacement, however, is actually a combination of the fibre elongation as well as the elongation of the crosshead, specimen grips, and the cardboard mounting card. It is therefore necessary to utilise a correction factor to determine the true displacement of the fibre, which involves the calculation of the testing system compliance. System compliance (C_s), as defined by ASTM Standard Test Method D 3379-75, is the portion of the indicated elongation contributed by the load train system and the specimen gripping system. This compliance must be determined experimentally for a given combination of test machine conditions, grip system and mounted specimen. It must be subtracted from the apparent elongation to yield true specimen elongation in the gauge length.

The procedure for determining system compliance is described in the ASTM D 3379-75 Standard Test method for Tensile Strength and Young's Modulus for High Modulus Single-Filament Materials, and was also used by Kromm et al. [65] to determine the system compliance of a particular tensile testing system. It requires the tensile testing of filaments of a material with a known Young's modulus, over a range of gauge lengths. For this experiment, E-glass was chosen as it has a known Young's modulus of 69 GPa, which is the same range for hemp fibres. From the corresponding load displacement curves for each gauge length of E-glass, the apparent compliance (C_a) for each gauge length could be determined by inverting the gradient of the straight-line section of each curve.

The apparent compliance is a linear function of gauge length, which can be extrapolated to zero gauge length to give the system compliance (C_s) (testing system compliance) (Figure 3.5)

y = 0.2189x + 0.5255

C_s = Zero gauge length intercept
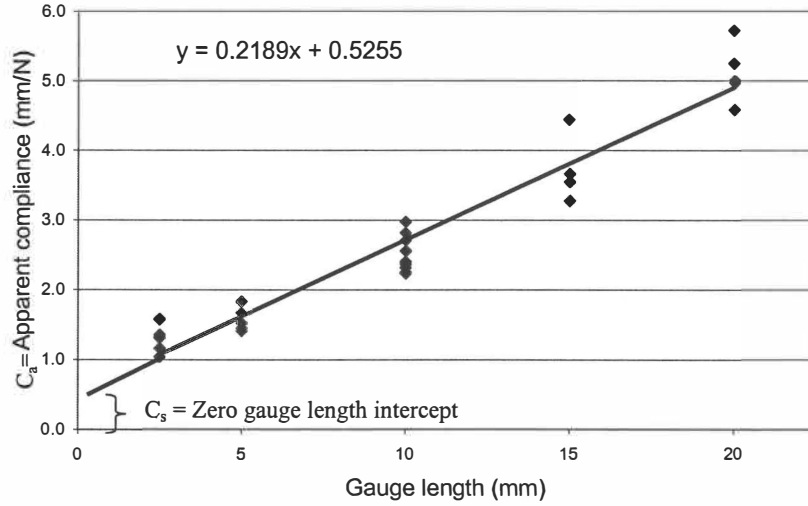
Figure 3.5 System compliance of tensile testing system

The true compliance (C) for any sample is thus the difference between the apparent compliance (C_a) and the system compliance (C_s):

$$C = C_a - C_s \qquad (3)$$

The Young's modulus of a 10mm gauge length e-glass fibre, with a cross sectional area of 7.178 x10^{-11} m^2 (an average CSA for all glass fibres tested) was calculated as 64 GPa using equations 3 and 4. This stiffness was thought to be sufficiently close to the manufacturers quoted value of 69 GPa, thus showing that the above method has a sufficient level of accuracy to be used to calculate the Young's modulus of single fibres using the same tensile testing system.

To calculate the Young's modulus of a fibre, the following formula could then be used:

$$Y_m = \frac{L}{CA} \qquad (4)$$

where:

Y_m = Young's modulus, Pa

L = specimen gauge length, mm

C = true compliance, mm/N

A = average cross sectional area of fibre, m^2

The true compliance (C) of the fibre could be calculated by using the system compliance trend-line formula (equation 5) and equation 3:

$$y = 0.2189x + 0.5255 \qquad (5)$$

where:

y = the indicated compliance (C_a) of the fibre, mm/N (the inverse of the slope of the straight line part of the load displacement curve)

x = the gauge length of the fibre, mm

0.5255 = the system compliance (C_s), mm/N

3.3 Fibre Treatment

For all the fibre treatment experiments, Hawkes-Bay hemp was used. Bast fibre was carefully removed from the hurd before being chopped into 10cm lengths. The chopped fibres were then dried in a drying oven at 80^0C for 24 hours. Biological treatments using fungi and alkali treatments using sodium hydroxide (NaOH) were then used to treat the fibres.

3.3.1 Biological Treatment

The purpose of treating hemp fibres with fungi is to modify the fibre surface by removing lignin and by roughening the fibre walls.

Three fungal strains were used to biologically treat samples of Hawkes-Bay hemp fibre. One strain was a *Basidiomycete* white-rot fungus (D2B), and the other two strains were albino *Ophiostoma floccosum* sap-stain fungi (F13 and F124).

Five samples of hemp fibre, each containing 12g of semi-dried fibre, were weighed equally and placed into double zip-lock bags. The 3 fungal strains were grown in a YM broth (nutrient substrate), and were incubated for a week at a temperature of 27^0C. After incubation, the supernatant for each fungus was aseptically tipped off and the hyphal mat inoculated into separate hemp-containing zip-lock bags. The fungus:hemp ratio was approximately 10mg fungus:12g semi-dried hemp (ie. equivalent to 80mg fungus per 100g dried hemp fibre). The 3 fungus-containing bags and 1 control bag were thoroughly shaken and then incubated in a darkroom at 27^0C for 3 weeks. A fifth bag of hemp was inoculated with F13 strain, and was incubated under the same conditions for 4 weeks.

After treatment, the biologically treated fibres and the control were washed in a fibre washer for 10 minutes before being dried in a drying oven at 80^0C for 24 hours. The fibres were then mounted on cardboard mounting-cards, and tensile tested using the same process as stated in 3.2.2 Single Fibre Tensile Testing.

3.3.2 Alkali Treatments

Sodium hydroxide (NaOH) digestion is a method commonly used by the pulp and paper industry to separate individual cellulose fibres from each other. This method can also be used for separating hemp bast fibres [66]. The purpose of this experiment was to optimise the alkali treatment process to achieve good fibre separation, to maximise lignin removal and to minimise fibre degradation. The variables that were manipulated to achieve this optimum process were:

(1) NaOH concentration: 10% or 15% NaOH solutions (by weight)
(2) Digestion process temperature: 160^0C or 180^0C
(3) Hold time at the maximum process temperature: 15 minutes or 45 minutes

3.3.2.1 Lab-Scale Pulp Digester

The digestion of hemp fibre was performed at high temperatures and high pressures inside a lab-scale pulp digester (Figure 3.6 and Figure 3.7). The upper temperature limit of the digester is 200^0C, and the processing temperature is regulated by controlled heating elements situated throughout the shell. During operation, the entire vessel is rotated cyclically through 110^0 (from an upright position) to ensure an even distribution of heat throughout the contents.

The digester has a minimum internal capacity of 15 litres, and therefore requires large amounts of alkali liquor (mixed NaOH solution) and fibre to become full. To prepare smaller batches of digested hemp for the purpose of single fibre and lignin testing, hemp fibre and alkali liquor were inserted into four 1L capacity stainless steel digesting canisters, which were then placed inside the digester cavity.
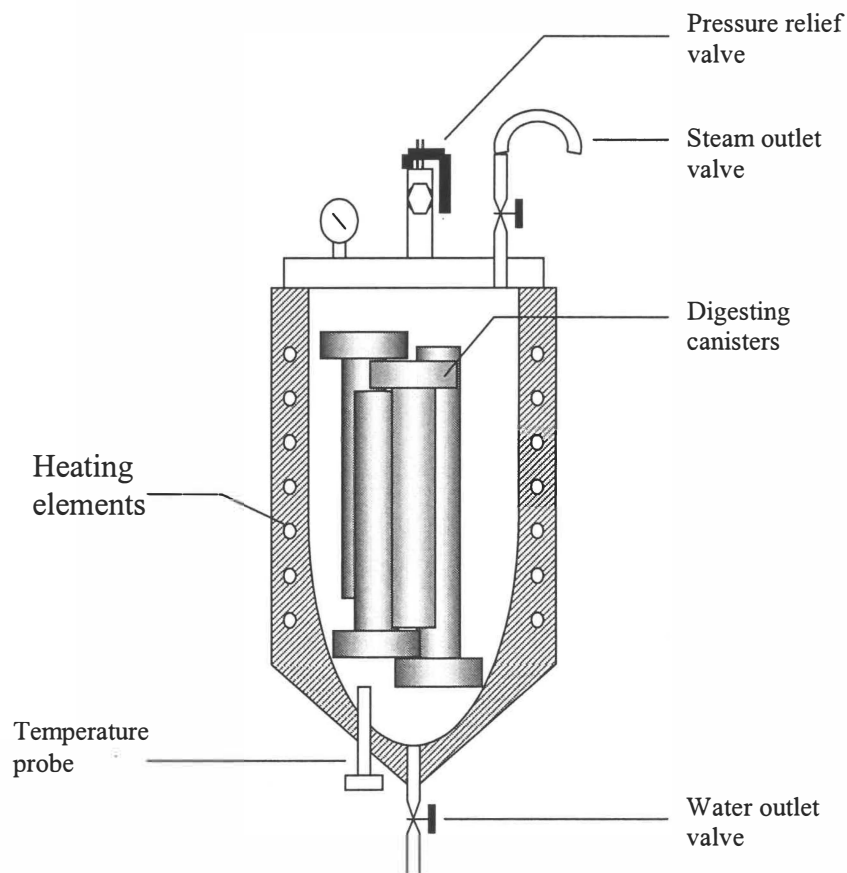
Figure 3.6 Schematic of pulp digester

Figure 3.7 Pulp digester

3.3.2.2 Alkali Preparation

Before fibre digestion could take place, it was necessary to carefully prepare the correct concentrations and volumes of alkali liquor. Sodium hydroxide solutions with concentrations of 10% and 15% were used to treat the hemp fibre, and the fibre: liquor ratio used was 1:6 (by weight). For each canister, 35g of oven dried Hawkes-Bay hemp fibre was combined with the appropriate volume of liquor. To maintain the 1:6 fibre: liquor ratio, 210g of sodium hydroxide solution was added to the dried fibre. To make up a 15% alkali solution, 31.5g of analytical grade NaOH pellets were dissolved in 178.5ml distilled water, and a 10% solution was made up by dissolving 21g NaOH pellets in 189ml distilled water.

3.3.2.3 Fibre Digestion

Once the appropriate amounts of fibre and liquor had been put into each of the four digestion canisters, they were inserted into the digester cavity. Water was then added to fill the remaining space in the digester so that heat could be transferred from the heating elements to the canisters. A cook schedule was programmed into the temperature controller to control the digestion process. Four cook schedules were used to digest the different batches of hemp, with the maximum processing temperature and hold time being varied. The cook schedule variables are summarised in Table 3.1.

Table 3.1 Summary of cook schedule variables

Hold time at maximum temperature	Maximum Temperature	
	$160^{o}C$	$180^{0}C$
15 min	✔	✔
45 min	✔	✔

Prior digester testing showed that the digester did not respond instantaneously to the cook schedules initially entered into the temperature controller, and a lag in temperature of about $15^{0}C$ was observed for each cook. The cook schedules were thus modified so that the maximum cook temperature could be achieved at the required time. Figures 3.8 to 3.11 show the effects of the programmed cook schedules on the actual cook process.

Figure 3.8 Digester cook process: 160^{0}C max temperature, 15 min hold time

Figure 3.9 Digester cook process: 160^{0}C max temperature, 45 min hold time

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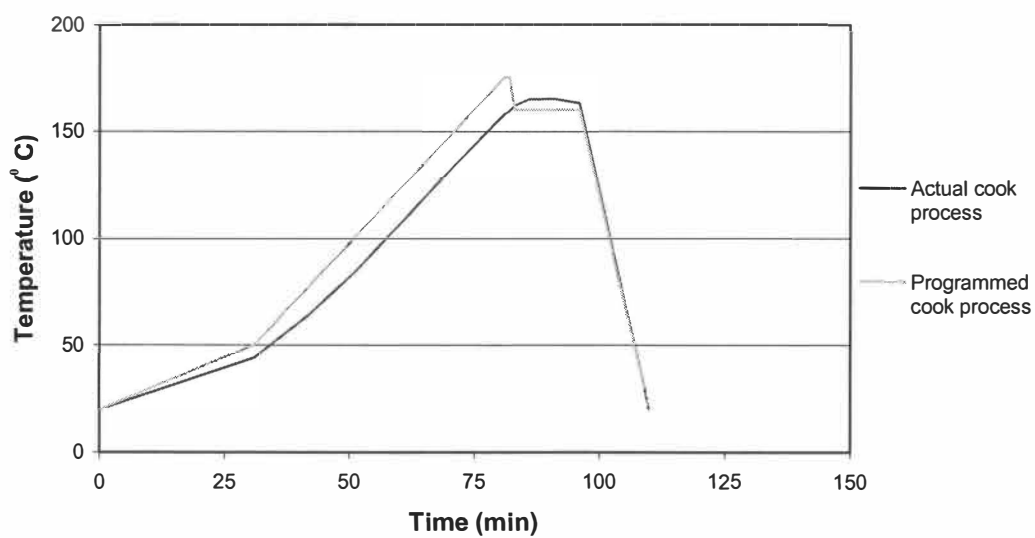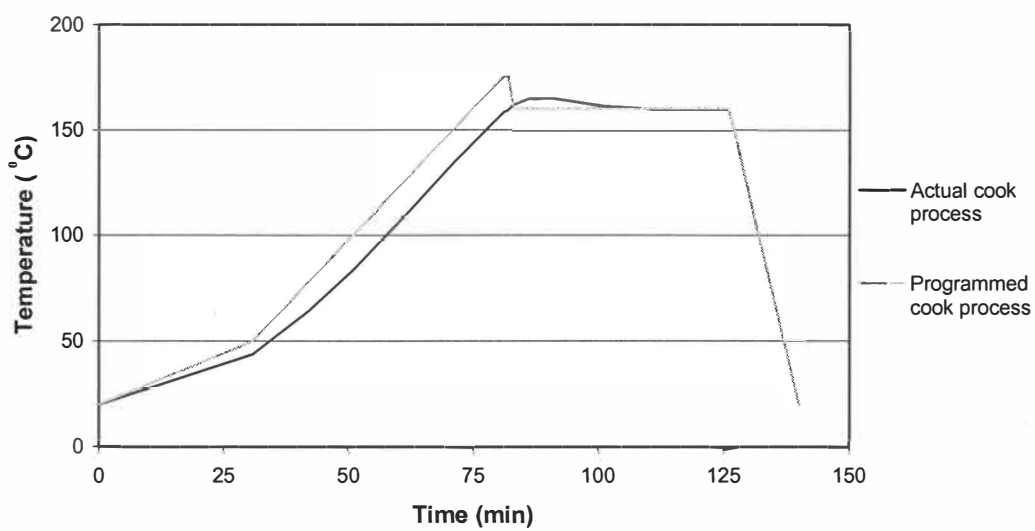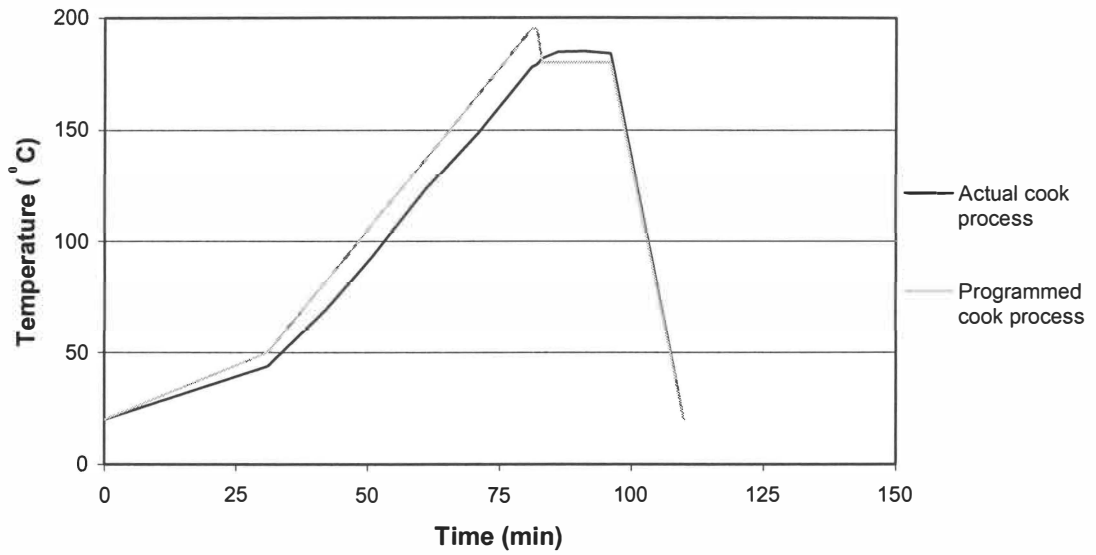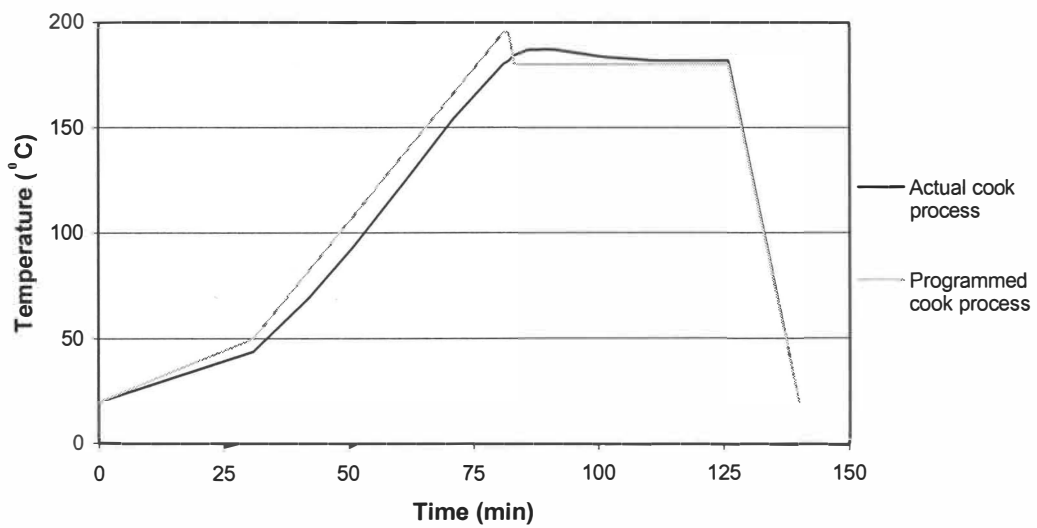**Figure 3.10 Digester cook process: 180^{0}C max temperature, 15 min hold time**

Figure 3.11 Digester cook process: 180^{0}C max temperature, 45 min hold time

Once the digestion process was complete, the digester and its contents were crash cooled (rapidly cooled from the maximum process temperature to 30^0C) to reduce the hemp fibre exposure time with the NaOH solution. This crash cooling process involved releasing the pressure within the digester by opening the steam outlet valve. Once the pressure had been released and the internal temperature had dropped to below 100^0C, the water outlet valve was opened to drain the hot water from inside the digester. A cold-water hose was then attached to the steam outlet pipe, so that cold water could be circulated in through the steam outlet valve and then out through the water outlet valve. The crash cool process took about 14-15 minutes to perform.

Once the crash cooling process was completed and the digestion canisters had reached manageable temperatures of 30^0C to 40^0C, the digested fibre was removed from each of the four canisters in turn and placed in a pulp and paper fibre-washer. Whilst the first batch of fibre was being washed, the remaining unopened canisters were kept in buckets of cold water until they too were washed. Fibres were washed for 10 minutes in clean water, before being dried in a drying oven at 80^0C for 48 hours. The fibres were then mounted on cardboard mounting-cards, and tensile tested using the same process as stated in 3.2.2 Single Fibre Tensile Testing. The alkali treated fibres that were tensile tested are summarised in Table 3.2:

Table 3.2 Summary of treatment processes for fibres that were tensile tested

Treatment Process	NaOH Concentration (%)	Maximum Processing Temperature (^{0}C)	Hold Time (min)
1	10	160	15
2	10	160	45
3	10	180	15
4	15	160	15
5	15	160	45
6	15	180	15
Untreated fibre (control)	-	-	-

Fibres treated using treatment processes 3 and 6 were not tensile tested as the fibres appeared to be very weak and disintegrated during handling. To further investigate the effects of alkali treatment on the fibre surface morphology, the fracture surfaces and cell walls of the control and treatment process 1 treated fibres were observed using a Hitachi S-4100 Field Emission Scanning Electron Microscope (SEM).

3.4 Lignin Measurement

One of the main aims of digesting hemp fibres with sodium hydroxide is to remove lignin. A suitable method of determining the amount of lignin remaining in the fibre after alkali treatment is the half-scale Kappa test. The half-scale Kappa test is a commonly used method for lignin determination in the pulp and paper industry, and is a scaled down version of the regular Kappa test for small samples.

The half-scale Kappa test involves the reaction of a known concentration of potassium permanganate solution with a predetermined amount of dried fibre. The mass of fibre is critical, as it is important that the fibre consumes around 50% of the potassium permanganate in the solution. The potassium permanganate reacts with lignin in the fibre, so the amount of potassium permanganate consumed is equivalent to the amount of lignin present in the fibre specimen. To determine the amount of potassium permanganate consumed, a solution of sodium thiosulphate of a known concentration is titrated against the fibre-permanganate mixture. By doing this, the amount of potassium permanganate remaining in the solution can be determined as can the amount of potassium permanganate consumed by the lignin. A formula (as can be seen in Appendix 1) is then used to determine the Kappa number of the fibre specimen.

The Kappa number is a measure of the amount of residual lignin within the fibre, and is by definition, the volume (in millilitres) of 0.1N (0.002M) potassium permanganate solution consumed by one gram of moisture free pulp under the conditions specified in the method. The results are corrected to 50% consumption of the permanganate added.

The half-scale Kappa test method used in this experiment is based on the AS/NZS 1301.201s:2002, the Papro 1.106 Kappa Number (half-scale modification), and TAPPI T236 Standards. The half-scale test gives the same results as the full-scale method, and can be used for all chemically and semi-chemically treated pulp up to a yield of 60%.

The half-scale Kappa test was performed on each of the fibre treatment processes mentioned in Table 3.2, and the test procedure can be seen in Appendix 1.

3.5 Composite Fabrication

Alkali treated fibres were combined with a polypropylene matrix, and in some instances a MAPP coupling agent, to produce hemp fibre reinforced polypropylene composite materials. The fibres were chopped into sizes that would enable composite processing, and then compounded with polypropylene powder in a twin-screw extruder. The resulting extruded composites were then chopped and injection moulded into tensile test specimens.

3.5.1 Composite Raw Materials

Composites were predominantly fabricated using Hawkes Bay hemp, although some composites were made with Waikato hemp. All hemp fibres were alkali treated using 10% NaOH, with a maximum processing temperature of 160^0C, and a maximum temperature hold time of 45 minutes (Treatment Process 2). The fibres were either chopped into lengths of 1-3mm using an industrial granulator, or manually chopped into 10mm lengths using a guillotine. The chopped fibres were dried at 80^0C for 48 hours.

The matrix polymer used was a standard polypropylene powder with a density of 0.9g/cm^3, and was supplied by Aldrich Chemical Company, Inc. A MAPP coupling agent with a high molecular weight, A-C 950P, was supplied by Honeywell International, Inc. USA.

Polypropylene absorbs small amounts of water, so to prevent water vapour induced voids from occurring in the composites, polypropylene and MAPP powders were dried under the same conditions as the fibre.

3.5.2 Composite Extrusion and Injection Moulding

Hemp fibres, polypropylene and MAPP were compounded in a ThermoPrism TSE-16-TC twin-screw extruder (Figure 3.12), such that composites with varying weight fractions of fibre, MAPP and polypropylene were produced. Composites were made using long guillotine-chopped fibres as well as the short granulator-chopped fibres to compare the effects of fibre length on the properties of the composite. The extruded composites were then granulated and dried at 80 ^{0}C for 48 hours, before being extruded and granulated a second time to improve homogeneity. The granulated composite pellets were then injection moulded into Type 1 tensile test specimens (as specified by the ASTM D638-01 standard) using a BOY15-S injection-moulding machine (Figure 3.13). The compositions of the composites that were produced can be seen in Table 3.3.
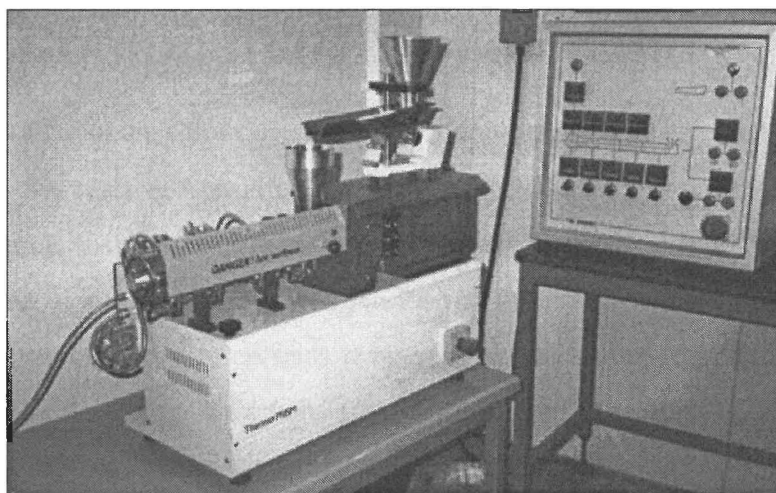

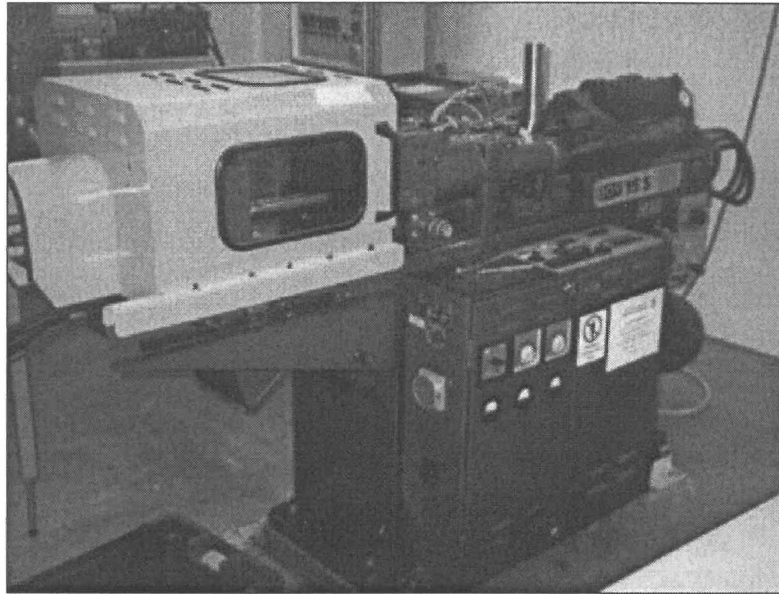**Figure 3.12 ThermoPrism TSE-16-TC twin-screw extruder**

Figure 3.13 BOY15-S injection-moulding machine

Table 3.3 Composite constituents

MAPP content (%)	Origin of Hemp	Hemp fibre length	Hemp fibre content (%)		
			0	30	40
0	Hawkes-Bay	Short	✔	✔	✔
1	Hawkes-Bay	Short	✔	✔	✔
2	Hawkes-Bay	Short	✔	✔	✔
2	Hawkes-Bay	Long			✔
2	Waikato	Long			✔

3.5.3 Composite Tensile Testing

Tensile test specimens were conditioned in a conditioning chamber at $23^0C \pm 3^0C$ and $50\% \pm 5\%$ relative humidity for 40 hours. The specimens were then tensile tested using an Instron-4204 tensile testing machine fitted with a 5kN-load cell, and operating at a rate of 5mm/min. An Instron 2630-112 extensometer was used to measure the strain. The composite specimens were tested to failure, whereas the non-fibre containing specimens (matrix and coupling agent only) were only tested to the point of maximum stress due to excessive necking.

Specimens that failed at the grips were disregarded, as stress concentrations caused by the gripping force may have lead to premature failure. Ten specimens were tested for each test of conditions.

To investigate the effects of the MAPP coupling agent on the fibre-matrix adhesion, the fracture surfaces of selected tensile test specimens were observed using a Hitachi S-4100 Field Emission Scanning Electron Microscope (SEM).

Chapter 4: Results and Discussion

Chapter 4:
Results and Discussion

4.1 Hemp Plant Cultivation Time

4.1.1 The Effects of Cultivation Time on Fibre Strength and Stiffness

The single fibre tensile test results performed on retted Waikato-grown hemp are shown in Figures 4.1 and 4.2. The error-bars each represent ± 1 standard deviation. From the results in Figure 4.1, it can be seen that there is a slight increase in the average tensile strength of hemp fibre during the growth period from 99 days to 114 days, and then a decrease from 114 days to 124 days. After 99 days of growth, the male plants had started to release their pollen (start of male plant flowering); and by 124 days, about 80% of the pollen had been released (near the end of male plant flowering). This increase and subsequent decrease in the average fibre tensile strength and stiffness is likely to be due to changes in fibre morphology and a change in the type of fibre being produced during the male plant flowering stage.

Mediavilla et al. [64] showed that initially, long and strong primary bast fibres are created almost empty (hollow), and are then progressively filled during the vegetative growth and flowering stages. The maximum degree of fibre filling was found to occur during male flower formation, and the filling of the primary fibres is thought to increase the average fibre tensile strength and stiffness. With the onset of the flowering and seed formation stages, shorter and weaker secondary fibres are produced in greater numbers, thus resulting in a decrease in the average fibre strength.
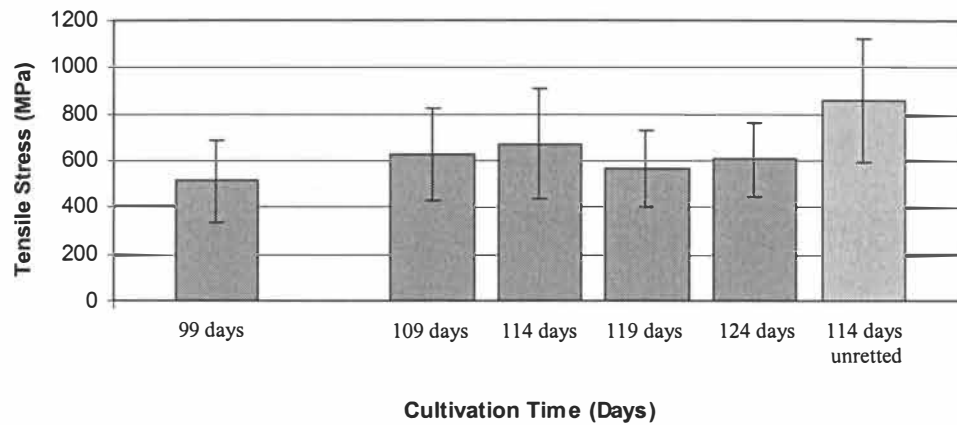
Figure 4.1 Effect of hemp plant cultivation time on single fibre strength (Waikato hemp).
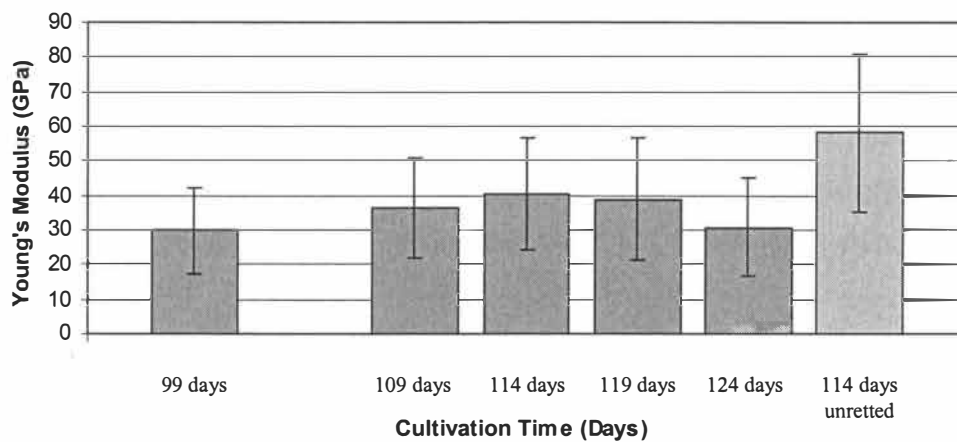
Figure 4.2 Effect of hemp plant cultivation time on single fibre stiffness (Waikato hemp).

During male plant flowering (the period of pollen release), the primary bast fibres become progressively stronger and stiffer due to an increase in fibre filling. At the same time, however, the average fibre strength and stiffness are reduced due to an increase in the numbers of weaker secondary bast fibres. A peak in average fibre strength and stiffness can therefore be identified at a point where the primary fibres have been filled to a large extent, but just before the secondary fibre content becomes high enough to significantly affect the average fibre strength.

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From the results in Figures 4.1 and 4.2, this peak occurs at a cultivation time of 114 days. Another reason for the increase and decrease in fibre strength could be due to the changing chemical composition of bast fibre during the aging of the plant [67]. No further investigations were performed to determine the chemical composition or changes in chemical composition of the fibre.

4.1.2 The Effects of Retting on Fibre Strength and Stiffness

It was observed that the average unretted fibre strength and stiffness appeared to be considerably higher than that of the average retted fibre (Figures 4.1 and 4.2). The retted hemp fibre appeared light yellow in colour, and no grey regions were present to indicate over-retting.

The fungi and bacteria commonly responsible for pectin and hemicellulose degradation do not generally attack and weaken the cellulose components of the cell wall during retting, and thus do not significantly weaken the fibres. In some cases, however, cellulolytic fungi such as *Epicoccul nigrum* can proliferate and weaken fibres that they come into contact with [37]. Fibre strength could also be compromised if structural hemicellulose, which exists in close association with cellulose, is removed along with the middle lamella hemicelluloses and pectins [37].

The reduction in fibre strength and stiffness of the retted Waikato-grown hemp was thought to be due to fibre damage caused by cellulose and structural hemicellulose degrading micro-organisms in the retting mixture.

4.1.3 The Effects of Fibre Diameter on Tensile Strength

The purpose of this investigation was to determine whether the diameters of the tensile tested hemp fibres influenced the fibre tensile strengths. For each sample of hemp fibre, all fibres tested (except failures and outliers) were plotted on a tensile stress vs diameter scatter plot (Figure 4.3(a) to 4.3(f)). From the trend-lines on each plot, with the exception of Figure 4.3(c), it can be seen that there is a general trend for the smaller diameter fibres to have slightly larger tensile strengths when compared to the larger diameter fibres. One explanation for this occurrence is that some of the larger fibres may have been slightly distorted and may have had elliptical, rather than circular cross-sectional shapes. Since the tensile strengths were calculated with the assumption that the fibres were cylindrical, the elliptical fibres would have been calculated as having larger cross-sectional areas than what was actually true. Tensile strength is calculated by dividing the tensile load by the fibre cross-sectional area, so fibres with larger than actual cross-sectional areas would then result in lower calculated tensile strengths.

Another reason for the reduction in tensile strength with an increase in fibre diameter could be due to the variability in primary cell wall degradation during retting. Retting is a highly variable process, and it is possible for the non-cellulose components of the primary cell wall to be degraded to a larger extent in some fibres compared to others. This could result in some fibres having greater amounts of non-strength contributing components (such as pectin, lignin and hemicellulose) that increase the fibre diameter, but do not add strength to the fibre. The increased fibre diameters lead to larger fibre cross sectional areas, and therefore lower tensile strengths.

Figure 4.3(a) Effect of fibre diameter on the tensile strength of 99-day old retted hemp fibres.

Figure 4.3(b) Effect of fibre diameter on the tensile strength of 109-day old retted hemp fibres.

Figure 4.3(c) Effect of fibre diameter on the tensile strength of 114-day old retted hemp fibres.

Figure 4.3(d) Effect of fibre diameter on the tensile strength 114-day old un-retted hemp fibres.
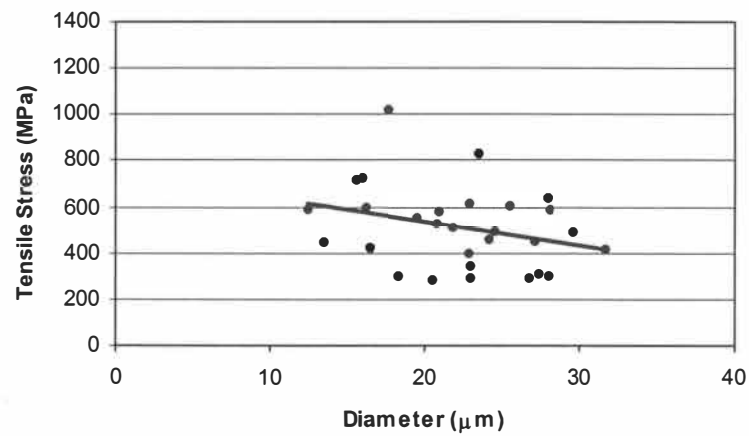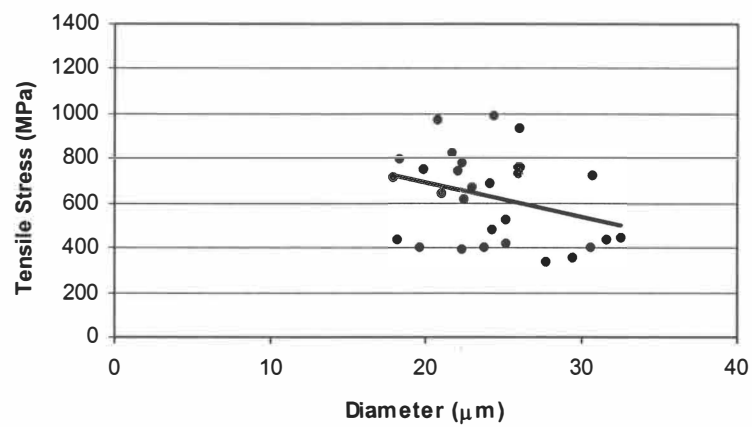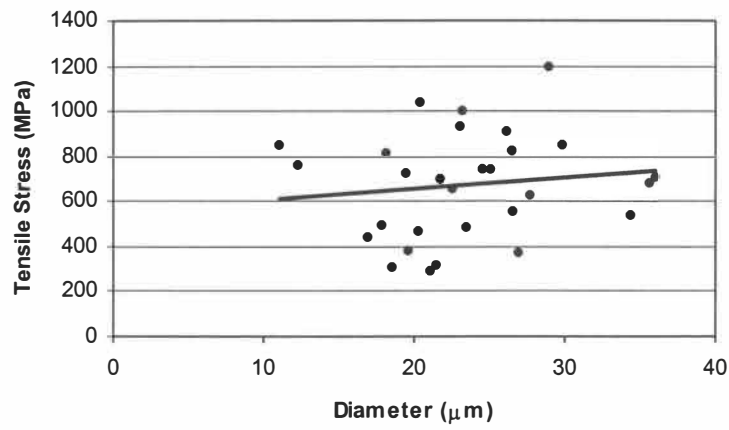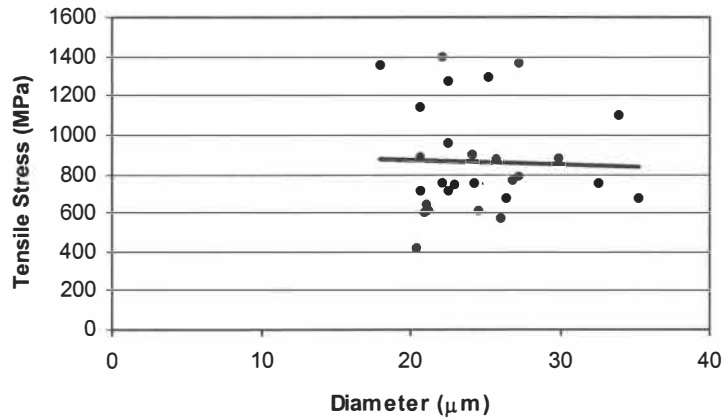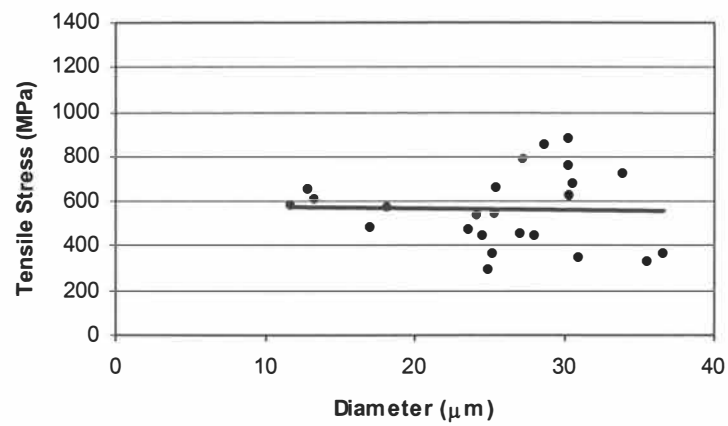
Figure 4.3(e) Effect of fibre diameter on the tensile strength of 119-day old retted hemp fibres.
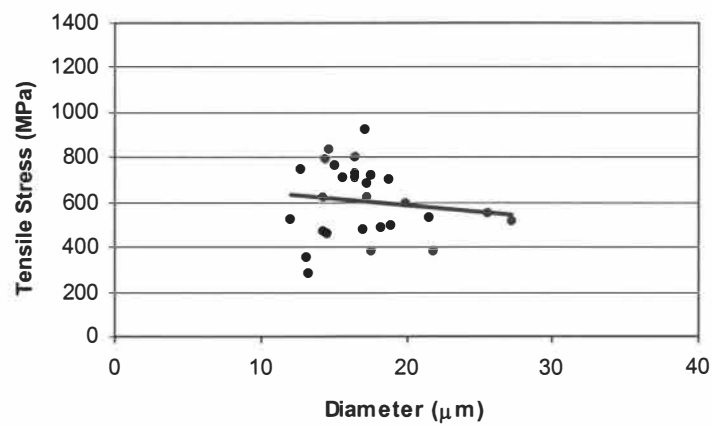
Figure 4.3(f) Effect of fibre diameter on the tensile strength of 124-day old retted hemp fibres.

4.2 Biological Fibre Treatments

4.2.1 The Effects of Fungal Treatment on Tensile Strength

The effects of the various fungal treatments on the strength of Hawkes-Bay hemp fibres can be seen in Figure 4.4. The results clearly show that the tensile strengths of all treated fibres were significantly reduced by fungal treatment. Each fungal treatment reduced the tensile strength of the fibres by 50% or more, therefore indicating that severe cellulose and structural degradation had taken place in each fibre. When viewed under a microscope, many of the treated fibres appeared to have severely decomposed regions along the fibre length. For the purpose of this experiment, only visually undamaged fibres were tensile tested.
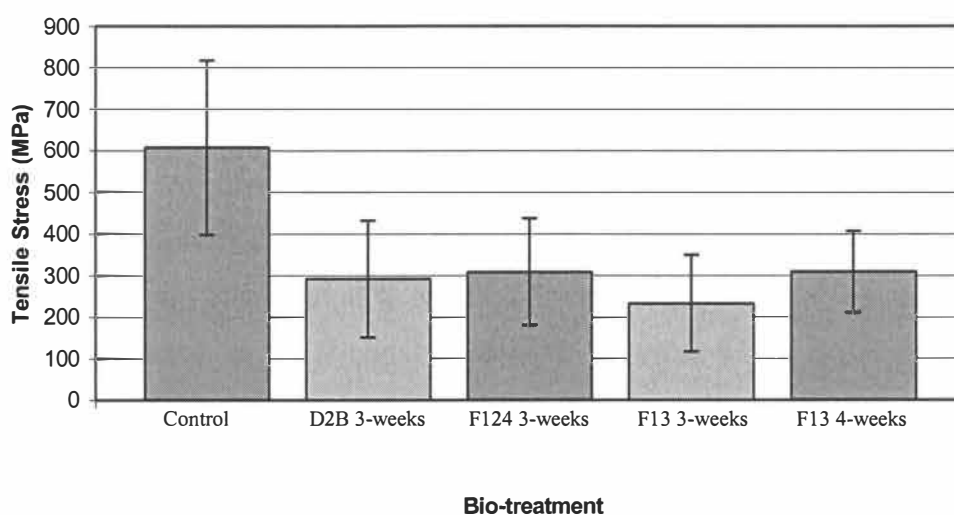
Figure 4.4 Effect of bio-treatment on the tensile strength of single hemp fibres.

It was expected that the *Basidiomycete* white-rot fungus (D2B) would have weakened the fibres to a larger extent than the *Ophiostoma floccosum* sap-stain fungi (F13 and F124) due to the fact that it causes larger boreholes in the fibre walls [40]. This however was not the case, as all the fungal treatments appeared to weaken the fibres to a similar degree.

It was also expected that an increase in the treatment time from 3 weeks to 4 weeks would further weaken the fibres. The results, however, show a slight increase in fibre strength from 3 to 4 weeks for the *Ophiostoma floccosum* F13 fungal treatments. This was thought to be due to the fact that fungal colonies growing on the hemp were not evenly distributed throughout the sample, and that a higher number of severely degraded fibres may have been randomly selected for the 3-week F13-treatment tensile tests.

The fungal treatments utilised in this experiment severely reduced the tensile strength of the fibres, thus making them undesirable for use in composite materials. The physical surface changes of the fibre brought about by fungal treatment, however, could aid the interfacial bonding of the fibres when combined with a thermoplastic matrix material. Shorter treatment times could therefore be used to reduce the extent of fibre degradation, while still modifying the fibre surface to improve its bonding ability.

4.2.2 The Effects of Fungal Treatment on Young's Modulus

The effects of fungal treatment on the fibre stiffness can be seen in Figure 4.5. With the exception of the F124 sample, the fungal treatments showed a Young's modulus reduction of around 30% when compared to the untreated control. This was to be expected, as the removal of some of the cross-linked compounds and cellulose in the cell wall would reduce the rigidity and stiffness of the fibres. A large amount of variation in fibre stiffness is present for each sample, as can be seen by the standard deviations shown by the error bars. This is thought to be due to the varying degrees of fibre degradation experienced by the treated fibres, as well as damage incurred on the fibres when manually separated from their fibre bundles.
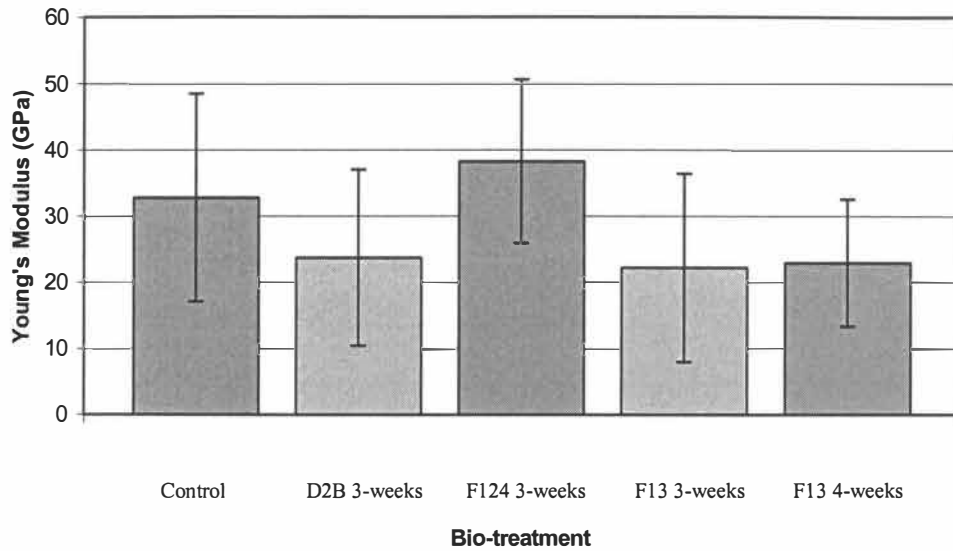
Figure 4.5 Effect of bio-treatment on the stiffness of single hemp fibres.

4.3 Alkali Fibre Treatments and Lignin Tests

The alkali treatments of Hawkes-Bay hemp fibres for use in hemp fibre reinforced thermoplastic composites have two main purposes: to remove lignin from the surface of the fibres, and to separate the fibres from their fibre bundles. It is also important, however, to maintain the tensile strength and stiffness of the fibres, as the fibres are the main contributors of these properties in the composite.

4.3.1 The Effects of Alkali Treatment on Tensile Strength

The results of the single fibre tensile tests performed for each alkali treatment can be seen in Table 4.1. Figures 4.6(a) and 4.6(b) further illustrate the effects of each treatment variable on the average fibre tensile strength.

Table 4.1 Summary of single fibre tensile test results for alkali treated hemp fibres

Treatment process number	Treatment variables	Tensile strength (MPa)	S.Dev	Young's Modulus (GPa)	S.Dev	Ave fibre diameter (μm)	S.Dev	Failure Load (N)	S.Dev
1	10% NaOH, 160°C, 15min	664	208	34.1	12.2	24.9	3.7	0.32	0.12
2	10% NaOH, 160°C, 45min	677	187	27.0	10.9	23.2	5.1	0.28	0.13
3	10% NaOH, 180°C, 15min	449	121	26.7	11.2	22.4	4.8	0.16	0.06
4	15% NaOH, 160°C, 15min	632	185	27.4	12.3	24.1	4.5	0.30	0.14
5	15% NaOH, 160°C, 45min	532	137	20.2	6.1	23.3	4.6	0.22	0.08
6	15% NaOH, 180°C, 15min	280	101	17.8	9.3	23.0	5.2	0.10	0.04
-	Untreated hemp	607	210	32.8	15.7	26.8	5.0	0.33	0.14

From these results, it can be seen that the alkali treatment that produced the strongest fibre was Treatment 2, closely followed by Treatment 1. These two alkali treatments were the mildest of the six treatments used, and actually resulted in fibre strength increases when compared to the untreated control. The process variable that most notably affected the fibre strength was alkali treatment temperature. For the 10% NaOH treatments, a 32% difference in tensile strength was observed between the 160^0C and 180^0C treatments. The difference in strength was even more pronounced at a NaOH concentration of 15%, and the fibre strength difference between the two alkali treatment temperatures was 56%. The large fibre strength reductions experienced at 180^0C were expected, as cellulose starts to degrade at that temperature [24]. It can also be seen from the results that the strength reduction due to increases in hold time and treatment temperatures were more pronounced at 15% NaOH concentrations.
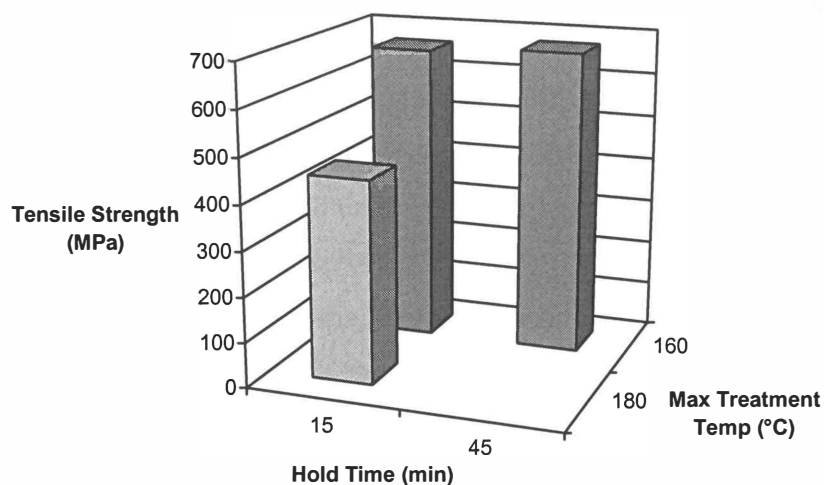
Figure 4.6(a) Effect of treatment temperature and hold time on the tensile strength of 10% NaOH treated hemp fibres.
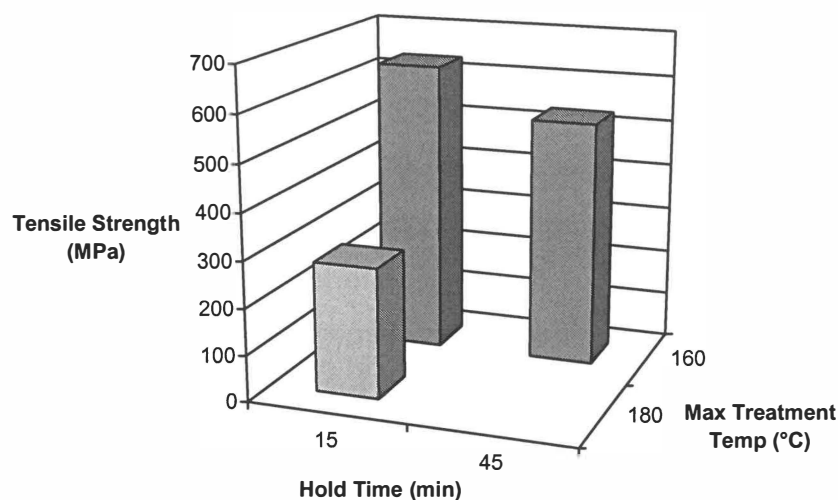
Figure 4.6(b) Effect of treatment temperature and hold time on the tensile strength of 15% NaOH treated hemp fibres.

In addition, the results in Table 4.1 show that the alkali treatments reduced the fibre diameters of the treated fibres, and that fibre diameter reductions appeared to be related to the severity of the alkali treatment. This was to be expected, as the NaOH removes much of the non-crystalline fibre components such as lignin, pectin and hemicellulose, and degrades the cellulose microfibrils to a much lesser extent. A reduction in fibre cross sectional area is thus evidence of the removal of alkali-soluble compounds in the fibre walls. This observation has been further investigated in section 4.3.4: Lignin Tests.

Alkali treatments 1, 2 and 4 appeared to have increased the tensile strength of the treated fibres compared to the control. This strength increase is likely to have been caused by the removal of non-strength contributing fibre wall components, which consequently would have led to a reduction in the average fibre cross sectional area. The alkali treatments may also have led to better packing of the cellulose microfibrils, a decrease in the microfibril spiral angle and an increase in the molecular orientation of the cellulose chains; all of which would have increased the tensile strength of the fibre. To identify the main reason for this fibre strength increase, the average tensile failure loads obtained during the single fibre tensile tests (as seen in Table 4.1) were compared to the tensile strength values. Unlike tensile strength measurements, tensile loads are not dependent on the magnitude of the fibre diameters. Tensile load is therefore a suitable measure for establishing whether the fibre strength increases for alkali treatments 1, 2 and 4 were due to reductions in fibre diameter or the strengthening of the cellulose fibre components.

From the results, it can be seen that the average tensile loads of the fibres treated using alkali treatments 1,2 and 4 were very close to those of the control. This shows that despite the removal of non-strength contributing components during alkali treatment, the cellulose component of the fibre was not weakened and the treated fibres could still withstand the same tensile loads as the untreated fibres. The increase in strength was therefore due to a reduction in fibre diameter as opposed to an increase in the strength of the cellulose fibre structure.

The other alkali treatments (treatments 3, 5 and 6), however, showed significantly lower values for load compared to the control. These load and tensile strength reductions indicate that the cellulose had been degraded and that the fibres had been significantly weakened.

It can therefore be seen that a reduction in the tensile load of a fibre is a good indicator of a loss in fibre strength due to cellulose degradation or fibre structure disruption.

4.3.2 The Effects of Alkali Treatment on Young's Modulus

The Young's moduli of the alkali treated Hawkes-Bay hemp fibres can be seen in Table 4.1, and are further illustrated in Figures 4.7(a) and 4.7(b). From the results, it can be seen that the average Young's modulus of treatment 1 treated fibres is slightly higher than that of the control. The control has a greater standard deviation than treatment 1, so it can be assumed that this difference is due to natural variation rather than an increase in fibre stiffness by the alkali treatment. There were, however, changes in fibre stiffness with the other alkali treatments, and the Young's modulus of the fibres seemed to decrease according to the severity of the treatment processes. It can therefore be said that the Young's modulus of the fibres decreased with an increase in the removal of alkali-soluble fibre-wall components, such as lignin, pectin and hemicellulose. This observation has been further investigated in section 4.3.4: Lignin Tests.
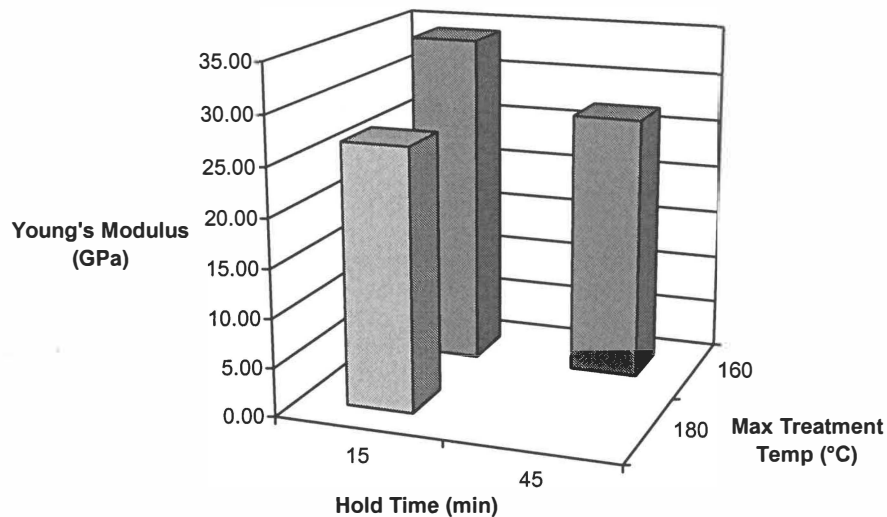

Figure 4.7(a) Effect of treatment temperature and hold time on the Young's modulus of 10% NaOH treated hemp fibres.
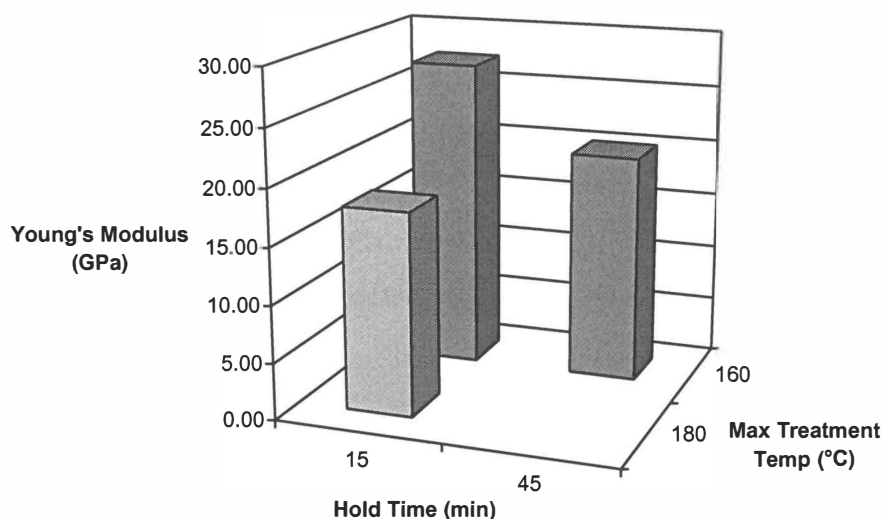
Figure 4.7(b) Effect of treatment temperature and hold time on the Young's modulus of 15% NaOH treated hemp fibres.
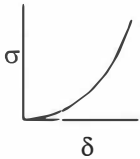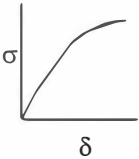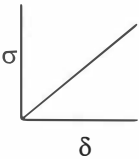
For alkali treatments 1, 2 and 4 (where very little cellulose degradation occurred), it can be seen that the removal of alkali-soluble fibre-wall components did not lead to a reduction in fibre strength, but did lead to a reduction in the fibre stiffness. Lignin, pectin and hemicellulose do not contribute much to the fibre tensile strength, but are often highly cross-linked or branched and provide a degree of structural integrity and rigidity to regions of the fibre wall in which they are present [24]. The removal of these intra-fibrillar binders could lead to stress releases and molecular relaxation of the cellulose fibre components, and hence a slight reduction in fibre stiffness. It was expected that the removal of lignin, pectin and hemicellulose would increase the fibre stiffness to some degree, as the release of active hydroxyl (OH) groups on the cellulose microfibril surfaces would lead to direct bonding between the microfibrils. It was thought that this inter-microfibrillar bonding did not occur to the extent that was expected, because the highly hydrophilic OH groups were bonding with water molecules as opposed to other microfibril OH groups.

To further investigate the effects of the removal of non-cellulose fibre components on the stress-strain behaviour of the fibres, the shape of the stress-displacement curves were observed for each fibre that was tensile tested. It should be noted that because an extensometer could not be used to obtain strain measurements during tensile testing, the shapes of the stress-crosshead displacement curves were considered instead. The shapes of the stress-displacement curves were expected to be almost identical to the stress-strain curves.

The load displacement curves showed 3 distinct shapes, namely an exponential curve, an inverted exponential curve and a straight line (Table 4.2). The frequency of each curve shape observed (expressed as a percentage of fibres tested) for each fibre treatment can be seen in Table 4.2. The exponential curve indicates non-linear elastic behaviour, the inverted exponential curve is very common for ductile materials, and a straight-line curve indicates brittle behaviour.

From the results, it can be seen that straight-line curves are more dominant for the untreated hemp fibres, and inverted exponential curves dominate the alkali treated fibres. This seems to indicate that the untreated fibres are mostly brittle in nature, and that the alkali treatments cause the fibres to become more ductile. This effect is thought to be due to the removal of highly cross-linked and branched intra-fibrillar binders that provide rigidity to the fibre wall, or to changes in the structure of the cellulose microfibrils.

Table 4.2 The frequency of stress-displacement curve shapes observed during single fibre tensile testing

Treatment Process	Exponential Curves (%)	Inverted Exponential Curves (%)	Straight line Curves (%)
1	7	68	25
2	3	55	42
3	10	66	24
4	3	57	40
5	0	79	21
6	21	54	25
Control	6	30	64

4.3.3 Microscopic Evaluation of Alkali Treated Fibres

The surfaces of untreated and alkali treated single fibres (treated using process 2) were observed using a Scanning Electron Microscope (SEM). The untreated fibres can be seen in Figures 4.8(a) to 4.8(c), and the alkali treated fibres can be seen in Figures 4.9(a) to 4.9(c). From the SEM micrographs, it can be seen that the gummy polysaccharides of lignin, pectin and hemicellulose are localized on the surfaces of the untreated fibres. In contrast, the alkali treated fibres have much reduced diameters and appear to have clean but rough surfaces with large numbers of etched striations. The rough surface morphology of the alkali treated fibres is expected to assist with mechanical interlocking when used in composites, and the clean surfaces are expected to provide direct bonding between the MAPP coupling agent and the microfibril cellulose.

Figure 4.8(a) Scanning Electron Micrograph (SEM) of untreated hemp fibre surface.
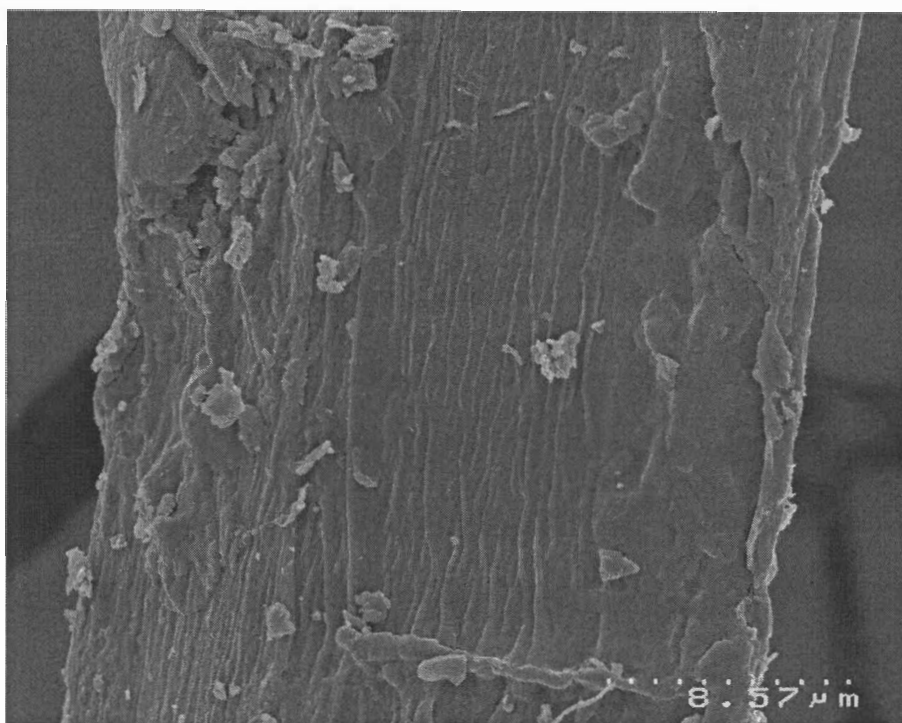
Figure 4.8(b) Scanning Electron Micrograph (SEM) of untreated hemp fibre surface.
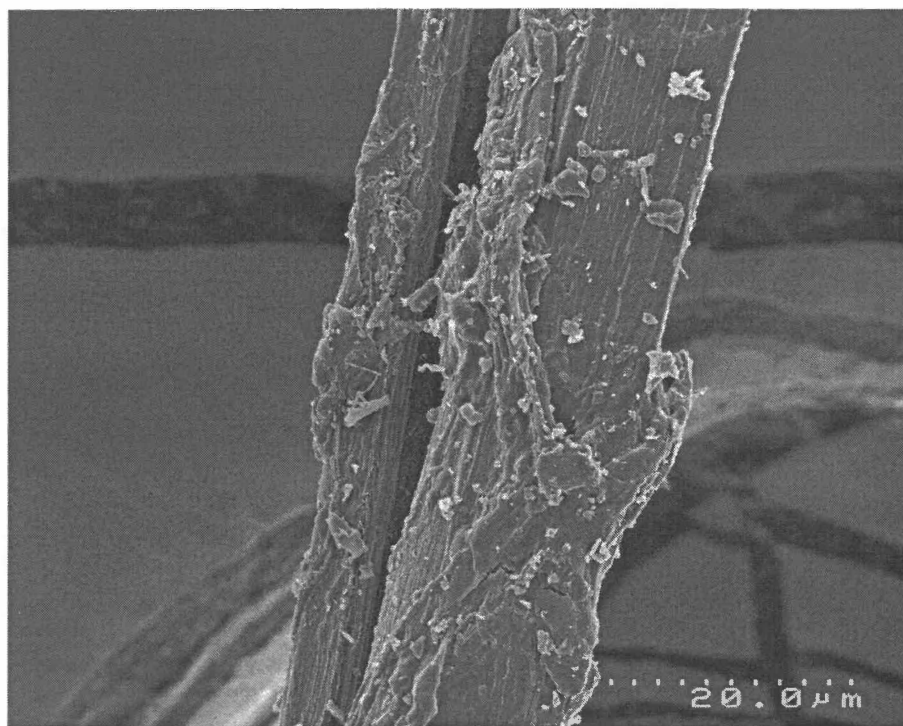
Figure 4.8(c) Scanning Electron Micrograph (SEM) of untreated hemp fibre surface.
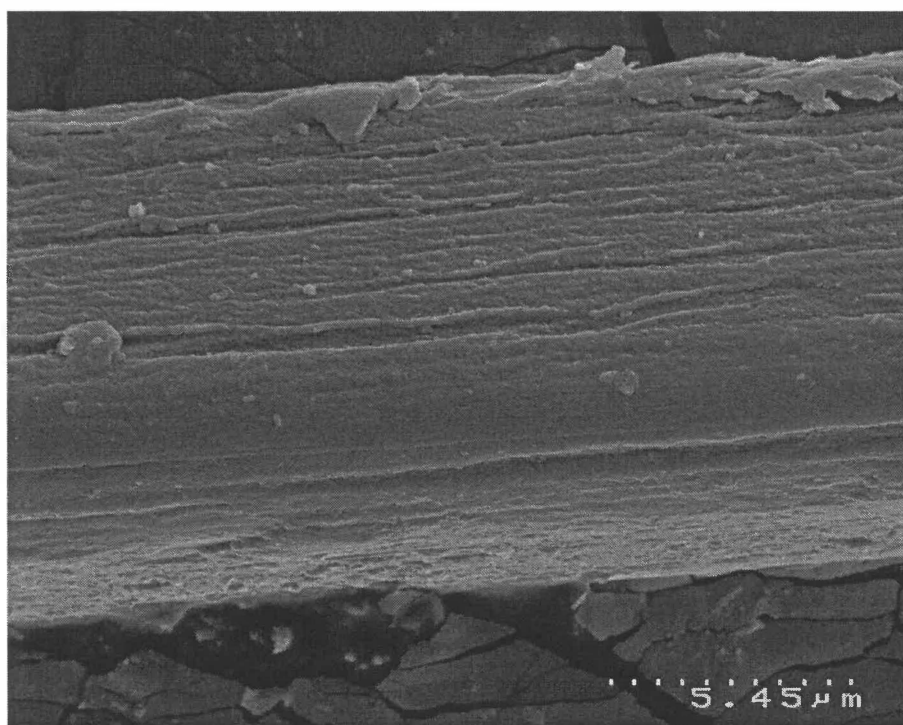
Figure 4.9(a) Scanning Electron Micrograph (SEM) of alkali treated hemp fibre surface.

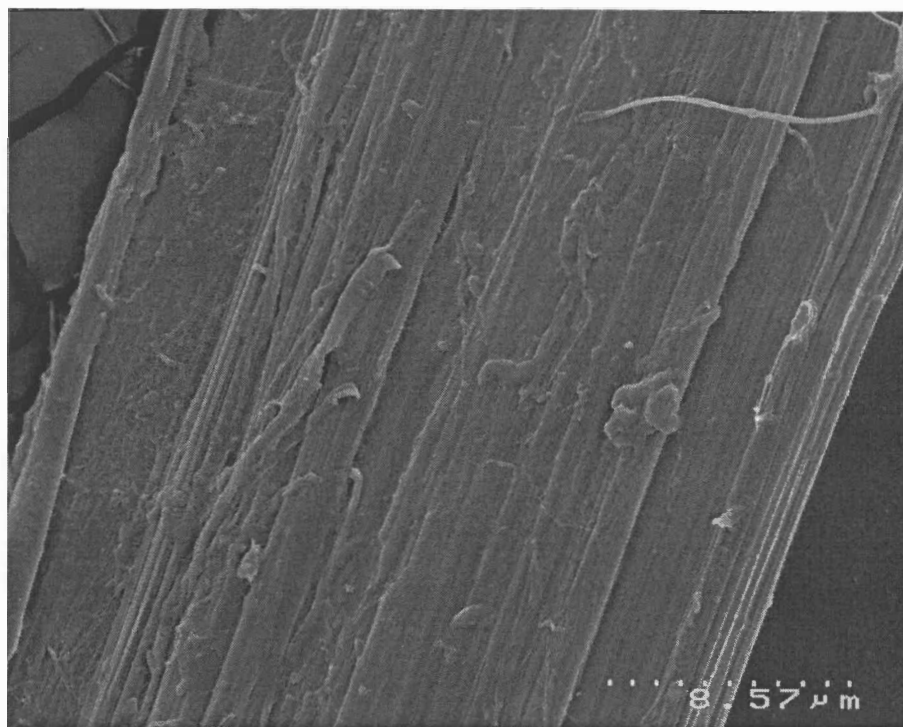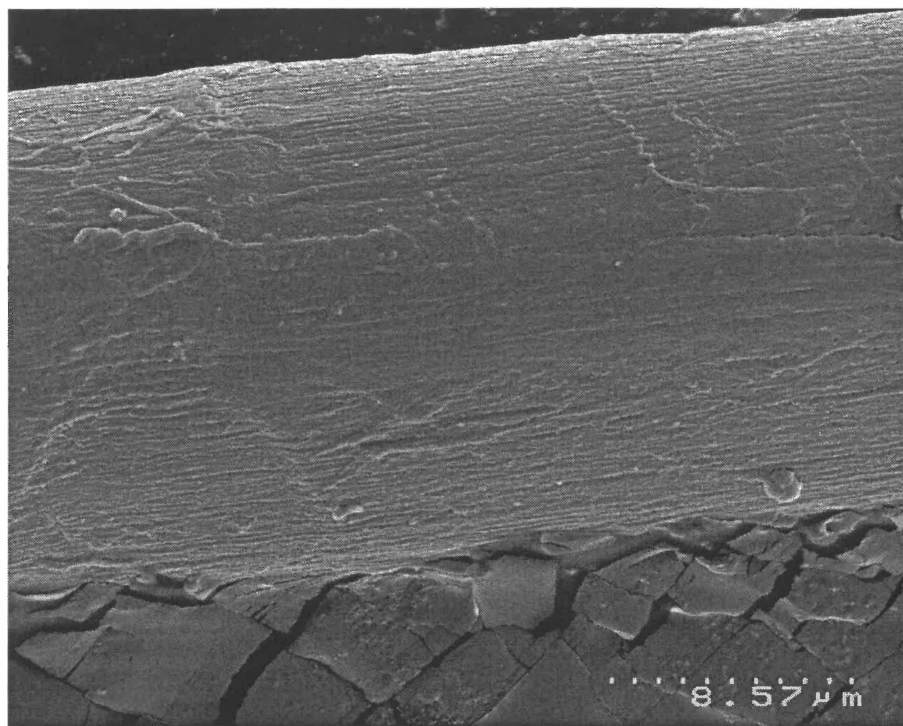**Figure 4.9(b) Scanning Electron Micrograph (SEM) of alkali treated hemp fibre surface.**
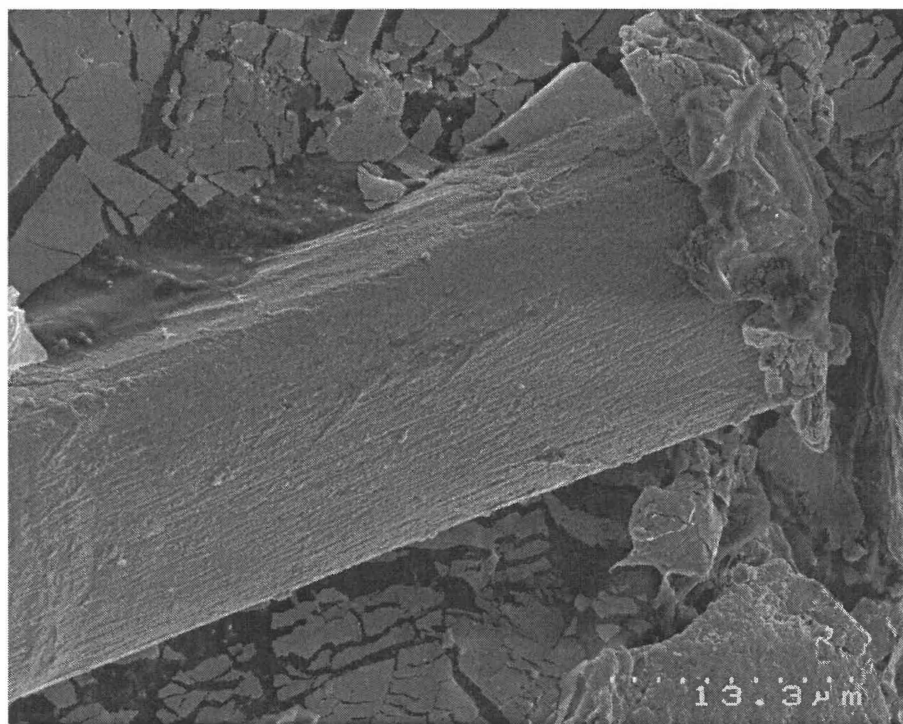
Figure 4.9(c) Scanning Electron Micrograph (SEM) of alkali treated hemp fibre surface.

4.3.4 Lignin Tests

The removal of lignin from natural fibres is important for producing strong and stiff natural fibre reinforced thermoplastic composites. Miller et al. [30] produced wood fibre reinforced polypropylene and polyethylene composites, and found that wood fibres with the lowest surface lignin contents showed the largest increases in tensile properties, both on their own and with coupling agents added.

The results of the Kappa tests performed for each alkali treatment can be seen in Figures 4.10(a) and 4.10(b). These results show that the degree of lignin removal is dependent on each of the process variables, namely NaOH concentration, maximum treatment temperature and hold time at the maximum temperature. The more severe treatment processes appeared to remove more lignin from the fibres compared to the less severe treatments.
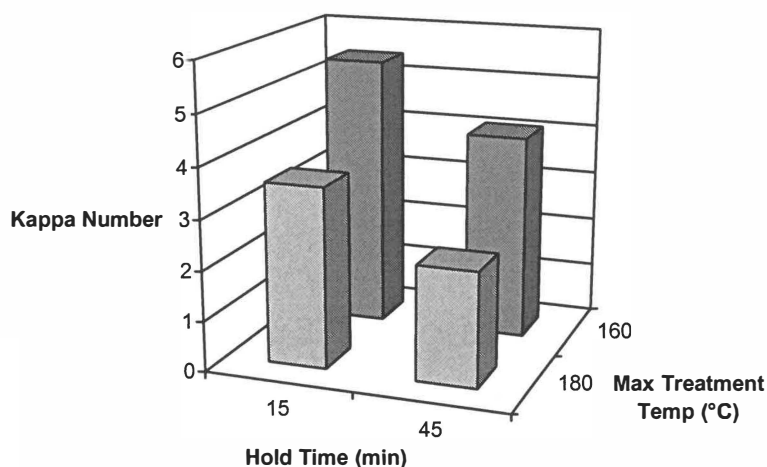
Figure 4.10(a) Effect of treatment temperature and hold time on the Kappa number of 10% NaOH treated hemp fibres.
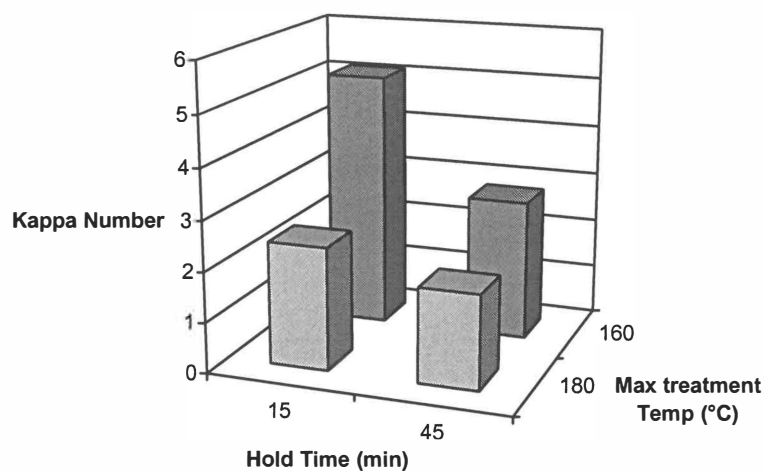
Figure 4.10(b) Effect of treatment temperature and hold time on the Kappa number of 15% NaOH treated hemp fibres.

As mentioned in the previous section, a reduction in the average alkali treated fibre diameter was thought to be due to the removal of alkali-soluble compounds in the fibre wall. The relationship between fibre diameter and Kappa number can be seen in Figure 4.11. This figure clearly shows that the average fibre diameter does in fact decrease with the removal of lignin in the fibre. As the lignin content of untreated hemp bast fibre is relatively low compared to hemicellulose and pectin contents (Table 2.5 in Chapter 2), it would be incorrect to say that the diameter reductions of alkali treated fibres were only due to the removal of lignin. It is known that lignin is less soluble in solvents and less prone to thermal degradation than hemicellulose and pectin [19],[21],[10],[9], so it can be assumed that these two constituents are removed to a greater extent than lignin during the alkali fibre treatment processes.

It was also mentioned in the previous section that the removal of alkali-soluble fibre-wall components resulted in a reduction of fibre stiffness. This phenomenon can be seen again in Figure 4.12, as a decrease in Young's modulus is linear with an increase in the amount of lignin removed from the fibres.
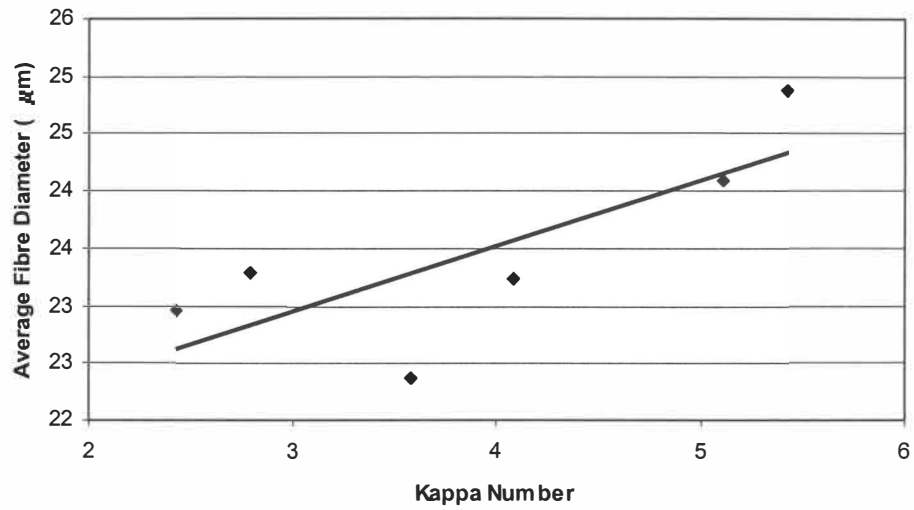
Figure 4.11 Effect of Kappa number on the average diameter alkali treated hemp fibres.
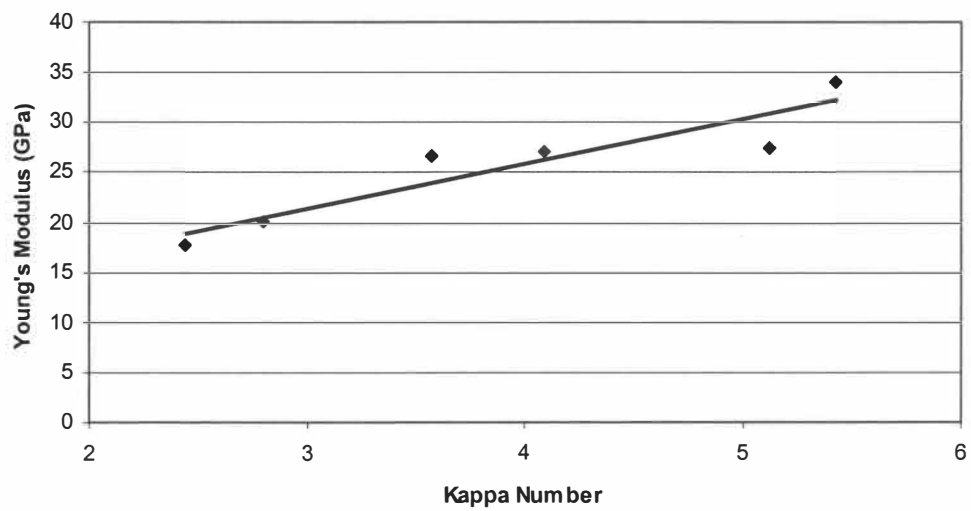
Figure 4.12 Effect of Kappa number on the Young's Modulus of alkali treated hemp fibres.

4.3.5 Fibre Separation

The alkali treated fibres were visually examined to determine the extent of fibre separation, and it was found that fibre separation improved with an increase in the amount of lignin removed during alkali treatment. This was expected as the pectins binding the individual fibres are removed along with hemicellulose and lignin during the alkali treatments. All alkali treatments resulted in satisfactory fibre separation, and it was noticed that treatments 1,2 and 4 had larger numbers of unseparated fibre bundles compared to the other treatments. Treatments 3, 5 and 6 appeared to be very well separated, but the fibres also appeared to be shorter and weaker than their counterparts.

4.4 Composite Results

Out of the alkali treated fibres, it was thought that the treatment 2 process (10% NaOH solution, 45 minute hold time and 160^0C treatment temperature) produced the most suitable fibres for use in composite materials. The average tensile strength of fibres treated by this method was 677 MPa, the average Young's modulus was 27 GPa, and the Kappa number was 5.43. This treatment appeared to have the best combination of fibre strength, stiffness, lignin removal and fibre separation. All of the composites produced contained hemp fibres that were treated using the alkali treatment 2 process. Hawkes-Bay hemp was used in all the composites, with the exception of one sample where Waikato hemp was used.

4.4.1 Composite Tensile Strength and Stiffness

The tensile strength and Young's modulus of each composite produced can be seen in Tables 4.3 and 4.4. The effects of fibre and MAPP contents on the tensile strength and Young's modulus of the short fibre composites are further illustrated in Figures 4.13 and 4.14. These results clearly show that the addition of MAPP to the pure polypropylene matrix had little effect on the tensile strength and Young's modulus of the matrix, and that increases in composite strength and stiffness could be gained by increasing the weight fraction of hemp fibre and MAPP content in the composite.

Table 4.3 Summary of composite tensile strengths (σ) (values are in MPa)

MAPP content (%)	Origin of hemp	Hemp fibre length	Hemp fibre content					
			0%		30%		40%	
			σ	s.dev	σ	s.dev	σ	s.dev
0	Hawkes-Bay	Short	22.8	0.1	25.9	0.7	28.1	0.7
1	Hawkes-Bay	Short	24.2	0.4	29.7	0.7	34.7	0.2
2	Hawkes-Bay	Short	24.0	0.2	36.7	0.7	37.6	1.3
2	Hawkes-Bay	Long					39.1	2.8
2	Waikato	Long*					38.3	2.8

*only 4 successful tests were conducted

Table 4.4 Summary of composite Young's modulus (E) (values are in GPa)

MAPP content (%)	Origin of hemp	Hemp fibre length	Hemp fibre content					
			0%		30%		40%	
			E	s.dev	E	s.dev	E	s.dev
0	Hawkes-Bay	Short	1.07	0.03	2.43	0.11	3.72	0.20
1	Hawkes-Bay	Short	1.15	0.04	2.95	0.13	3.94	0.20
2	Hawkes-Bay	Short	1.11	0.03	2.93	0.10	4.02	0.33
2	Hawkes-Bay	Long					4.38	0.35
2	Waikato	Long*					4.10	0.42

*only 4 successful tests were conducted

The strongest short fibre composite contained 40% Hawkes-Bay hemp and 2% MAPP (weight % of composite), and it had a tensile strength of 37.6 Mpa, and a Young's modulus of 4.02 GPa. The improvements in the tensile strength and Young's modulus of this composite compared to polypropylene with 2% MAPP were 57% and 262% respectively.

The alkali treated hemp fibres that were used had an average tensile strength of 677 MPa, compared to 22.8 MPa for the polypropylene matrix, so it was expected that an increase in the fibre content would considerably increase the tensile strength of the composite. However, due to inefficient adhesion between the fibres and matrix, the tensile strengths of the uncoupled composites were far below their potential values (see 4.4.4 Composite Strength Predictions). By adding 2% MAPP to the 30% hemp fibre composite, the composite tensile strength and Young's modulus were increased by 42% and 21% respectively (compared to the 30% fibre composite with no MAPP). For the 40% fibre composite, the addition of 2% MAPP increased the tensile strength and Young's modulus by 34% and 8% respectively (compared to the 40% fibre composite with no MAPP). The modest increase in strength and stiffness observed by increasing the composite fibre content from 30% to 40% (both with 2% MAPP) suggests that the interfacial bonding had not been optimised, and further improvements could have been made by adding more MAPP.

From the results in Tables 4.3 and 4.4, it can be seen that the use of longer Hawkes-Bay hemp fibres improved the strength and stiffness of the composites. The long-fibre Hawkes-Bay composites were the strongest and stiffest of all the composites produced, and had a tensile strength of 39.1 MPa, and a Young's modulus of 4.38 GPa. The longer fibres were initially cut to 10mm lengths, but the extrusion and granulating processes were thought to have reduced the mean fibre length to below 5mm. It can therefore be concluded that further increases in fibre length could considerably improve the strength and stiffness of the composites.

The results in Tables 4.3 and 4.4 also show that the use of long Waikato hemp fibres, as opposed to long Hawkes-Bay fibres, showed very little difference in affecting the composite strength and stiffness. It was expected that the Waikato hemp composites would have had larger tensile strength and Young's modulus values compared to the Hawkes-Bay hemp composites, because the Waikato hemp fibres were stronger and stiffer than their Hawkes-Bay counterparts.
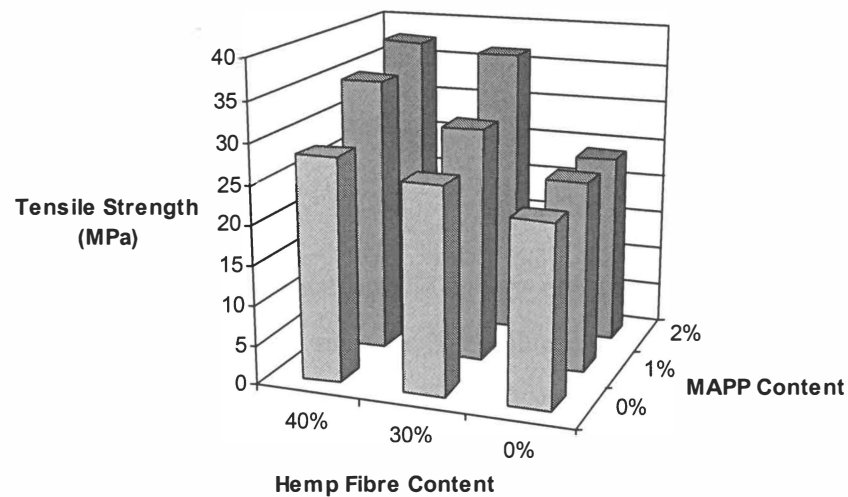
Figure 4.13 Effect of hemp fibre content and MAPP content on composite tensile strength.
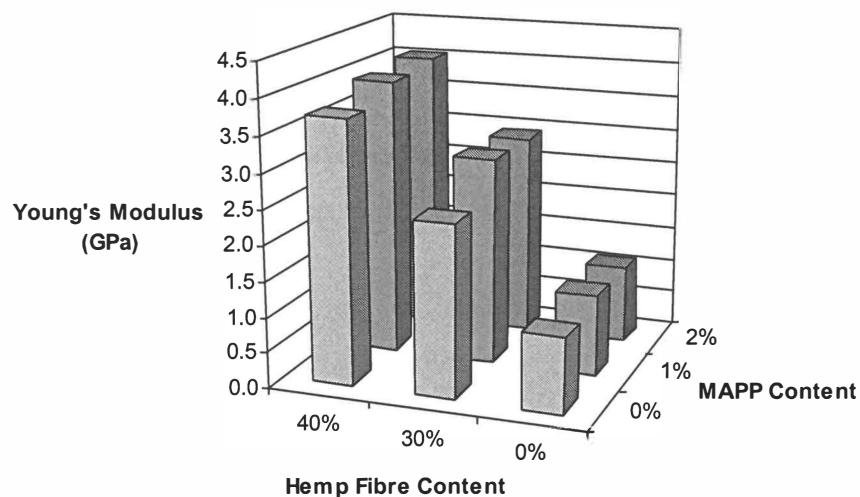
Figure 4.14 Effect of hemp fibre content and MAPP content on composite Young's modulus.

4.4.2 Microscopic Evaluation of Composites

The fracture surfaces of selected hemp fibre reinforced polypropylene composites were observed using a Scanning Electron Microscope (SEM). The SEM micrographs in Figures 4.15(a) to 4.19(b) show the effects of hemp fibre and MAPP coupling agent contents on the extent of fibre/matrix interfacial bonding. Comparing the fracture surfaces of 30% fibre composites with 0% MAPP (Figures 4.15(a) and 4.15(b)) and 2% MAPP (Figures 4.16(a) to 4.16(c)), it can be seen that the matrix did not adhere to the fibre surface without the aid of a coupling agent, and that good interfacial bonding occurred with the addition of 2% MAPP.

The improvements in interfacial bonding were not as pronounced with the 40% fibre composites as they were with the 30% fibre composites. In Figures 4.17(a) and 4.17(b), and Figures 4.18(a) to 4.18(c), it can be seen that only a moderate degree of bonding occurred between the fibre and matrix with the addition of 2% MAPP. This explains why only a small difference in tensile strength was observed between the 30% fibre, 2% MAPP and 40% fibre, 2% MAPP composites. It is thought that for the 40% fibre composite, a 2%(wt) MAPP content was not sufficient to optimise interfacial bonding for all the fibres in the composite. It is possible that the tensile strength of the 40% fibre composites could be greatly improved by adding more than 2% (wt) MAPP.

No distinct differences were observed between the 40% short fibre and 40% long-fibre composites, as can be seen in Figures 4.18(a) to 4.18(c), and Figures 4.19(a) and 4.19(b).

**Figure 4.15(a) Scanning Electron Micrograph (SEM) of composite fracture surface
[30 % fibre, 0% MAPP].**

**Figure 4.15(b) Scanning Electron Micrograph (SEM) of composite fracture surface
[30 % fibre, 0% MAPP] showing poor interfacial bonding.**

Figure 4.16(a) Scanning Electron Micrograph (SEM) of composite fracture surface [30 % fibre, 2% MAPP].

Figure 4.16(b) Scanning Electron Micrograph (SEM) of composite fracture surface [30 % fibre, 2% MAPP] showing good interfacial bonding.

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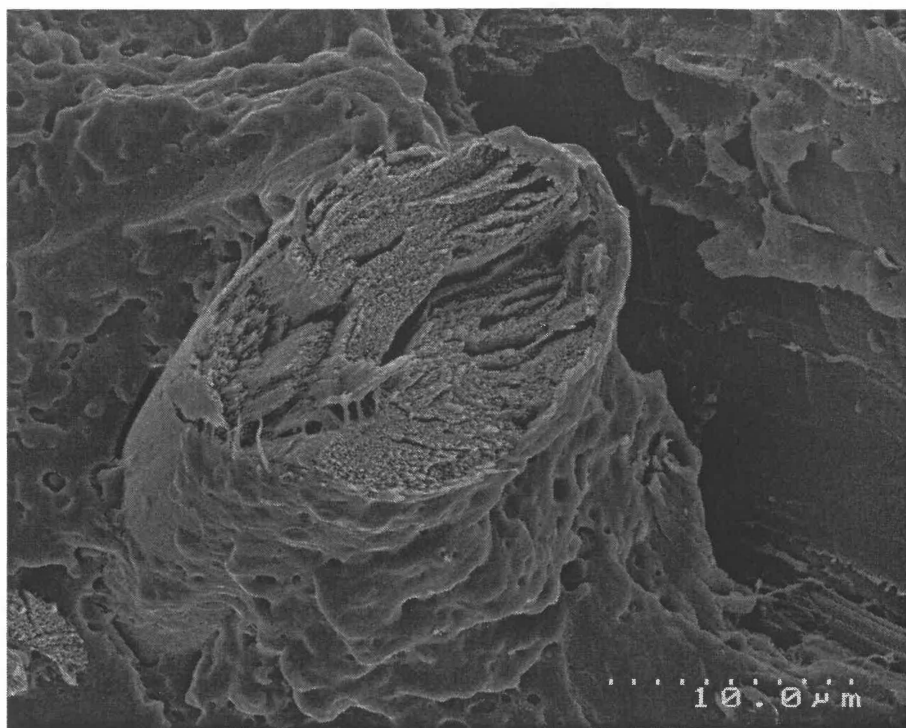
**Figure 4.16(c) Scanning Electron Micrograph (SEM) of composite fracture surface
[30 % fibre, 2% MAPP] showing good interfacial bonding.**
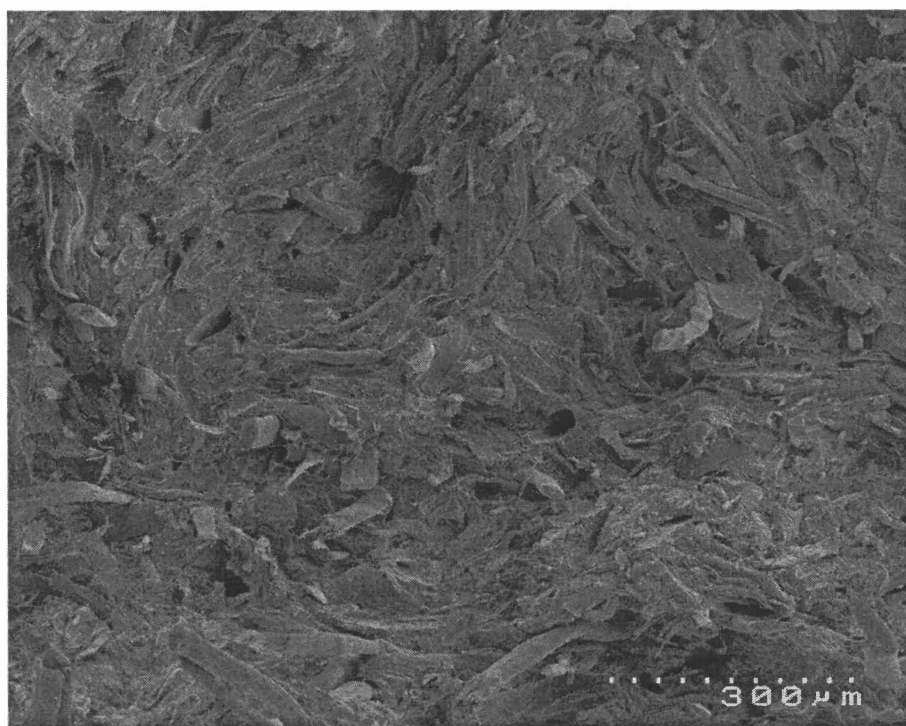
**Figure 4.17(a) Scanning Electron Micrograph (SEM) of composite fracture surface
[40 % fibre, 0% MAPP].**

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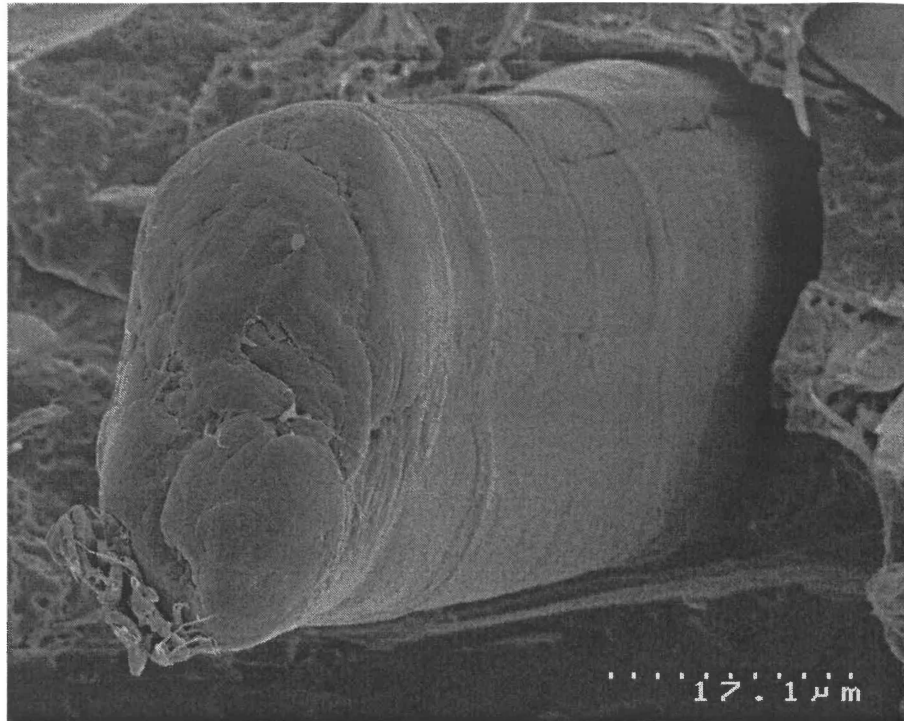
Figure 4.17(b) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % fibre, 0% MAPP] showing poor interfacial bonding.
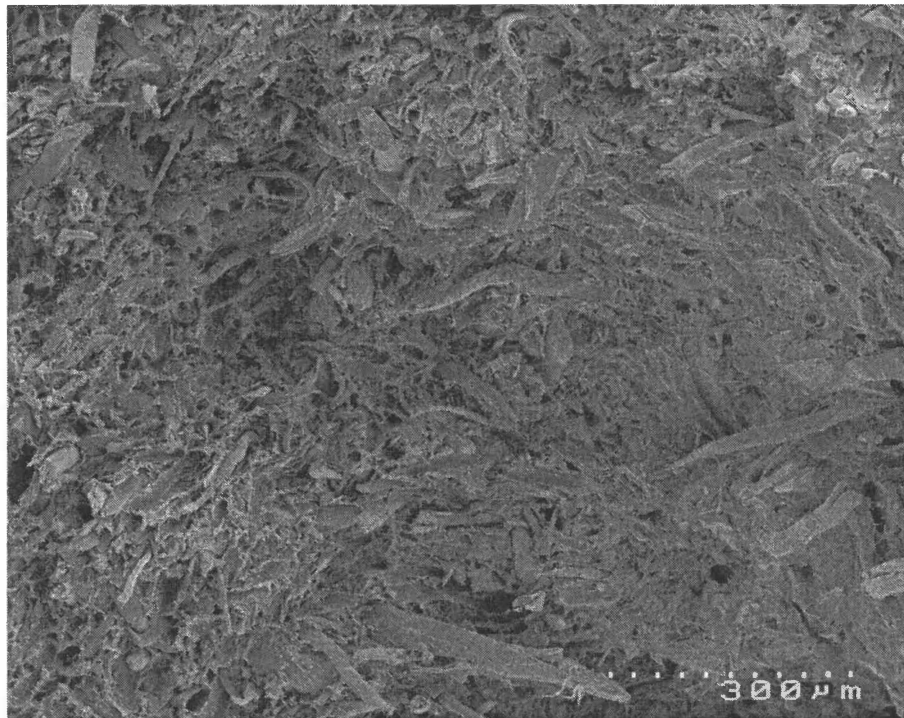
Figure 4.18(a) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % short fibre, 2% MAPP].
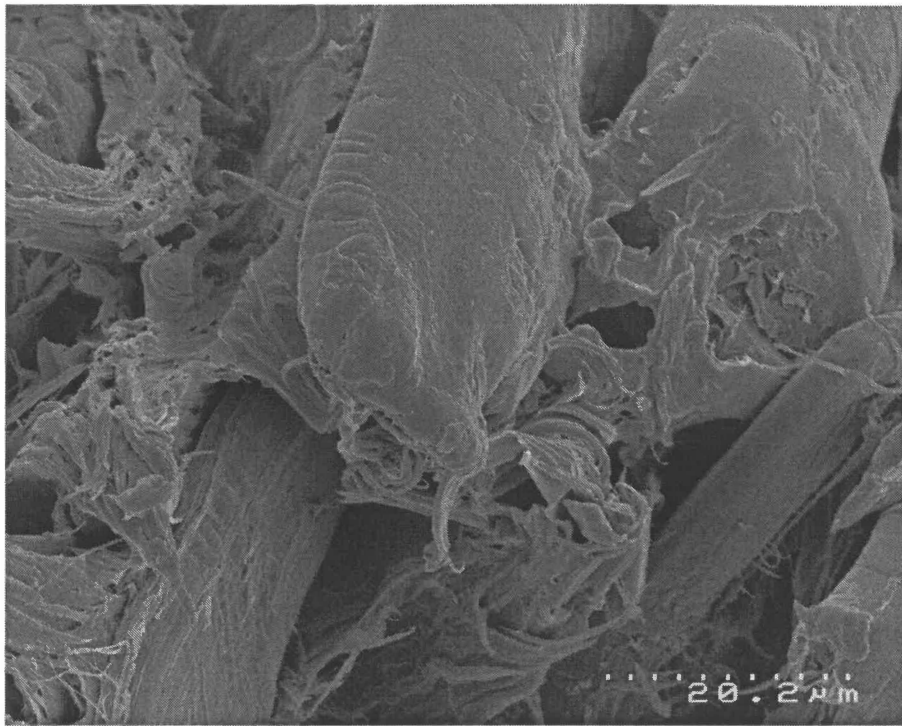
Figure 4.18(b) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % short fibre, 2% MAPP] showing moderate bonding.
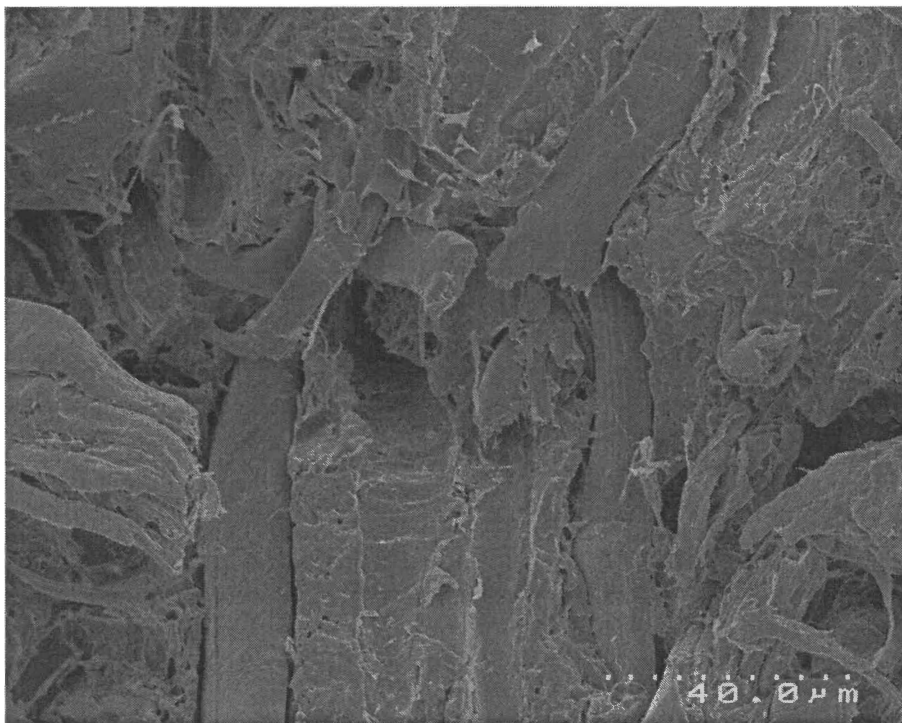
Figure 4.18(c) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % short fibre, 2% MAPP] showing moderate bonding.
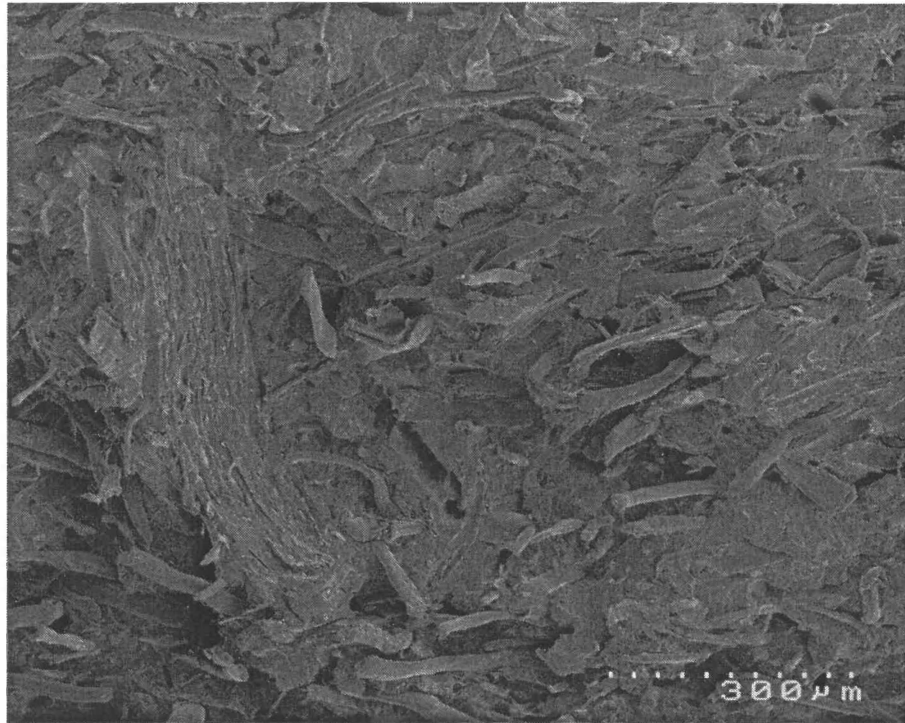
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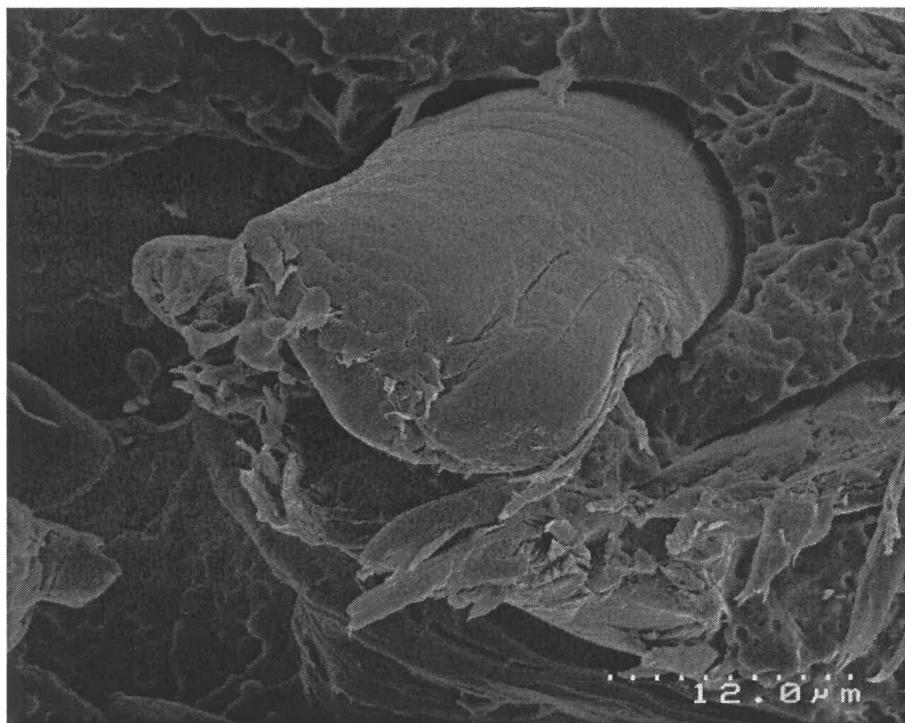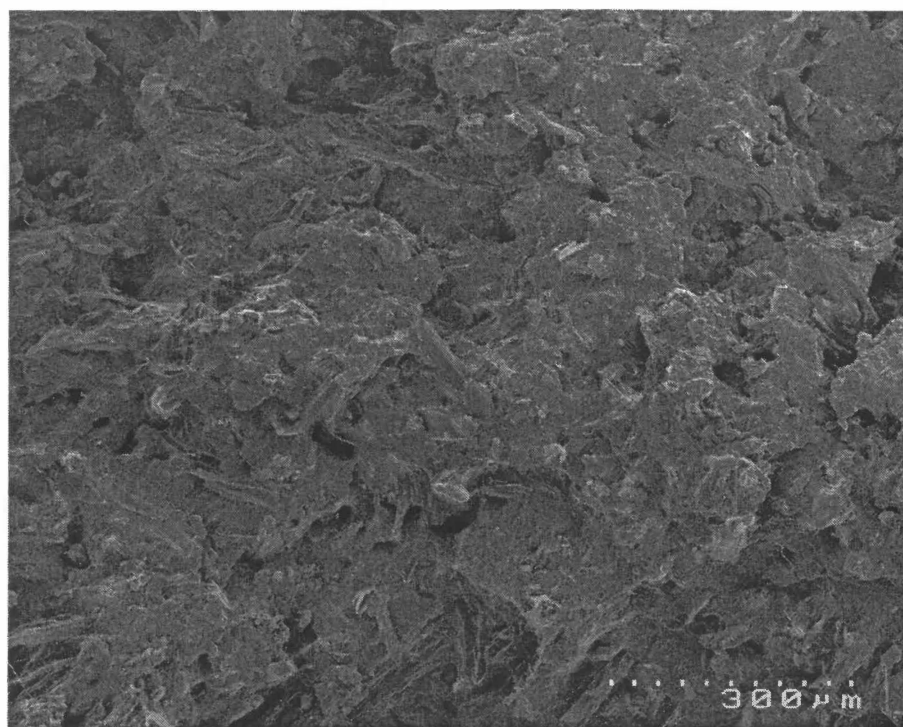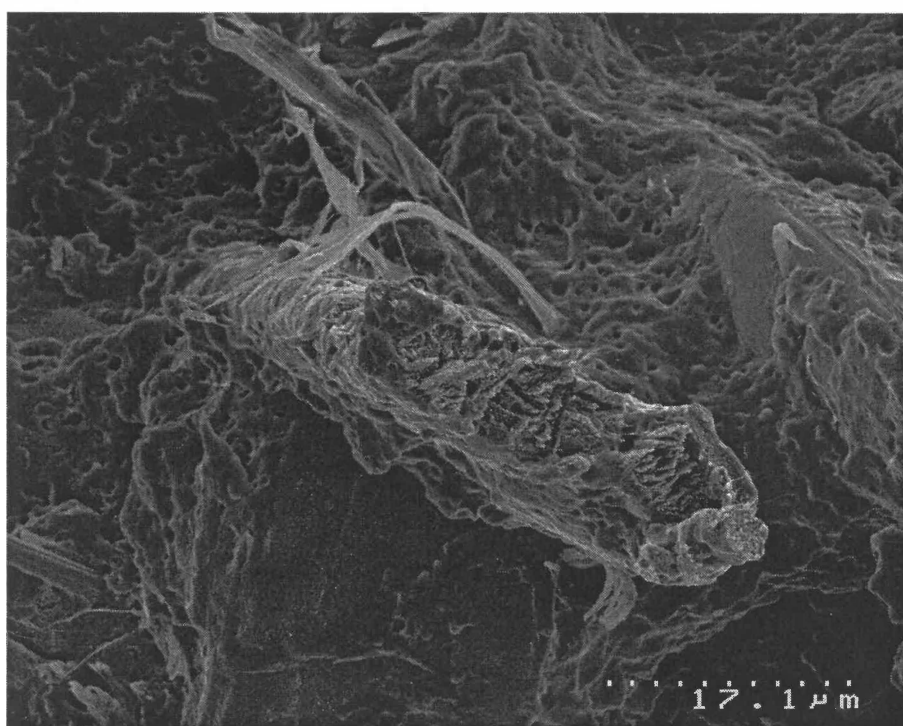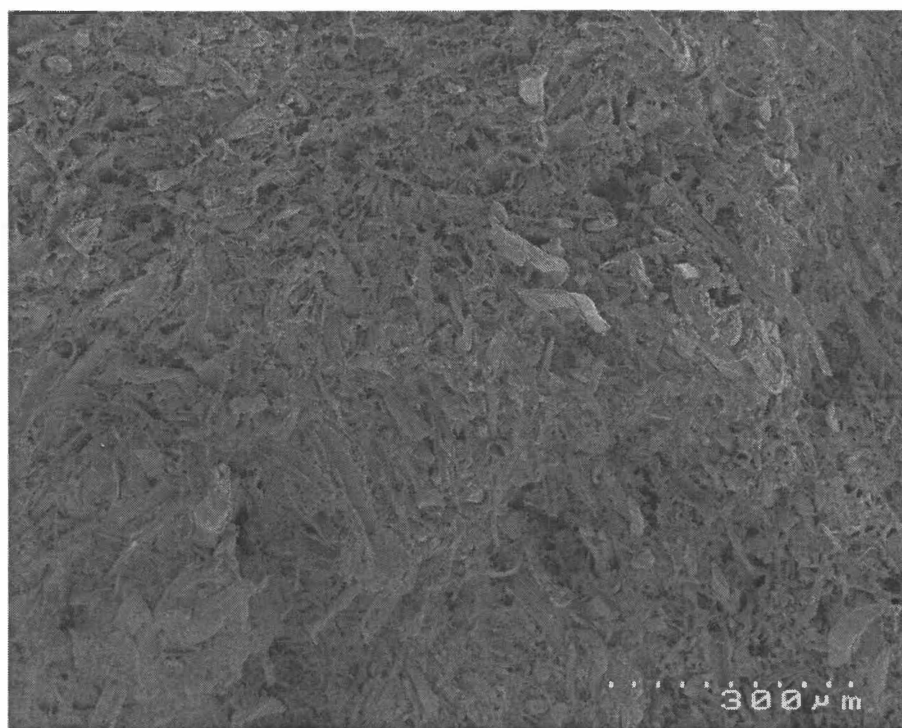**Figure 4.19(a) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % long fibre, 2% MAPP].**
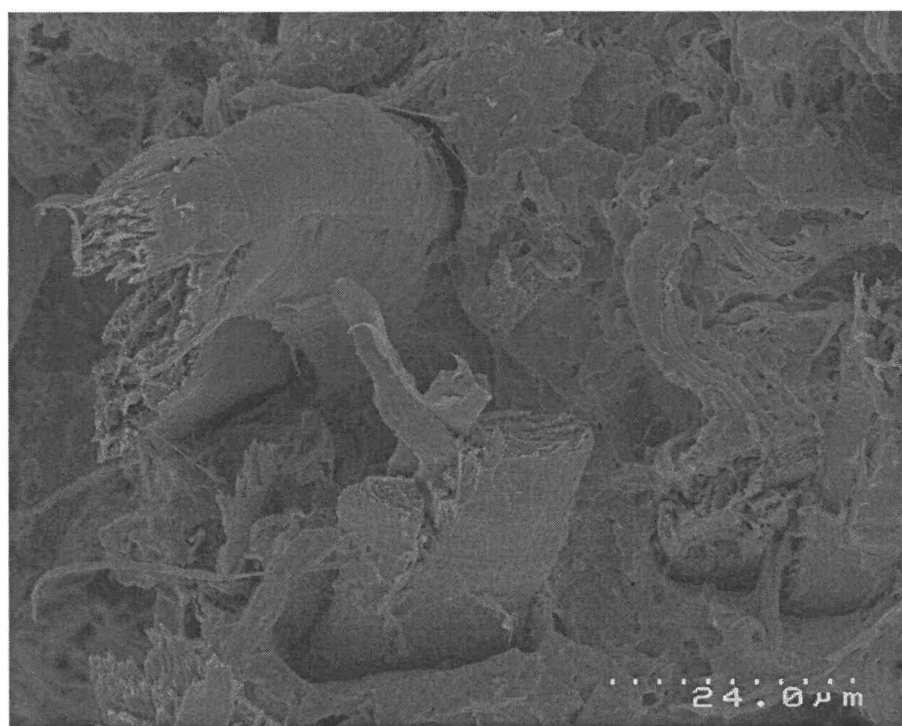
Figure 4.19(b) Scanning Electron Micrograph (SEM) of composite fracture surface [40 % short fibre, 2% MAPP] showing moderate bonding.

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4.4.3 Composite Density

One of the most appealing physical characteristics of natural fibre reinforced thermoplastic composites is their low density compared to synthetic fibre composites and other engineering materials. Sanadi et al. [4] showed that a glass fibre reinforced polypropylene composite with a fibre content of 40% (by weight) has density of $1.23g/cm^3$, and a kenaf fibre reinforced polypropylene composite with a fibre content of 50% (by weight) has a density of $1.07g/cm^3$.

The densities of hemp fibre composites were thus determined so that a comparison could be made with the composites stated in the literature. These densities were simply determined by weighing each composite test specimen, and then submerging the test specimens in a measuring cylinder to determine the volume of water displaced. The densities of each composite were then calculated by dividing the specimen mass by the volume of water displaced. The composite densities can be seen in Table 4.5.

Table 4.5 Composite densities

Composite fibre content (wt %)	Composite density (g/cm^3)
0	0.90
30	1.03
40	1.10

4.4.4 Composite Strength Predictions

By using the modified rule of mixtures (equation 1), it was possible to calculate the theoretical tensile strengths of some of the hemp-fibre composites, and then to compare them to the actual strengths obtained during tensile testing.

The Modified Rule of Mixtures strength prediction method is as follows [1]:

$$\sigma_c = V_m\sigma_m{}^* + V_f\sigma_f K_1 K_2 \qquad (1)$$

where:

σ_c = the tensile strength of the composite

V_m = the matrix volume fraction

V_f = the fibre volume fraction

K_1 = orientation factor

K_2 = a factor dependant on the stress transfer between the matrix and the fibres

σ_f = the tensile strength of the fibres

$\sigma_m{}^*$ = the tensile contribution of the polymer matrix at the failure strain of the composite

The first two variables that need to be determined for this calculation are the volume fractions of the matrix (V_m) and the reinforcing fibres (V_f). For a 100g mass of a 30% fibre (by weight) composite, the fibres would contribute 30g and the polypropylene would contribute 70g to the total composite mass. The volumes occupied by the fibres and matrix were determined by dividing the mass of each component by their respective densities. The density of hemp fibre is 1.48 g/cm^3 [2] and the density of polypropylene is 0.9 g/cm^3 [22]. The total composite volume was determined by adding together the calculated matrix and fibre volumes. The fibre and matrix volume fractions could then be calculated by dividing the fibre and matrix volumes by the total composite volume. The fibre and matrix volume fractions for each composite can be seen in Table 4.6.

Table 4.6 Theoretical composite tensile strengths

Fibre content (wt %)	Vf	Vm	Theoretical tensile strength (MPa)		
			Fibre orientation:		
			3-D random	Planar random	Aligned
30%	0.21	0.79	47.4	72.3	161.0
40%	0.29	0.71	56.3	90.7	213.0
50%	0.38	0.62	66.4	111.0	272.1

The next two variables, namely the orientation factor (K_I) and the factor dependent on the stress transfer between the matrix and the fibre (K_2) can only be determined experimentally. To calculate the maximum theoretical tensile strength, however, it is possible to make certain assumptions on these variables [1]:

- $K_I = \frac{1}{5}$ for a 3-dimensional random orientation

- $K_I = \frac{3}{8}$ for a planar random configuration

- $K_I = 1$ for aligned fibres

- $K_2 = 1$ assuming perfect adhesion between the fibres and matrix

The tensile strength of the alkali treated fibre (σ_f) is 677 MPa, and the tensile strength of the polypropylene matrix (σ_m*) is 24 MPa. The theoretical tensile strengths for each composite were then calculated using equation 1, and the results are summarised in Table 4.6.

It can be seen from these results that improving the fibre alignment, as well as increasing the fibre volume fraction in the composite could lead to great improvements in tensile strength.

When comparing the theoretical tensile strength values in Table 4.6 to the actual composite tensile strength values in Table 4.3, it can be seen that there are large differences between the theoretical and actual strengths. The injection-moulded composites were thought to have had a planar random fibre configuration, which was caused by linear flow of the molten composite into the mould. The results show that the difference between the actual and theoretical strengths of the 30% and 40% fibre composites (with 2% MAPP) are 36 MPa and 53 MPa respectively.

The composites would never actually be as strong as the theoretical values due to fibre damage incurred during composite processing, variations in MAPP distribution and variations in interfacial bonding, but the theoretical values do provide a benchmark from which to judge the performance of the composites. The main reasons why the composites appeared to be so much weaker than the theoretical values were thought to be partly due to poor interfacial bonding and partly due to the presence of sub-critical fibre lengths.

It can therefore be concluded that to improve the strength of hemp fibre reinforced polypropylene composites:

- fibre volume fractions in the composite must be increased
- fibres need to be aligned in the direction of the applied tensile loads
- fibres need to be longer than the critical fibre length
- fibre-matrix interfacial bonding needs to be improved.

Chapter 5:
Conclusions

Chapter 5:
Conclusions

5.1 Hemp Plant Cultivation Time

From the results obtained by tensile testing retted hemp fibres of varying degrees of maturity, it was found that the tensile strengths of hemp bast fibres changed throughout the male hemp-plant flowering stage. At the start of male plant flowering (99 day cultivation time), the bast fibres were weaker and less stiff due to the fact that they were hollow. The fibres were then progressively filled during this stage, with resulting increases in fibre strength and stiffness. This increase in strength and stiffness reached a maximum at 114 days cultivation time, after which a decrease in the average fibre strength and stiffness occurred due to increases in the formation of weaker secondary bast fibres.

It was also observed that the retting process reduced the tensile strength and stiffness of the fibres. This was thought to be due to fibre damage caused by cellulose and structural-hemicellulose degrading micro-organisms in the retting mixture.

The tensile strength of retted hemp fibres appeared to decrease with an increase in fibre diameter. This was thought to be mainly due to fibre shape distortions, which may have led to slight increases in the calculated cross-sectional areas, and therefore slight reductions in the tensile strength of some fibres. The retting process may also have removed some lignin and hemicellulose constituents without degrading the cellulose fibre components, thus reducing the fibre cross-sectional area and increasing the tensile strength.

5.2 Biological Fibre Treatments

The biological fibre treatments involving the exposure of hemp fibres to a D2B white rot fungus and to F13 and F124 sap-stain fungi significantly reduced the strength and stiffness of the hemp fibres. All 3 fungal treatments seemed to reduce the tensile strength of hemp fibre to the same extent, and significant reductions in fibre stiffness were also observed as a result of the bio-treatments. No genuine differences were observed between the 3 and 4-week F13 treatments. Shorter treatment times could be used in future to reduce the extent of fibre degradation, while still modifying the fibre surface to improve the interfacial bonding with a thermoplastic matrix.

5.3 Alkali Fibre Treatments and Lignin Tests

The single fibre tensile tests for alkali treated fibres showed that the alkali treatments 1, 2 and 4 did not reduce the strength of the fibres. The more extreme conditions experienced by fibres during alkali treatments 3, 5 and 6 resulted in significant tensile strength reductions, and this was thought to be due to cellulose degradation and fibre structure disruption. The most significant process variable that affected fibre strength was the process temperature. Large fibre strength reductions were experienced at processing temperatures of 180^0C (compared to 160^0C) due to the degradation of structural cellulose in the fibre. It was also noticed that fibre strength reductions due to increases in hold time and treatment temperature were more pronounced at NaOH concentrations of 15%.

The alkali treatments removed alkali-soluble constituents such as lignin, hemicellulose and pectin from the fibre walls. A decrease in the average fibre diameter was observed for each alkali treatment, and this decrease appeared to be related to the severity of the alkali treatment. Kappa tests were performed on the alkali treated fibres to determine the lignin contents, and it was found that the extent of lignin removal increased with increases in the NaOH concentration, hold time and processing temperature. SEM micrographs comparing the surfaces of alkali treated and untreated fibres showed that the alkali treatments removed lignin and other alkali soluble components from the cell wall, as well as causing striations on the fibre surface.

The single fibre tensile test results also showed that the alkali treatments reduced the Young's modulus of the hemp fibres. These fibre stiffness reductions appeared to be consistent with an increase in the severity of the alkali treatments, and it was also noted that the fibre stiffness decreased with an increase in the lignin removal. The removal of lignin and other intra-fibrillar binders was thought to lead to stress releases and molecular relaxation of the cellulose fibre components, and hence a slight reduction in fibre stiffness.

The alkali treatments also appeared to make the fibres more ductile in behaviour. The average shape of the stress-displacement curves obtained during the single fibre tensile tests were predominantly straight-lines for untreated fibres, and inverted exponential curves for alkali treated fibres. This behaviour was thought to have occurred due to decreases in fibre rigidity with the removal of lignin, hemicellulose and pectin.

The alkali treatment process that produced fibres with the best combination of strength and stiffness retention, lignin removal and fibre separation was treatment 2. Fibres treated by this process were digested in a 10% NaOH solution at 160^0C, with a maximum temperature hold time of 45 minutes. These alkali treated fibres had an average strength and stiffness of 677 MPa and 27 GPa respectively, and a Kappa number of 5.4.

5.4 Composite Results

A series of composites were produced with varying weight fractions of Hawkes-Bay hemp fibre and MAPP. The strongest short-fibre reinforced composite consisted of 40% fibre (by weight) and 2% MAPP, and had a tensile strength of 37.6 MPa and a Young's modulus of 4.02 GPa. It was found that increases in composite strength and stiffness could be made by adding 2% MAPP to the composite. Composites containing 30% fibre showed a 42% increase in tensile strength and a 21% increase in Young's modulus with the addition of 2% MAPP, while composites containing 40% fibre showed a 34% increase in tensile strength and an 8% increase in Young's modulus with the addition of 2% MAPP.

It was also found that an increase in the average length of reinforcing fibres improved the strength and stiffness of the composites, and that the use of Waikato grown hemp, as opposed to the use of Hawkes-Bay hemp, had little effect on the strength and stiffness of the composites.

SEM micrograph evaluations of the short fibre Hawkes-Bay hemp composites showed that poor interfacial bonding occurred in the 30% and 40% fibre composites with no MAPP. The micrographs also showed that the addition of 2% MAPP produced good interfacial bonding in the 30% fibre composites, and moderate interfacial bonding in the 40% fibre composites. No differences were observed between the 40% long fibre composites with 2% MAPP and the 40% short fibre composites with 2% MAPP. It was thought that the interfacial bonding of all the composites could be improved further by the addition of more than 2% MAPP.

It can thereby be concluded that New Zealand grown industrial hemp fibre is stiff and strong, and has the potential to be combined with a polypropylene matrix to produce stiff, strong, lightweight, cheap and recyclable composite materials. The benefits and advantages of using natural fibre reinforced thermoplastic composites are rapidly becoming more recognised in industry, and further improvements in these composites are likely to lead to more widespread use in the near future.

Chapter 6:
Recommendations

Chapter 6:
Recommendations

The results obtained during the course of this research exercise laid an important platform from which to further improve the properties of hemp fibre reinforced polypropylene composites. Some recommendations for future work include the following:

- Increase the volume fraction of hemp fibre in the composites.
- Determine the optimum amount of MAPP for each volume fraction of hemp fibre used in the composite.
- Improve the fibre alignment in the composites. This may involve the use of continuous hemp yarns to produce uniaxially aligned thermoplastic matrix pre-preg composites for the compression moulding if composite components.
- Determine the fibre-matrix interfacial shear stress for each combination of coupling agent and matrix.
- Calculate the critical fibre length of hemp fibres to be used with each combination of coupling agent and matrix.
- Dissolve the matrix for each type of composite produced to determine the fibre length distribution within the composite.
- Increase the fibre lengths in the composite to well above the critical fibre length.
- Investigate the effects of extrusion and injection moulding process variables on fibre length reductions. These process variables include extruder screw configuration, extrusion speed and temperature, and injection moulding pressure.
- Investigate the effects of using other coupling agents or combinations of coupling agents to improve the fibre-matrix interfacial bonding.

- Investigate the effects of coating the fibres with the coupling agent, as opposed to adding the coupling agent to the matrix polymer.
- Use a solvent to remove bound water molecules from the alkali treated fibres, and then remove the solvent from the fibres in a vacuum. This may enhance the inter-microfibrillar bonding, and improve the tensile strength and Young's modulus of the alkali treated fibres.

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Appendices

Appendix 1

Half-Scale Kappa Test Method

This method is based on the AS/NZS 1301.201s: 2002; the Papro 1.106 Kappa Number (Half Scale Modification); and TAPPI T236 Standards.

1 Method Requirements

1.1 Apparatus

- Mechanical stirrer with 100 r.p.m stirring capabilities
- Magnetic stirrer
- Waring blender
- Constant temperature water bath set at 25 ^{0}C
- Sintered funnel
- Conical funnel
- Burette: 50ml, graduated at 0.1ml
- A range of pipettes: 5ml, 10ml, 25ml, 50ml
- Measuring cylinders
- Timer
- Heating device
- Electronic balance
- Glass beakers

1.2 Reagents

- Distilled water

- Potassium permanganate ($KMnO_4$) solution standardised to 0.02M (0.1N) ± 0.0001M. (Should be standardised weekly)

- Sodium thiosulphate ($Na_2S_2O_3$) solution standardised to 0.2M (0.2N) ± 0.0005M. (Should be standardised weekly)

- Potassium iodide (KI) solution, 1M (1N)

- Potassium iodide (KI) solution, 10%

- Sulphuric acid (H_2SO_4), 2M (4N)

- Starch indicator solution, 2%

- Potassium Iodate (KIO_3) solution (0.1N)

1.3 Reagent Volumes Required for Each Titration

For each half-scale Kappa test, 4 titrations are required: 3 titrations with fibre and one blank.

For each titration, the following amounts of reagent are required:

- 50ml 0.02M $KMnO_4$ solution

- 50ml 2M H_2SO_4 solution

- 400ml distilled water

- 10ml 1M KI solution

- 25ml or less 0.2M $Na_2S_2O_3$ solution

- A predetermined amount of fibre that will consume between 30% and 70% $KMnO_4$ (see 4.2).

2 Potassium Permanganate Solution

For each half-scale Kappa Test, 200ml of standardised $KMnO_4$ solution is required. (i.e. enough for 4 titrations). It should be noted that extra potassium permanganate needs to be made up for the standardisation titrations. (an extra 200ml of permanganate is required – ie. 8 titrations, each using ± 25ml of permanganate).

It is necessary to calculate the amount of potassium permanganate that will be needed for the standardisation titrations <u>and</u> Kappa tests.

2.1 Preparation of Potassium Permanganate Solution

- A 0.02M $KMnO_4$ solution (0.1N) is required for the Half Scale Kappa Test.

- To mix up 250ml of the ± 0.02M $KMnO_4$, measure exactly 0.85g $KMnO_4$ powder and dissolve in exactly 250ml distilled water.

- Transfer solution to a beaker and heat to about 90 ^{0}C for 15 minutes (in a fume cupboard).

- Cool to room temperature, and then filter through a sintered glass funnel.

2.2 Standardisation of Potassium Permanganate Solution

- Weigh accurately 0.134g Sodium Oxalate ($Na_2C_2O_4$) that has been dried at a temperature of 100 ^{0}C to 110 ^{0}C.

- Add to a conical flask

- Dissolve in 20ml hot distilled water, and then cool. Store at 4 ^{0}C.
  (i.e. 134g $Na_2C_2O_4$ in 20ml water gives a 0.05M (0.1N) solution).

- Add 50ml 2M H_2SO_4 (98% analytical grade acid, at 109ml acid/L water)

- Heat to 80 ^{0}C and titrate slowly with permanganate (shake flask well)

- Continue until permanent pink tinge is achieved
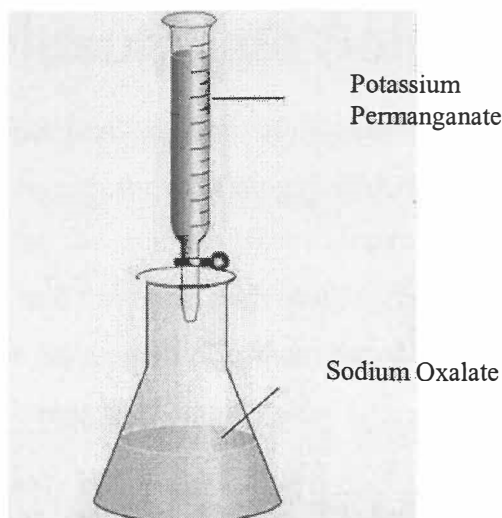
In this reaction, 20 ml of 0.05M Oxalate reacts with 20M $KMnO_4$

The mole ratio of this reaction is as follows: 2.5 mol Oxalate reacts with 1 mol $KMnO_4$ (Note: There are 4×10^{-4} mol in 20ml $KMnO_4$).

- So, if exactly 20ml of $KMnO_4$ reacts with 20ml oxalate, then the concentration of $KMnO_4$ is exactly 0.02M

- If more than 20ml $KMnO_4$ is used, then the concentration of $KMnO_4$ is < 0.02M, and the amount of $KMnO_4$ that needs to be added to the solution to get the concentration to 0.02M needs to be calculated.

- If less than 20ml $KMnO_4$ is used, then the concentration of $KMnO_4$ is > 0.02M, and the amount of water that needs to be added to the solution to get the concentration to 0.02M needs to be calculated.

- To calculate the $KMnO_4$ concentration, the following formula can be used:

Conc. of $KMnO_4$ = no. moles in 20ml $KMnO_4$ / vol $KMnO_4$ titrated against oxalate

* Three successful titrations need to be performed, and the average concentration of the three titrations needs to be determined.

- The potassium permanganate solution needs to be stored in a dark environment.

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3 Sodium Thiosulphate Solution

For each half-scale Kappa Test, ±100ml of standardised sodium thiosulphate solution is required. (i.e. enough for 4 titrations). But, extra sodium thiosulphate needs to be made up for the standardisation titrations (an extra 200ml of thiosulphate is required – ie. 8 titrations, each using ± 25ml of thiosulphate).

It is necessary to calculate the amount of sodium thiosulphate that will be needed for the standardisation titrations <u>and</u> Kappa tests.

3.1 Preparation of Sodium Thiosulphate Solution

- A 0.2M sodium thiosulphate solution is required for the Half Scale Kappa Test.

- To mix up 200ml of sodium thiosulphate, measure 9.928g $Na_2S_2O_3.5H_2O$ granules, and add water to make the solution up to 200ml. (ie. the concentration of $Na_2S_2O_3.5H_2O$ is 49.64 g/L)

- The sodium thiosulphate solution must then be titrated against a solution consisting of a mixture of KIO_3, KI and H_2SO_4.

3.2 Standardisation of Sodium Thiosulphate Solution

For each thiosulphate standardising titration, the following are required:
- Exactly 50ml 0.1N (0.0167M) KIO_3 solution (0.178g KIO_3 powder (dried) + 50ml water).
- 20ml 10% KI solution (2g KI + 20ml water)
- 20ml 2M H_2SO_4 (must allow to cool)
- Distilled water
- 1% starch solution (20ml H_2O + 0.2g soluble starch)

Method: Take 50ml potassium iodate solution and add 20ml potassium iodide solution and 20ml acid. Dilute to 200ml with distilled water and titrate with thiosulphate solution (0.2M thiosulphate is required).

When the solution has become a pale straw colour, add 2ml starch solution and continue the titration until the colour changes from blue to colourless (titrate slowly).

Sodium
Thiosulphate

KI, KIO_3, H_2SO_4
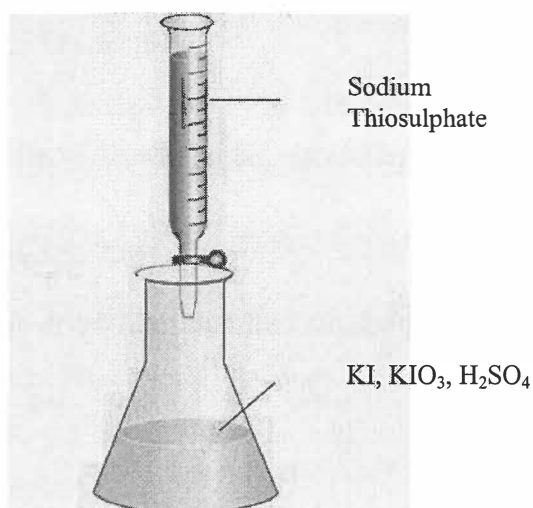
In this reaction, 25ml 0.2M thiosulphate reacts with 50ml 0.0167M KIO_3.

The mole ratio of this reaction is as follows: 6 mol thiosulphate reacts with 1 mol KIO_3 (Note: There are 8.35×10^{-4} mol in 50ml 0.0167M KIO_3, and 5×10^{-3} mol in 25ml 0.2M thiosulphate).

- So, if exactly 25ml thiosulphate reacts with 50ml KIO_3, then the concentration of the thiosulphate is exactly 0.2 mol/L

- If more than 25ml is used, then the concentration of thiosulphate is < 0.2M

- If less than 25ml is used, then the concentration of thiosulphate is > 0.2M

- The thiosulphate solution needs to be standardised to between 0.1995M, and 0.2005M.

4 Half Scale Kappa Test

See the reagents needed for each Kappa test (1.3).

Perform 4 titrations for each half-scale Kappa test: 3 titrations with fibre, and 1 blank.

4.1 Test Method

Use enough fibre to consume 30% - 70% of the permanganate (ie titre should be 30% to 70% of the blank determination). Most accurate results are obtained when the permanganate consumption is near 50%.

*See 4.2 for instructions on how to determine the amount of fibre to use.

- Weigh out 3 samples of fibre.

- For each sample, cut the dried fibre mat into smaller pieces, and place in a blender with 300ml water. Blend for 45 seconds. Pour water and fibres into a large beaker, and rinse the blender with an additional 100ml water. Add this extra water to the beaker.

- Place beaker into a 25^0C water bath, and allow the fibre/water mixture to attain this temperature.

For each titration:

- Pipette 50ml 0.02M $KMnO_4$ solution into a flask, and add 50ml H_2SO_4.

- Bring the mixture to 25^0C, and then add to the fibre suspension.

- Start stopwatch immediately, and place the suspension in a mechanical stirrer set at 100 R.P.M.

- Use a small amount of distilled water to wash the remaining permanganate out of the beaker and into the fibre suspension.

- After exactly 10 minutes, terminate the reaction by adding 10ml (exactly) 1M KI. (to mix a 1M solution of KI, measure exactly 41.5g KI, and add water to make up to 250ml). NB: KI solution photo-decomposes, so store in a dark environment away from sunlight. Discard if the solution turns yellow.

- Titrate immediately with sodium thiosulphate, until a pale yellow colour develops.

- Add 10 drops of starch solution, and continue titration until the solution is clear. NB: use a magnetic stirrer to stir the fibre suspension during the titration.

- Titrate very carefully, and do not overshoot the equilibrium point. Measure the amount of thiosulphate used to within 0.01ml.

The blank determination is performed in a similar manner, but without using any fibre.

4.2 Permanganate Consumption

- For the Half-scale Kappa test, the amount of fibre used must consume between 30% and 70% of the permanganate (with a 50% consumption being the most desirable)

- To do this, a minimum of 2 titrations must be performed. (1 titration with fibre and 1 bank)

Step1:

- Estimate a mass of fibre that will consume the required amount of permanganate (e.g. 4g).

Step 2:

- Perform a titration as mentioned in 4.1

Step 3:

- Use the following formulas to calculate the % of permanganate consumed:

$$P = n(b-a)/0.1$$
$$\text{and}$$
$$\% \text{ permanganate consumed} = P \times 100/n$$

where:

P = permanganate consumption (ml)

n = normality (molarity) of thiosulphate

b = vol in ml of thiosulphate consumed in blank determination

a = vol in ml of thiosulphate consumed in the test

Step 4:

- The Kappa number can then be calculated as follows:

$$K^1 = [(P \times f)/m] \times C$$

where:

K^1 = the half-scale Kappa number

P = permanganate consumption (ml)

f = factor for correction to a 50% permanganate consumption (see Table 1)

C = temperature correction factor (see Table 2)

m = mass of moisture free fibre (g)

Table 1. Factor f to be used in equation

p	0	1	2	3	4	5	6	7	8	9
30	0.958	0.960	0.962	0.964	0.966	0.968	0.970	0.973	0.975	0.977
40	0.979	0.981	0.983	0.985	0.987	0.989	0.991	0.994	0.996	0.998
50	1.000	1.002	1.004	1.006	1.009	1.011	1.013	1.015	1.017	1.019
60	1.022	1.024	1.024	1.028	1.030	1.033	1.035	1.037	1.039	1.042
70	1.044									

Table 2. Factor C to be used in equation

Temperature	Correction	Temperature	Correction	Temperature	Correction
t	c	t	c	t	c
20.0	1.065	23.5	1.020	27.0	0.974
20.5	1.059	24.0	1.013	27.5	0.968
21.0	1.052	24.5	1.007	28.0	0.961
21.5	1.046	25.0	1.000	28.5	0.955
22.0	1.039	25.5	0.994	29.0	0.948
22.5	1.033	26.0	0.987	29.5	0.942
23.0	1.026	26.5	0.981	30.0	0.935