The Improvement of Interfacial Bonding, Weathering and Recycling of Wood Fibre Reinforced Polypropylene Composites

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

by

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The University of Waikato, Hamilton, New Zealand
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Abstract

This study deals with medium density wood fibre (MDF) and Kraft fibre reinforced polypropylene (PP) composites produced using extrusion followed by injection moulding. Initially, composites were produced with MDF fibre using 10, 20, 30, 40, 50 and 60 wt% fibre, and 1, 2, 3 and 4 wt% maleated polypropylene (MAPP) as a coupling agent. A fibre content of 50 wt% with 3 wt% MAPP was found to be optimum. Alkali treatment of fibre was carried out to improve the interfacial bonding. After treatment, fibre surface charge was found to increase, but single fibre tensile strength (TS) and Young's modulus were (YM) decreased. Alkali treatment reduced composite TS but increased YM.

The effects of hemicellulose and residual lignin content were assessed with Kraft fibre (subjected to different stages of a standard Kraft pulping process and therefore consisting of different hemicellulose and residual lignin contents). Fibre surface charge was found to increase with decreasing residual lignin content. Composites containing higher amounts of lignin lead to lower TS and lower thermal stability. Composites were subjected to accelerated weathering for 1000 hours. TS and YM were found to decrease during weathering, and the extent of reduction was found to be higher for composites with higher residual lignin. The reduction of mechanical properties was found to be due to degradation of lignin and PP chain scission as evaluated by increase in PP crystallinity after weathering. As low lignin (bleached) Kraft fibre composites were found to provide superior mechanical properties, as well as more stable during accelerated weathering, further study including optimisation of MAPP content, effects of fibre contents, fibre length, fibre beating, hygrothermal ageing and recycling were carried out with bleached Kraft fibre.

MAPP contents of 1, 2, 3, 4, 5, 7 and 10 wt% were used in Kraft fibre reinforced PP composites, and 3-5 wt% was found to be most favourable. Composite fibre content was varied between 30-50 wt%, and 40 wt% found to provide the maximum TS. To investigate the effects of fibre length on composites, fibre fractions of different length distribution were separated using a pressure screen. TS, YM and impact strength were found to decrease and failure strain (FS) increased with decreasing fibre length. To improve the interfacial bonding, the fibre was treated by mechanical beater. Fibre beating increased the TS of composites up to a certain point, beyond which TS decreased. Hygothermal ageing of composites was carried out by immersing specimens in distilled water at 30, 50 and 70°C over an 8-month period. Equilibrium moisture content and diffusion coefficient increased with increased fibre content in composites as well as with increased immersion temperature. Composites without coupling agent showed higher water uptake and diffusion coefficient than that of with coupling agent. After hygrothermal ageing the TS and YM decreased but FS and impact strength were found to increase.

An investigation into the effects of recycling was carried out with composites containing either 40 wt% or 50 wt% fibre (bleached Kraft) with 4 wt% MAPP, and recycled up to eight times. For composites with 40 wt% fibre, TS and YM were found to decrease with increased recycling by up to 25% for TS and 17% for YM (after being recycled 8 times). Although TS was lower for virgin composites with 50 wt% fibre than for those with 40 wt% fibre, this initially increased with recycling by up to 14% (after being recycled 2 times), which was considered to be due to improved fibre dispersion, but then decreased with further recycling, and an overall

11% reduction of TS was found after recycling 8 times compared to the virgin composites. YM was higher for virgin composites with 50 wt% fibre than those with for 40 wt% fibre, and also initially increased with recycling but decreased upon further recycling. Recycling was found to increase thermal stability. The TS of composites made by combining recycled with virgin materials was also assessed. Hygrothermal ageing behaviour of recycled composites was also investigated by immersing specimens in distilled water at 50°C over a 9 month period. It was found that the diffusion coefficient and the equilibrium moisture contents of composites decreased with increased number of times the materials were recycled. After hygrothermal ageing, TS and YM of composites were found to decrease. However, the extent of reduction was found to decrease with increased recycling.

Dedicated

To

My beloved wife and daughter

Acknowledgement

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3. Beg MDH and Pickering KL. Pickering. Effect of Coupling Agent and Fibre Pre-Treatment on the Mechanical Properties of Wood / Polypropylene Composites. SCENZ Conference, 2nd July, 2004, New Zealand.
4. Beg MDH and Pickering KL. Effect of Fibre Pre-Treatment on the Mechanical Properties of Wood / Polypropylene composites. The 2nd International Conference on Structure, Processing and Properties of Materials, SPPM2004, 25-27 February 2004, Dhaka, Bangladesh.
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Symbols and Abbreviations

ABS	Acrylonitrile butadiene styrene
BKP	Bleached Kraft pulp
D	Diffusion coefficient (m^2/s)
DMM	Dimethylol melamine resin
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_a	Activation energy (kJ/mol)
EU	European Union
FS	Failure strain (%)
HDPE	High density polyethylene
I_{DSC}	% Crystallinity determined by DSC
I_{XRD}	% Crystallinity determined by XRD
l_N	Average fibre length (mm)
l_0	Length of virgin fibre (mm)
L	Thickness of the sample (m)
LDPE	Low density polyethylene
MAPP	Maleated polypropylene
MDF	Medium density fibre
MAPP	Maleic anhydride grafted polypropylene
MA	Maleic anhydride
M_c	Modulus of composite
M_m	Modulus of matrix
M_f	Modulus of fibre
M_e	Chain length between entanglements
M_t	Moisture content at time t
M_∞	Moisture content at the equilibrium

PP	Polypropylene
PE	Polyethylene
PS	Polystyrene
PVC	Polyvinyl chloride
PF	Phenol-formaldehyde resin
SMA	Styrene/maleic anhydride
S_c	Strength of composite (MPa)
S_m	Strength of matrix (MPa)
S_f	Strength of fibre (MPa)
SEBS-MA	Styrene-ethylene-butylene-styrene/maleic anhydride
SEM	Scanning electron microscopy
T_{max}	Temperature at maximum reaction rate (^oC)
T_m	Melting temperature (^oC)
T_g	Glass transition temperature (^oC)
TS	Tensile strength (MPa)
TMP	Thermomechanical pulp
TGA	Thermogravimetric analysis
UV	Ultra-violet
US	United States
WPC	Wood plastic composites
x	Stress transfer factor
XRD	X-ray diffraction
y	Fraction of materials not been decomposed
YM	Young's modulus (MPa)
β	Heating rate (^oC/min)
σ_N	Tensile strength of the composites recycled N times
N	Number of times the materials were recycled
ξ	Zeta potential (mV)
ΔH	Heat of fusion (J/g)

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Symbols and Abbreviations

ABS	Acrylonitrile butadiene styrene
BKP	Bleached Kraft pulp
D	Diffusion coefficient (m^2/s)
DMM	Dimethylol melamine resin
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_a	Activation energy (kJ/mol)
EU	European Union
FS	Failure strain (%)
HDPE	High density polyethylene
I_{DSC}	% Crystallinity determined by DSC
I_{XRD}	% Crystallinity determined by XRD
l_N	Average fibre length (mm)
l_0	Length of virgin fibre (mm)
L	Thickness of the sample (m)
LDPE	Low density polyethylene
MAPP	Maleated polypropylene
MDF	Medium density fibre
MAPP	Maleic anhydride grafted polypropylene
MA	Maleic anhydride
M_c	Modulus of composite
M_m	Modulus of matrix
M_f	Modulus of fibre
M_e	Chain length between entanglements
M_t	Moisture content at time t
M_∞	Moisture content at the equilibrium

PP	Polypropylene
PE	Polyethylene
PS	Polystyrene
PVC	Polyvinyl chloride
PF	Phenol-formaldehyde resin
SMA	Styrene/maleic anhydride
S_c	Strength of composite (MPa)
S_m	Strength of matrix (MPa)
S_f	Strength of fibre (MPa)
SEBS-MA	Styrene-ethylene-butylene-styrene/maleic anhydride
SEM	Scanning electron microscopy
T_{max}	Temperature at maximum reaction rate (^oC)
T_m	Melting temperature (^oC)
T_g	Glass transition temperature (^oC)
TS	Tensile strength (MPa)
TMP	Thermomechanical pulp
TGA	Thermogravimetric analysis
UV	Ultra-violet
US	United States
WPC	Wood plastic composites
x	Stress transfer factor
XRD	X-ray diffraction
y	Fraction of materials not been decomposed
YM	Young's modulus (MPa)
β	Heating rate (^oC/min)
σ_N	Tensile strength of the composites recycled N times
N	Number of times the materials were recycled
ξ	Zeta potential (mV)
ΔH	Heat of fusion (J/g)

CHAPTER-ONE

PROJECT INTRODUCTION

1.1 Introduction

Composites are comprised of combinations of two or more materials with different composition or form. The constituents retain their identities in a composite and do not dissolve or merge, but act together [1]. A composite may have a ceramic, metallic or polymeric (thermoset or thermoplastic) matrix. The fibres can also be ceramic, metallic or polymeric, however, a more common classification relates to whether they are synthetic (e.g. glass fibre, carbon fibre, Kevlar fibre) or natural (wood fibre, hemp fibre, flax fibre, jute fibre etc). Therefore, the number and variety of composites available are very large. Fibre-reinforced composite materials commonly consist of fibres of high strength and Young's modulus embedded in, or bonded to, a matrix with a distinct interface between them. In general, the fibres are the principal load carrying members, while the surrounding matrix holds them in the desired location and orientation, acting as a load transfer medium between them.

The idea of using natural fibres as reinforcement in composite materials is not new. Natural fibres were used over 3000 years ago in composite systems in ancient Egypt, where straw and clay were mixed together to build walls [2]. Many centuries later, in 1896, aeroplane seats were made of natural fibres with a small content of polymeric binders. As early as 1908, the first composite materials were applied in the fabrication of large quantities of sheets, tubes and pipes [3]. However, during the 70's and 80's, cellulose fibres were gradually substituted by newly developed synthetic fibres due to better performance. Over the past few years, there has been a renewed interest in using natural fibres as reinforcement materials in the plastics industry [3]. More recently, critical discussion about the preservation of natural resources and recycling has led to further interest concerning natural materials with the focus on renewable raw materials [4]. As mentioned earlier, there is a wide variety of different natural fibres which can be applied as reinforcement. Wood fibre is the most widely used lignocellulosic fibre for reinforcing plastics. It can be obtained from variety of processes, namely: thermomechanical, soda, sulphite, sulphate (Kraft) and semi-chemical pulping [5,6]. Wood fibre composites offer several advantages over synthetic fibre composites such as: low density, improved acoustic properties, favourable processing properties (e.g. low wear on tools), occupational health benefits compared to glass fibres, as well as positive effects on agriculture with comparable mechanical properties [7].

There are many applications of wood plastic composites (WPC) in everyday life. Wood fibre/polypropylene (PP) composites are used in cars behind the vinyl carpeting on the doors, consoles and seat backs. Residential construction applications include windows, sidings, and roof tiles. Many window and door manufacturers are considering WPC as an alternative to solid wood in cladding components [8]. In North America, building products, particularly decking, account for 75% of the total WPC market [9].

As the outdoor applications of WPC become more widespread, the durability of its products against weathering, particularly ultra-violet (UV) light becomes of concern. UV exposure can cause changes in the surface chemistry of the composite, also known as photodegradation, which may lead to discoloration making the products aesthetically unappealing [10,11,12]. Composites reinforced with natural fibres containing large amounts of lignin have been shown to be more susceptible to UV degradation than those with negligible amounts of lignin [13,14]. Removal of lignin, hemicellulose and water soluble components has the potential to reduce UV degradability [15]. Scientists have begun to investigate the UV durability of WPC. Work with wood fibre reinforced polyolefin composites has focused mainly on changes in appearance and mechanical properties [10,11,12]. However, little work has provided insight into the mechanism of change of WPC properties containing different lignin contents due to UV exposure [16].

Another main concern is the hydrophilic nature of wood fibre, which results in an incompatibility with hydrophobic polymeric matrices leading to poor mechanical properties. Further, in moist environment, due to this hydrophilicity, swelling by water uptake can lead to micro-cracking of the composite and degradation of mechanical properties [17]. For this to be predictable, an understanding is required of the relationship between water absorption kinetics with mechanical properties.

It might be expected that treatments which improve interfacial bonding would improve mechanical properties as well as moisture resistance. Good wetting of the fibre by the matrix and adequate fibre–matrix bonding has been shown to decrease the rate and amount of water absorption in the interfacial region of the composite [18]. Optimisation of interfacial adhesion between cellulose-based fibres and thermoplastics has been the focus of a large amount of research conducted during the last two decades [19,20,21]. However, it has proved difficult to entirely eliminate the absorption of moisture in the composites without using expensive surface barriers [22]. The most cost effective benefit for improving moisture resistance along with mechanical performance of WPC’s has been found with coupling agents, which play an important role in improving compatibility and adhesion between polar wood fibre and non-polar polymer matrices by forming bridges of chemical bonds between the fibre and the matrix. So far, more than forty coupling agents have been used in production and research. Among them, maleated polypropylene (MAPP) is the most popular one as well as the most effective [23]. However, these studies tend to focus on only a small range of fibre contents and do not include coverage of New Zealand radiata pine Kraft fibre. Alkali treatment, which could improve UV resistance by removing lignin as mentioned previously, could also increase the number of reactive hydroxyl groups (-OH) on the fibre surface available for chemical bonding, thus improving composite strength [24]. Mechanical beating of fibre is also widely used in paper making as a method of improving interfacial bonding. It has been suggested that beaten fibres should exhibit increased fibre–matrix bonding due to the increase in fibre surface area [25,26], and some work has been done on the effects of fibre beating in cement fibre composites [25,26]. However, no literature was found concerning the effect of beating of wood fibre in PP composites. Therefore, beating needs to be attempted as a fibre pre-treatment process to improve the interfacial bonding between the fibre and the matrix.

As mentioned earlier, concern for the environment has led to increasing pressure to recycle materials at the end of their useful life, but very little work has been done on recycling of WPC and the associated mechanism. Therefore, extensive study is needed to investigate the extent to which WPC materials are recyclable.

1.2 Objectives

The specific objectives of this thesis were to study:

The effects of coupling agent and alkali treatment on medium density fibre (MDF) fibre reinforced PP composites:

- Assessing the effects of maleated polypropylene (MAPP) coupling agent on composite properties over a wide range of fibre volume fractions

- Study the effects of alkali fibre pre-treatment on composite mechanical properties
- Comparison with models for tensile strength and Young's modulus.

The effects of residual lignin and hemicellulose content on the accelerated weathering of wood fibre (Kraft) reinforced PP composites:

- Evaluate the effects of residual lignin and hemicellulose content on composite properties
- Investigate the degradation behaviour of wood fibre reinforced PP composites under accelerated weathering conditions.

Fibre pre-treatment and hygrothermal ageing of wood fibre (Kraft) reinforced PP composites:

- Optimisation of coupling agent for bleached Kraft fibre reinforced PP composites
- Investigation of the effects of fibre volume fraction and fibre length on composite properties
- Assessing fibre pre-treatment by mechanical beating and its effects on composite properties
- Study of hygrothermal ageing at different temperatures and its effects on composites properties.

Effects of recycling on wood fibre (Kraft) reinforced PP composites:

- Evaluation of the effects of recycling on mechanical properties
- Investigate the effects of recycling on thermal and crystalline behaviour
- Relate hygrothermal aging with recycling of composites.

CHAPTER-TWO

LITERATURE REVIEW

2.1 Introduction

This chapter describes the physical, chemical and mechanical properties of wood fibre, and some methods of pulping process. Matrix, its types and role of matrix in composites were also discussed. Major factors controlling the performance of composites were briefly described. Special emphasis was given on the methods of modification of fibre-matrix interface as it plays an important role on mechanical properties of composites. Both hygrothermal and UV degradation behaviour of composites were assessed mentioning some previous work in these fields. As the disposal option for composites are becoming limited, degree of recyclability has been an important issue. Therefore, current status on recycling of composites was also presented.

2.2 Natural Fibre

2.2.1 Natural Fibre and Its Source

There is a wide variety of cellulose fibres that can be used to reinforce thermoplastics. These include wood fibres, and a variety of agro-based fibres such as stems, stalks, bast, leaves and seed hairs. These fibres are abundantly available throughout the world. Cellulose fibres, depending on the part of the plant from which they are taken, can be classified as [27,28]:

Grasses and reeds: These fibres come from the stems of monocotyledonous plants such as bamboo and sugar cane. Both types of fibres can be used to reinforce plastics.

Leaf fibres: Leaf fibres are fibres that run lengthwise through the leaves of most monocotyledonous plants such as sisal, henequen, abaca and esparto. These fibres, which are also referred to as 'hard fibres', are the most commonly employed as reinforcing agents in plastics.

Bast fibres: These fibres (bundles) come from the inner bark (phloem or bast) 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 come from the xylem of angiosperm (hardwood) and gymnosperm (softwood) trees. Examples include maple, yellow poplar, pine and spruce.

Wood fibre is the most abundantly used cellulosic fibre due to their extensive use in pulp and paper industries. Commercially important fibre sources and world production are listed below:

Table 2.1: Commercially important fibre sources and annual production [29]:

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	*Hibiscas cannabinus*	970	Stem
Flax	*Linum usitatissimum*	830	Stem
Sisal	*Agave sisilana*	378	Leaf
Hemp	*Canabis sativa*	214	Stem
Coir	*Cocos nucifera*	100	Fruit
Abaca	*Musta textiles*	70	Leaf

2.2.2 Wood Fibre

Wood is comprised primarily of spindle-shaped cells. The thickened walls are composites of the three structural component polymers, with contiguous cells held together by lignin. Figure 2.1 provides a common representation of the organization of wood cell wall structure and ultra structure.

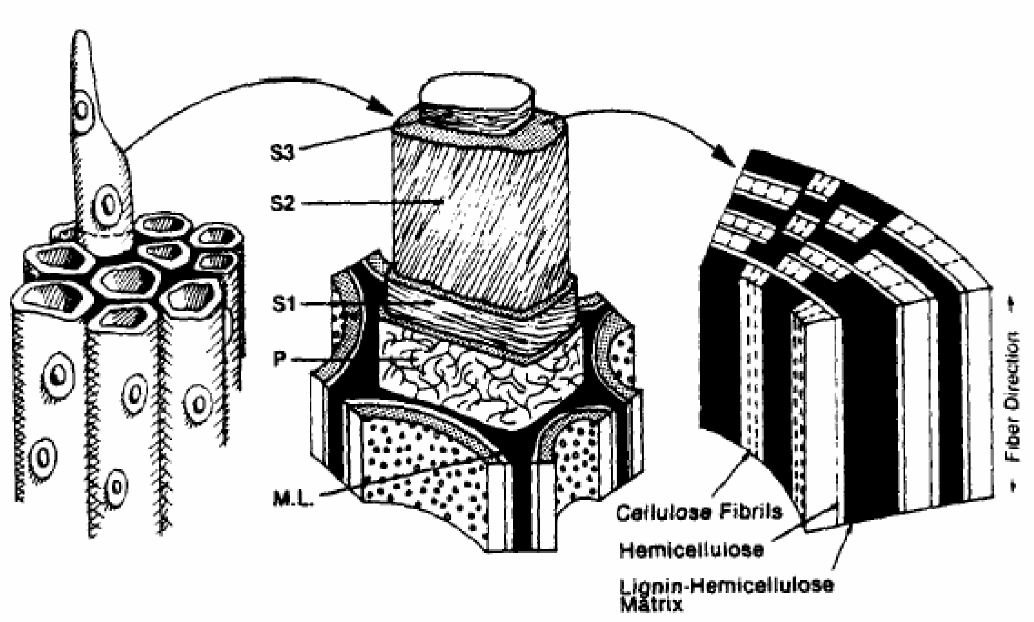


Figure 2.1: Schematic illustration of the molecular architecture of wood tissue, showing the relationship of contiguous cells (left), cutaway view of the cell wall layers, S1-S3- secondary cell wall layers; P- Primary wall; and M.L- middle lamella [30].

The basic morphology of wood cell walls is determined by the cellulose, which makes up approximately 45% of the weight of wood. It is a linear polymer of anhydrocellobiose units linked by β-1,4-glycosidic bonds. Van der Waals forces and hydrogen bonding interactions between and within cellulose molecules, make natural cellulose structurally complex. The individual cellulose molecules are arrayed in bundles known as microfibrils, each of which contains approximately 40 individual cellulose molecules. Within these bundles the cellulose is highly ordered and thus appears crystalline in diffraction measurements. Because the fibrils have long-range curvature in their native state and are subjected to torsional deformation, diffractometric measurements indicate some amorphous character. The microfibrils are arranged in lamella that are in the plane of the cell wall. The cell wall is comprised of layers of microfibrils: the primary wall, which is laid down first by the living cell, the fibrils appear to be randomly oriented within a matrix consisting of xyloglucan and pectic substances at the cell surface. Nests are the secondary layers (the bulk of the weight of wood), in which the cellulose microfibrils are organized parallel to each other in lamellae. Within the lamellae, the microfibrils spiral at an angle to the long axis of the cell. Three regions are identified within the secondary wall: the S1, S2, and S3 layers (see Figure 2.1); within these, the microfibrils have different parallel orientations in respect to the axis of the cell. The bulk of the wall is the S2 layer, in which the microfibrils are at an acute angle to the long axis of the cell; the angle diminishes from juvenile to mature wood and eventually the fibrils are essentially parallel to the cell axis. The cellulose fibrils nearest the lumen of the cell comprise the tertiary layer and are oriented nearly perpendicular to the long axis of the cell [30].

2.2.3 Chemical Composition of Wood Fibre

Climatic conditions, age and the digestion process influences not only the structure of the fibre but also the chemical composition. Wood is composed of cellulose, hemicelluloses, and lignin. Softwoods (like Radiata pine) and hardwoods (like Eucalyptus) have fairly similar cellulose contents, but the lignin content of softwoods is somewhat higher. Radiata pine contains typically 42% cellulose, 29% lignin and 7% hemicelluloses. In addition to these basic constituents, most woods also contain extractives. When pulping coniferous species (like Radiata pine) according to the kraft process, these extractives can be recovered as by products (turpentine and tar oil) [31]. Chemical constituent of some natural fibre are shown in Table 2.2.

Table 2. 2: The chemical constituents of some important plant fibres [32]:

Fibre	Type	Cellulose content (%)	Lignin content (%)	Pectin content (%)
Flax	Bast	65-85	1-4	5-12
Hemp	Bast	60-77	3-10	5-14
Jute	Bast	45-63	12-25	4-10
Kenaf	Bast	45-57	8-13	3-5
Sisal	Leaf	50-64	-	-
Abaca	Leaf	60	12-13	1
Coir	Seed	30	40-45	-
Cotton	Seed	85-90	-	0-1
Softwood	Wood	40-45	26-34	0-1
Hardwood	Wood	40-45	20-30	0-1

Cellulose: Cellulose is the essential component of wood. In 1838, Anselme Payen suggested that the cell walls of large numbers of plants consist of the same substance, to which he gave the name cellulose [33]. It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units (often abbreviated as anhydroglucose units or even as glucose units for convenience) joined together by β-1,4-glycosidic bonds. It is thus a 1,4-β-D-glucan. The pyranose rings are in the 4C1 conformation, which means that the $–CH_2OH$ and –OH groups, as well as the glycosidic bonds, are equatorial with respect to the mean planes of the rings. The Haworth projection formula of cellulose is shown in Figure 2.2. The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its chemical and physical properties. In the fully extended molecule, adjacent chain units are orientated by their mean planes at an angle of 180° to each other. Thus, the repeating unit in cellulose is the anhydrocellulobiose unit and the number of repeating units per molecule is half the degree of polymerisation. This may be as high as 14,000 in native cellulose, but purification procedures usually reduce it to in the order of 2,500 [33]. The mechanical properties of natural fibres depend on its cellulose type, because each type of cellulose has its own cell geometry and the geometrical conditions determine the mechanical properties [33,34].

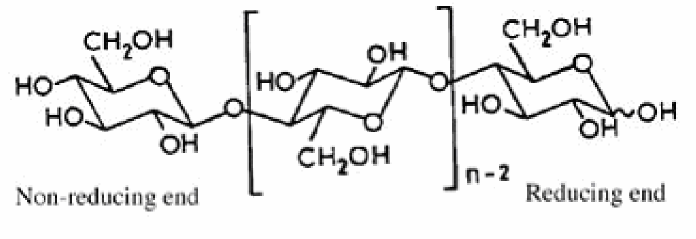


Figure 2.2: Structure of Cellulose.

Hemi-cellulose: Hemi-cellulose is not a form of cellulose; it comprises a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The hemi-cellulose differs from cellulose in three important aspects. In the first place, they contain several different sugar units whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to one hundred times higher than that of hemi-cellulose. Unlike cellulose, the constituents of hemi-cellulose differ from plant to plant [33].

Lignin: Lignins are the reinforcing substance that make tree cells wood ‘hard’ and 'woody' rather than soft which are complex hydrocarbon polymer with both aliphatic and aromatic constituents [33]. Their chief monomer units are various ring-substituted phenyl-propanes linked together (see Figure 2.3) in ways, which are still not fully understood. Structural details differ from one source to another [33]. The mechanical properties are lower (Young’s modulus of about 4 GPa) than those of cellulose (average of about 30 GPa) [35].

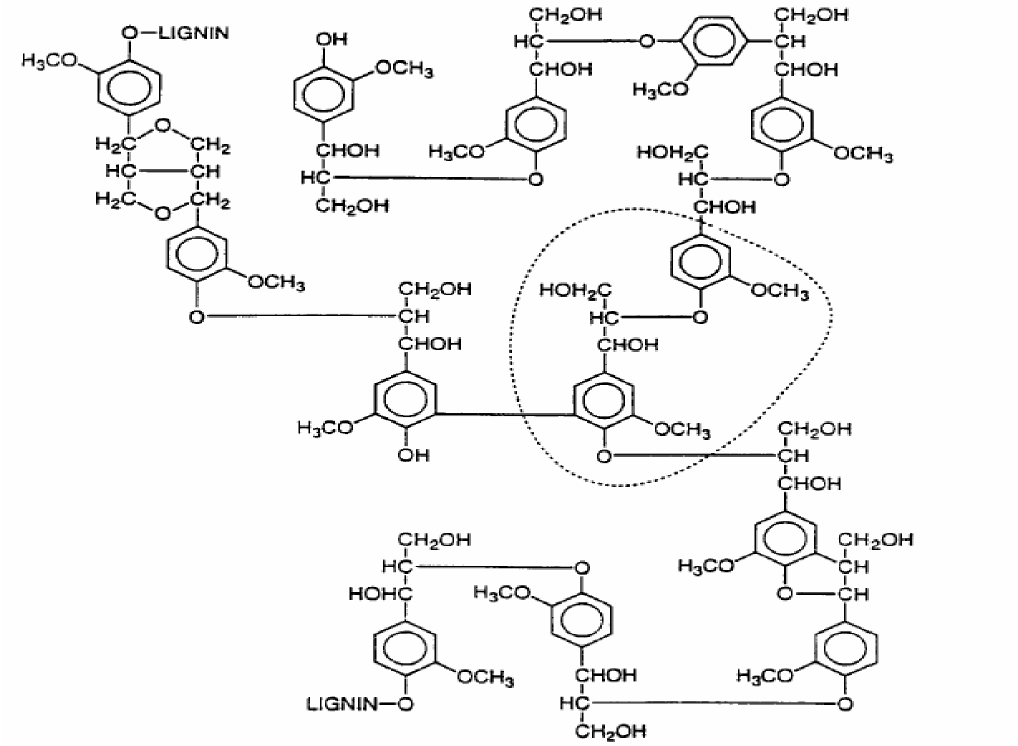


Figure 2. 3: Structure of lignin.

2.2.4 Physical and Mechanical Properties of Fibre

Natural fibres are in general suitable to reinforce plastics, due to their relative high strength and stiffness and low density (see Table 2.3) [36]. The range of the characteristic values is one of the drawbacks for all natural fibre, which can be explained by differences in fibre structure due to the overall environmental conditions during growth. Natural fibres can be processed in different ways to yield reinforcing elements having different mechanical properties. The modulus of bulk wood is about 10 GPa. Cellulose fibre with modulus up to 40 GPa can be separated from wood, for instance, by chemical pulping processes. Such fibres can be further subdivided by hydrolysis followed by mechanical disintegration into microfibrils with an elastic modulus of 70 GPa. Theoretical calculations of the elastic modulus of cellulose chains have given values of up to 250 GPa, however, there is no technology available to separate these from microfibrils [37,38].

Table 2. 3: Physical and mechanical properties of some natural fibres [32]:

Fibre	Density (gcm^{-3})	Tensile strength (MPa)	Young's modulus (GPa)	Specific strength (Pam^3/g)	Specific Young's modulus ($kPam^3/g$)
Flax	1.4-1.5	500-900	50-70	357-600	36-47
Hemp	1.48	300-800	30-60	203-541	20-41
Jute	1.3-1.5	200-500	20-55	154-333	15-37
Sisal	1.45	100-800	9-22	69-552	6-15
Banana	1.4	500-700	7-20	375-500	5-14
Softwood	1.4	100-170	10-50	71-121	7-36
Hardwood	1.4	90-180	10-70	64-129	7-50

2.2.5 Wood Type

Wood fibre can be obtained from two types of wood namely, soft wood and hard wood.

2.2.5.1 Soft wood

Softwood is the wood from conifers; include, pine, spruce, cedar, fir, larch, douglas-fir, hemlock, cypress, redwood and yew. Softwood and hardwood differ in microscopic structure. The structure of softwood is fairly uniform, with only two types of cells: tracheids and parenchyma cells. Softwood never has vessel elements for water transport, but relies on tracheids.

Softwood has a huge range of uses: it is a prime material for structural building components, also found in furniture and other products such as millwork (mouldings, doors, windows). Softwood is also harvested for use in the production of paper, and for various types of board [39].

2.2.5.2 Hardwood

The term hardwood designates wood from broad-leaved (mostly deciduous, but not necessarily, in the case of tropical trees) or angiosperm trees. Hardwood contrasts with softwood, which comes from conifer trees. On average, hardwood is of higher density and hardness than softwood, but there is considerable variation in actual wood hardness in both groups, with a large amount of overlap; some hardwoods (e.g. balsa) are softer than most softwood, while yew is an example of hard softwood. Hardwoods have broad leaves and enclosed nuts or seeds such as acorns. They often grow in subtropical regions like Africa and also in Europe and other regions, such as Asia. Hardwood species are more varied than softwood.

Hardwoods serve an enormous range of applications, including: buildings, furniture, flooring, utensils etc. Hardwoods are generally far more resistant to decay than softwoods when used for exterior work [40].

2.2.6 Radiata Pine

Radiata pine *(Pinus Radiata)* is the dominant New Zealand wood spices. Pine is used extensively due to many factors, including the fact that pine grows relatively fast in New Zealand, it resists pest and diseases, responds well to intensive management and selective breeding programs. Pine is used for wide range of products including wood panels, veneers, fuel sources and paper. Radiata pine is made up of cells that are relatively uniform in terms of density and strength across the stem, although those nearest the centre are definitely shorter and weaker. This central zone or core wood is therefore usually not permitted in timber sawn for uses where strength is important. Wood from the outside of the stem has longer and stronger cells, so is well suited to structural timber and pulps where greater strength is important. The wood also has lower resin/lignin content, an important factor for pulping [41].

2.2.7 Pulping

Pulping is the process of converting wood or nonwood material to separated pulp fibres for paper making. Processes range from mechanical, in which the wood is ground into fibres by disk refiners or grindstones, namely: stone groundwood, pressurised groundwood, refiner mechanical pulp, thermomechanical pulp to chemical, in which the fibres are separated by chemically degrading and dissolving, namely: soda pulp, sulphite pulp, sulphate (Kraft) pulp and semi-chemical pulps [42,43]. This study will concentrate on thermomechanical pulp for the production of MDF and Kraft pulp.

2.2.7.1 Thermomechanical pulp (TMP)

Medium density fibres (MDF) also called TMP are prepared by breaking up of wood chips by heat, pressure and steam. The chips are heated up to 80^0C in the pre-steaming bin, which softens the chips and creates uniform moisture content. The chips are then compressed and de-watered by a tapered screw in the pre-heater, which forms a plug that seals the screw against pressure from the pre-heater. Steam is injected into the pre-heater at $165\text{-}180^o$C with a pressure of 0.7-1.0 MPa. The final step in the production of wood fibres is the refining stage. The chips are forced into the eye of the refiner by plug screw, and then forced readily outwards between the refiner plates by steam pressure and a centrifugal force to break down the chips into fibres. Due to high temperature used, plasticization occurs, which aid the fibres shear in the middle lamella region and further soften the lignin component of the chips. The resulting pulp is light, both in colour and weight, of fine fibres which is also fluffy [44]. Mechanical pulping processes all use a lot of electrical energy and water.

However, they provide 80-90% recovery of total fibre. Mechanical pulping processes are cheaper to operate than more sophisticated chemical based systems. There are also fewer environmental issues, such as chemical contamination of sites and unpleasant smells [45].

2.2.7.2 Kraft pulp

Internationally, Kraft is the most widely used pulp making process which is a partly mechanical and partly chemical process that produces a strong pulp. In Kraft pulping process, after de-barking, the wood chips are heated in a solution of NaOH and Na_2S in a pressure cooker, during which time a lot of lignin is removed from the wood. The pressure is then released suddenly, causing the chips to fly apart into fibres. The pulp is washed with water to wash out the cooking chemicals and lignin from the fibre, so that they do not interfere with further processing steps. A sieve is used to remove knots and clumped-together uncooked fibres from the pulp. Bleaching commonly used to increase the brightness of pulp, largely removes lignin from wood fibres. This is done in two stages. Firstly, the pulp is treated with NaOH in the presence of O_2. The NaOH removes hydrogen ions from the lignin and O_2 breaks down the polymer. Then, the pulp is treated with ClO_2, then a mixture of NaOH, O_2 and peroxide and finally, again with ClO_2 to remove the remaining lignin [46]. Typically, unbleached Kraft fibres consists of 65–75% cellulose, 17–32% hemicellulose, and 3-8% lignin, while bleached fibres contain 70–80% cellulose and 20–30% hemicellulose [47]. The removal of lignin from the fibre has the potential to increase fibre-matrix adhesion due to more open or rougher fibre surface leading to increased physical bonding with the matrix [48].

2.3 Matrix

The matrix plays a crucial role in the performance of polymers composites. Both thermosets and thermoplastics are attractive as matrix materials for composites.

2.3.1 Thermosets

Thermoset composites are normally chemically cured to a highly cross linked, three dimensional network structures. These cross linked structures are highly solvent and creep resistant. The fibre loading can be as high as 80% [49]. Thermosets used in composites include epoxy, phenols and polyesters.

Advantages of thermosets matrix:

- Chemical make up of thermosets being the most similar to natural fibres
- Production is a lot simpler, as resin moulders can be used allowing the matrix and the reinforcing agent to be cured under mild processing conditions
- Thermosets have a highly cross linked chain structure which does not allow the chains to slide and rotate easily
- This chain structure gives thermosets high strength and good stiffness properties but ductility suffers, with thermosets generally showing a brittle form of failure.

Disadvantages of thermosets matrix:

- Complex formulation
- Long processing cycle
- High material cost
- Brittle (may crack)
- Require careful installation
- High installation cost

2.3.2 Thermoplastics

Thermoplastics are made up of flexible linear chains, which allowed thermoplastics to undergo elastic deformation due to the stretching of covalent bond within the chain.

The advantages of the thermoplastic matrices:

- Lower cost of processing them than thermosets
- Design flexibility and ease of moulding complex parts; simple methods such as extrusion and injection moulding are used for processing these composites
- They are flexible and tough, and exhibits good mechanical properties
- Thermoplastics such as polypropylene have the lower level of moisture absorption
- Recycling of composites is possible with thermoplastics.

Disadvantages of thermoplastic matrices:

- The percentage of loading is limited by the processability of the composite
- The fibre orientation in the composites is random and the property modification is not as high as is observed in the thermoset composites [49,50].
- Thermoplastics have a different chemical structure compared to natural fibres as they have a high non polar nature, so methods of improving the interfacial region between the two materials need to be investigated.

However, after assessing the limitations and the benefits of thermoplastics and thermosets in the present study, thermoplastic was chosen.

In thermoplastics, most of the work reported so far, deals with polymers such as polypropylene (PP), polyethylene (PE), polystyrene (PS), polyamide and polyvinyl chloride (PVC). This is mainly because the processing temperature of thermoplastic is restricted to temperature below 200°C to avoid thermal degradation of natural fibres [51]. PP and PE have the lowest densities with low level of moisture absorption. PP has the best combination of strength and stiffness, therefore, PP was selected as a matrix for this study.

2.3.2.1 Polypropylene (PP)

Polypropylene (PP) is a thermoplastic polymer, can be made by addition polymerisation process. PP has a melting point of about 165°C, glass transition temperature (T_g) about -10°C [52]. Most commercial PP has an intermediate level of crystallinity, between 40-60% [53]. Depending on their crystallinity, density ranges from 0.85 g/cm^3 to 0.95 g/cm^3. Its Young's modulus is also intermediate. Although, it is less tough than high density polyethylene (HDPE) and less flexible than low density polyethylene (LDPE), it is much more brittle than HDPE. This allows PP to be used as a replacement for engineering plastics, such as acrylonitrile butadiene styrene (ABS). PP can be made translucent when uncoloured but not completely transparent as polystyrene or acrylic. Polypropylene has very good resistance to fatigue [52].

There is a wide variety of applications of PP, including, food packaging, plastic parts and reusable containers of various types, thermal pants and shirts made for the military, laboratory equipment, loudspeakers, automotive components, and polymer banknotes [52].

2.4 Wood Fibre Reinforced Plastics

Wood fibre reinforced plastic are hybrid with their properties, with characteristics of both wood and plastics. Incorporation of wood fibres into plastic is now a standard technology to improve the mechanical properties of plastics. Physical properties like

Young's modulus and tensile strength are enhanced in the end product with the aesthetic appeal look like wood. The mechanical properties of the fibres determine the stiffness and tensile strength of the composite [54].

2.4.1 Mechanism of Reinforcement

Reinforcement of a low modulus polymer with a high modulus, high strength fibre uses the plastic flow of the polymeric material under stress to transfer the load to the fibre; this gives a moderate strength high modulus composite. The aim of the combination is to produce a two phase material in which the primary phase (i.e. the fibres) is well dispersed and bonded by a weak secondary phase (i.e. the polymer matrix). The principal constituents influencing the strength and stiffness of composites are the reinforcing fibres, the matrix and the interface between the fibres and the matrix.

The functional requirements of fibres in a composite should have [55]:

- High modulus of elasticity to give stiffness to the composite
- High ultimate strength
- Low variation of strength between individual fibres
- Stability during handling
- Uniform diameter.

The matrix should fulfil certain functions:

- Bind the fibres together to protect their surfaces from damage during the service life of the composite
- Transfer stresses to the fibres efficiently by adhesion/friction
- Disperse and separate the fibres
- Be chemically and thermally compatible with fibres.

2.5 Factors Controlling Performance of Fibre Reinforced Composites

The performance of a fibre reinforced composite depends largely upon the strength of the interfacial bond between the fibre and the matrix. A major concern for thermoplastic materials therefore is incompatibility between natural fibre and thermoplastic. The details, which have been identified, are as follows [56]:

2.5.1 Dispersion of Fibre in the Matrix

The incorporation of fibres in thermoplastics leads to poor dispersion of the fibres due to the strong inter fibre hydrogen bonding which holds the fibre together. Treatment of the fibres and/or use of external processing aids can reduce these problems [57]. The surface adhesion between the fibre and the polymer plays an important role in the transmission of stress from matrix to the fibre and thus contributes toward the performance of the composite. Most polymers, especially thermoplastics, are non-polar (hydrophobic) substances that are not compatible with polar (hydrophilic) fibres; it prevents efficient fibre-matrix bonding. Therefore, the result is poor adhesion between polymer and fibre. In order to improve the affinity and adhesion between fibres and thermoplastic matrices, chemical coupling agents have been employed [58]. Maleic anhydride (MA)-grafted polypropylene (MAPP) has been reported to function efficiently for lignocelluloses-PP systems. Earlier results suggest that the amount of MA grafted and the molecular weights are both important parameters that determine the efficiency of the additive. The Maleic anhydride present in the MAPP not only provides polar interactions, but can covalently link to the hydroxyl groups on the lignocellulosic fibre. Grafting chemical series on to the fibre surface has also been reported to improve the interaction properties between the fibres and matrix. Although grafting can improve properties of the composites to a significant extent, this process increase the materials cost of the system. The use of dispersing agent and/or coupling agents is a cheaper route to improve properties and makes more practical sense for high volume, low cost composites systems [60].

2.5.2 Thermal Stability of the Fibre

The primary drawback of the use of agro-fibres is the lower processing temperature permissible due to possibility of lignocelluloses degradation and/or the possibility of volatile emissions that could affect composites properties. The processing temperatures are thus limited to about 200^{o}C, although it is possible to use higher temperatures for short periods of time. This limits the type of thermoplastics that can be used with agro-fibres to commodity thermoplastics such as polyethylene, polypropylene, polyvinyl chloride, and polystyrene [60].

2.5.3 Hydrophilic Nature of Organic Fibre

Moisture absorption can result in swelling of the fibres and concern about the dimensional stability of the agro-fibre composites. It affects the mechanical properties of composites. The absorption of moisture by the fibre is minimized in the composites due to encapsulation by the polymer. It is difficult to entirely eliminate the absorption of moisture without using expensive surface barriers on the composite surface. If necessary, the moisture absorption of the fibres can be dramatically reduced through the acetylating of some of the hydroxyl groups present in the fibre, but with increase in the cost of the fibre [59]. Good fibre-matrix bonding can also decrease the rate and amount of water absorbed by the composite [60].

2.5.4 Critical Fibre Length

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 [61]. If the fibre aspect ratio is, lower than its critical value, insufficient stress will be transferred and reinforcement of the fibre will be insufficient (i.e. the fibre 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 [61].

2.5.5 Fibre Orientation

Orientation of fibres related to one another plays an important role in composites. The strength of the unidirectional aligned composites normal to the fibre alignment (transverse) is less than that of the randomly oriented fibre composite. When the fibres are aligned perpendicular to the direction of force (transverse), fibres are not reinforcing the matrix to increase the strength of the composite in the direction of applied load [61]. Short fibre composites rarely consist of fibres oriented in a single direction. During extrusion and injection moulding, the polymer melt will undergo both extensional and shear flow. There will be rotation of the fibre during shear flow and alignment during elongation flow. Thus, it is possible to achieve some degree of fibre alignment by using extrusion and injection moulding [62].

2.5.6 Fibre Volume Fraction

One of the most significant factors determining the mechanical properties of composite is the content of reinforcing fibre. At low fibre volume 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 concentrations, and cause the bond between fibre and matrix to break. At higher volume fractions, the matrix is sufficiently restrained and the stress is more evenly distributed. This results in reinforcing effects 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. At very high fibre volume fractions, the strength of composites start to decrease due to insufficient filling of the matrix materials [63]. Another explanation for the decrease in composites mechanical processing could be due to the fact that, during the processing (extrusion and injection moulding) of short fibre reinforced polymer composites, fibre damage takes place as a result of fibre polymer interaction, fibre-fibre interaction and the fibre contact with the surface of the processing equipment. At high fibre volume fractions, there is an increase in fibre-fibre interaction and fibre equipment contact, leads to the reduction in mean fibre length, and if the mean fibre length is very smaller than the critical fibre length the reinforcing efficiency would be reduced [64].

A large number of theoretical models based on the Rule of Mixtures have been developed to predict the tensile strength (TS) and Young's modulus (YM) of composites as a function of fibre volume fraction [65]. The most widely applied models to predict TS and YM of composites are Parallel and Series models, which assumes a state of uniform strain and the latter, a state of uniform stress in the individual components, respectively. The Parallel model represents the upper bound and the Series model represents the lower bounds for the TS and YM. These models assume a perfect interface [66]. The Hirsch's model is a weighted average of the series and parallel models. An empirical parameter x is introduced in Hirsch model that characterises the stress transfer between the fibre and matrix, which depends on fibre orientation, fibre length and fibre distribution. The value of x can be varied from 0 to 1 to give best fit.

Parallel model:

$$M_c = M_f V_f + M_m V_m \tag{2.1}$$

$$S_c = S_f V_f + S_m V_m \tag{2.2}$$

Series model:

$$M_c = \frac{M_m M_f}{M_m V_f + M_f V_m}$$

$$S_c = \frac{S_m S_f}{S_m V_f + S_f V_m} \tag{2.4}$$

Hirsch's model:

$$M_c = x\left(M_m V_m + M_f V_f\right) + (1-x)\frac{M_f M_m}{M_m V_f + M_f V_m} \tag{2.5}$$

$$S_c = x\left(S_m V_m + S_f V_f\right) + (1-x)\frac{S_f S_m}{S_m V_f + S_f V_m} \tag{2.6}$$

where, M_c, M_m and M_f are the Young's modulus of composite, matrix and fibre, respectively. S_c, S_m and S_f are the tensile strength of composite, matrix and fibre, respectively. V is the fibre volume fraction, and subscripts c, f and m indicate composite, fibre and matrix, respectively.

2.6 Methods for Surface Modification of Natural Fibres

The quality of the fibre–matrix interface is significant for the application of natural fibres as reinforcement for plastics. Physical and chemical methods can be used to optimise this interface. These modification methods are of different efficiency for the adhesion between fibre and matrix [67].

2.6.1 Physical Methods of Modification

Physical treatments change structural and surface properties of the fibre and there by influence the mechanical bonding to polymers [68]. Physical methods, such as stretching, calendaring and thermo treatment can be used by no change of the chemical composition of the fibres.

Electric discharge (corona, cold plasma) is another way of physical treatment. Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibres and in case of wood, surface activation increases the amount of aldehyde groups [69].

The physical definition of plasma (glow-discharge) is an ionized gas with an essentially equal density of positive and negative charges. It can exist over an extremely wide range of temperature and pressure. The solar corona, a lightening bolt, a flame and a neon sign are all examples of plasma. For the purposes of textile modification, the low pressure (0.01 to 1 mbar) plasma, that is found in the neon sign or fluorescent light bulb are used. However, for the plasma treatment of polymeric substrates, the extremely energetic chemical environment of the plasma is utilized.

The same effects are reached by cold plasma treatment. Depending on the type and nature of the gases used, a variety of surface modification could be achieved. Surface cross linking could be introduced, surface energy could be increased or decreased, reactive free radicals and groups could be produced [69].

Electric discharge methods are known to be very effective for non-active polymer substrates as polystyrene, polyethylene, polypropylene etc. They are successfully used for cellulose fibre modification, to decrease the melt viscosity of cellulose polyethylene composites and improve mechanical properties of cellulose polypropylene composites [70].

Mechanical beating is another physical method of modification of fibre which is widely used in paper making to improve interfacial bonding. The process of beating has three main effects, namely: 1) the fibres become shortened, 2) external fibrillation occurs, causing partial or sometimes total removal of the primary wall and causing fibrils to form on the surface of the fibre, thereby increasing the fibre surface area, and 3) internal fibrillation occurs, causing the fibres to become more conformable [71]. Thus, it is believed that beaten fibres should exhibit increased fibre–matrix bonding due to the increase in fibre surface area [72].

Nishi et al. [73] studied the refining on physical and electrokinetic properties of various cellulosic fibres. Refining increased the surface charge, specific surface area and specific volume of fibres, but did not change the total fibre charge. When refined to the same freeness, the pine kraft pulp had a higher surface charge, surface area and specific volume than the eucalyptus pulps. The pine kraft pulp required a higher refining energy than the eucalyptus pulps to reach the same freeness. The increased specific surface area as well as the increased surface charge of the fibres was apparently relevant to the improvement of fibre–fibre bonding. In other study

Nishi et al. [74] found that, the fibre surface charge increased with the degree of refining.

No authors reported the effects of beating on wood fibre reinforced PP composites. Although, some work has been done on the effects of fibre beating on cement fibre composites [71,72]. However, no significance improvement on mechanical properties was observed for beating.

2.6.2 Chemical Methods of Modification

2.6.2.1 Alkali treatment of natural fibres (Mercerization)

Mercerization is the most common method of fibre treatment. The standard definition of mercerization (proposed by ASTM D 1965) is, the process of subjecting a vegetable fibre to an interaction with a fairly concentrated aqueous solution of a strong base, to produce great swelling with resultant changes in the fine structure, dimension, morphology and mechanical properties [75].

Sodium hydroxide treatment of cellulose fibres leads to the irreversible mercerisation effect, which increases the amount of amorphous cellulose at the expense of crystalline cellulose. The cellulose–sodium hydroxide reaction is thought to be as follows.

$$\text{Cell-OH} + \text{NaOH} \longrightarrow \text{Cell } O^{-}Na^{+} + H_2O + [\text{surface impurities}] \qquad (2.7)$$

Mercerisation improves adhesion, characteristics by removing surface impurities, thus exposing micro-fibrils, which then render the fibre topography with a rough texture. The rough and cleaned surface facilitates mechanical adhesion in addition to improved wetting ability of the resin. The composites produced from fibres treated with sodium hydroxide are in principle, expected to have improved mechanical properties but only if there is no increase in the amorphous cellulose [76].

As discussed earlier cellulose forms the main structural component of natural fibres, although, the non-cellulosic components, e.g. lignin and hemicellulose, also play an important part in the characteristic properties of the fibre. Hemicellulose, which is thought to consist principally of xylan, polyuronide and hexosan, has been shown to be very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or α-cellulose. Later studies about the alkali treatment of jute-fibres, for instance, reports about the removal of lignin and hemicellulose which affects the tensile characteristics of the fibres. When the hemicelluloses are removed, the inter-fibrillar region is likely to be less dense and less rigid and thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation. When natural fibres are stretched, such rearrangements amongst the fibrils would result in better load sharing by them and hence result in higher stress development in the fibre. In contrast, softening of the inter-fibrillar matrix adversely affects the stress transfer between the fibril and thereby, the overall stress development in the fibre under tensile deformation. As lignin is removed gradually, the middle lamella joining the ultimate cells is expected to be more plastic as well as homogeneous due to the gradual elimination of micro voids, while the ultimate cells themselves are affected only slightly.

Further, some authors reported about changes in the crystallinity through alkaline treatment on coir and flax fibres. The increase in the percentage crystallinity index of alkali treated fibres occurs because of the removal on the cementing materials, which leads to a better packing of cellulose chains. Additionally, treatment with NaOH leads to a decrease in the spiral angle, i.e. closer to fibre axis, and increase in molecular orientation. A fair amount of randomness is introduced in the orientation of the crystallites due to the removal of non-cellulosic matter. The Young's modulus of fibres, for instance, is expected to increase with increasing degree of molecular orientation. Well oriented cellulosic fibres such have much higher Young's modulus than fibres with medium orientation. In addition to the modification of orientation and the consolidation of weak points, other important factors with regard to the mechanical properties could be the crystallite length and degree of crystallinity as well as the removal of fractions of cellulose at a very low degree of polymerization [77, 78, 79].

Ray et al. [80] studied effects of alkali treated jute fibres on the mechanical properties of vinylester resin composites. They found that the alkali treatment improves the mechanical properties such as Young's modulus, flexural strength and flexural modulus of the composite. Jochen Gassan et al. [81] studied on the influence of alkali treatment on the mechanical properties of jute/epoxy composites. They found the the rougher surface morphology after alkali treatment did not improve the adhesion. Sreenivasan et al. [82] studied the influence of delignification and alkali treatment on the fine structure of coir fibres. The effect of successive removal of lignin and hemicelluloses on the fine structure has also been studied. Unlike other cellulosic fibres, alkali treatment failed to produce any increase in fibre elongation in coir. Reddy et al. [83] studied the effect of alkali treatment (sodium hydroxide and potassium hydroxide) on the crystal structure and properties of jute fibres. The accessibility of jute treated at higher alkali concentrations increased with a decrease in crystallinity. Van de Weyenberg et al. [84] studied on the influence of chemical treatment and processing of flax fibres on their composites. A treatment consisting of a combination of alkali and dilute epoxy gave the highest improvement of the flexural properties. Rout et al. [85] studied the effect of alkali treatment of coir fibre in polyester/coir composite system. They reported that 2% alkali-treated coir/polyester composites showed a significant improvement in tensile strength. Valadez-Gonzalez et al. [86] showed that alkali treatment of henequen fibre improved the fibre/matrix mechanical interlocking as well as interaction between fibre and matrix.

2.6.2.2 Coupling agents

Coupling is an important chemical modification method, which improves the interfacial adhesion. When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material (also called coupling agent) that has properties intermediate between those of the other two. Strongly polarized cellulose fibres are inherently incompatible with hydrophobic polymers. Therefore, scientists have investigated a variety of coupling agents to improve the compatibility of the fibre and matrix [87].

Mechanism of Coupling Agents:

There are several mechanisms of coupling in materials [87]:

- Weak boundary layers – coupling agents eliminate weak boundary layers
- Deformable layers – coupling agents produce a tough, flexible layer
- Restrained layers – coupling agents develop a highly crosslinked interface region, with a modulus intermediate between that of substrate and of the matrix
- Wettability – coupling agents improve the wetting between polymer and substrate
- Chemical bonding – coupling agents form covalent bonds with both

materials.

- Acid–base effect – coupling agents alter acidity of substrate surface.

The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. The main chemical bonding theory alone is not sufficient. So, the consideration of other concepts appears to be necessary, which include the morphology of the interface, the acid–base reactions at the interface, surface energy and the wetting phenomena [87,88,89].

Classification of coupling agents:

Coupling agents are classified into organic, inorganic and organic-inorganic groups. Organic coupling agents are iso-cyanates, anhydrides, amides, imides, acrylates, chlorotriazines, epoxides, organic acids, monomers, polymers and copolymers. Inorganic coupling agents include silicates while organic-inorganic agents include silanes and titanates [57].

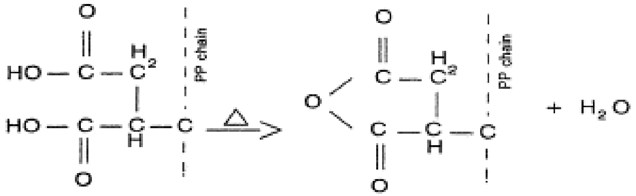
Organic coupling agents normally have bi-or multifunctional group in their molecular structure. These functional groups, such as (-N=C=O) of isocyanates, [-$(CO)_2O$-] of maleic anhydrides, and (Cl-) of dichloro triazine derivatives, interact with the polar groups [mainly hydroxyl groups (-OH)] of cellulose and lignin to form covalent or hydrogen bonding. Alternatively, organic coupling agents can modify the polymer matrix by graft copolymerization, thus resulting in strong adhesion, even crosslinking at the interface [90].

Inorganic coupling agents possibly act as dispersing agents to counteract the surface polarity of cellulose fibre and improve the compatibility between fibre and polymer. Only a few inorganic coupling agents have been used so far in wood fibre polymer composites [57]. Organic-inorganic coupling agents are hybrid compounds in structure. For example, titanates usually contain a titanium centre and an organic part surrounding this inorganic atom. The functionalities of the organic part in these agents determine their coupling effectiveness. Organic-inorganic coupling agents are between organic and inorganic agents in functions [90,91].

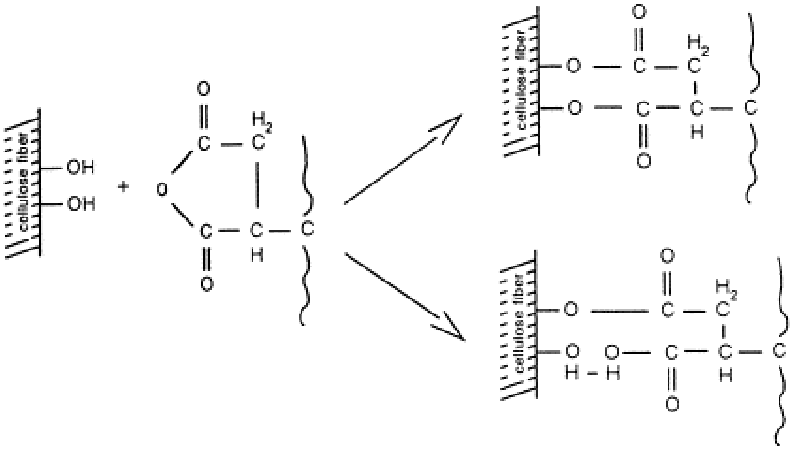
Of the organic coupling agents, anhydrides sush as maleic anhydride (MA), acetic anhydride, succinic anhydride and phthalic anhydride are popular coupling agents in wood fibre reinforced plastic composite. Acetic anhydride, succinic anhydride and phthalic anhydride have two functional groups i.e. carboxylate groups (-COO-), which can link wood fibre through esterification and hydrogen bonding. However, maleic anhydride is an, β-unsaturated carbonyl compound, containing one carbon carbon double bond (-C=C-) and two carboxylate groups (-COO-). This conjugated structure greatly increase the graft reactivity of the carbon-carbon double bond on the heterocyclic ring with the polymer matrix through the conjugate addition under a radical initiator, resulting in crosslinking or strong adhesion at the interface [92]. However, the molecular chain of maleic anhydride is much shorter than that of polymer matrix and wood fibres. This discrete nature makes maleic anhydride not so effective to improve the interfacial adhesion. Therefore, long chains of high molecular weight are obtained usually by grafting maleic anhydride with polyethylene, polypropylene, and polystyrene to make it an ideal coupling agent for fibre-polymer composites [93]. The formed copolymer maleated polyethylene (MAPE or maleic anhydride-modified-polyethylene), maleated polypropylene (MAPP or maleic anhydride-modified-polypropylene), styrene/maleic anhydride (SMA), styrene-ethylene-butylene-styrene/maleic anhydride (SEBS-MA) are used as coupling agents [94] in fibre-polymer composites, creating both covalent bonding to the fibre surface and extensive molecular entanglement to improve properties of the interface. Theoretically, extremely long chains may reduce the possibility of migration of the coupling agents to the fibre surface because of the short processing time [93]. If the molecular weight of the coupling agent is too high, it may entangle with the PP molecules so that the polar groups on the coupling agent have difficulty "finding" the –OH groups on the fibre surface [93].

The treatment of cellulose fibres with hot polypropylene–maleic anhydride (MAH–PP) copolymers provides covalent bonds across the interface [95]. The mechanism of reaction can be divided into two steps:

- activation of the copolymer by heating (t=170°C) (before fibre treatment) and

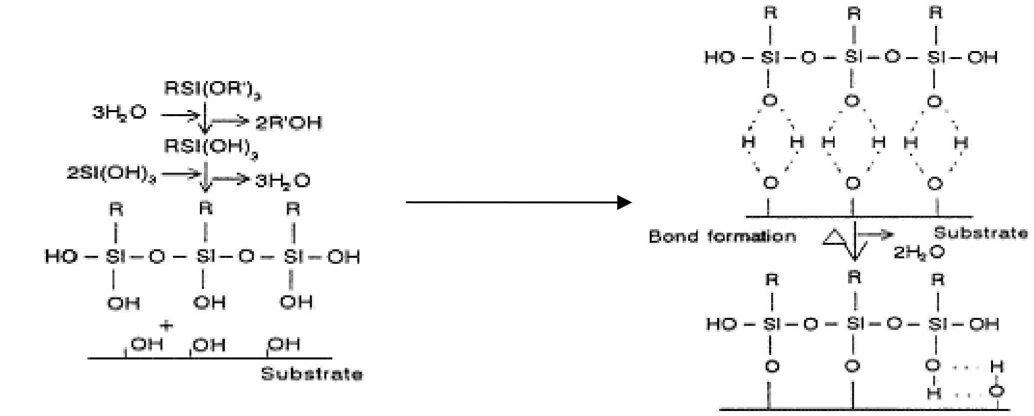


- esterification of cellulose.



The interactions between non-polar thermoplastics such as PP and any coupling agents such as MAPP are resulted in predominant chain entanglement between them. Stresses applied to one chain can be transmitted to other entangled chains, and stress is distributed among many chains. These entanglements function like physical cross links, that provide some mechanical integrity up to and above the glass transition temperature, (T_g), but become ineffective at much higher temperatures [96]. When polymer chains are very short, there is a little chance of entanglement between chains and they can easily slide past one another [97]. When the polymer chains are longer, entanglement between chains can occur and the viscosity of polymer becomes high. A minimum chain length or a critical molecular weight (M_e) is necessary to develop these entanglements and typical polymer has a chain length between entanglements equivalent to M_e varying from 10,000 to about 40,000 [97].

Silanes, represented as $R\text{-}Si(OR')_3$, have better performance in organic-inorganic coupling agents, recently used in wood fibre plastic composite, because the attachment of silanes to hydroxyl groups of cellulose or lignin is accomplished either directly to the alkoxy group (-OR') attached to silocon or via its hydrolyzed products (i.e silanol) by the hydrogen bond or ether linkage. The functional group (R-) in silanes also influences the coupling action [98]. The general mechanism of how alkoxysilanes form bonds with the fibre surface which contains hydroxyl groups is as follows [99]:



Dichlorotriazines and derivatives have multifunctional groups in their molecular structure. These groups have different functions in the coupling reactions. On heterocyclic ring, the reactive chlorines react with the hydroxyl group (-OH) of wood fibre and give rise to the ether linkage between the cellulose and the coupling agent. The electronegative nitrogen may link hydroxyl group through hydrogen bonding. On the alkyl chain, the carbon carbon double bonds (C=C) form covalent bonds with polymer matrix by grafting. At the same time, the electronegative nitrogen in the amino group and oxygen in the carboxylate groups also link the cellulose phase through hydrogen bonding [90].

Some thermosetting resin adhesives, such as phenol-formaldehyde resin (PF) and mono- or dimethylol melamine resin (DMM) has been introduced as a bonding agent in wood fibre plastic composites. PF and DMM resins can crosslink wood fibre with methylene ($-CH_2-$) linkage resulting from the condensation reaction between their reactive methylol groups ($-CH_2OH$) and hydroxyl groups (-OH) group of wood fibre. Although these methylol groups can not react with the thermoplastic matrix. PF and DMM improve the interfacial adhesion through molecular entanglement with the matrix [100].

Pre-Treatment:

Pre-treatment of fibre and polymer with coupling agents is extensively applied before mixing to improve the mechanical properties. There are two pre-treatment methods:

1. Coating coupling agents on fibre.
2. Modifying fibre and polymer by graft co-polymerization.

Coating coupling agents on fibre:

The compatibility between fibre and polymer is enhanced by coating fibres with coupling agents. This process can either cause hydroxyl groups (-OH) of fibres to react with coupling agents which have a linear molecular structure similar to the polymer matrix, or create a chemical interaction between coupling agents and matrix [101].

Four kinds of coating methods have been used in wood plastic composites (WPC) production: compounding, blending, soaking and spraying. The compounding method mixes coupling agents at high temperature with fibres and polymers in an extruder. This method is mostly used in melt blending process. For the blending method, a coupling agent is coated on the surface of the fibre, polymer or both in a roll mill or a magnetic stirrer at low or high temperature. For the soaking method, fibre can be first impregnated in the form of sheets of paper with a coupling agent solution containing initiators or other additives. Then the impregnated paper is removed from the solution and placed between two pieces of polymer release film for moulding. In the spraying process, coupling agents are emulsified and sprayed on to the surface of the fibre. Both blending and spraying are suitable for the pre-coating of wood fibre and polymer before mixing. Spraying and soaking are better than compounding and blending for coating process because, coupling agents are distributed at the interface more evenly and efficiently in the former two cases. However, it is difficult to accurately control the impregnating amount of coupling agents for the soaking method [101].

Modifying fibre and polymer by graft co-polymerization:

An effective method of chemical modification of natural fibres is graft copolymerization. This reaction is initiated by free radicals of the cellulose molecule. The cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the cellulose molecule cracks and radicals are formed. Afterwards, the radical sites of the cellulose are treated with a suitable solution (compatible with the polymer matrix), for example vinyl monomer, acrylonitrile, methyl methacrylate, polystyrene. The resulting co-polymer possesses properties characteristic of both, fibrous cellulose and grafted polymer [102].

MAPP for Wood/PP composites:

Meyer was possibly the first person who suggested using a coupling agent (which he called a cross linking agent) to improve the mechanical properties of wood-polymer materials [103]. Bridgeford (1963) invented a method to graft olefinically unsaturated monomers onto wood fibre with a catalyst system containing ferrous cations and hydrogen peroxide to modify the compatibility between wood fibre and thermoplastic polymer [104]. Gaylord patented to combine cellulose and polyvinyl chloride in the presence of free radical initiator [105]. As pioneers in the applications of coupling agents in wood fibre plastic composite, Kalson and co-workers made an initial study on using maleic anhydride as the coupling agent in the cellulose flour and polypropylene composite [91]. Woodhams et al. successfully introduced Epolene E-43, a kind of maleic anhydride-modified-polypropylene (MAPP) with low molecular weight, as a coupling agent in thermo mechanical pulp (TMP) and PP composites [106]. Kazayawoko et al. [107] investigated the effectiveness of MAPP in bleached Kraft pulp (BKP) and unbleached thermo-mechanical pulp (TMP)-PP composites and reported that surface treatment of BKP increased the tensile strength of the composites by 28% and TMP by 27%. Yuan et al. [108] used MAPP as a coupling agent for PP-waste news paper flour composites and reported improved compatibility and hence mechanical properties of PP and paper flour. Sanadi et al. [109] reported that improvement in properties by using MAPP depended on the amount of MA in the graft copolymer and the molecular weight of the copolymer. Bledzki et al. incorporated three compounding techniques (two-roll mill, high speed mixer and twin-screw extruder) for preparation of wood fibre/PP composites and found that application of MAPP (independently on way of introduction) resulted in an important increase of tensile and flexural strength, but in negligible effect on tensile and flexural modulus.

2.7 Processing Methods

There are various methods for processing of randomly oriented fibre reinforced composites. These include the spray-up method, where polymer and resin are sprayed onto the mould simultaneously, centrifugal casting, where polymer and fibre are placed inside a cylinder mould which is rotated at high speed, vacuum bag and pressure bag processes, where fibre and polymer are placed on the mould and a pressure or vacuum is applied, hot and cold press, where fibre and polymer are placed on a mould and pressure is applied with and without heat, extrusion and injection moulding , where fibre and polymer are melted and mixed together then forced through a die to form a shape. This study will concentrate on extrusion and injection moulding processes.

2.7.1 Extrusion

The process of extrusion is similar to the squeezing of toothpaste or forming of spaghetti. As the viscosity of most plastic melt is high, extrusion requires the production of pressure in order to force the melt through the die. A screw pushes thermoplastic granules or powder through a heated cylinder, changing the plastic from solid to liquid and mixing the plastics as it moves through the barrel, then through the die which will give the plastic a constant cross section area. The plastic is melted in the barrel by the mechanical energy from the rotating screws and the heat, transferred from the high temperature barrels. There are two common types of extruders, single screw and double screw extruder. For single screw extruders, friction between the plastic and the rotating crew makes the resin rotate with the screw. The friction between the rotating resin and the barrel pushes the materials forward and generate heat. Single screw extruders are not positive displacement, so they are not effective mixing device [110]. A twin screw extruder is a compounding device to uniformly blend plasticizers, fillers etc. into the plastic melt. Twin screw extruders have intermeshing screws, the relative motion of the flight of one screw inside the channel of another, pushes the material forward with very low friction. Heat is controlled from an outside force and is not controlled by the speed [110].

2.7.2 Injection Moulding

Injection moulding is the most widely used polymeric fabrication process. A large force must be used to inject polymer into the hollow mould cavity. More melt must be packed into the mould during solidification to avoid shrinkage in the mould. Identical parts are produced through a cycle process involving the melting of pellet or powder resin followed by the injection of the polymer melt into the hollow mould cavity under higher pressure. Injection moulding can be used to form a wide variety of products, for both thermosets and plastics. Complexity is virtually unlimited, sizes can vary and excellent tolerance is also possible. With respect to reinforced composites, only randomly oriented short fibres can be used in this process, the orientation of the fibres in the composite are determined by the flow of the composite melt during filling of the mould cavity. The incorporation of short fibres in an injection moulded polymer increases the strength, modulus, impact, creep and heat resistance while decreasing the failure strain. Extrusion is used prior to injection moulding when mixing of a thermoplastic, filler and additive is required. Pellets of the compounded mix are then fed into the hoper are melted, the liquid melt is then injected into the closed mould cavity with a force. The melt is then allowed to cool and solidify before the mould is opened and the final product removed. The process can then be repeated [111]. Advantages and disadvantages of injection moulding are as follows [112]:

Advantages:

- High production rates
- Design flexibility
- Repeatability within tolerances
- Can process a wide range of materials
- Relatively low labour
- Little to no finishing of parts required
- Minimum scrap losses

Disadvantages:

- High initial equipment investment
- High start-up and running costs possible
- Part must be designed for effective moulding
- Accurate cost prediction for moulding job is difficult

2.8 Recycling

Concern for the environment, both in terms of limiting the use of finite resources and the need to manage waste disposal, has led to increasing pressure to recycle materials at the end of their useful life. In the metals industries, for instance, materials recycling operations are already well established and are driven by economics [113]. Polymers are generally more difficult to recycle and the economic incentives to recycle have been less favourable, particularly when waste disposal in landfills is relatively cheap. On the other hand, due to their low cost, large amount of post-consumed plastic waste generated daily in large cities worldwide. To give an example, a city in an emergent country with a population of three million inhabitants produces each day around 400 tonnes of plastic waste [114]. As a consequence, municipalities are becoming concerned about a 25% increase in plastic waste generation per year while the landfill area is only increasing at a 7.5% annual rate. Therefore, as Scott [118] points out, by the year 2015, there will be no disposal options for plastic waste. However, waste management is now a high priority within the European Union. As a consequence, it is already illegal to landfill composites waste in many EU countries. The “End-of-Life Vehicle Directive” (Directive 2000/53/EC) regulates the disposal of vehicles and the requirements include that from 2015, 85% of the weight of all “End-of-Life” vehicles must be re-used or recycled, a further 10% may be subject to energy recovery with a maximum of only 5% of the vehicle allowed to be disposed of in landfill. As vehicles have a life expectancy of more than 10 years, vehicles currently being manufactured must meet the 2015 requirements [113]. As a consequence of increasing legislation, there is a need for recycling routes to be established [113]. Although there are governmental regulations in countries such as Germany, recycled materials are avoided, not only due to their physical properties, but mainly because of their surface appearance. Indeed, many designers are reluctant to use them as they can be rejected by the market. However, this is an attitude that can change [115], as demonstrated in Brazil where around 15% of all rigid plastics and films consumed, are recycled and returned to industry [116]. Some states in the US are also concerned with recycling. For example, in Michigan, the recycling rate is close to 100% and proves the potential for recycling plastic waste as well as changes in market attitude [117].

Plastic waste management can be carried out using three different approaches namely: thermo-mechanical recycling, energy recovery and biological recycling.

Thermo-mechanical recycling first involves mechanical recycling where the thermoplastics are granulated, followed by techniques as extrusion or thermoforming. Energy recovery can be performed in two distinct ways. One is incineration where the hydrocarbon polymers replace fossil fuels. The second approach is pyrolysis or by hydrogenation to low molecular weight hydrocarbons for use either as portable fuels or as polymer feedstock. Biological recycling takes advantage of polymer biodegradation, which is highly dependent on the polymer type and environmental conditions. However, this type of recycling most often involves not only high costs and complex procedures but also potential damage to the environment [118]. Of these three techniques, thermo-mechanical would be expected to involve the least energy in terms of the product "life cycle".

It may be considered that, to be economical, a thermo-mechanical recycling process must be designed in such a manner that the energy to recover the post-consumer materials plus the energy to reprocessing must be equal to the amount of energy needed to produce the virgin material plus the energy required to dispose of the material. This balance does not, however, take into consideration environmental benefits. When those environmental gains are considered, higher energy consumption could be allowed during thermo-mechanical recycling for which the increase in cost could be compensated by indirect costs due to reduction in landfill, for example.

Several authors have investigated the reprocessing of polypropylene. Guerrica-Echevarria et al. [119] have studied the evolution of rheological and mechanical properties of PP after repetitive injection moulding cycles. The main effect of reprocessing was found to decrease in molecular weight of the PP, the chemical structure, however, remains unchanged, melt viscosity and failure strain also decreased. While, Xiang [120] has shown an important change in chemical structure and rheological values after 7 cycles of injection moulding. Another study [121] showed an increase in crystallinity and decrease in tensile strength and elongation at break after 7 extrusion cycles for virgin PP.

Agro-based fibres are less brittle and softer than glass fibres and are likely to be easier to recycle than mineral based fibres. Although no post-consumer based recycling studies have been done on agro-based fibres [93], a study on the effects of reprocessing had been conducted by Walz et al. [122] where, 50% Kenaf fibre reinforced PP composites were reprocessed for 9 times. Both tensile and flexural properties were found to decrease with increase number of times the materials were recycled. Arbelaiz et al. discussed about recycling of flax fibre bundle/polypropylene composites. After passing 4 times through injection moulding, tensile properties only showed a small decrease. A similar trend was shown by Joseph et al. [123] for 20 wt% sisal fibre/LDPE matrix composites. Johan et al. [124] studied the properties of second generation composites made from recycled materials (60% wood fibre, 30% HDPE, 5% PET and 5% tackifier). In general, the mechanical properties, water resistance, and dimensional stability of second-generation panels were equivalent to or better than properties obtained from first-generation panels.

2.9 Degradation and Environmental Effects

Wood fibre is the most widely used lignocellulosic fibre for reinforcing plastics. There are many applications of wood plastic composites (WPC) in everyday life (discussed earlier in 1.1). However, the main disadvantage of natural fibre is their hydrophilic nature that lowers the compatibility with hydrophobic polymeric matrices. They also present poor environmental and dimensional stability that prevent a wider use of natural fibre composites. The possibility for using these materials in outdoor applications makes it necessary to analyse their mechanical behaviour under the influence of the weathering action [17,125].

2.9.1 Degradation by Moisture Absorption

Amorphous cellulose and hemicellulose are mostly responsible for the high water uptake of natural fibres, since they contain numerous easily accessible hydroxyl groups which give a high level of hydrophilic character to fibres. Due to this hydrophilicity, swelling by water uptake can lead to micro-cracking of the composite and degradation of mechanical properties [17]. Moisture penetration into composite materials occurs by three different mechanisms. The main process consists of diffusion of water molecules inside the micro-gaps between polymer chains. The other mechanisms are capillary transport into the gaps and flaws at the interfaces between fibres and polymer due to incomplete wettability and impregnation, and transport by micro-cracks in the matrix, formed during the compounding process [126,127]. The capillary mechanism involves the flow of water molecules into the interface between the fibres and the matrix. It is particularly significant when the interfacial adhesion is weak and when the debonding of the fibres and the matrix has started. In addition, transport by micro-cracks includes the flow and storage of water in the cracks, pores or small channels in the composite structure. These imperfections can be originated during the processing of the material, or due to environmental and service effects. The diffusion coefficient is the most important parameter for water absorption, as this shows the ability of solvent molecules to penetrate inside the composite structure. Over short times such that $M_t/M_\infty \leq 0.5$ the following equation can be used to determine the diffusion coefficient [128]:

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \tag{2.8}$$

where M_t is the moisture content at time t, M_∞ is the moisture content at the equilibrium, L is the thickness of the sample and D is the diffusion coefficient. Rearranging equation (1) gives:

$$D = \frac{\pi L^2 (M_2 - M_1)^2}{16 M_\infty (t_2^{1/2} - t_1^{1/2})^2} \tag{2.9}$$

D can be obtained from the slope of the linear part of the plot of M_t versus the square root of time t.

A lot of work has been done on hygrothrmal ageing on composites. Ana et al. [129] studied the water absorption on natural fibres/PP composites and was proved to follow the kinetics of a Fickian diffusion process, where the kinetics parameters were influenced by the content of fibre and the temperature. Mechanical properties were dramatically affected by the water absorption. Water-saturated samples presented poor mechanical properties such as lower values of Young's modulus and tensile strength. For samples with low fibre content, water acted in some way as a plasticizer leading to slightly higher values of strain, although this effect disappeared with the increase in temperature or in fibre content. Joseph et al. [53] studied the environmental effects on sisal fibre reinforced PP composites. Water uptake of the composite was found to increase with fibre content and levelled off at longer periods. The chemically modified fibre composites showed a reduction in water uptake because of better interfacial bonding. Water uptake of the composite was found to increase with temperature since temperature activates the diffusion process. Reduction in tensile properties was observed due to the plasticisation effect of water. The fibre/matrix bonding becomes weak with increasing moisture content, resulting in interfacial failure. Rongzhi Li studied environmental degradation of wood-HDPE composite [130], and it was found that, the interaction of the water absorption and desorption by the wood phase and the environmental stress cracks of the HDPE phase became the most damaging element to the wood-HDPE composite.

2.9.2 Degradation by Ultra-Violet (UV) Radiation

UV exposure can cause changes in the surface chemistry of the composite also known as photodegradation which may lead to discoloration making the products aesthetically unappealing [131,132133]. Furthermore, prolonged UV exposure may ultimately lead to loss in mechanical integrity [133]. The composites reinforced with fibres containing large amounts of lignin are more susceptible to natural weathering than those with negligible amounts of lignin. This is because lignin and hemicelluloses existing in the middle lamellae of wood fibre are more susceptible to chemical degradation than cellulose [134,135]. Hemicelluloses are responsible for moisture sorption and biological degradation in wood to a much greater extent than cellulose. Lignin is responsible for ultraviolet degradation [136]. Table 2.4 shows the cell wall polymers involved in each fibre property [137].

The photodegradation mechanisms of wood and plastic separately are well documented in the literature. However, the photodegradation mechanisms of WPC is complicated, because each component, namely wood and plastic, may degrade via a different mechanism. The photodegradation of wood is attributed to the degradation of its components namely cellulose, hemicellulose, lignin and extractives [138]. Research has shown that the breakdown of lignin to water soluble products which eventually leads to the formation of chromophoric functional groups such as carboxylic acids, quinones and hydroperoxy radicals, is the main cause for discoloration, mainly yellowing in wood [139, 140]. Lignin undergoes photodegradation via many different pathways. Ultimately, they all lead to the formation of chromophoric groups which have a characteristic yellow colour [141].

Table 2. 4: Cell wall polymers responsible for the properties of lignocellulosics in order of importance [137]:

Strength	**Moisture absorption**
Crystalline cellulose	Hemicellulose
Non-crystalline cellulose	Non-crystalline cellulose
Hemicellulose +Lignin	Lignin
Lignin	Crystalline cellulose
Thermal degradation	**Ultraviolet degradation**
Hemicellulose	Lignin
Cellulose	Hemicellulose
Lignin	Non-crystalline cellulose
Biological degradation	Crystalline cellulose
Hemicellulose	
Non-crystalline cellulose	
Crystalline cellulose	
Lignin	

The degradation of PP is due to photo-oxidation promoted by UV irradiation [142]. Oxidative reaction initiated by UV radiation is represented in Figure 2.4 [53].

Initiation

$$RH \xrightarrow{h\upsilon} R^{\bullet} \tag{2.10}$$

Propagation

$$\begin{aligned} &\mathrm{R}^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \\ &ROO^{\bullet} + R^{'} \longrightarrow ROOH + R^{\bullet '} \end{aligned} \tag{2.11}$$

Branching

$$\begin{aligned} &ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH \\ &2ROOH \longrightarrow ROO^{\bullet} + RO^{\bullet} + H_2O \end{aligned} \tag{2.12}$$

Figure 2. 4: Oxidation reactions initiated by UV radiation [53].

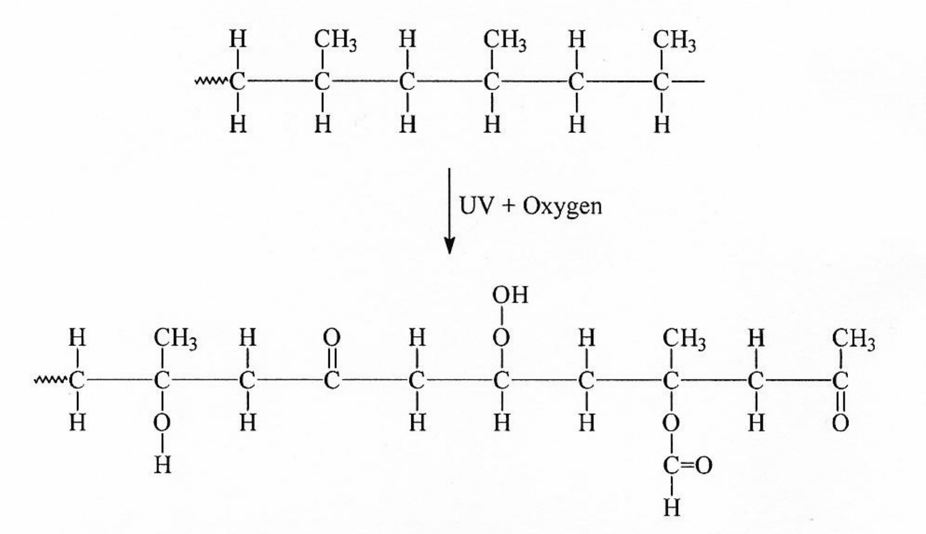


Figure 2. 5: **PP molecules after extensive photodegradation [53].**

For the reaction, oxygen is used up before it can diffuse to the interior so that degradation is concentrated near the surface, even in polymers in which high UV levels are present in the interior. The photo oxidation process takes place mainly in the amorphous region because of the higher permeability to oxygen [53,143,144]. Schematic representation of PP molecules after extensive photodegradation is shown in Figure 2.5 [53].

The long-term behaviour of materials due to environmental influences can be evaluated by the real time observations of the materials exposed to natural conditions for several years [145]. However, research programme lasting 10 years or more are rare for organizational and economic reasons. Accelerated aging tests seem to be useful for this purpose. However, during accelerated weathering measured variables can include exposure time, UV exposure as radiant energy over a specific wavelength range, and water exposure as number of cycles or time. To allow better comparison between studies it is recommended that performance after weathering be reported after a specific radiant exposure, the time integral of irradiance [146].

Accelerated weathering in presence of water enhances the rate of degradation of WPC. Wood cell walls swell when penetrated by water, facilitating light penetration further into the wood providing sites for further degradation [147]. Furthermore, washing the degraded surface with water exposes new surfaces for degradation. Therefore, weathering of WPC results in a cyclical erosion of the surface as the lignin is degraded and subsequently washed away, exposing more lignin to degradation. Washing can also remove some water soluble extractives that impart colour to wood [146].

Joseph et al. [53] studied the environmental degradation of sisal/PP composites. They found that, the tensile properties of both untreated and chemically treated composites decrease after exposure to UV radiation due to chain scission as a result of photooxidation. The decrease in tensile properties was greater for chemically treated rather than untreated composites. Nicole et al. [148] reported that, exposing the wood fibre/HDPE composites to either UV radiation with water spray or UV radiation alone showed that the majority of the loss in mechanical properties after weathering was caused by moisture effects. In addition to the acceleration of oxidation reactions caused by water absorption, the swelling of the wood cell wall compromises the interface between the wood and HDPE. Rongzhi Li [149] conducted long term degradations in weathering condition and in controlled environment conditions for wood flake reinforced HDPE composites and reported that, it retained about half of its initial strength and two thirds of its initial toughness after outdoor weathering for 205 days. Thermal degradation plays an important role in the environmental ageing of the wood-HDPE composite. Oxidative degradation was not significant at the low temperature of 37°C, demonstrated an impact at higher temperature than 67°C. In dry and indoor conditions, UV radiation had small but noticeable influence over the composite. It mainly promotes environmental stress cracks of HDPE. UV exposure causes crosslinking and dissociation of HDPE molecular chains, embrittles HDPE. However UV degradation was limited to a thin layer at the surface of the composite. In the outdoor weathering experiment of the wood-HDPE composite, a mutual promotion of the water adsorption and desorption by the wood phase and the environmental stress cracks of the HDPE phase was the main factor in the degradation of the composite. Ragnar et al. [150] studied UV aging of PP/wood fibre composites and found that the PP matrix and the PP/wood fibre composite both displayed good UV-resistance with regard to mechanical properties. The PP matrix displayed a 10% reduction in flexural strength and a 50% reduction in impact strength. The wood-fibre composites displayed a maximum 20% reduction in flexural strength and almost retained impact strength. The degradation of the composites was restricted to a thin surface layer, owing to the screening effect of the wood fibres. The degraded layer had a chalky appearance, due to degradation of the PP matrix, leading to chemicrystallization and extensive surface cracking. The rate of degradation of the PP matrix was approximately twice as high in samples with 50 wt% wood-fibres, compared to samples with 25 wt% fibres, owing to the higher number of chromophores in the former. DSC scans (second melting) of degraded surface layers revealed a maximum 33°C decrease in PP melting temperature, due to molecular chain scission and the formation of extraneous groups, such as carbonyls and hydroperoxides.

CHAPTER -THREE

THE EFFECTS OF COUPLING AGENT AND ALKALI TREATMENT ON MDF FIBRE REINFORCED PP COMPOSITES

3.1 Introduction

This study investigates the effect of coupling agent and alkali fibre treatment on the physical and mechanical properties of MDF fibre reinforced PP composites. Initially composites were produced with 10, 20, 30, 40, 50 and 60 wt% fibre content and 1, 2, 3 and 4 wt% maleated polypropylene (MAPP) as a coupling agent. The effects of alkali treatment were assessed for composites with 50 wt% fibre content. Prior to compounding, the fibre was treated with NaOH. The effects of treatment were assessed using single fibre tensile testing, kappa testing, zeta potential, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Tensile testing and SEM were carried out to assess the effect of modification on composite mechanical properties and fracture behaviour.

3.2 Experimental

3.2.1 Materials

High temperature thermomechanically pulped (TMP) radiata pine *(Pinus Radiata*) medium density wood fibre (MDF) was supplied by Forest Research, New Zealand. The fibre length ranged from 2-4 mm. The matrix polymer was a standard polypropylene (PP) powder with a density of 0.9 g/cc supplied by the Aldrich Chemical Company, Inc and maleated polypropylene (MAPP-AC 950P) with a saponification value of 35-40 mg KOH/g, a density of 0.93 g/cc and free maleic anhydride content of less than 0.5% was supplied by Honeywell International, Inc, USA.

3.2.2 Methods

Alkali Treatment: Predetermined amounts of fibre was placed in a stainless steel canisters with pre-mixed NaOH solutions of concentrations 2%, 4%, 7% and 10% NaOH (by weight), such that the fibre: solution ratio was 1:20 by weight. The canisters were then inserted into a small lab-scale pulp digester for alkali treatment, with the predetermined treatment cycles, controlled by a 10-step controlled program. The treatment temperature was 110^{o}C with a hold time at the maximum temperature of 25 minutes. After treatment, the fibres were thoroughly washed (until the pH reached 7-7.5) using a pulp and paper fibre-washer. Fibres were then dried at 80^{o}C for 48 hours.

Zeta potential: The pH dependent zeta (ξ) potential measurements on fibres were carried out using a Mutek SZP 06 System zeta potential based on the streaming potential method. An electrolyte solution of 0.001M KCl was forced by external pressure through a fibre plug. The pH value was varied between 3-11 by the addition of 0.1M HCl or KOH.

Kappa testing*:* The half scale kappa test method used in this experiment was based on the AS/NZS 1301.201.2002, the Papro 1.106 kappa number (half scale–modification) and TAPPI T 236 standards. The kappa number is a measure of the amount of residual lignin with the fibre and by definition, the volume (in ml) of 0.1N (0.0002M) potassium permanganate solution consumed by one gram of moisture free pulp. Kappa testing involves the reaction of a known concentration of potassium permangante solution with a predetermined amount of dried fibre. 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. To determine the amount of potassium permanganate consumed, a solution of sodium thiosulfate of a known concentaration was titrated against the fibre-permanganate mixture.

The amount of lignin was determined from the kappa number using the relation [151]:

$$\text{Lignin } (\%) = (\text{Kappa number} \times 0.00147) \times 100 \qquad (3.1)$$

Single fibre tensile testing: The tensile testing of wood fibre was carried out according to the ASTM D3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials, using an Instron 4204 tensile test machine fitted with a 10 N load cell and operated at a cross-head speed of 0.5 mm/min.

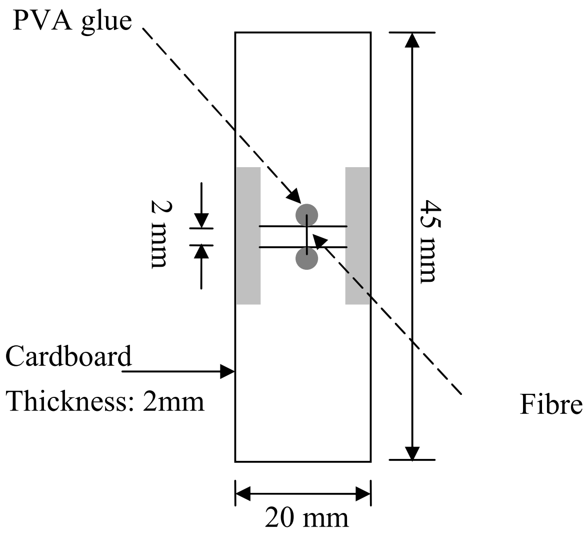


Figure 3. 1: Schematic diagram of cardboard window with mounted single fibre.

Individual fibres were mounted on cardboard windows using poly-vinyl acetate (PVA) glue to provide a gauge length 2 mm (See Figure 3.1). An Olympus BX 60 optical microscope was used to measure the diameter of single fibre. Approximately 35/40 single fibres were tested for each batch.

Scanning electron microscopy (SEM): Fibre and composite surfaces were examined using a Hitachi S-4000 field emission scanning electron microscope, operated at 5 kV. Samples were mounted with carbon tape on aluminium stubs and then sputter coated with platinum and paladium to make them conductive prior to SEM observation.

X-ray diffraction (XRD): X-ray diffraction was carried out using a Philip's X-ray diffractometer with a current of 15 mA and a voltage of 54 kV using CuKα radiation and a graphite monochromator with the range of $2\theta = 6\text{-}60^o$.

Composite fabrication: Composites were fabricated using a TSE-16-TC twin-screw extruder with a 15.6 mm screw blade diameter at 180°C (maintaining 5 different temperature zones 100, 130, 160, 180 and 175°C from feed zone to exit die) and a screw speed setting of 100 rpm. Prior to extrusion, wood fibre, PP and coupling agent were dried in an oven at 80°C for a minimum of 48 hours. Following extrusion, the material was pelletised into lengths of less than 5 mm and injection moulded into specimens for tensile and 4-point bend testing using a BOY 15-S injection moulder using 100 rpm screw speed and 40% injection pressure. The screw speeds and injection pressure was maintained same for the production of all composites to reduce the anisotropy of the samples. Impact test specimens were produced from standard 4-point bend test samples by polishing to give a suitable sample width.

Composite tensile testing: Tensile testing was carried out according to ASTM 638-03: Standard Test Method for Tensile Properties of Plastics. Test specimens were placed in a conditioning chamber at 23°C ± 3°C and 50 % ± 5 % relative humidity for 40 hours. The specimens were then tested using an Instron-4204 tensile testing machine fitted with a 5 kN load cell and operated at a cross-head speed of 5 mm/min. An Instron 2630-112 extensometer was used to measure the strain. Six specimens were tested for each batch with a gauge length of 50 mm.

Four point bend testing: Four point bend testing was carried out according to the ASTM D6272-02: Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials, using a Lloyd LR 100 K tensile tester fitted with a 50 kN load cell and a cross head speed of 15 mm/min. Six specimens were tested for each batch.

Impact testing: Charpy impact testing was carried out based on ISO 179: Plastics-Determination of Charpy Impact Strength. Dimensions of the samples were 80 mm x 8 mm x 3.2 mm with a 0.25 mm single notch (type A). Testing was carried out using a Polytest advanced universal pendulum impact tester with an impact velocity of 2.9 m/s at 21°C.

Hardness testing: The surface hardness of composites was measured using a LM 700 micro hardness tester with a test load of 25 g and dwell time of 20 s.

Melt flow index: The melt flow index was obtained using a Dynisco MFI2 Melt flow indexer following ASTM D1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, using an applied load of 3.80 kg at 230°C. Three independent tests were carried out on each sample.

Density: Density of composite was determined following the ASTM D 792-00: Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, using the following formula:

$$Specific\,gravity = \frac{apparent\ mass\ of\ specimen\ in\ air}{appearent\ mass\ of\ specimen\ in\ water} \tag{3.2}$$

3.3 Results and Discussion

3.3.1 Effects of MAPP and Fibre Content

The tensile strength (TS) and Young's modulus (YM) of pure polypropylene samples moulded using the same conditions as the composites were 25 MPa and 1418 MPa respectively (see Figure 3.2 and 3.3).

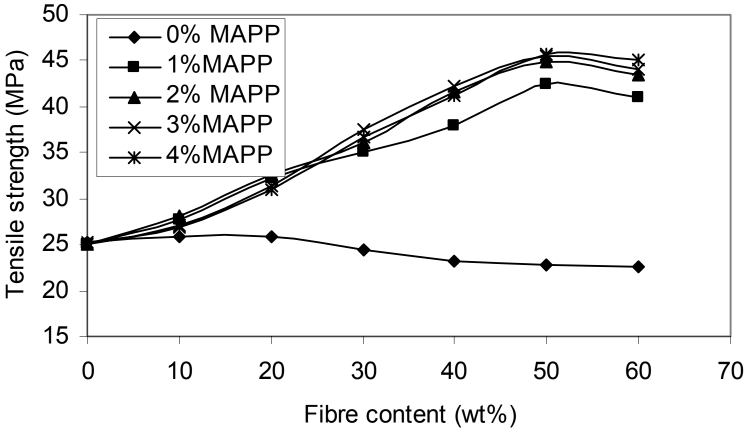


Figure 3. 2: Tensile strength versus fibre content (wt%) of composites.

Without the use of a coupling agent, the TS of the composites (see Figure 3.2) decreased with increasing fibre content. This suggests that the interfacial bond between the fibre and the matrix is poor without coupling agent. This is supported by SEM (see Figure 3.4a) in which fibre pull-out and debonding predominates at the fracture surface. However, the YM was found to increase (see Figure 3.3) with increasing fibre content.

By using a coupling agent (MAPP), TS increased with increasing fibre content up to 50 wt% fibre, then a reduction was observed for 60 wt% fibre content, which could be due to the increase in viscosity, as indicated by reduction of melt flow index (see Table 3.1) resulting limited fibre distribution. TS was found to increase with increasing MAPP content up to 4 wt%, although, little difference on TS was found between 3 and 4 wt% MAPP content. YM was found to increase with increasing MAPP content in composites, and again, the difference in YM between 3 and 4 wt% MAPP was very little (see Fig. 3.3). Therefore, 3 wt% MAPP content was taken to be an optimum amount, and the rest of the studies were carried out with 3 wt% MAPP. The increase in TS and YM using MAPP appeared to be due to better interfacial bonding (see Figure 3.4b).

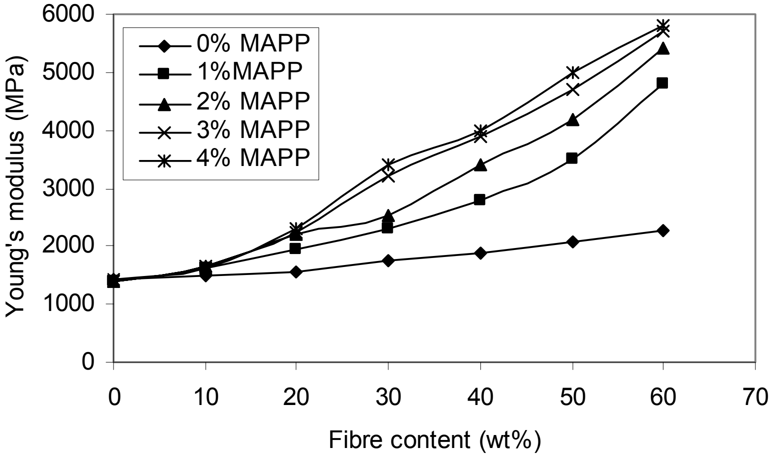
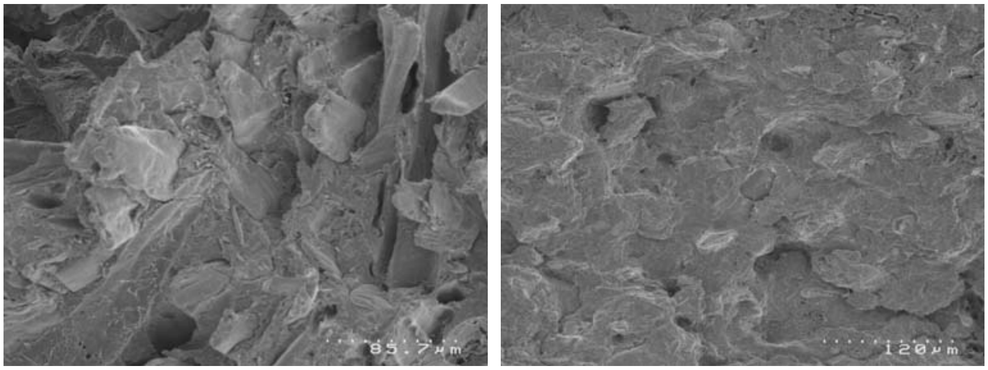


Figure 3. 3: Young's modulus versus fibre content (wt%) of composites.

Failure strain (FS) decreased with increasing fibre content in composites (see Figure 3.5) from about 7% for 10 wt% fibre to about 1.2% for 60 wt% fibre content, which was due to the more brittle nature of the fibre than the matrix PP. A slight increase in FS was found for increasing MAPP content in composites which could be due to better interfacial bonding.



(a) Without MAPP (b) With 3 wt% MAPP

Figure 3. 4: SEM of 60 wt% fibre composites fracture surfaces with and without MAPP.

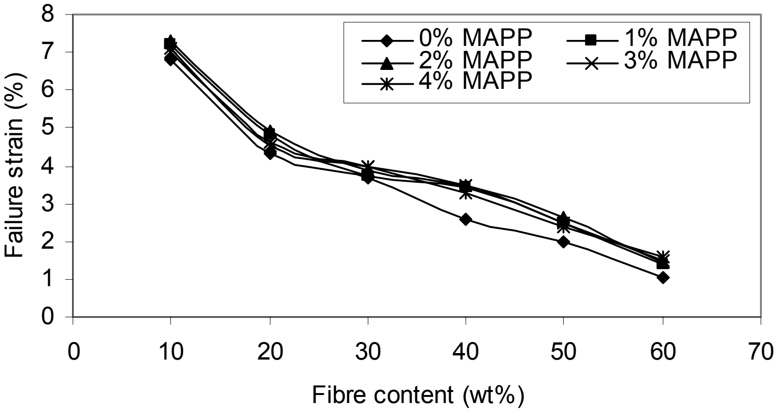


Figure 3. 5: Failure strain versus fibre content (wt%) of composites.

Flexural strength, flexural modulus and hardness of composites increased (see Table 3.1) with increasing fibre content, which could be due to the presence of fibres reducing plastic flow. Impact strength was found to decrease with increasing fibre content (see Table 3.1), which could be due to more brittle nature of fibre reinforced PP compared to PP alone. Density of composites was found to increase with increasing fibre content due to the density of the fibre being higher than that of PP [37,38].

Table 3. 1: Properties of composites with different fibre content with 3 wt% MAPP:

Fibre Content (wt %)	**PP**	**10**	**20**	**30**	**40**	**50**	**60**
Flexural strength (MPa)	-	27	33	45	48	66	78
Flexural modulus (MPa)	-	3437	4088	5634	6369	7294	9510
Vickers' hardness number	6	6.4	7.1	7.8	8.5	9.9	10.5
Impact strength (kJ/m^2)	10.62	4.57	3.98	3.87	3.81	3.76	3.68
Melt flow index (g/10 min)	29.4	19.4	15.8	10.6	6.3	5.4	2.7
Density (g/cm^3)	0.90	0.91	0.97	1.05	1.12	1.17	1.25

3.3.2 Effects of Alkali Treatment

3.3.2.1 Characterisation of fibre

Residual lignin content decreased with increasing NaOH concentration in the digestion medium (see Table 3.2). The residual lignin content for untreated fibre was 3% and decreased to 1.8% for 10% NaOH treated fibre. The surface charge of treated and untreated fibre was measured using the streaming potential method over a range of pH values for which the results are shown in Figure 3.6 with the ζ_{plateau} values given in Table 3.2. Natural cellulose fibres are negatively charged due to the presence of carboxyl and hydroxyl groups [152]. It has been evaluated elsewhere [153,154] that, the number of hydroxyl groups present at the surface of wood fibre is only approximately 1% of the total number in cellulose.

The surface charge of fibre increased with increasing NaOH concentration in the digestion medium. This may be because, alkali reacts with the cementing materials of the fibre, particularly hemicellulose, and leads to the destruction of the mesh structure of the fibre, splitting the fibres into finer filaments [155]. The break-down of the fibre bundles would increase the effective surface area, exposing further hydroxyl and carboxyl groups and increasing the surface charge, which is supported by zeta potential measurements, where the magnitude of zeta potential increased from $\zeta_{plateau}$= -9mV for untreated fibre to $\zeta_{plateau}$= -13mV for 10% NaOH treated fibre (see Figure 3.6 and Table 3.2).

Table 3. 2: Physical and mechanical properties of fibre before and after alkali treatment:

Fibre type	Single fibre tensile strength (MPa)	Single fibre Young's modulus (GPa)	Residual lignin content (%)	Zeta potential $\zeta_{plateau}$ (mV)	I_{XRD}
Untreated	300 ±95	32±4.5	3.0	-9	77
2% NaOH	-	-	2.5	-9.8	74
4% NaOH	-	-	2.3	-11.5	71
7% NaOH	-	-	-	-12.5	71
10% NaOH	220±85	24±4.7	1.8	-13	69.5

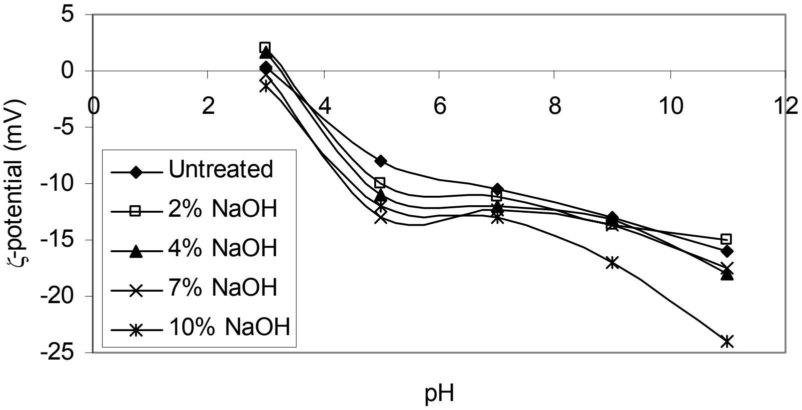


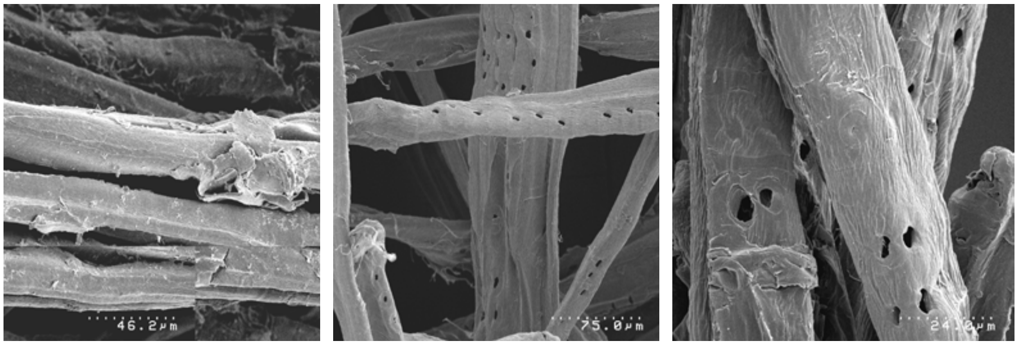
Figure 3. 6: Zeta Potential of treated and untreated fibre against pH.

Evidence of surface roughness was seen using SEM (see Figure 3.7). In addition, porosity and pore size on the fibre surface was found to increase with increasing alkali concentration resulting in a reduction of TS and YM of fibre respectively from 300 MPa and 32 GPa for untreated fibre to 220 MPa and 24 GPa for 10% NaOH treated fibre (see Table 3.2).

The crystallinity index *(I_{XRD})* was determined from the XRD (see Figure 3.8) traces by using Equation 3.3, where $I_{(002)}$ is the peak intensity at an angle 22° representing crystalline material and $I_{(am)}$ is the peak intensity at 18° representing amorphous material in cellulosic fibres.

$$I_{XRD} = \frac{I_{(200)} - I_{(am)}}{I_{(200)}} x100 \qquad (3.3)$$

The crystallinity index was found to decrease with increasing NaOH concentration (see Table 3.2).



(a) Untreated (b) 2% NaOH treated 10% NaOH treated

Figure 3.7: SEM of fibre surfaces before and after alkali treatment.

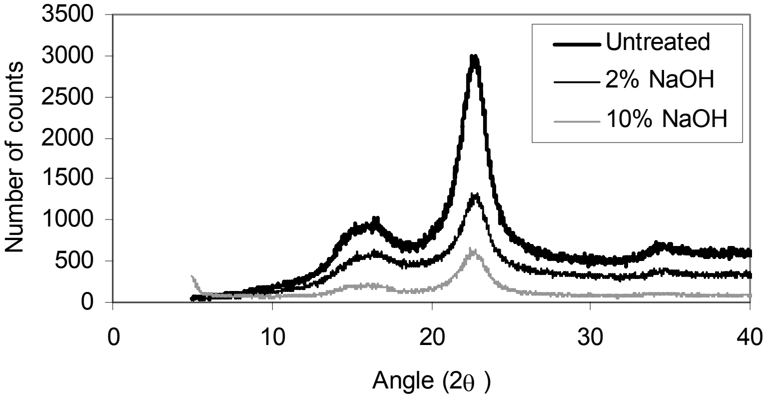


Figure 3.8: XRD traces of untreated and alkali treated fibre.

3.3.2.2 Characterisation of composites

As 50% fibre content in composites was found to be optimum (see section 3.3.1) the effects of fibre pre-treatment were assessed on composites containing 50 wt% fibre. TS and FS decreased and YM increased with increasing NaOH concentration as shown in Table 3.3. The decrease in TS and FS could be due to the reduction of single fibre TS resulting from increase in fibre porosity. However, porosity appears to have improved physical interlocking leading to better interfacial bonding that resulted in an increase in YM.

Table 3. 3: Mechanical properties of composites:

Concentration of NaOH (%)	0	2	4	7	10
Tensile strength (MPa)	45	43	41	40	38
Young's modulus	4700	4851	4912	5100	5200
Failure strain (%)	2.5	2.1	1.8	1.2	1.0

3.3.4 Modelling of Tensile Strength and Young's modulus

Figures 3.9 and 3.10 shows the experimental data of TS and YM as a function of fibre volume fraction, together with the predicted values (considering density of wood fibre=1.4 g/cc [32]) from the different models applied, namely: Series, Parallel and Hirsch's model (see Equations 2.1-2.6 in section 2.5.6). It can be seen that, in all cases, TS and YM increased gradually with increasing fibre volume fraction. The best correlation between the experimental and theoretical values of TS and YM was found with the Hirsch model using fitting parameter x=0.2, but a deviation was observed for TS at higher fibre content, and approached to x=0.1, which could be due to fibre agglomeration.

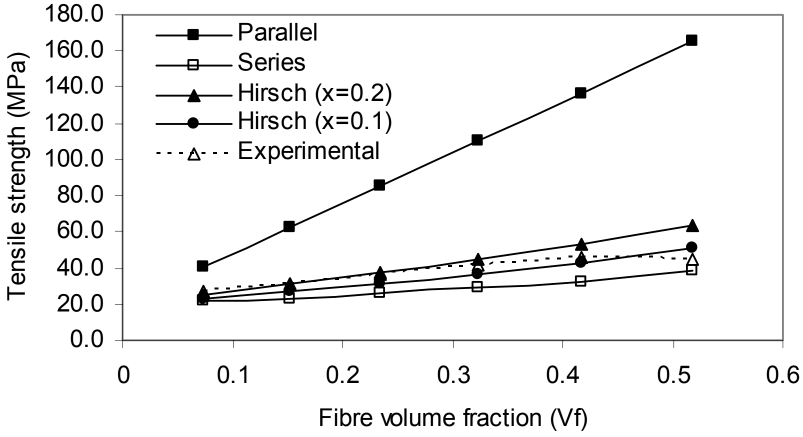


Figure 3. 9: Tensile strength versus fibre volume fraction of composites (predicted values –solid line and experimental values---dotted line).

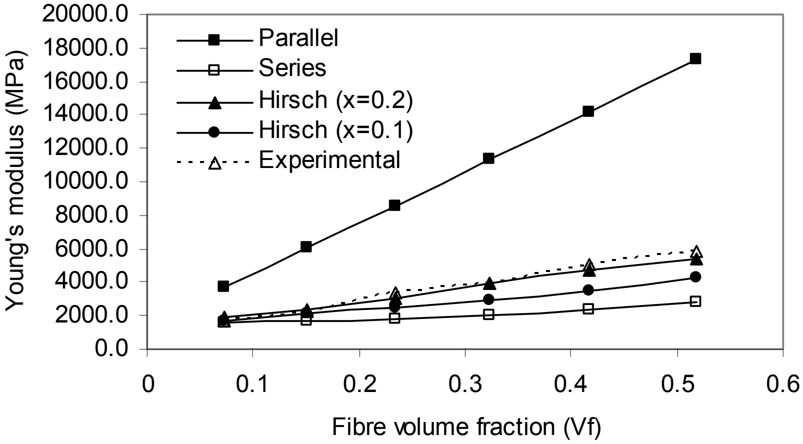


Figure 3. 10: Young's modulus versus fibre volume fraction of composites (predicted values –solid line and experimental values---dotted line).

CHAPTER-FOUR

THE EFFECTS OF RESIDUAL LIGNIN AND HEMICELLULOSE CONTENT ON THE ACCELERATED WEATHERING OF WOOD FIBRE (KRAFT) REINFORCED PP COMPOSITES

4.1 Introduction

In this chapter the ultraviolet (UV) weathering performance of wood fibre (subjected to different stages of a standard Kraft pulping process and therefore consisting of different hemicellulose and residual lignin contents) reinforced polypropylene (PP) composites were studied. Fibre was characterised by kappa testing, zeta potential, thermogravimetric analysis (TGA) and SEM. Composites were fabricated with 40 wt% fibre, 3 wt% coupling agent (maleated polypropylene-MAPP) as 3. Accelerated weathering was carried out for 1000 hours on composites, and mechanical properties were evaluated before and after weathering by tensile testing, impact testing, differential scanning calorimetry (DSC), XRD, TGA and SEM.

4.2 Experimental

4.2.1 Materials

Radiata pine *(Pinus Radiata)* wood fibre collected from different point of the Kraft pulping process was supplied by Tasman Pulp & Paper Co Ltd, New Zealand. The matrix polypropylene (PP) and coupling agent MAPP used in this study were the same as mentioned in 3.2.1.

4.2.2 Methods

Fibre characterisation: Fibre properties were assessed using kappa testing, zeta potential, SEM and TGA (as described in 3.2.2) and also by determination of hemicellulose content as outlined below.

Determination of hemicellulose content: After removing pectin and wax by using organic solvent (methanol and benzene, 50:50 v/v), about 3-4 g of oven dried wood fibre was boiled for 3 hours in 20 g/L NaOH solution, then washed into a filter, dried overnight at 105°C and weighed again. The hemicellulose content was determined by the weight difference.

Composite fabrication: Composites were fabricated using extrusion followed by injection moulding described in section 3.2.2.

Accelerated weathering Testing: Accelerated weathering testing of composites was carried out using an accelerated weathering tester (Model QUV/ spray with solar eye irradiance control) following the ASTM G 154-00a: Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Non-Metallic Materials. A fluorescent bulb UVA with 0.68 W/m^2 irradiance (at 340 nm) was used, with cycles consisting of UV irradiation for 1 hr followed by 1 min spray of de-ionized water, then 2 hours condensation. The temperature was maintained at 50°C. The samples were submitted to the aging process for durations of 150 hours, 400 hours, 600 hours, 800 hours and 1000 hours.

Composite characterisation: Composites were characterised using tensile testing, impact testing, hardness testing, melt flow index, SEM, TGA, DSC and XRD (methods described in 3.2.2).

4.3 Results and Discussion

4.3.1 Characterisation of Fibre

Physical properties of fibres are summarised in Table 4.1. Residual lignin and hemicellulose content decreased with progressive washing and bleaching. Pre-washed fibre, collected from the digester just after Kraft pulping process, contained the highest residual lignin (3.9%) and hemicellulose (21%) contents.

Table 4. 1: Physical properties of pre-washed, washed and bleached fibre:

Fibre	Hemi-cellulose content (%)	Kappa number	Residual lignin content (%)	Zeta potential ($\zeta_{plateau}$) (mV)
Pre-washed	21	27	3.9	-
Washed	20	17	2.4	-12
Bleached	17	≤1	≈0	-16

Intermediate residual lignin and hemicellulose contents were found for washed fibre, at which stage all the dissolved lignin had been removed by washing. The lowest lignin (virtually zero) and hemicellulose (17%) was found for bleached fibre. The surface charge of washed and bleached fibre was measured using the streaming potential method over a range of pH values for which the results are shown in Figure 4.1 (with plateaux values shown in Table 4.1). Generally, natural cellulose fibres are negatively charged due to the presence of carboxyl and hydroxyl groups as mentioned in 3.3.2.1 [152]. In the case of washed fibre, these groups are covered by lignin, present in the primary wall of the fibre shown in Figure 4.2a, where a resinous second phase can be seen on the fibre surface, while the surfaces of bleached fibre which appear more smooth (see Figure 4.2b). This could explain the lower magnitude of zeta potential found for washed fibre ($\zeta_{plateau}$=-12) compared to bleached fibre ($\zeta_{plateau}$=-16) [156].

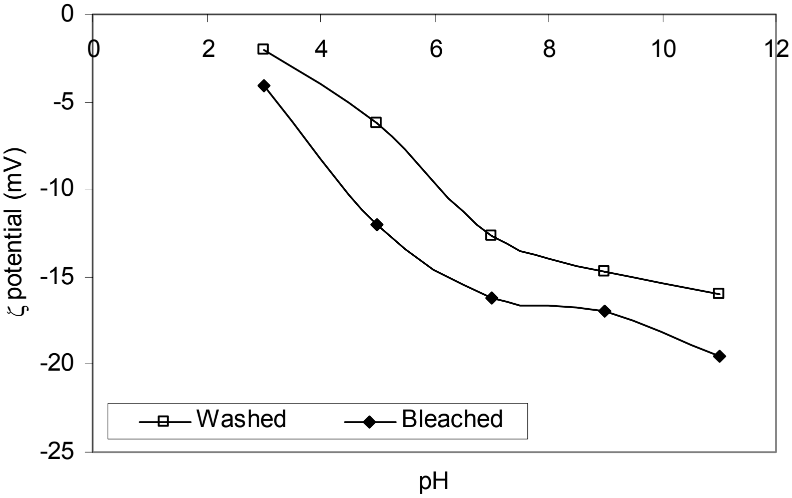
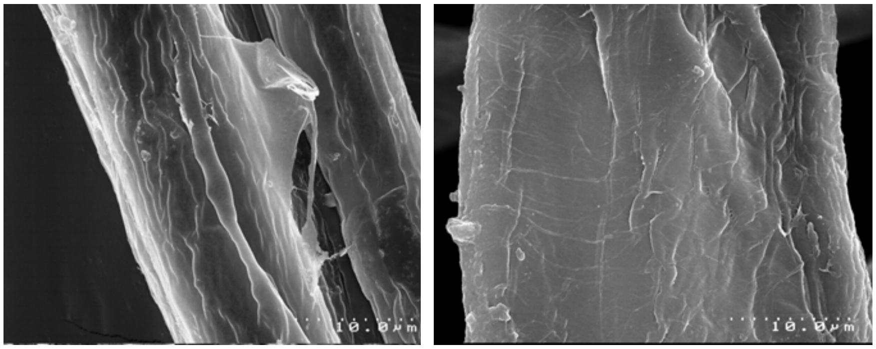


Figure 4. 1: Zeta potential of washed and bleached fibre.



(a) Washed fibre (b) Bleached fibre

Figure 4. 2: SEM of pre-washed and bleached fibre surfaces.

Typical DTA and TGA traces for fibres are shown in Figures 4.3 and 4.4. Two main stages of decomposition were observed for all fibres, starting with dehydration combined with emission of volatile components at a temperature of about 260^{o}C, followed by a rapid weight loss due to oxidative decomposition corresponding to formation of char as the temperature increased (see Figure 4.3) [157]. Kinetic parameters for the various stages of thermal degradation were determined from the TGA graphs using the following equation, given by Broido [158]:

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

where y is the fraction of nonvolatilized material not yet decomposed, T_{max} is the temperature of maximum reaction rate, β is the heating rate, Z is the frequency factor, and E_a is the activation energy. Initially plots of lnln(1/y) versus 1/T for various stages of decomposition were drawn, such as in Figure 4.5 and generally found to be linear, suggesting good agreement with the Broido equation. The activation energies, E_a, determined from the slopes of these plots are given in Table 4.2. Both Ea and T_{max} generally increased for pre-washed through to bleached fibre. The positions of weight loss on the TGA traces shifted to higher temperatures (see Figure 4.4) for increased processing stages from pre-washed to bleached fibre, suggesting increased thermal stability, which can be supported by the increased E_a and T_{max} (see Table 4.2). This increase in thermal stability could be due to the decreased lignin and hemicellulose content.

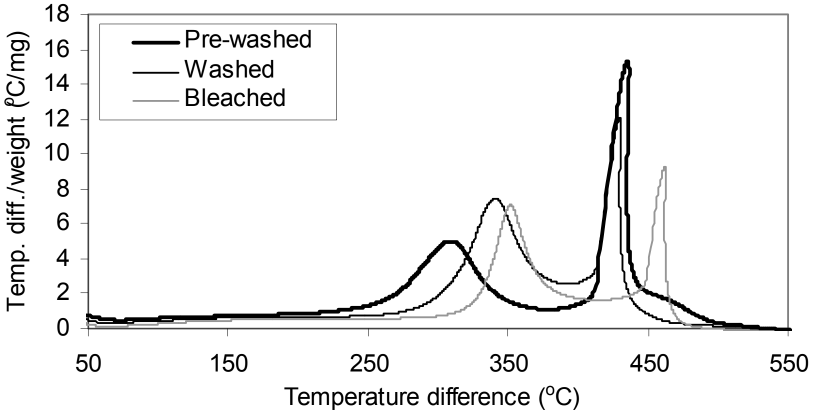


Figure 4. 3: DTA curves of pre-washed, washed and bleached fibre.

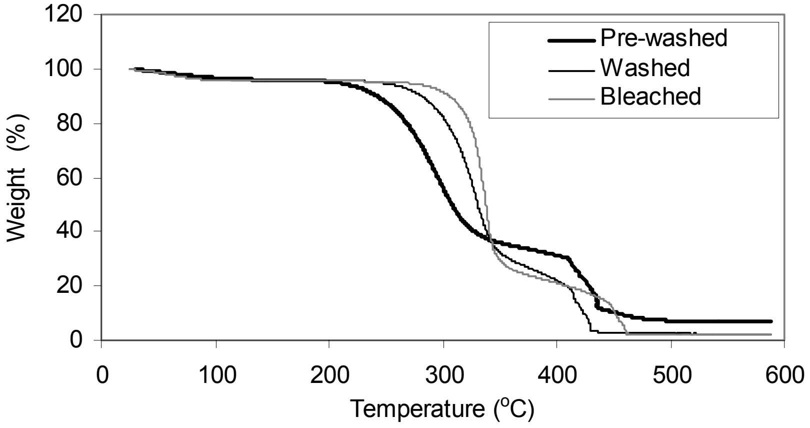


Figure 4. 4: TGA curves of pre-washed, washed and bleached fibre.

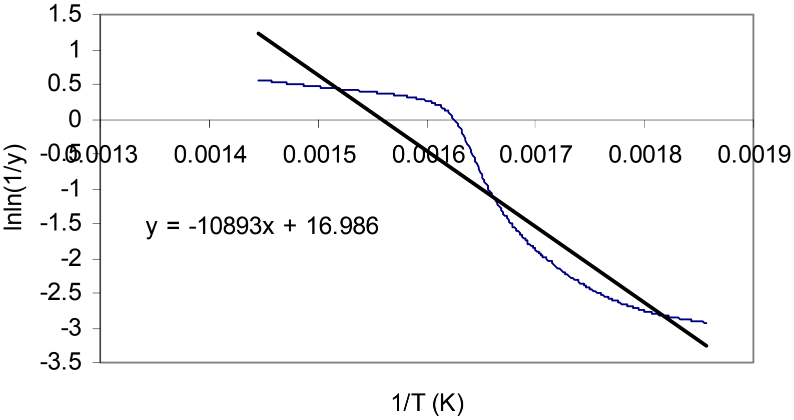


Figure 4. 5: lnln(1/y) versus 1/T for 1st decomposition stage of bleached fibre.

Table 4. 2: Thermal properties of pre-washed, washed and bleached fibre:

Fibre type	Stages	Temp range (°C)	T_{max} (°C)	Residue (%)	Activation energy E_a (kJ/mol)
Pre-washed	1st	285-376	311	6.61	40
	2nd	411-446	436		67
Washed	1st	275-385	343	2.36	79
	2nd	413-477	427		98
Bleached	1st	308-405	354	1.82	91
	2nd	446-480	462		125

It is also noted that the higher the amounts of lignin in the fibre the higher the residue obtained after TGA analysis (see Table 4.2), which could be due to the lignin component contributing to char formation such that a charred layer helps to insulate against further thermal degradation [159].

4.3.2 Characterisation of Composites

For easy processing 40 wt% fibre was selected for the production of composites to evaluate the effects of accelerated weathering and 3 wt% MAPP was used as it was found to be optimum (see section 3.3.2). Properties of composites are presented in Table 4.3. A significant increase of TS was found for bleached compared to pre-washed fibre composites respectively from 31 MPa to 41 MPa. FS increased, but very little change in YM was noted for pre-washed through to bleached fibre composites.

Table 4. 3: Properties of pre-washed, washed and bleached fibre composites:

Fibre type	TS (MPa)	YM (MPa)	FS (%)	Vicker's hardness number	Impact strength (kJ/m^2)	Melt flow index (g/10 min)	I_{DSC}
Pre-washed	31	4584	0.7	8.7	3.9	2.20	36.9
Washed	39	4500	1.6	8.2	5.6	1.10	37.2
Bleached	41	4450	2.1	7.7	6.1	0.90	42.8

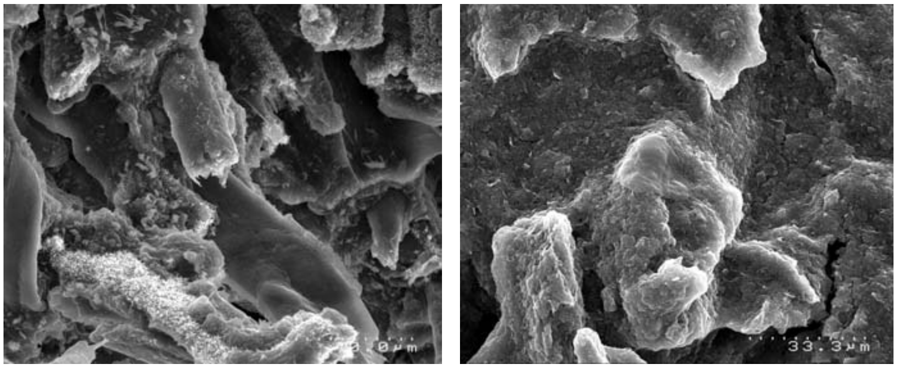
Hardness was found to decrease from 8.7 Vicker's hardness number to 7.7 Vicker's hardness number and impact strength increased from 3.9 kJ/m^2 to 6.1 kJ/m^2 for pre-washed through to bleached fibre composites. Melt flow index was found to decrease for pre-washed through to bleached fibre composites. For the pure PP, melt flow index was found to be 29.40 g /10 min, while pre-washed fibre composites showed a melt flow index of 2.20 g/10 min and bleached fibre composites showed 0.90 g/10 min.

The increase in TS with an increase degree of fibre processing could be due to the removal of hemicellulose and lignin which have less contribution to TS than cellulose [137]. Also, lignin appears to hinder the efficiency of stress transfer between PP and fibre [160] which may result in poor interfacial bonding between the fibre and the matrix as supported by Figure 4.6a, where a lot of fibre pull out was observed from the fracture surface of pre-washed fibre composites compared to better interfacial bonding of bleached fibre composites (see Figure 4.6b). Removal of bulky groups of lignin may increase the FS and impact strength, and decrease hardness of bleached fibre composites.

The crystallinity of PP in composites was determined from the DSC analysis using the relation [161]:

$$\%\, Crystallinity, I_{DSC} = \frac{\Delta H}{\Delta H_m} X \frac{100}{W} \tag{4.2}$$

where ΔH and ΔH_m are the heat of fusion of PP and 100% crystalline PP respectively, and W is the fraction of PP in composites. Taking ΔH_m=148 J/g for PP [162], the crystallinity of PP in composites was calculated and is presented in Table 4.3.



(a) Pre-washed (b) Bleached

Figure 4. 6: SEM of pre-washed and bleached fibre composites fracture surfaces.

The crystallinity index for PP in pre-washed fibre composites was 36.9%, increased to 42.8% for bleached fibre composites (see Table 4.3), which may be due to the removal of amorphous lignin from the fibre. The increase in composite crystallinity was also supported by XRD (see Figure 4.7). This increase in crystallinity may be another reason for the increase in TS for bleached fibre composites.

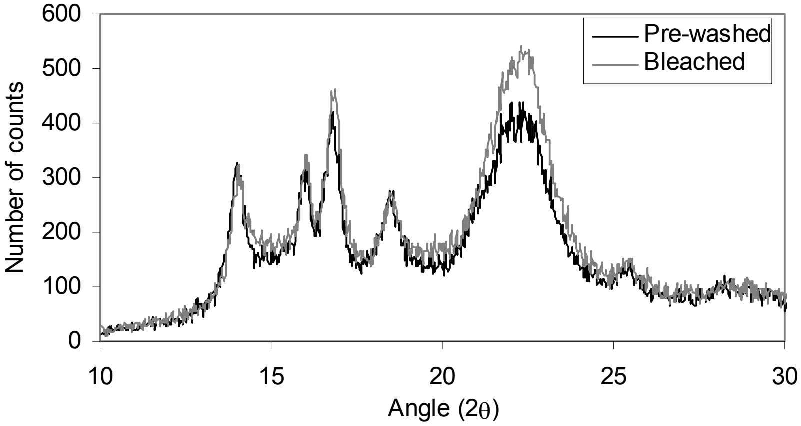


Figure 4. 7: XRD traces of pre-washed and bleached fibre composites showing higher intensity for bleached fibre composites.

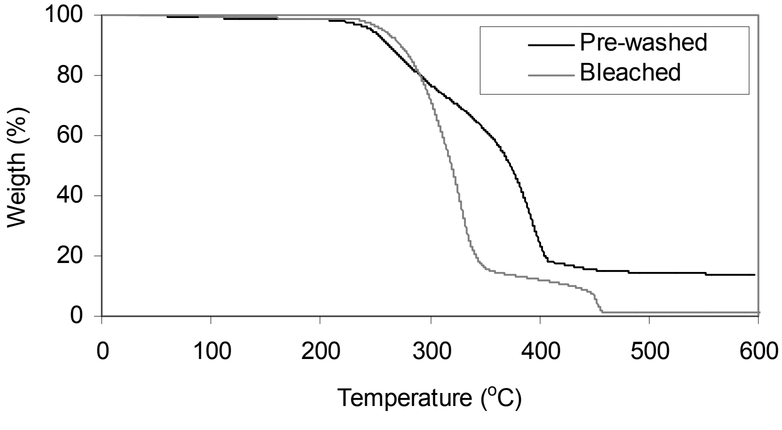


Figure 4. 8: TGA curves of pre-washed and bleached fibre composites.

TGA traces of composites are presented in Figure 4.8. Pre-washed fibre composites started to decompose earlier than bleached fibre composites, but this trend changed at higher temperature (with the pre-washed fibre composites leaving a greater of residue). For pre-washed fibre composites 13.8% was residue remained and for bleached fibre composites 1.55% residue was left. This may be due to pre-washed fibre containing higher amounts of residual lignin which contributes to char formation, and a charred layer helping to insulate against further thermal degradation of the sample [159].

4.3.3 Effects of Weathering

The surface texture of samples exposed to the accelerated weathering environment slightly deteriorated, in the form of colour fading and deposition of white powdery material on the surface (see Figure 4.9). Progressive weight gain during weathering is presented in Figure 4.10. For PP, there was no significant change in weight during weathering. The weight of pre-washed fibre composites decreased considerably with exposure time, however, washed and bleached fibre composites showed an increase in weight. The change of weight is likely to be due to effects of leaching of lignin from the samples and absorption of water during the water spray and condensation cycle. For pre-washed fibre composites, the former mechanism appears to be predominant, but for washed and bleached fibre composites, the latter appears to be predominant.

Unweathered 150 hours weathered 1000 hours weathered

Figure 4. 9: Visual change during weathering of composites consisting bleached, washed and pre-washed fibre, denoted by its kappa number respectively 1, 17 and 27.

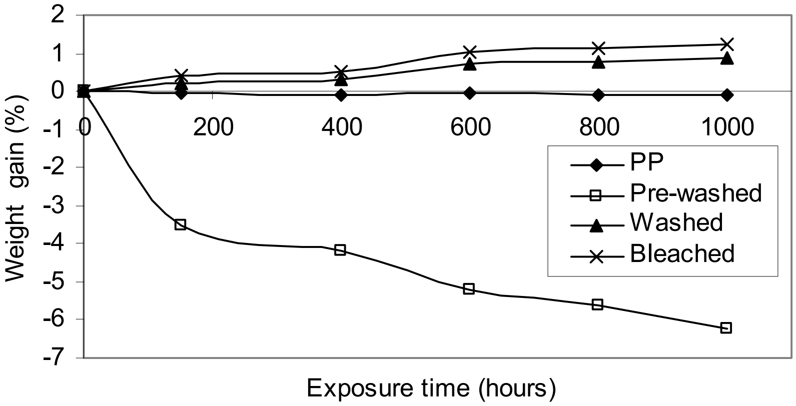


Figure 4. 10: Weight gain of composites during weathering.

Loss of lignin from composites can be supported by Figure 4.9 where pre-washed fibre composites changed their colour after 150 hours weathering from blackish brown to light brown and finally after 1000 hours to a yellow colour, which is likely to be due to the breakdown of lignin to water soluble products [163,164].

The change in mechanical properties due to weathering for different periods of time is presented in Figures 4.11-4.16. Very little change in TS and YM was found for PP, but both TS and YM decreased for composites with increasing duration of irradiation (see Figures 4.11 and 4.12). The highest reduction was found for pre-washed fibre composites. TS and YM of pre-washed fibre composites reduced respectively from 31 MPa and 4584 MPa before weathering to 19 MPa and 1197 MPa after 1000 hours weathering.

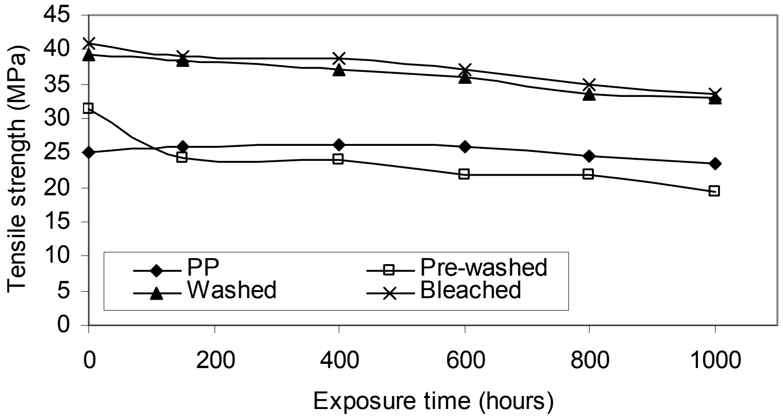


Figure 4. 11: Tensile strength of composites and PP versus weathering time.

FS (see Figure 4.13) was found to increase with increasing irradiation time for pre-washed and washed fibre composites, but was found to decrease for bleached fibre composites. A dramatic reduction of FS was found for PP (see Figure 4.14), reducing from 128% for 150 hours weathering to 2.5% for 1000 hours weathering.

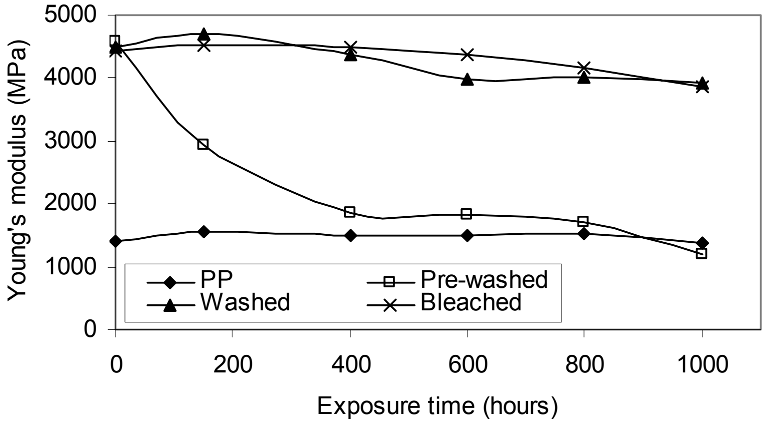


Figure 4. 12: Young's modulus of composites and PP versus weathering time.

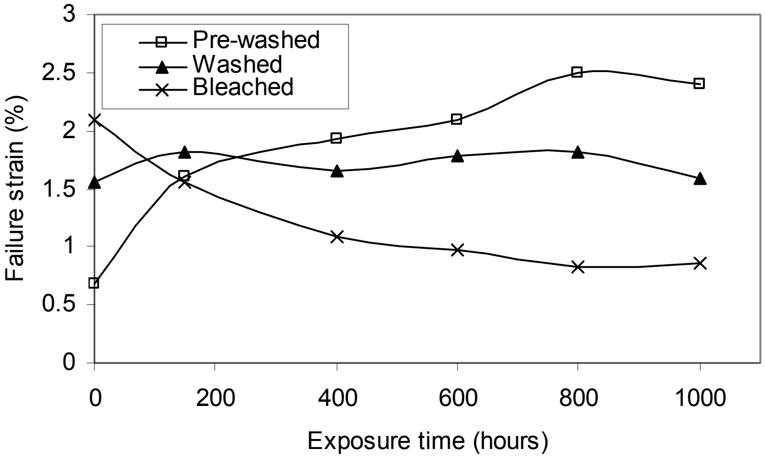


Figure 4. 13: Failure strain of composites versus weathering time.

Impact strength (see Figure 4.15) was found to increase slightly with increasing irradiation time for pre-washed and washed fibre composites, but was found to decrease for bleached fibre composites. A dramatic reduction of impact strength was found for PP, from 10.5 kJ/m^2 for virgin PP to 3.3 kJ/m^2 for the PP after 1000 hours weathering. It is interesting to note that FS and impact strength of composites are less affected than PP alone during weathering (see Figures 4.13-4.15).

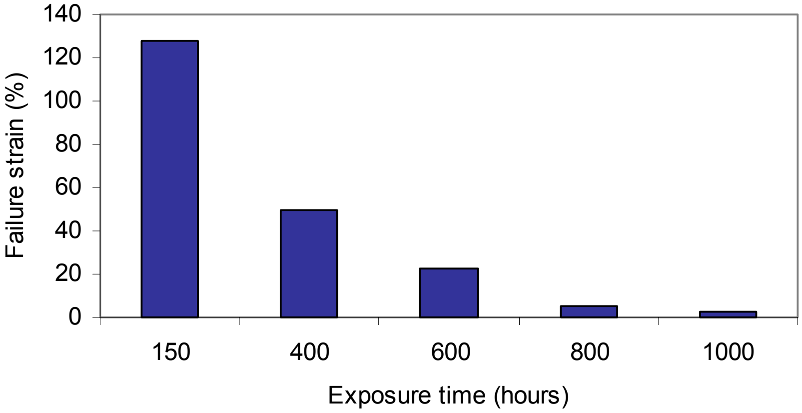


Figure 4. 14: Failure strain of PP versus weathering time.

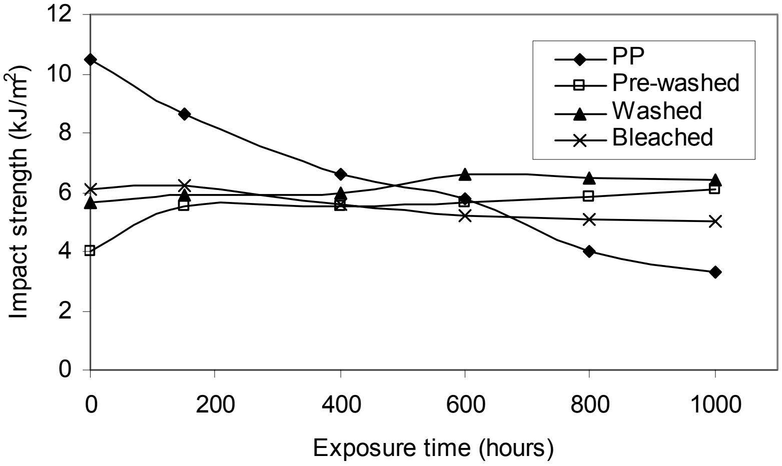


Figure 4. 15: Impact strength of composites and PP versus weathering time.

Hardness was generally found to decrease for PP and all of the composites. Among them, pre-washed fibre composites showed the greatest reduction of hardness, with most of the reduction happening within 200 hours of weathering (see Figure 4.16).

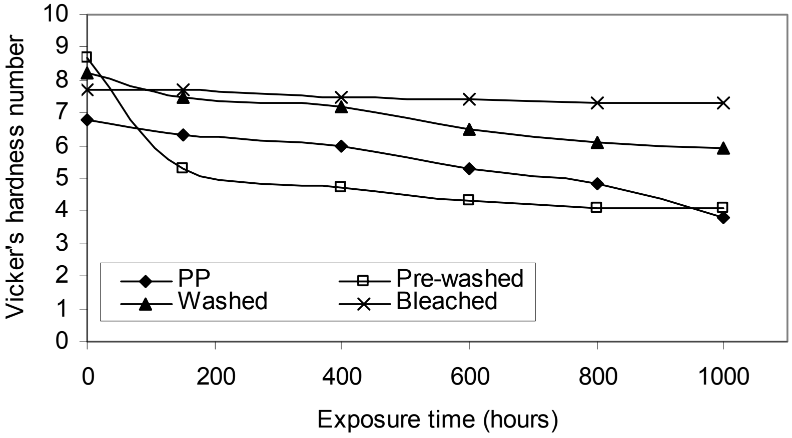
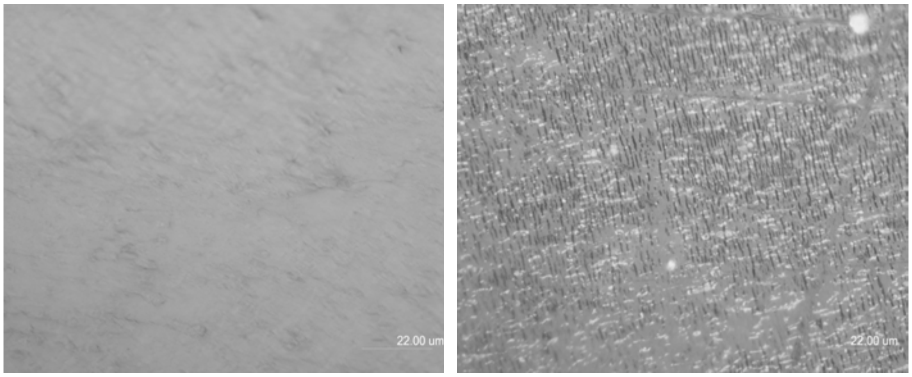


Figure 4. 16: Vicker's hardness of composites and PP versus weathering time.

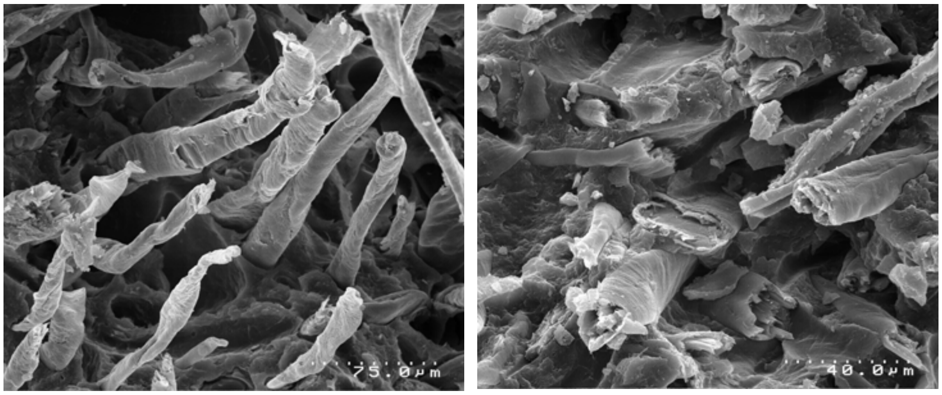
The reduction of TS and YM found during weathering could be due to chain scission and degradation occurring to PP molecules [53]. The degree of crystallinity of virgin PP is 38.8% (Table 4.4). Therefore, a large fraction of the material is in the non-crystalline state, which favours the permeability of oxygen and the photo-oxidation process which takes place mainly in these amorphous regions [165,166,167]. Since the glass transition temperature of PP (-10^{o}C) [168] is below the exposure temperature (50^{o}C), the freed segments in the amorphous region have sufficient mobility to rearrange into a crystalline phase, resulting in higher crystallinity after weathering [169] during exposure leading to shrinkage of the degraded material. In thick samples, the changes take place only near the moulded surfaces (where chemical degradation occurs), and as the interior remains unchanged, the tendency of surface contraction ultimately leads to the formation of surface cracks as can be seen in Figure 4.17 [170].



(a) Unweathered (b) 1000 hours weathered

Figure 4. 17: Micrographs of PP surfaces before and after weathering.

The other reason for reduction of TS and YM of composites could be due to the breakdown of lignin to water soluble products [139,140]. A high content of water soluble substances leached from the composites during water spray and condensation leding to the initiation of debonding between the fibre and the matrix [171] and ultimately resulting in fibre pull out (see Figure 4.18).



(a) Pre-washed (b) Bleached

Figure 4. 18: Composites fracture surfaces after weathering showing higher degree of pull out for pre-washed fibre composites.

The reduction of FS and impact strength of PP (Figures 4.14 and 4.15) could be due to the formation of surface cracks, as shown in Figure 4.17, and chain break down of PP. The increase in FS and impact strength for pre-washed and washed fibre composites during weathering could be due to the removal of lignin resulting in leaching of the debonded fibre and giving a porous structure. As the porosity increases, water molecules can become trapped inside the composite structure, which may act as a plasticizer resulting in an increase of FS and impact strength [53]. The reduction of FS and impact strength for bleached fibre composites could be due to less fibre pull out and chain scission of PP leading to more brittle behaviour.

Table 4. 4: Crystallinity of PP alone samples and PP in composites before and after weathering:

	Before weathering		After 1000 hours weathering	
Sample	T_m (^oC)	I_{DSC}	T_m (^oC)	I_{DSC}
PP	169.2	38.8	163.7	40.9
Pre-washed	168.2	36.9	167.0	29.0
Washed	169.6	37.2	168.4	34.6
Bleached	170.5	42.8	169.3	41.1

The crystallinity calculated (using equation 4.2) from DSC analysis was found to increase from 38.8% for virgin PP to 40.9% for 1000 hours weathered PP. However, for the PP in composites, the crystallinity decreased after weathering (see Table 4.4). This observation was supported by XRD (see Figures 4.19-4.21), where a higher intensity was found for PP after weathering, as opposed to the composites where a decrease in intensity with weathering was found.

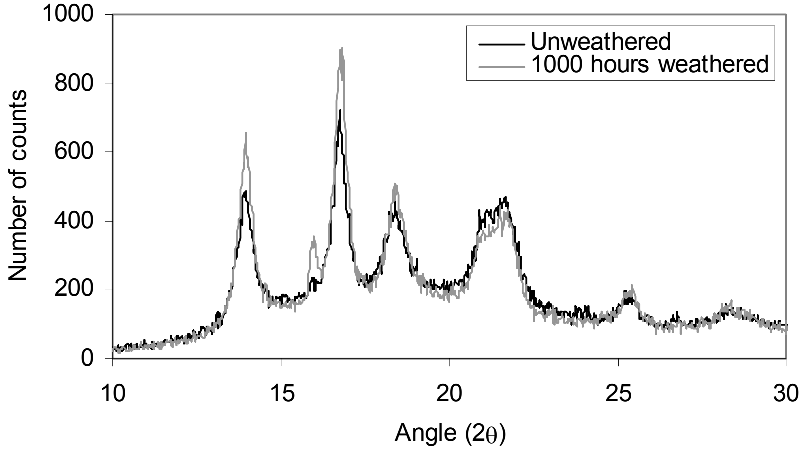


Figure 4. 19: XRD traces of PP before and after weathering.

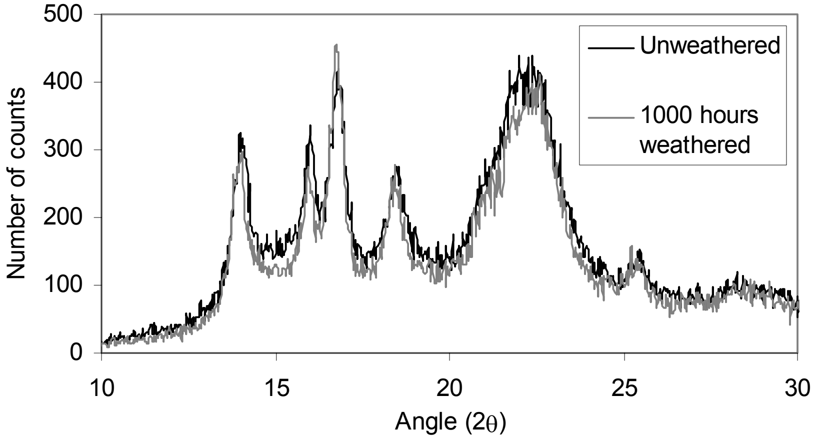


Figure 4. 20: XRD traces of pre-washed fibre composites.

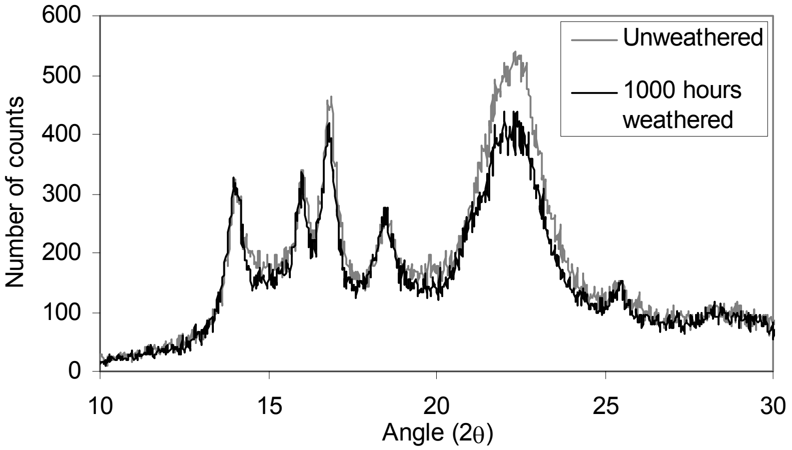


Figure 4. 21: XRD traces of bleached fibre composites.

TGA traces of PP are presented in Figure 4.22, where, it may be seen that the TGA traces shifted to lower temperatures with increasing weathering time. The decrease in thermal stability when weathering time was increased could be due to reduction of molecular weight. TGA traces of composites also shifted to lower temperature after 1000 hours weathering (see Figures 4.23 and 4.24) as observed for PP.

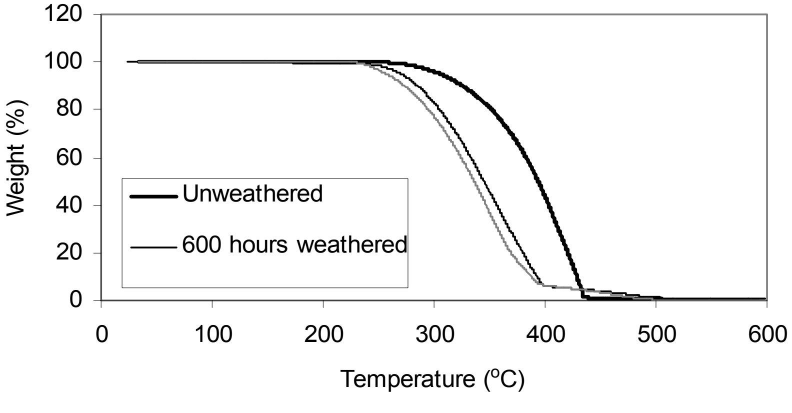


Figure 4. 22: TGA traces for PP before and after weathering.

For pre-washed fibre composites the amount of residue left after TGA was found to be much less than with the unweathered composites (see Figure 4.23), with 13.8% for unweathered composites and 4.6% residue after 1000 hours weathering. This appeared to be due to the removal of residual lignin which contributes to char formation [154]. The decrease in thermal stability of composites during weathering could be due to the PP chain scission and degradation of both the fibre and the fibre matrix interfacial bonding as supported by Figure 4.18.

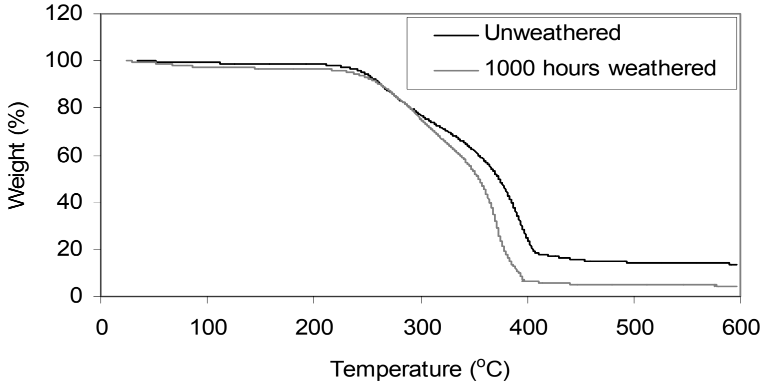


Figure 4. 23: TGA traces for pre-washed fibre composites before and after weathering.

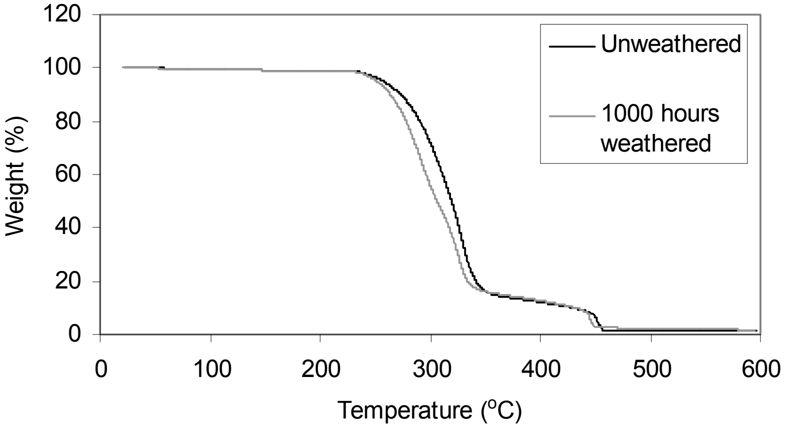


Figure 4. 24: TGA traces for bleached fibre composites before and after weathering.

After weathering, the crystalline melting temperature (T_m) was found to decrease for PP and all composites (see Table 4.5). Virgin PP showed a T_m of 169.2°C and after 1000 hours weathering it was 163.7°C (see Figure 4.25). The reduction of T_m for all composites due to weathering was approximately 1°C. The reduction of T_m could be due to the break down of polymer chains and a reduction of molecular weight [53], which may be less for PP in composites than PP alone, as supported by T_m (see Table 4.5).

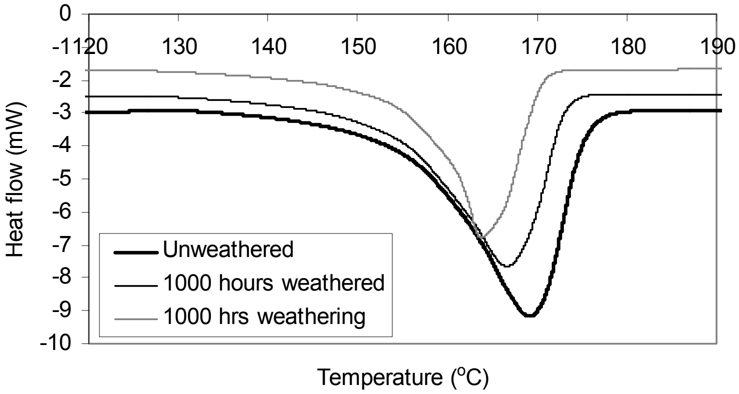


Figure 4. 25: DSC curves of PP before and after weathering.

Table 4. 5: Crystallinity of PP alone samples and PP in composites before and after weathering:

	Before weathering		After 1000 hours weathering	
Sample	T_m (°C)	I_{DSC}	T_m (°C)	I_{DSC}
PP	169.2	38.8	163.7	40.9
Pre-washed	168.2	36.9	167.0	29.0
Washed	169.6	37.2	168.4	34.6
Bleached	170.5	42.8	169.3	41.1

CHAPTER-FIVE

FIBRE PRE-TREATMENT AND HYGROTHERMAL AGEING OF WOOD FIBRE (KRAFT) REINFORCED PP COMPOSITES

5.1 Introduction

In this chapter, the effects of fibre beating and hygrothermal ageing on bleached Kraft wood fibre reinforced PP composites were investigated. Initially, coupling agent content in composites was optimised. Coupling agent contents of 1, 2, 3, 4, 5, 7 and 10 wt% were used in composites. A 30-50 wt% fibre was loaded in composites. To investigate the effects of fibre length, fibre fractions of different length distribution were separated using a pressure screen. Fibre pre-treatment by mechanical beating was used to improve the interfacial bonding. Hygrothermal ageing on composites was carried out by immersing specimens in distilled water at 30, 50 and 70°C over an 8-month period. Fibre pre-treatment was assessed by zeta potential, freeness testing and SEM. Composites were characterised using tensile testing, impact testing, melt flow index, SEM and TGA.

5.2 Experimental

5.2.1 Materials

Radiata pine *(Pinus Radiata)* bleached wood fibre (Kraft) was supplied by Tasman Pulp & Paper Co Ltd, New Zealand. The average fibre length was 2.36 mm. The matrix PP and coupling agent MAPP used in this study were the same as mentioned in 3.2.1.

5.2.2 Methods

Fibre beating: Fibre was beaten using a Sprout-Waldron disc refiner with a specific edge load of 0.89 Ws/m for 10 minutes. The refiner was operated at 1450 rpm so that the disc peripheral velocity was in the range of 20-25 m/s. The plates used were Papro R^3 plates, with a cutting length of 223 m/rev. Refined pulps were removed at regular intervals.

Freeness testing: Freeness testing was carried out according to the AS/NZS 1301.206: Methods of Test for Pulp and Paper-Freeness of Pulp using a Freeness tester.

Fibre separation: Fibre was separated into long and short fibre fractions using a Beloit MR8 Pressure Screen with 1 mm holes (a standard fractionation basket used for obtaining different paper grades). The pulp was split into a long fibre fraction and a short fibre fraction. This process was repeated for half an hour for the long fibre fraction in order to increase the average fibre length.

Composite fabrication: Composites were fabricated using extrusion followed by injection moulding as described in chapter 3.2.2.

Water absorption: Water absorption studies were performed following the ASTM D 570-98: Standard Test Method for Water Absorption of Plastics. Six specimens of tensile and bending from every batch were submerged in distilled water at 30, 50 and 70°C. The specimens were removed from the water after certain periods of time, weighed in a high precision balance to find the amount of water taken up and then resubmerged in water.

Composite characterisation: Composites were characterised using tensile testing, impact testing, melt flow index, SEM and TGA (methods described in 3.2.2).

5.3 Results and Discussion

5.3.1 Effects of MAPP

No significant effect on TS and YM was found for MAPP addition to PP alone (see Figure 5.1 and 5.2). For composites without the use of coupling agent, the TS decreased from 25 MPa for pure PP to 23 MPa for composites (see Figure 5.1). This suggests that the interfacial bond between the fibre and the matrix is poor. This can be supported by SEM (see Figure 5.3a), where fibre pull-out and debonding predominate at the fracture surface. Using MAPP of 1 wt% in the composites, the TS increased to 37 MPa from 23 MPa. Both the TS and YM increased with increasing MAPP content in composites up to 4 wt% (see Figure 5.1 and 5.2), which appeared to be due to better interfacial bonding between the fibre and the matrix (see Figure 5.3b).

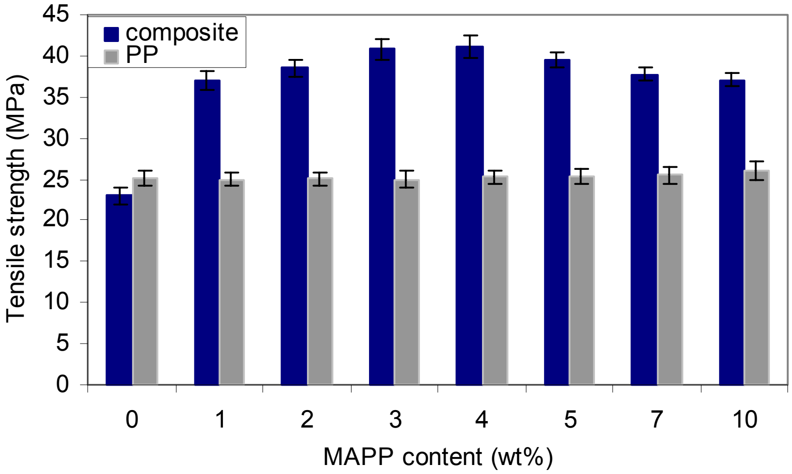


Figure 5. 1: Tensile strength versus coupling agent concentration in composites (40 wt% fibre).

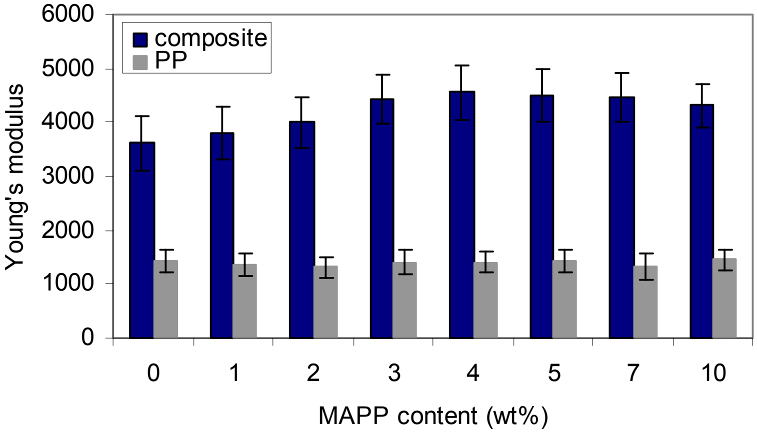
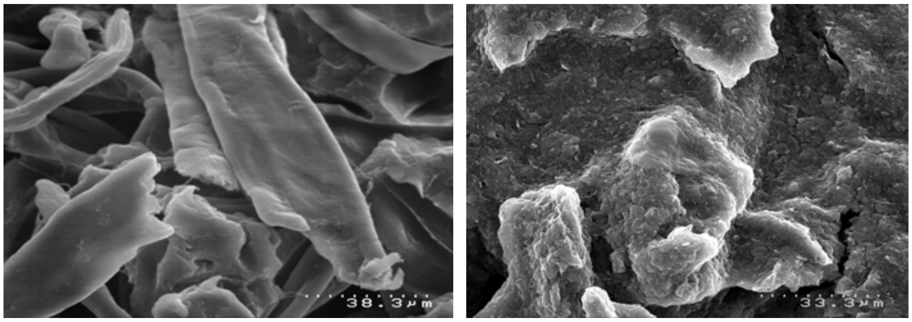


Figure 5. 2: Young's modulus versus coupling agent concentration in composites (40 wt% fibre).



(a) Without MAPP (a) With 4 wt% MAPP

Figure 5. 3: SEM of composites (40 wt% fibre) fracture surfaces with and without MAPP.

A slight reduction of TS and YM was observed for 5 wt% MAPP and the extent of reduction of TS and YM increased for 7 and 10 wt% MAPP. The reduction of TS and YM at higher MAPP content has been attributed to self-entanglement among the compatibilizer chains rather than with the polymer matrix, thus resulting in slippage [172,173]. As there was very little difference on TS and YM for 3-5 wt% MAPP content in composites, it was considered that any concentration within this range could be used to achieve the most favourable mechanical properties. For the rest of this study 4 wt% MAPP was used in composites.

5.3.2 Effects of Fibre Content

The TS increased from 39 MPa for 30 wt% fibre composites to 41 MPa for 40 wt% fibre composites, but was found to decrease down to 38 MPa for 50 wt% fibre composites (see Table 5.1).

Table 5. 1: Properties of composites containing 4% MAPP with different fibre content:

Fibre content (wt%)	MAPP content (wt%)	TS (MPa)	YM (MPa)	FS (%)	Impact strength (kJ/m^2)	Melt flow index (g/10min)
30	4	39±0.94	3616±208	2.48±0.8	7.5	2.80
40	4	41±1.43	4553±500	1.99±0.5	6.2	0.90
50	4	38±1.50	4888±555	1.06±0.5	4.1	0.14

This is in contradiction to Rule of Mixtures type models, where increasing the fibre content would be expected to increase TS [174]. Departure from this trend is considered likely to be due to the limited dispersion of fibre in composites at higher fibre content, due to the increase of viscosity as indicated by the reduction of melt flow index (see Table 5.1). As expected, the YM was found to increase with increasing fibre content, due to the high modulus of the fibre. FS and impact strength decreased with the increase in fibre content, due to the brittle nature of fibre relative to PP.

DTA and TGA traces are shown in Figure 5.4 and 5.5. Three stages of decomposition were observed for all composites, such as for the 30 wt% fibre composites shown in Fig. 5.4. As the temperature increased, dehydration and decomposition of volatile components was observed at about 260^{o}C, followed by rapid weight loss for oxidative decomposition, and finally slow decomposition corresponding to the formation of char [175].

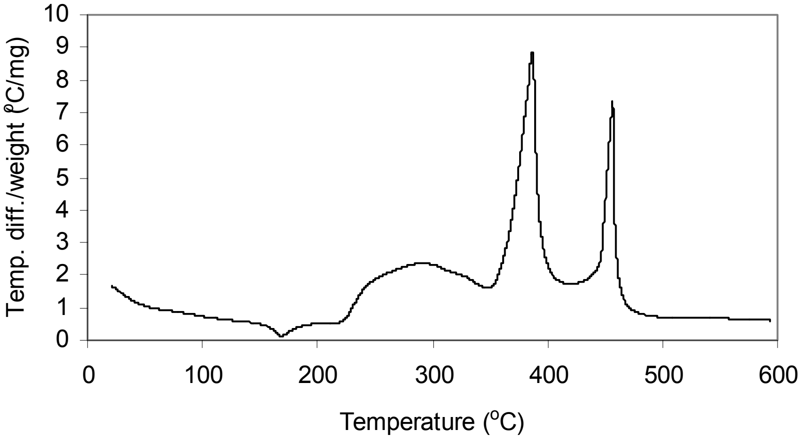


Figure 5. 4: TDA traces of 30 wt% fibre content composites with 4 wt% MAPP.

Activation energies for the various stages of thermal degradation were determined from the TGA graphs using the Broido equation (Equation 4.1) following the methods described in 4.3.1. The results are presented in Table 5.2.

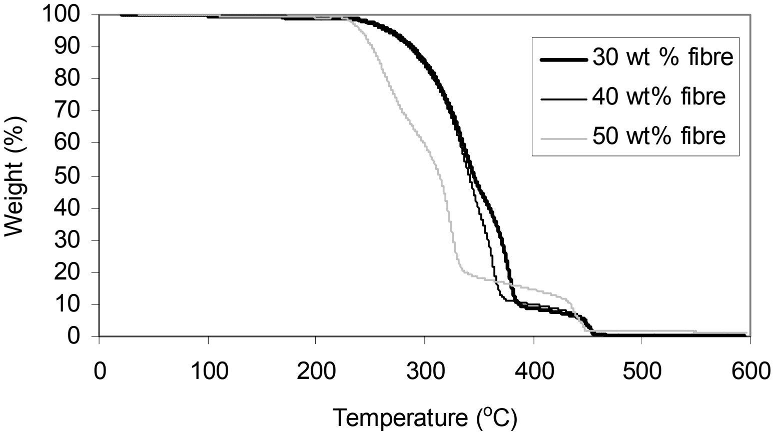


Figure 5. 5: TGA traces of composites with different fibre content (with 4 wt% MAPP).

Both E_a and T_{max} decreased with increased fibre volume fraction in composites. The positions of weight loss on the TGA trace shifted to lower temperatures (see Figure 5.5) with increased fibre volume fraction, suggesting decreased thermal stability, can be supported by decreased activation energies with increase fibre volume fraction in composites (see Table 5.2).

Table 5. 2: Thermal properties of composites:

Fibre content (wt%)	MAPP content (wt%)	Stage	Temperature range (^{o} C)	T_{max} (^{o}C)	Activation energy (kJ/mol)
30	4	1st	215-352	291	89
		2nd	352-422	387	67
		3rd	422-491	456	84
40	4	1st	221-343	282	80
		2nd	343-413	370	61
		3rd	413-491	455	83
50	4	1st	215-310	264	78
		2nd	310-413	342	60
		3rd	413-477	448	83

5.3.3 Effects of Fibre Length

TS and YM decreased with decreasing fibre length in composites (see Table 5.3), which could be due to a decrease in the reinforcing efficiency with decreasing fibre length [176]. Impact strength was found to decrease with decrease in fibre length, may be due to less stress transfer for short fibre. On the other hand, FS increased with decreasing fibre length, which could be due to the fibre shorter than the critical fibre length, would easily debond from the matrix inducing an increase in FS.

Table 5. 3: Properties of composites containing 40 wt% fibre (of different fibre length) and 4 wt% MAPP:

Fibre length (mm)	TS (MPa)	YM (MPa)	FS (%)	Impact strength (kJ/m^2)
3.07	43±1.4	4600±460	1.91±0.6	6.5
2.36	41±1.4	4553±500	1.99±0.5	6.2
0.95	37±1.2	3879±340	2.47±0.5	5.6

5.3.4 Effects of Fibre Beating

With increasing beating time, fibre length and fibre freeness decreased (see Figure 5.6 and 5.7). External fibrillation occurred resulting from partial or total removal of the primary wall [25] (see Figure 5.8).

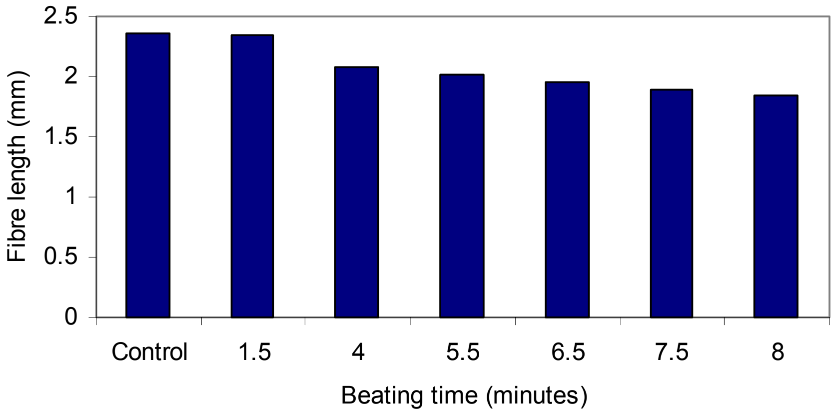


Figure 5. 6: Fibre length versus beating time of beaten and unbeaten fibre.

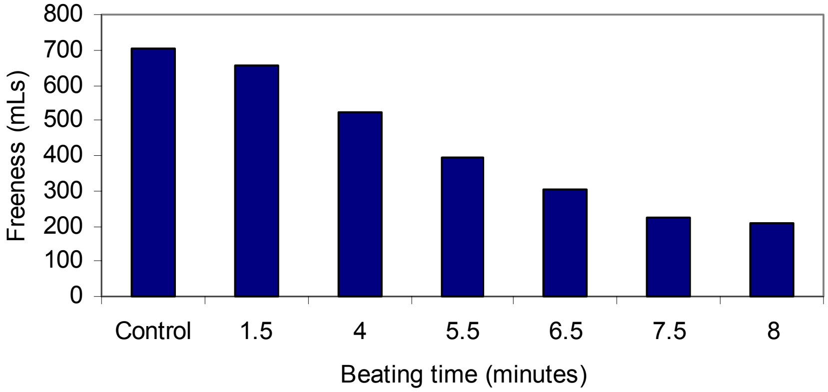
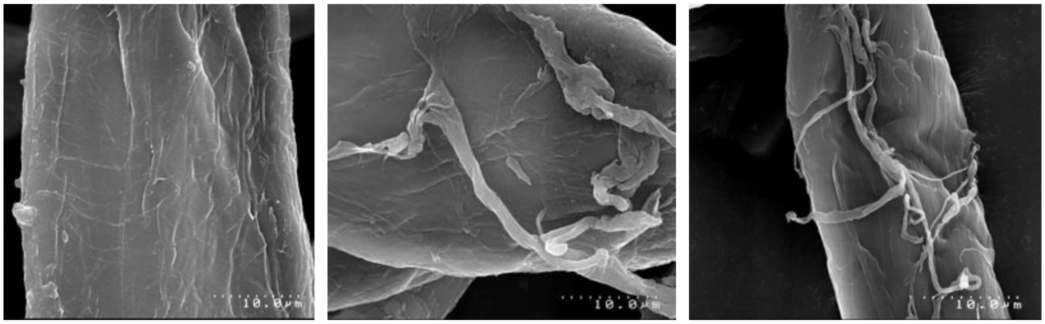


Figure 5. 7: Fibre freeness versus beating time of beaten and unbeaten fibre.

The surface charges of beaten and unbeaten fibre were measured using the streaming potential method over a range of pH values. Natural cellulose fibres are negatively charged as described in 3.3.2.1. The magnitude of negative zeta potential increased with increasing beating time (see Figure 5.9), which could be due to an increased specific surface area of the fibre after beating [25,177]. The $\zeta_{plateau}$ value for unbeaten fibre was -16 while the value was -20 for fibre beaten for 8 minutes.



(a) Control (b) 5.5 mins beaten (c) 8 mins beaten

Figure 5. 8: SEM of beaten and unbeaten fibre surfaces.

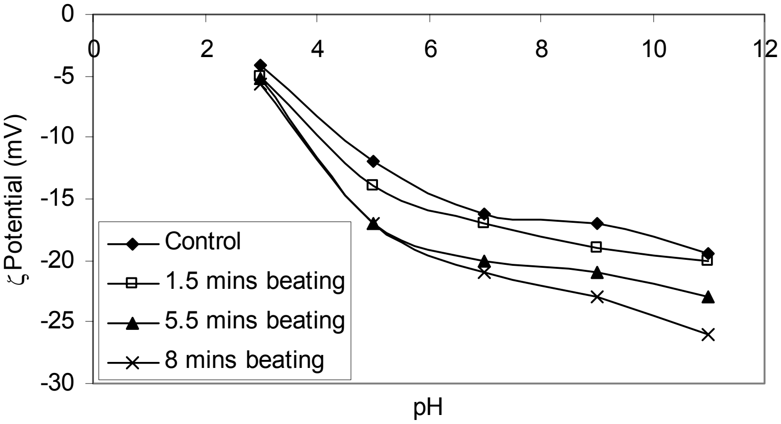


Figure 5. 9: Zeta potential versus pH of beaten and unbeaten fibres.

The properties of composites prepared with beaten fibre are presented in Figure 5.10 and 5.11. TS increased up to 45 MPa with increase in beating time up to 5.5 minutes, which could be due to the improvement of interfacial bonding between the fibre and the matrix resulting from the formation of micro fibrils and increased surface area, then decreased upon further beating, could be due to the fibre damage and reduction of fibre length [25]. YM was found to decrease with increasing beating time (see Figure 5.11), which may be due to the reduction of fibre length as observed in section 5.3.3.

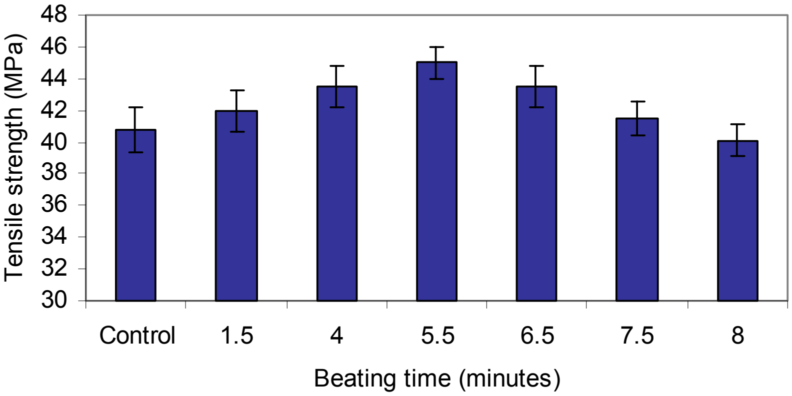


Figure 5. 10: Tensile strength of composites (40 wt% fibre and 4 wt% MAPP) versus fibre beating time.

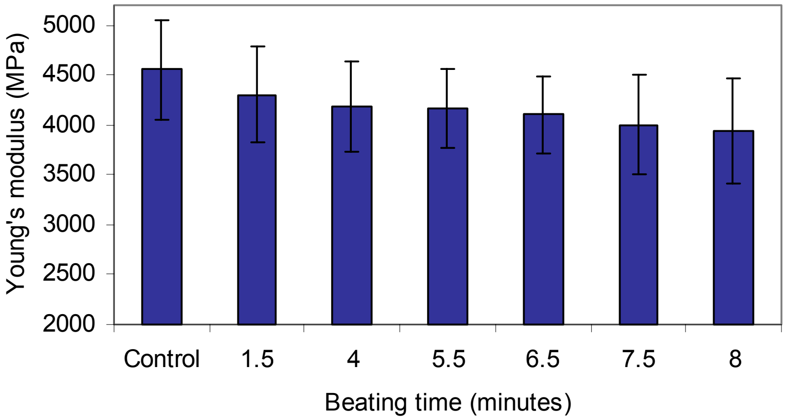
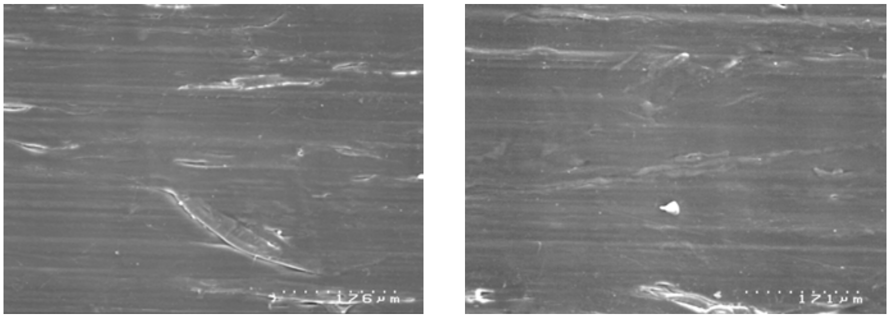


Figure 5. 11: Young's modulus of composites (40 wt% fibre and 4 wt% MAPP) versus fibre beating time.

5.3.5 Effects of Hygrothermal Ageing

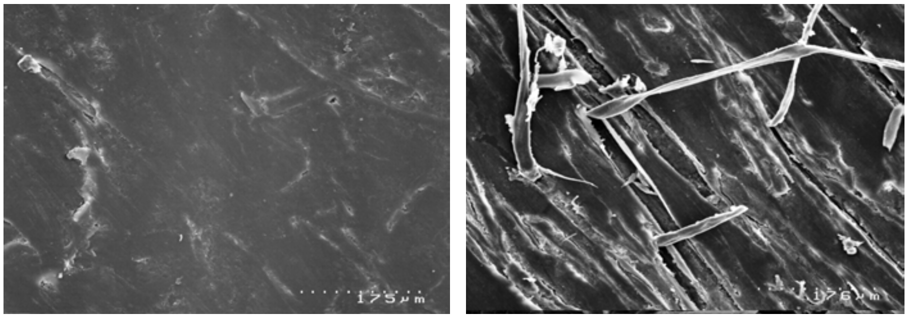
Hygrothermal ageing was carried out for four batches of composites (30, 40, 50 wt% fibre content with MAPP and 40 wt% fibre content without MAPP). The exposure of the samples to hygrothermal environments resulted in slight deteriorations of the surface texture, in the form of colour fading. Fibre became discernible from the matrix, where 30 wt% fibre composites with 4 wt% MAPP was found to be least affected and 40% fibre composites without MAPP was most affected (see Figure 5.12).

Hygrothermal ageing also resulted in increased sample thickness (see Figure 5.13). Degree of swelling increased with increased temperature and fibre content in composites. The composites without coupling agent showed swelling to a level almost twice that of composites with coupling agent.



(a) Composites of 30% fibre with 4% MAPP (unaged)

(b) Composites of 40% fibre without MAPP (unaged).



(a) Composites of 30% fibre with 4% MAPP (aged)

(b) Composites of 40% fibre without MAPP (aged)

Figure 5. 12: Least and most affected composite surfaces after ageing at 70^{o}C compared to unaged surface.

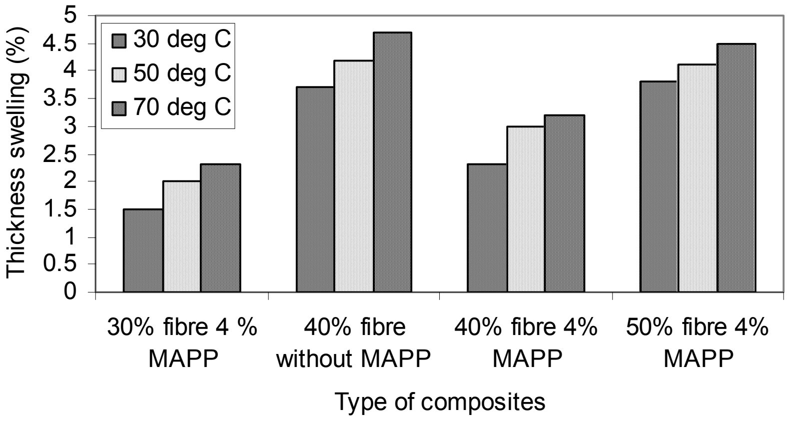


Figure 5. 13: Thickness swelling of composites after hygrothermal ageing.

Moisture absorption increased with increasing time for all composites until saturation at about 5 months (see Figure 5.14 and 5.15). As PP did not show any significant weight gain during this period, it seems likely that moisture only penetrated composites through the fibre and fibre matrix interface. The composites without coupling agent reached the saturation point more quickly than the composites with coupling agent. With increasing temperature, the rate of moisture absorption increased and the saturation point was reached quickly. Composites containing a higher amount of fibre showed higher rates of water absorption.

The diffusion coefficient calculated from the plot of M_t versus the square root of time (t) using Equation 2.9 (see section 2.9.1) is presented in Table 5.4. The equilibrium moisture content and the diffusion coefficient increased with increasing fibre content in composites as well as with increasing temperature.

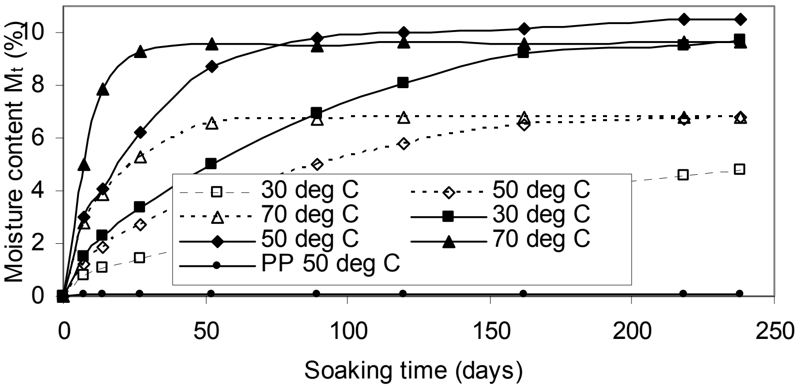


Figure 5. 14: Soaking time versus moisture content of 40 wt% fibre composites with 4 wt% MAPP (dotted line) and without MAPP (solid line) at 30, 50 and 70°C.

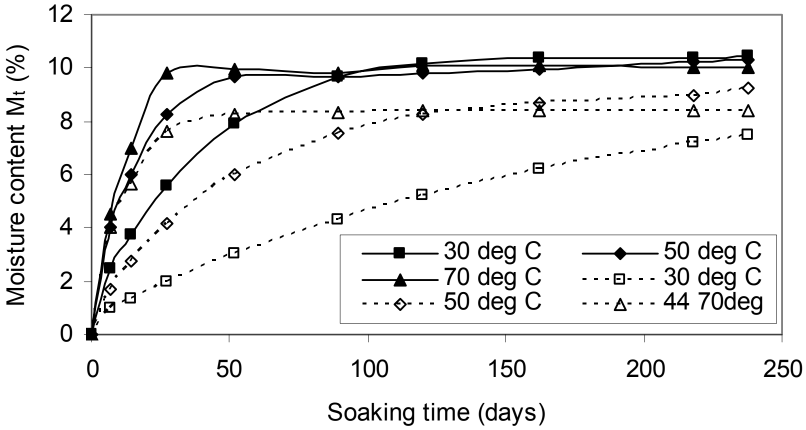


Figure 5. 15: Soaking time versus moisture content of 30 wt% fibre (dotted line) and 50 wt% fibre composites (solid line) (containing 4 wt% MAPP) at 30, 50 and 70°C.

As the fibre volume fraction increased, it would become more likely to have networked fibre which would serve as passages for water molecules to travel through the lattice from one side to another [178], resulting in increased diffusion coefficients and equilibrium moisture contents with increased fibre contents. Higher equilibrium moisture contents and diffusion coefficients for composites without coupling agent could be due to poor interfacial bonding, evident from SEM (see Figure 5.3).

Table 5. 4: Composites equilibrium moisture contents and diffusion coefficients:

Fibre content (wt%)	MAPP content (wt%)	Equilibrium moisture content (%), Diffusion coefficient (m^2/s)		
		30°C	50°C	70°C
30	4	4.60, -	6.75, $1.68x10^{-13}$	6.77, $5.08x10^{-13}$
40	0	10.41, $2.92x10^{-13}$	10.25, $5.68x10^{-13}$	10.05, $8.77x10^{-13}$
40	4	7.21, -	8.95, $2.43x10^{-13}$	8.40, $6.24x10^{-13}$
50	4	9.50, $1.80x10^{-13}$	10.47, $3.23x10^{-13}$	9.65, $10.60x10^{-13}$

TS and YM were found to decrease after hygrothermal ageing for all composites, and the extent of reduction was found to be higher for higher fibre content composites and for higher immersion temperatures (see Figure 5.16 and 5.17).

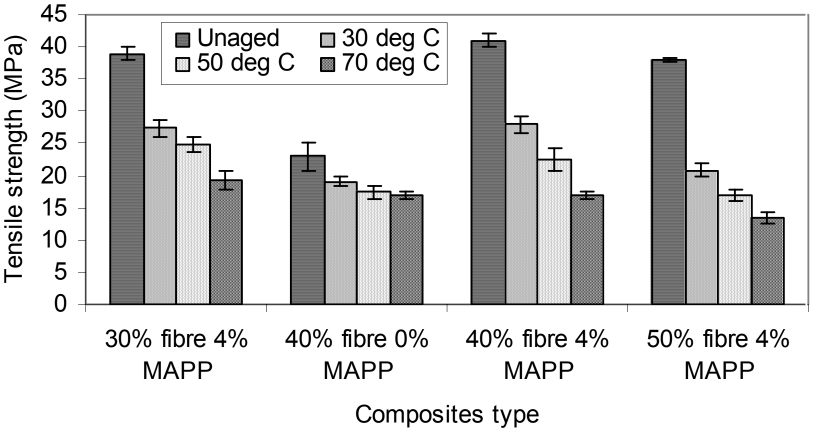


Figure 5. 16: Tensile strength of composites before and after hygrothermal ageing at different temperatures.

The reduction of TS and YM may be due to the degradation of fibre and /or the fibre matrix interface. SEM micrographs clearly showed the loss of adhesion between the fibre and matrix, characterised by the apparition of voids and fibre pull out (see Figure 5.18), where the most severely damaged composite fracture surfaces are presented. Degradation of the fibres by the water absorption can be seen and the microfibrils can be clearly observed (Figure 5.18) compared to virgin fibre (Figure 5.8a).

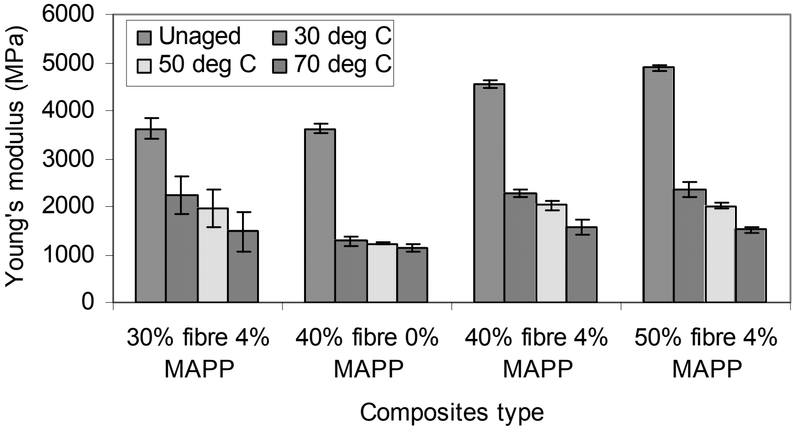
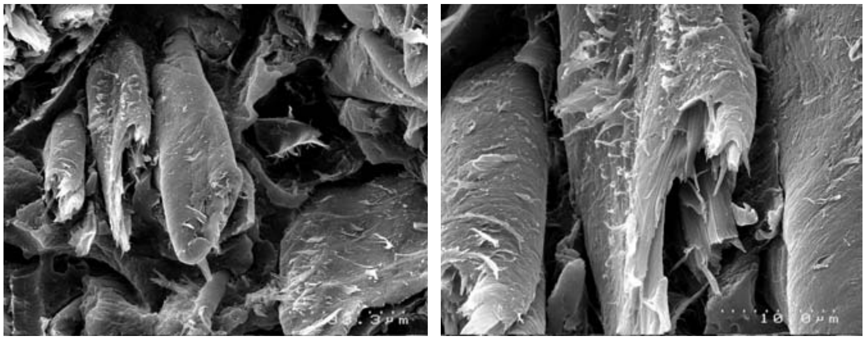


Figure 5. 17: Young's modulus of composites before and after hygrothermal ageing at different temperatures.



(a) Composites of 50% fibre with 4% MAPP

(b) Composites of 40% fibre without MAPP.

Figure 5. 18: Most affected composites fracture surfaces after hygrothermal ageing (at 70 °C).

The FS and impact strength were found to increase after hygothermal ageing for all composites (Figure 5.19 and 5.20), which may be due to water molecules acting as a plasticizer in the composite material [53]. However, the increment was found to be the highest for 30°C immersion. For increasing immersion temperature, both the FS and impact strength were generally found to decrease, which could be due to the increase in degradation of the fibre and /or fibre matrix interface at higher temperature.

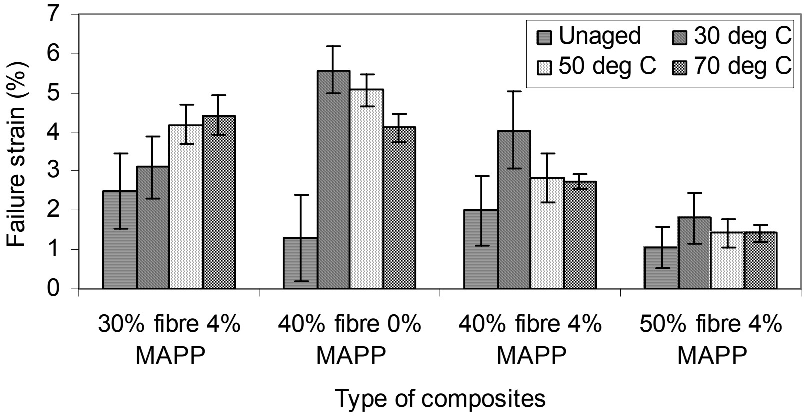


Figure 5. 19: Failure strain of composites before and after hygrothermal ageing at different temperatures.

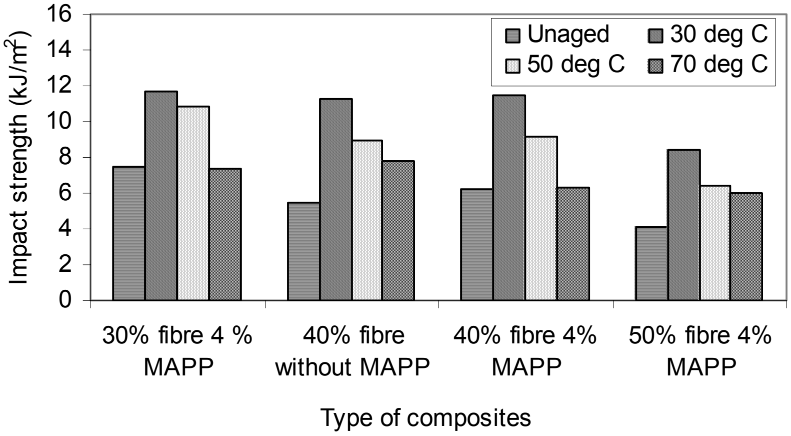


Figure 5. 20: Impact strength of composites before and after hygrothermal ageing at different temperatures.

CHAPTER -SIX

EFFECTS OF RECYCLING ON WOOD FIBRE (KRAFT) REINFORCED PP COMPOSITES

6.1 Introduction

This chapter describes the effects of recycling on the physical and mechanical properties of composites based on Kraft fibre reinforced PP composites. Composites, containing either 40 wt% or 50 wt% fibre, were recycled up to eight times. Composites were characterised using tensile testing, four point bend testing, impact testing, hardness testing, melt flow index, density measurement, digital microscopy, SEM, TGA, DSC and XRD. Change in fibre length during reprocessing was correlated with some empirical equations. Hygrothermal ageing behaviour of recycled composites was also investigated by immersing specimens in distilled water at 50°C over a 9 month period. Changes in physical and mechanical properties due to aging were correlated with number of times the materials were recycled.

6. 2 Experimental

6.2.1 Materials

Radiata pine *(Pinus Radiata)* bleached wood fibre (Kraft) was supplied by Tasman Pulp & Paper Co Ltd, New Zealand. The average fibre length was 2.36 mm. The matrix PP and coupling agent MAPP used in this study were the same as mentioned in 3.2.1.

6.2.2 Methods

Composite fabrication: Composites were fabricated with 40 wt% or 50 wt% fibre with 4 wt% MAPP and PP using a TSE-16-TC twin-screw extruder with a 15.6 mm screw blade diameter at 180^{o}C (maintaining 5 different temperature zones 100, 130, 160, 180 and 175°C from feed zone to exit die) and a screw speed setting of 100 rpm. Prior to extrusion, wood fibre, PP and coupling agent were dried in an oven at 80°C for a minimum of 48 hours. Following extrusion, the material was pelletised into lengths of less than 5 mm and injection moulded into specimens for tensile and 4-point bend testing using a BOY 15-S injection moulder. Specimens for tensile, 4-point bend testing and impact testing were randomly selected from approximately one hundred and fifty of each type to evaluate the mechanical properties. Impact test specimens were produced from standard 4-point bend test samples by polishing to give a suitable sample width. The remaining specimens were granulated and injection moulded. Again, specimens were randomly selected from these recycled materials for physical and mechanical property evaluation. The procedure of injection moulding and granulation was repeated a total of eight times.

Composite characterisation: Composites were characterised using tensile testing, four point bend testing, impact testing, hardness testing, melt flow index, density measurement, SEM, TGA, DSC and XRD (methods described in 3.2.2). In addition, digital microscopy was used to analyse the fibre distribution in composites.

Digital microscopy: Following mounting, grinding and polishing, the fibre distribution and alignment of the fibre in the composites was observed using an Olympus B X 60 microscope.

Extraction of fibre from composites: Fibre was extracted from composites by dissolving the matrix in hot xylene at 110°C, followed by soxhlet extraction in xylene for 72 hours.

Fibre length measurement: The length and fibre distribution of virgin and extracted fibre from the composites was measured using a Kajaani FS-200 electronic sequential fibre analyzer. Fibre counts of about 15,000-20,000 were used to determine the fibre length distribution.

Water absorption: Water absorption studies were performed at 50^{o}C following the ASTM D 570-98: Standard Test Method for Water Absorption of Plastics (methods described in 5.2.2).

6.3 Results and discussion

6.3.1 Effects of Recycling on Mechanical Properties

Very little change on TS and YM was found for PP during recycling (see Figure 6.1 and 6.2). The TS and YM of the 40 wt% fibre composites decreased with increased number of times the materials were recycled in a linear fashion (see Figure 6.1 and 6.2). The virgin composites showed an average TS of 41 MPa and YM of 4553 MPa which reduced after being recycled 8 times to 31 MPa and 3800 MPa respectively.

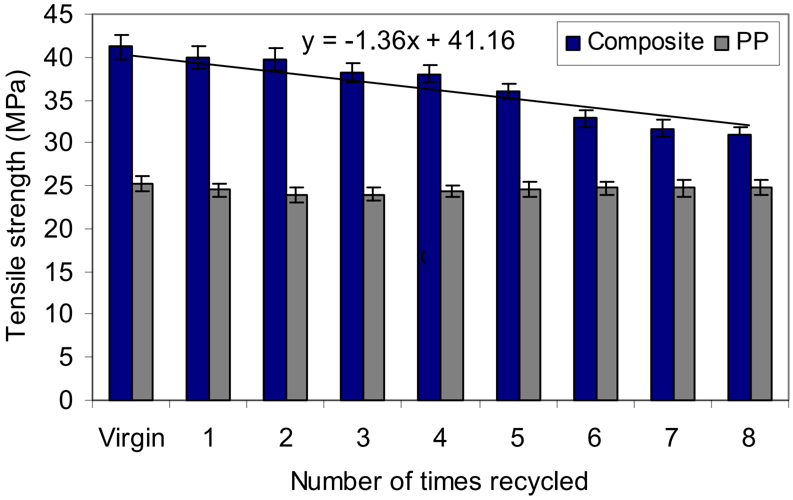


Figure 6. 1: Tensile strength of virgin and recycled composites (40 wt% fibre) and PP.

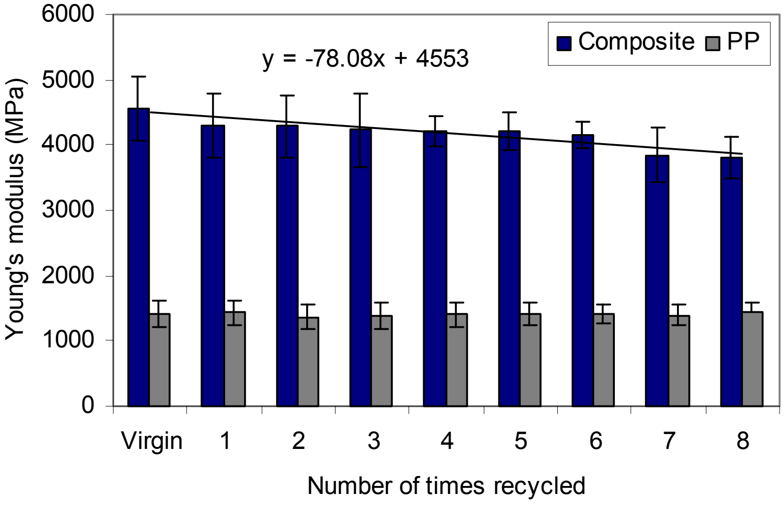


Figure 6. 2: Young's modulus of virgin and recycled composites (40 wt% fibre) and PP.

TS and YM for the 50 wt% fibre composites are presented in Figure 6.3 and 6.4. Based on a Rule of Mixtures type model (see equation 2.1-2.4) the increase in fibre content in composites would be expected to increase the TS and YM.

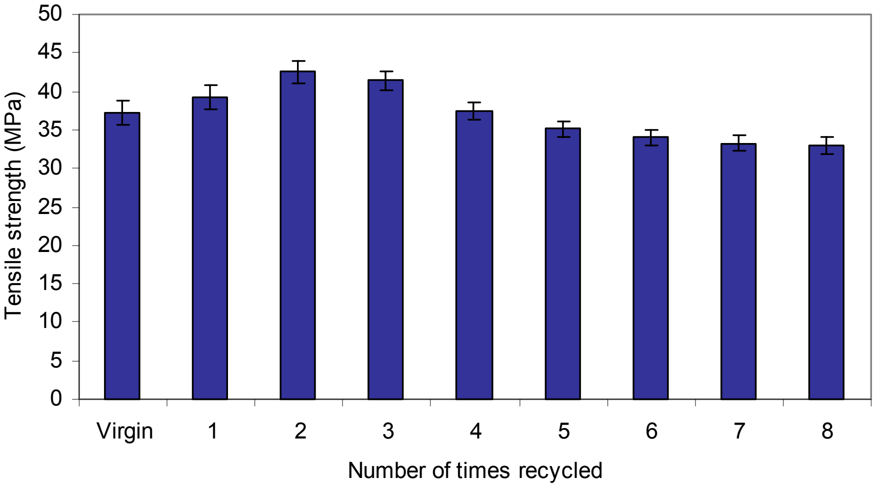


Figure 6. 3: Tensile strength of virgin and recycled composites (50 wt% fibre).

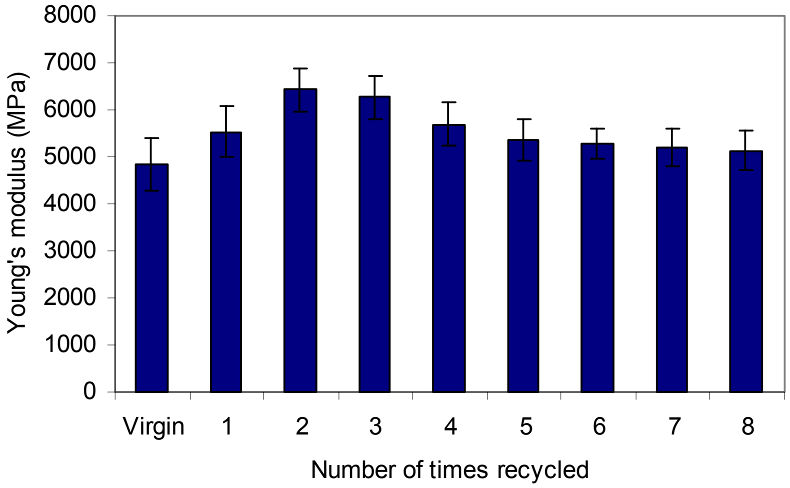


Figure 6. 4: Young's modulus of virgin and recycled composites (50 wt% fibre).

However, TS was initially lower for 50 wt% fibre than for 40 wt% fibre content composites (see Figure 6.1 and 6.3) which is likely to be due to the limited dispersion of fibre in composites at higher fibre content due to the increase in viscosity as indicated by the reduction of melt flow index (see Table 6.1).

Table 6. 1: Melt flow index of composites and PP:

Type	Melt flow index (g/10 min)
PP	29.40
Composite with 40 wt% fibre	0.90
Composite with 50 wt% fibre	0.14

However, TS of 50 wt% fibre composites increased with increased number of times the materials were recycled up to 2 times from 37 MPa for virgin composites to 42 MPa for the composites recycled 2 times (see Figure 6.3), which was considered to be due to improved fibre dispersion, but then decreased with further recycling and overall 11% reduction of TS was found for the composites after recycled 8 times, compared to the virgin composites. As expected by the Rule of mixtures, YM was higher for 50 wt% fibre content than 40 wt% fibre content composites (see Figure 6.2

and 6.4) and also increased with increased number of times the materials were recycled up to 2 times, and then decreased upon further recycling. During recycling, the occurrence of improvement of fibre dispersion and fibre damage occur simultaneously, but at lower levels of recycling the former seems to be predominant, although at higher levels of recycling the latter appears to have an overriding influence.

The trend for TS of the 40 wt% composites versus the number of times the materials were recycled (see Figure 6.1) was found to be closely represented by the empirical equation:

$$\sigma_N = \sigma_0 + aN \tag{6.1}$$

where σ_N is the tensile strength of the composites recycled N times and a is the slope of the TS versus number of times recycled graph. A 25% reduction in TS and 16% reduction in YM was observed for the composites after they were recycled 8 times (see Figure 6.5).

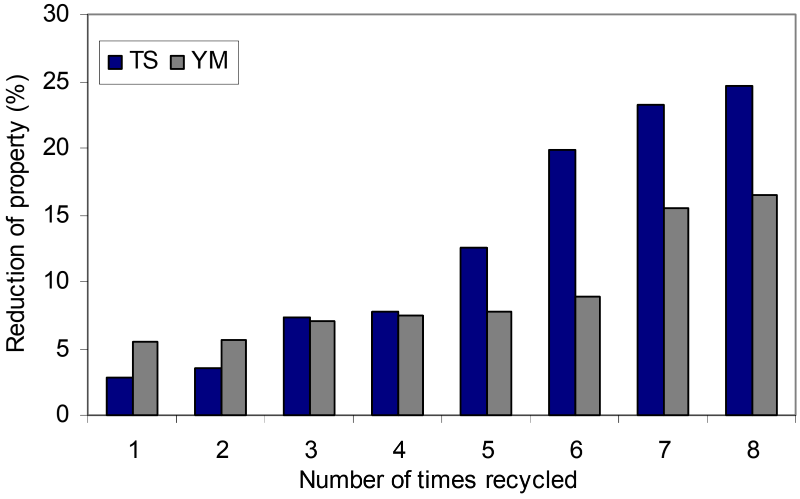


Figure 6. 5: Reduction in TS and YM of composites during recycling (40 wt% fibre).

FS of PP was found to be greater than 500% (the maximum range of the tensile tester), but was found to be reduced drastically by the addition of fibre to about 2% for 40% fibre composites and 1.3% for 50 wt% fibre composites (see Figure 6.6 and 6.7). The FS of both 40 wt% and 50 wt% fibre composites increased exponentially with increased number of times the materials were recycled.

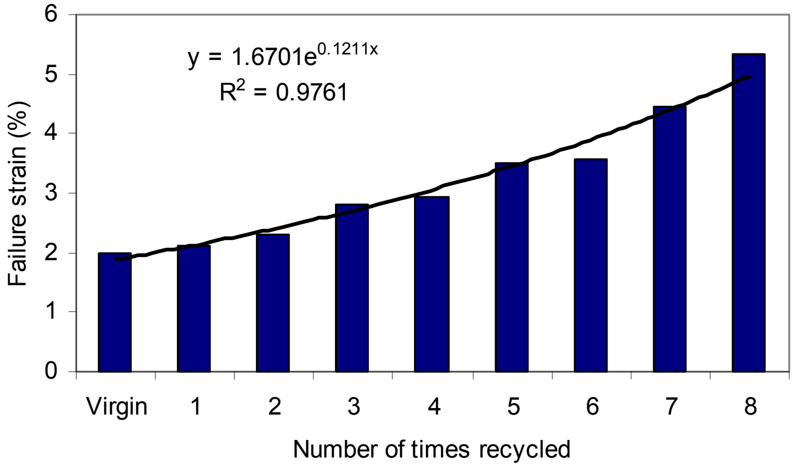


Figure 6. 6: Failure strain of virgin and recycled composites (40 wt% fibre).

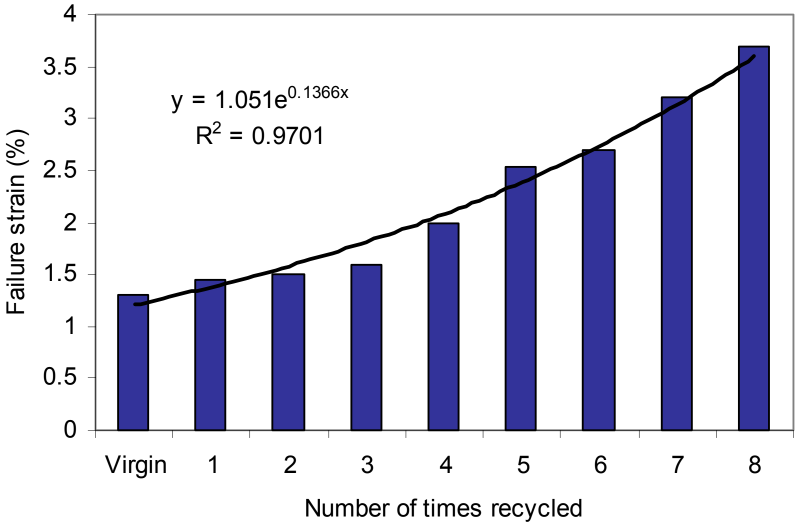


Figure 6. 7: Failure strain of virgin and recycled composites (50 wt% fibre).

Flexural tests, impact tests and hardness tests were also carried out for 40 wt% fibre composites. Flexural strength and flexural modulus were found to decrease with increased number of times the materials were recycled (see Figure 6.8 and 6.9).

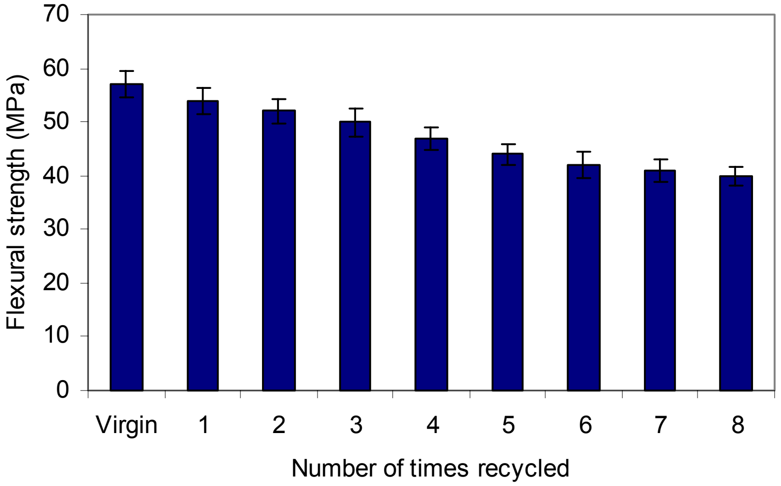


Figure 6. 8: Flexural strength of virgin and recycled composites (40 wt% fibre).

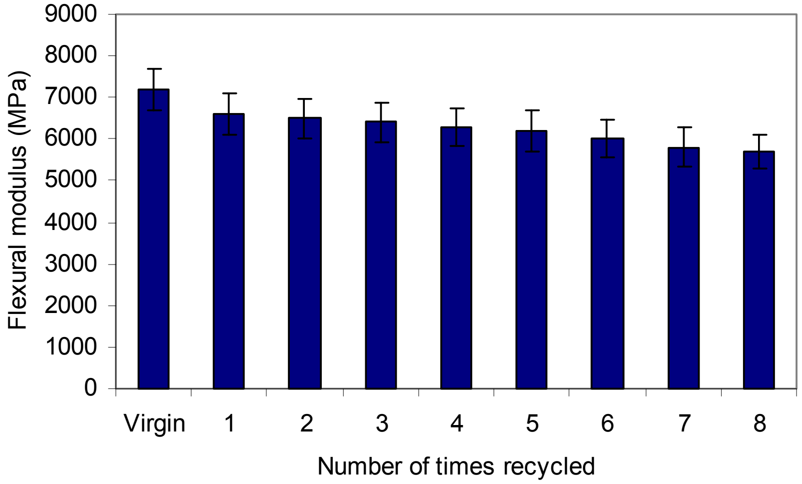


Figure 6. 9: Flexural modulus of virgin and recycled composites (40 wt% fibre).

The virgin 40 wt% fibre composites showed an average flexural strength and flexural modulus of 57 MPa and 7200 MPa respectively, which reduced after being recycled 8 times to 40 MPa and 5700 MPa respectively (see Figure 6.8 and 6.9). Impact strength was also found to decrease for both PP and composites containing 40 wt% fibre during recycling from 10.5 kJ/m^2 and 6.2 kJ/m^2 respectively for virgin PP and composites to 6.2 kJ/m^2 and 3.2 kJ/m^2 respectively after the materials were recycled 8 times (see Figure 6.10). The hardness of the composites increased with recycling (see Figure 6.11).

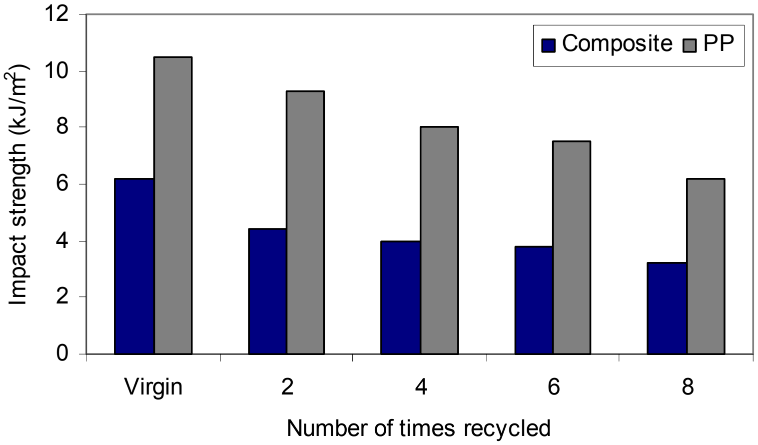


Figure 6. 10: Impact strength of virgin and recycled composites and PP (40 wt% fibre).

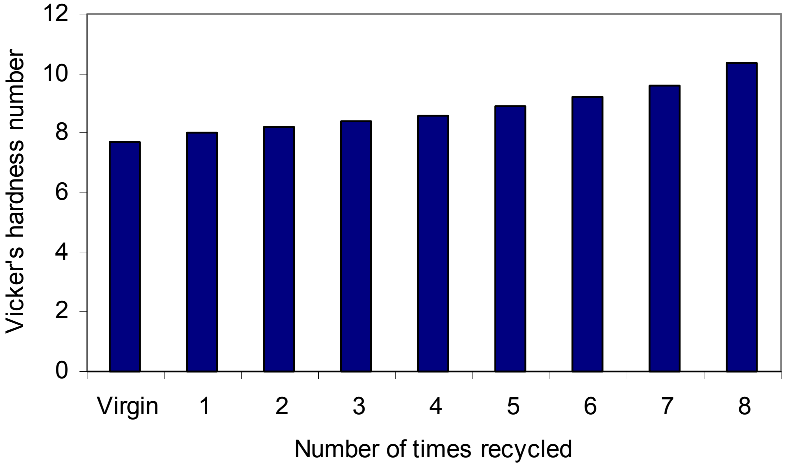


Figure 6. 11: Vicker's hardness of virgin and recycled composites (40 wt% fibre).

One of the reasons for the changes in mechanical properties is likely to be due to the fact that reprocessing incurred some fibre damage. The average fibre length was found to decrease from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the 40 wt% fibre composites recycled 8 times (see Figure 6.12). In addition, the amount of fibre fines (fibre length less than 0.20 mm) was found to increase (see Figure 6.13) and the length distribution of fibres became narrower and reduced to shorter fibre lengths (see Figure 6.14 a-d) with increased number of times the materials were recycled. The shorter fibre lengths and the increased fines percentage with recycling were also observable by light microscopy (see Figure 6.15). This would be expected to reduce reinforcing efficiency leading to the observed reduction in TS, YM, flexural strength and flexural modulus [179].

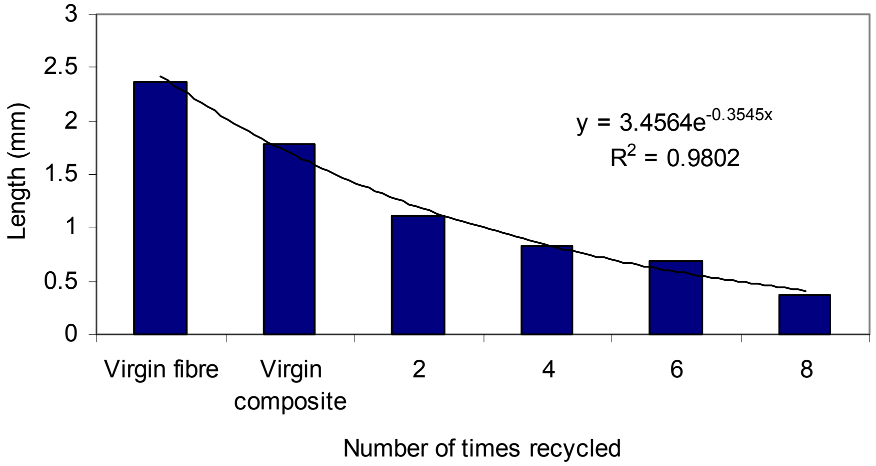


Figure 6. 12: Weighted average fibre length of virgin fibre and the fibre extracted from composites.

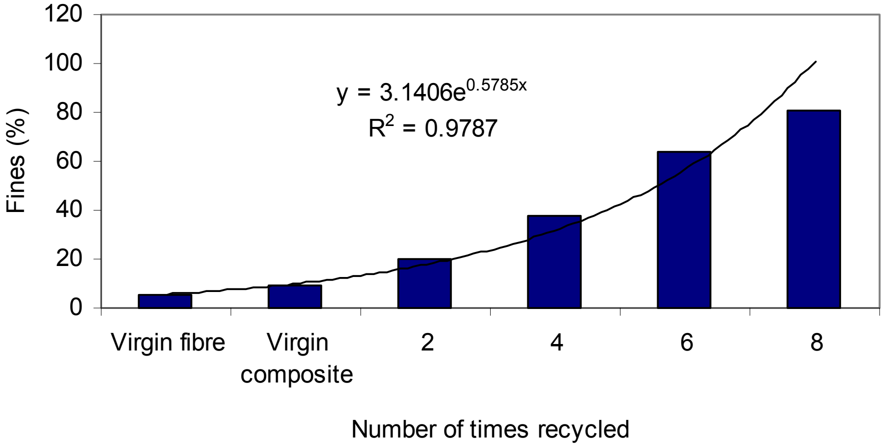


Figure 6. 13: Fines (fibre length less than 0.20 mm) in the virgin fibre and the fibre extracted from composites.

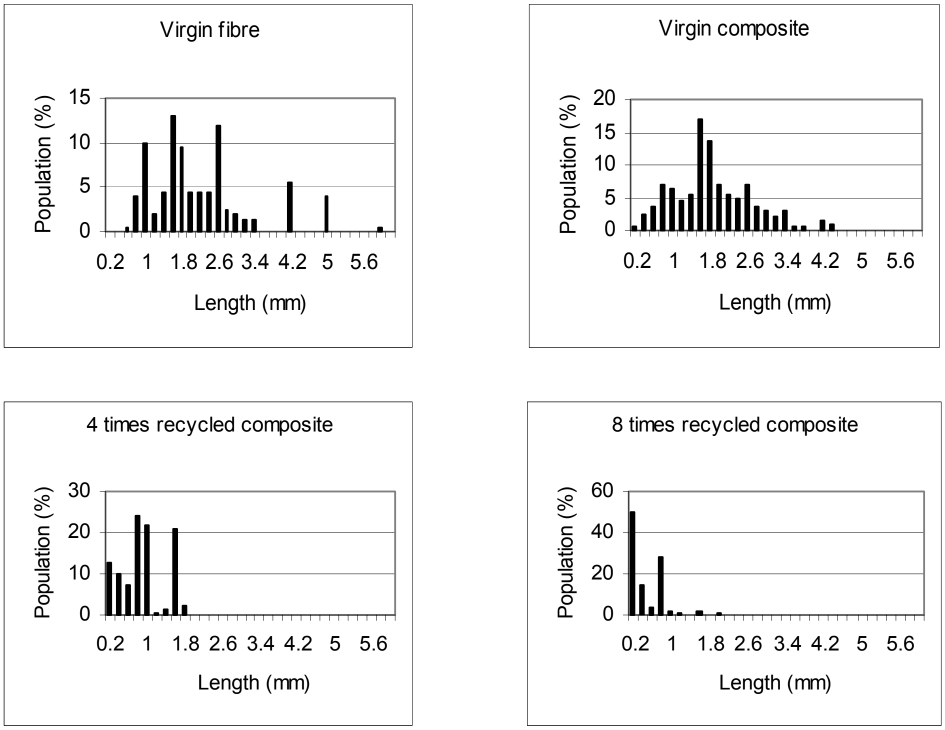
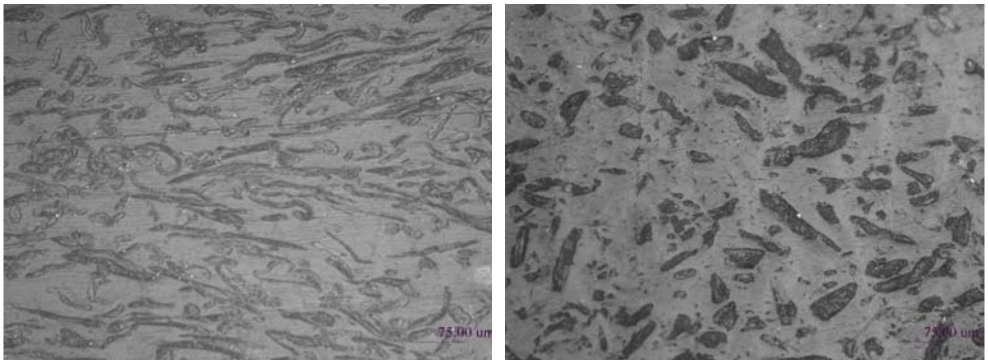


Figure 6. 14: Fibre length distribution of virgin fibre and the fibre extracted from composites.



(a) virgin composite (b) 8 times recycled composite

Figure 6. 15: Micrographs of composites surface showing fibre distribution in composites.

The increase in FS was likely to be due to less constraint from shorter fibre and the reduction of micro voids as evaluated by the increased density of composites (see Figure 6.16). The reduction of impact strength could be due to the reduction of molecular weight of PP during recycling. The increase in hardness may have resulted from the reduction of micro voids and the increase in composite density with increased recycling.

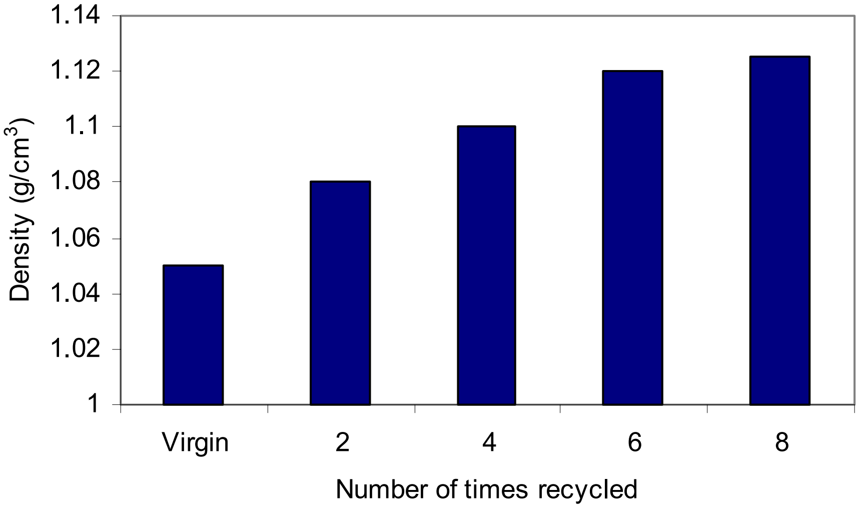


Figure 6. 16: Density of virgin and recycled composites.

The change in average fibre length can be correlated with the number of times the composite materials were recycled by the following empirical equation:

$$l_N = l_0 e^{-bN} \tag{6.2}$$

where l_N is the average fibre length at any recycled composites, l_0 is the length of virgin fibre, and b is the slope of fibre length versus number of times recycled graph. Rearranging Equation 6.2 to give:

$$\ln\left(\frac{l_0}{l_N}\right) = bN \tag{6.3}$$

and combining with Equation 6.1 gives TS as a function of the ratio of the original fibre length to the reduced length that has occurred with recycling as follows:

$$\sigma_N = \sigma_0 + \frac{a}{b}\ln\left(\frac{l_0}{l_N}\right) \tag{6.4}$$

The theoretical TS calculated by using Equation 6.4 is compared with experimental values in Figure 6.17 and shows good agreement.

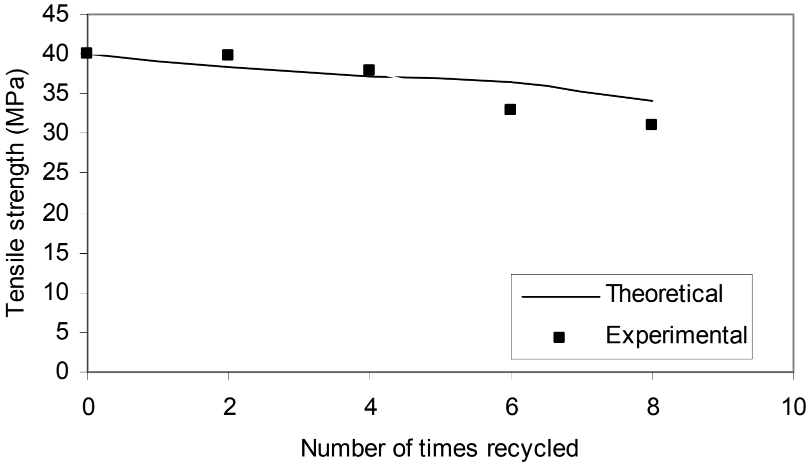


Figure 6. 17: Theoretical and experimental value of TS (Verification of Equation 6.4) for mixture of virgin and recycled composites.

6.3.2 Effects of Recycling on Thermal Stability and Crystallinity

The DSC curves for PP and 40 wt% fibre composites are shown in Figure 6.18 and 6.19 suggesting the reduction of melting temperature (T_m) with recycling. The percentage crystallinity of virgin and recycled PP and that of the PP in the composites was calculated using Equation 4.2 (see section 4.3.2) and is presented in Table 6.2. The crystallinity of PP only samples and PP in the composites increased with increased number of times the materials were recycled (see Table 6.2) which is likely to be as a result of molecular weight reduction [180]. The increase in crystallinity was also supported by the XRD traces (see Figure 6.20 and 6.21).

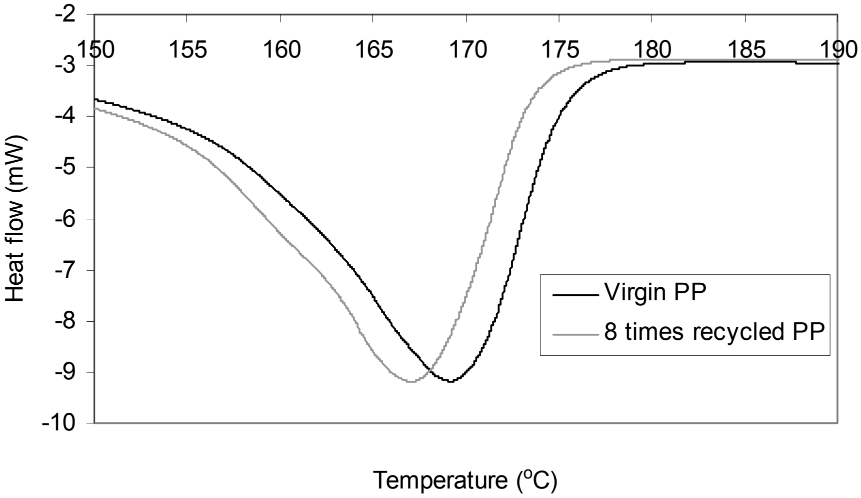


Figure 6: 18 DSC curves of virgin and recycled PP.

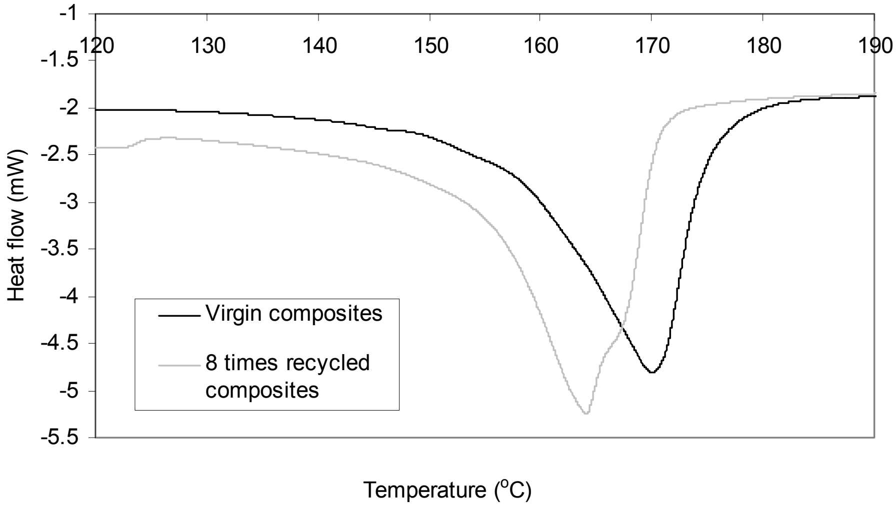


Figure 6. 19: DSC curves of virgin and recycled 40 wt% fibre composites.

The T_m for PP alone showed very little change during recycling (see Table 6.2). The T_m for PP in virgin composites was found to increase slightly from 169.2°C for virgin PP to 170.5 °C for PP in the virgin composites, which is likely to be due to the fibres acting as nucleating sites and increasing the crystallinity [181], however, the T_m for PP in composites decreased slightly with increased number of times the materials were recycled which could be due to the reduction of molecular weight [180].

Table 6. 2: Melting point and crystallinity of PP only samples and the PP in composites:

Sample	Melting Point T_m (°C)	I_{DSC}
Virgin PP	169.2	38.8
4 times recycled PP	168.8	39.0
8 times recycled PP	168.7	40.1
Virgin composite	170.5	43.7
4 times recycled composite	167.7	44.9
8 times recycled composite	167.0	45.2

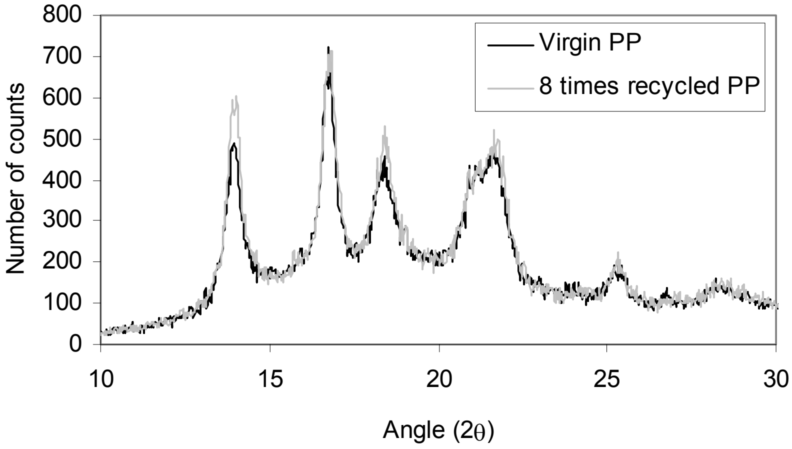


Figure 6. 20: XRD traces of virgin and recycled PP showing higher intensity for recycled PP.

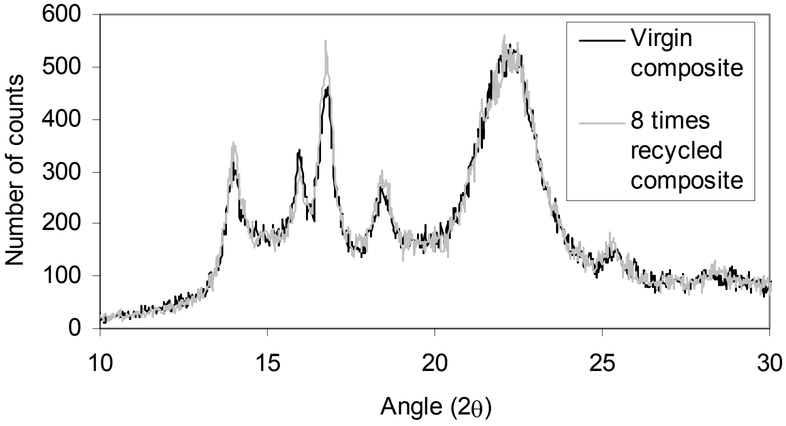


Figure 6. 21: XRD traces of virgin and recycled 40 wt% fibre composites showing higher intensity for recycled composites.

Typical DTA and TGA traces for virgin PP as well as recycled PP and the composites are shown in Figures 6.22-6.25. Three stages of decomposition were observed for all composites and PP samples (see Figure 6.22 and 6.23), starting with dehydration and decomposition of volatile components at around 260°C, followed by rapid weight loss for oxidative decomposition and finally slow decomposition corresponding to formation of char as the temperature increased [182]. Activation energies for the various stages of thermal degradation were determined from the TGA graphs using the Broido equation (Equation 4.1), following method described in 4.3.1 and are presented in Table 6.3. T_{max} and E_a for PP and composites were generally found to increase with increased number of times the materials were recycled. The positions of weight loss on the TGA traces both for PP and composites shifted to higher temperatures with increased number of times the materials were recycled (see Figure 6.24 and 6.25) suggesting increased thermal stability. The increase in thermal stability is likely to be due to the increase in crystallinity of PP [183] resulting from molecular weight reduction [180] and better interfacial bonding during recycling, supported by observations of fracture surfaces (see Figure 6.26).

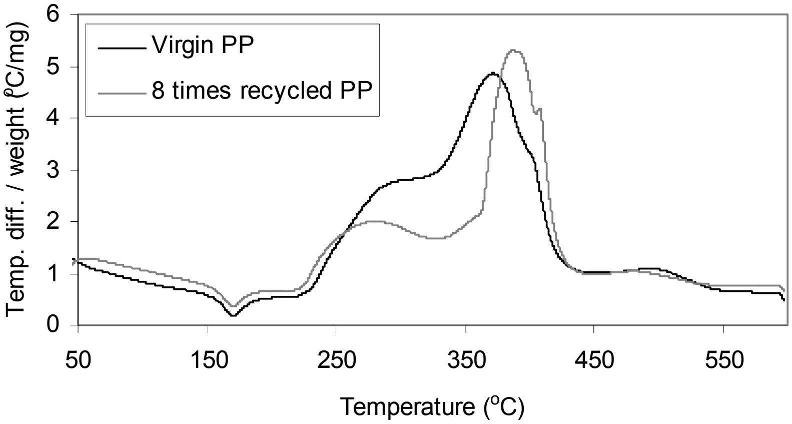


Figure 6. 22: DTA traces for virgin and recycled PP.

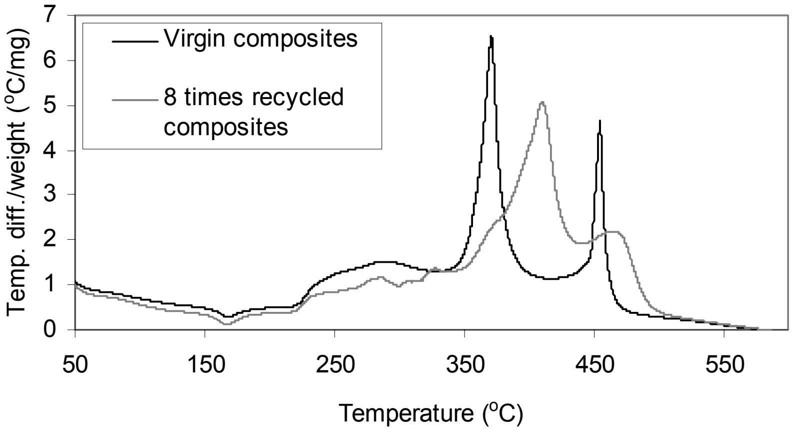


Figure 6. 23: DTA traces for virgin and recycled 40 wt% fibre composites.

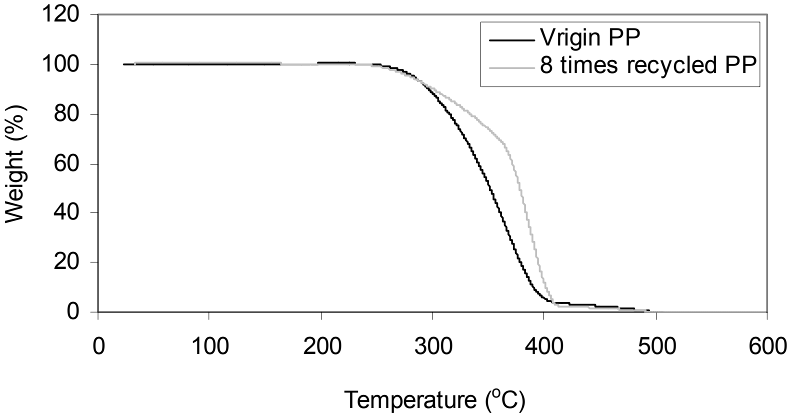


Figure 6. 24: TGA curves of virgin and recycled PP.

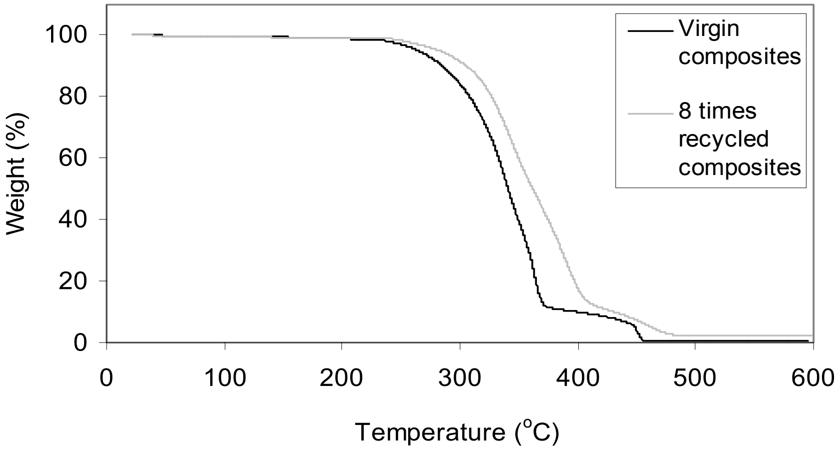
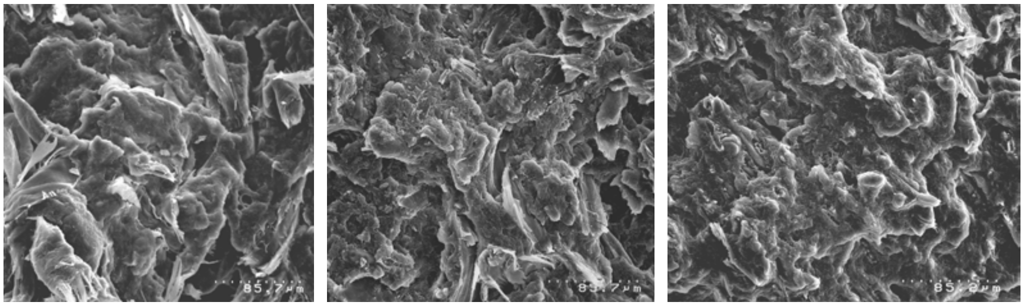


Figure 6. 25: TGA curves of virgin and recycled 40 wt% fibre composites.



Virgin 4 times recycled 8 times recycled

Figure 6. 26: SEM of composite fracture surface showing less pull out at higher number of times the materials were recycled.

Table 6. 3: Thermal properties of PP and composites:

Sample	Stage	Wt. loss (%)	Temp. range (^{o} C)	T_{max} (^{o}C)	Activation energy E_a (kJ/mol)
Virgin PP	1st	26	224-320	293	104
	2nd	70	320-445	375	78
	3rd	3	445-534	504	43
8 times recycled PP	1st	18	224-328	285	115
	2nd	79	320-445	390	84
	3rd	2	445-534	506	50
Virgin composite	1st	61	226-351	285	85
	2nd	31	351-436	371	68
	3rd	7	436-508	455	60
8 times recycled composite	1st	30	230-340	289	87
	2nd	52	340-447	412	71
	3rd	15	470-512	470	81

6.4.3 Mixing Virgin and Recycled Composites

The TS of composites prepared with the mixture of 50 wt% virgin and 50 wt% (2-8 times) recycled composites are shown in Figure 6.27, and it can be seen that TS decreased from 41 MPa for virgin composites to 37.5 MPa for 50 wt% virgin + 50 wt% 8 times recycled composites. TS of the mixture are expected to follow the Rule of Mixtures equation (Equation 2.1 in section 2.5.6) rewritten for more clarity as follows:

$$\sigma_{mix} = \left(\sigma_0 \chi_0 + \sigma_N \chi_N\right) \tag{6.5}$$

where σ_o and σ_N are the TS of virgin and recycled composites, χ_0 and χ_N are the volume fraction of virgin and recycled composites, and *N* is the number of times the materials were recycled. Good agreement with the Rule of Mixtures equation was obtained (see Figure 6.27).

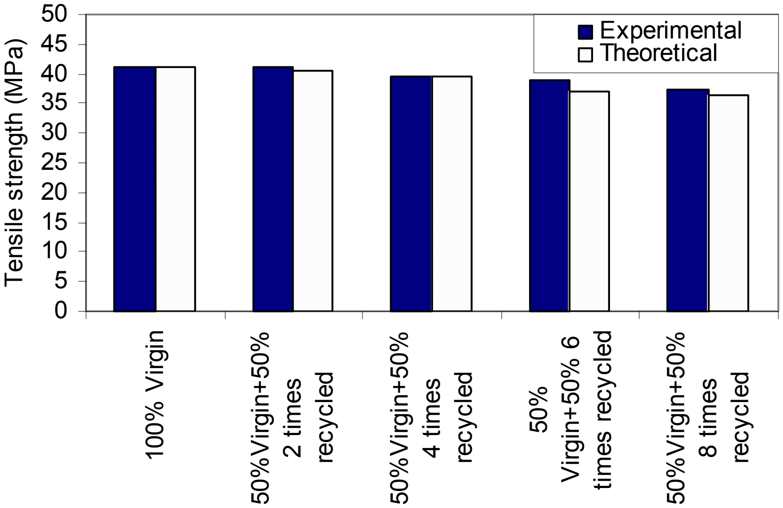
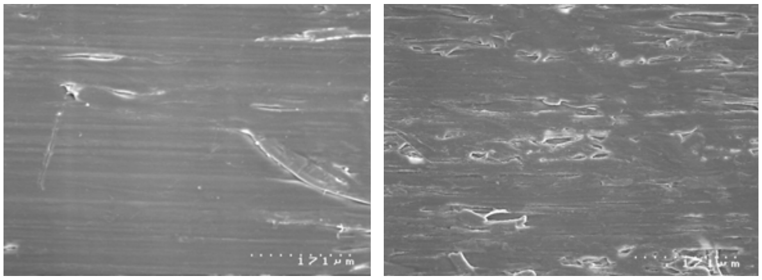


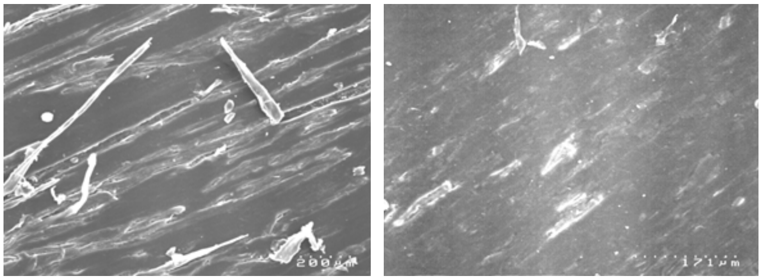
Figure 6. 27: Tensile strength of composites produced from the mixture of virgin and recycled composites (40 wt% fibre)

6.4.4 Hygrothermal Ageing of Recycled Composites

The exposure of the samples to hygrothermal ageing resulted in slight deterioration of the surface texture in the form of colour fading. Fibre also became discernible from the matrix as compared to unaged composites (see Figure 6.28). However, after aging, less fibre can be seen from the composites surface recycled 8 times than that from the virgin composites surface, which could be due to the better interfacial bonding between fibre and matrix as observed in Figure 6.26.



(a) Unaged virgin (b) Unaged 8 times recycled



(c) Aged virgin (d) Aged 8 times recycled

Figure 6. 28: SEM of virgin and recycled composites surface before and after hygrothermal ageing.

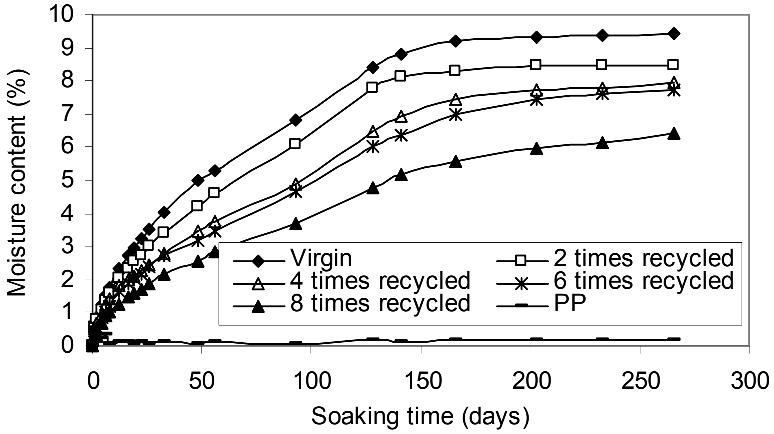


Figure 6. 29: Moisture content versus soaking time of virgin and recycled composites and PP.

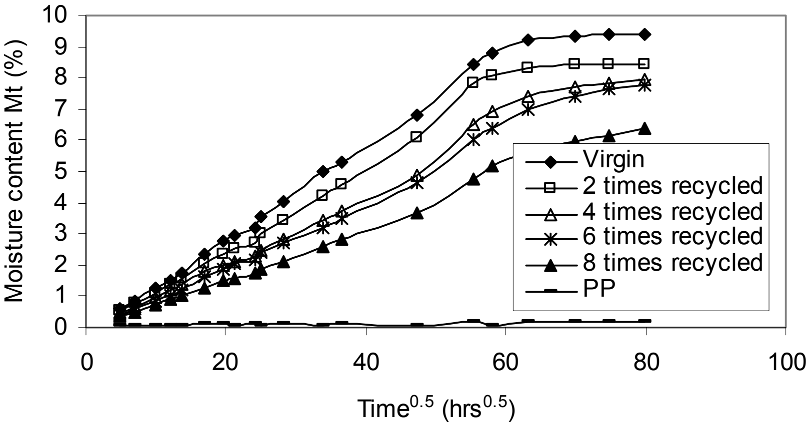


Figure 6. 30: Moisture content versus square root of time of virgin and recycled composites and PP.

Moisture absorption increased with increasing time for all composites until saturation at about 5 months (see Figure 6.29). As no significant weight gain was found for PP during this period, it seems likely that moisture only penetrated into the composites through the fibre and fibre matrix interface. The diffusion coefficient of moisture absorption was calculated using Equation 2.9 (see section 2.9.1) from the plot of M_t versus the square root of time (t) (see Figure 6.30). Both the equilibrium moisture content and diffusion coefficient decreased with increased number of times the materials were recycled (see Table 6.4).

Table 6. 4: Equilibrium moisture content and diffusion coefficient of virgin and recycled composites:

Number of times recycled	Equilibrium moisture content M_∞(%)	Diffusion coefficient D (m^2/s)
Virgin composite	9.42	$2.54x10^{-13}$
2 times recycled composite	8.46	$1.53x10^{-13}$
4 times recycled composite	7.93	$1.19x10^{-13}$
6 times recycled composite	7.75	$1.10x10^{-13}$
8 times recycled composite	6.41	$1.01x10^{-13}$

Equilibrium moisture content and diffusion coefficient decreased respectively from 9.42% and 2.54×10^{-13} m^2/s for virgin composites to 6.41% and 1.01×10^{-13} m^2/s for composites recycled 8 times. The decrease in moisture content and diffusion coefficient with increased number of times the materials were recycled can be explained by a number of effects. As the fibre length decreased with increased number of times the materials were recycled, it would have been more difficult to form finite clusters which serve as passages for water molecules to travel through the lattice from one side to another [184]. Also, reduction of micro voids as evaluated by the increased density of composites would be expected to result in a decrease in moisture content and diffusion coefficient with increased recycling. In addition, recycling increased the crystallinity of PP and improved the interfacial bonding between the fibre and the matrix, as supported by SEM (see Figure 6.26), which would also be expected to reduce the moisture absorption.

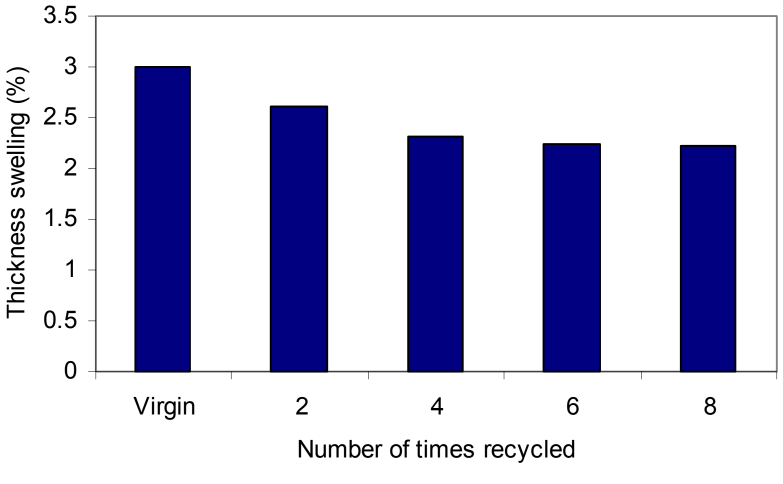


Figure 6. 31: Thickness swelling of virgin and recycled composites after hygrothermal ageing.

Thickness swelling was found for virgin and recycled composites after hygrothermal ageing (see Figure 6.31) the extent of which was found to decrease with recycling, such that after ageing, the virgin composites showed an increase in swelling by 3.7% which reduced down to 2.2% for composites recycled 8 times. This again could be due to the reduction of micro voids and better interfacial bonding with an increased number of times the materials were recycled.

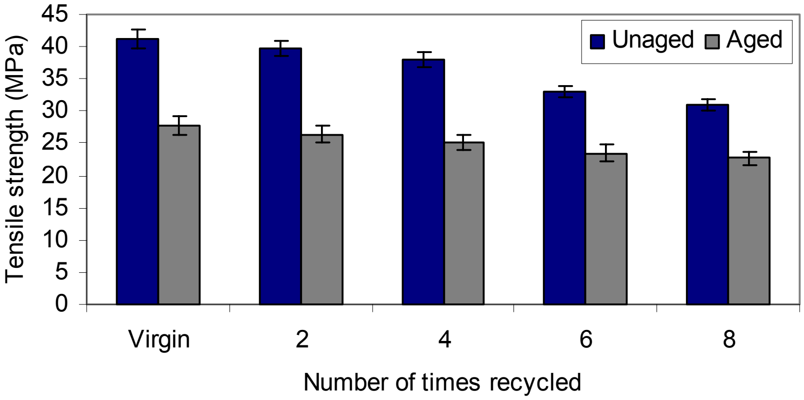


Figure 6. 32: Tensile strength of virgin and recycled composites before and after hygrothermal ageing.

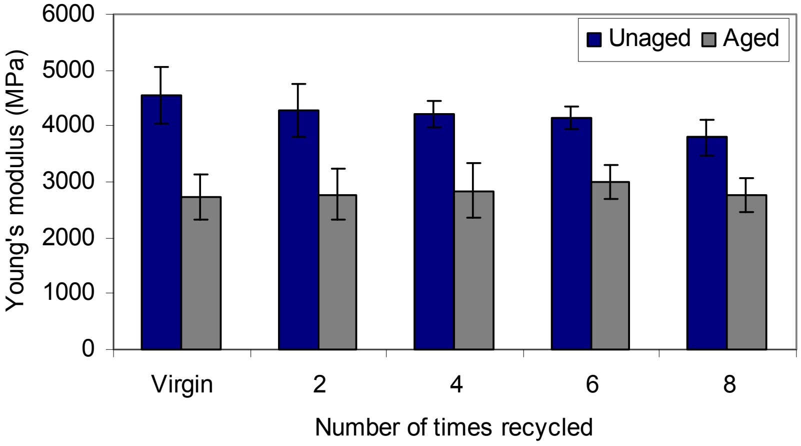


Figure 6. 33: Young's modulus of virgin and recycled composites before and after hygrothermal ageing.

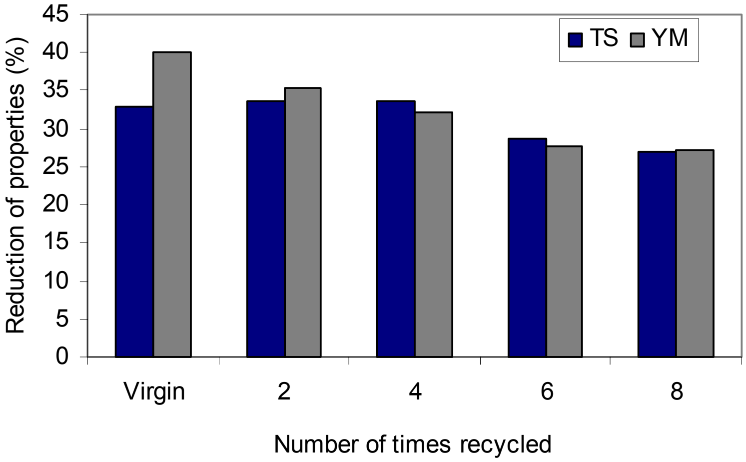
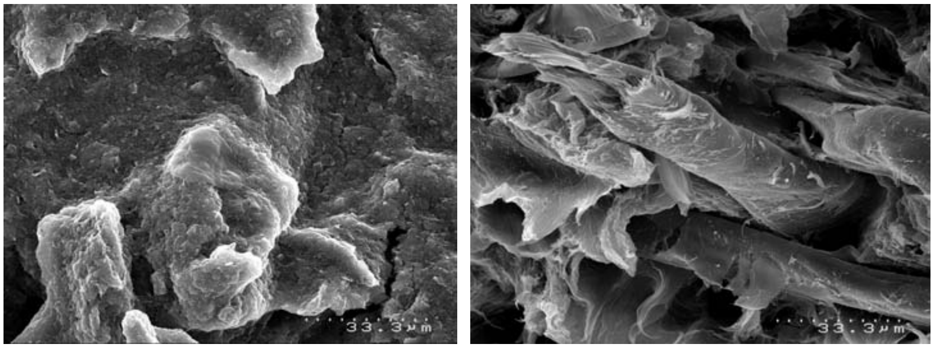


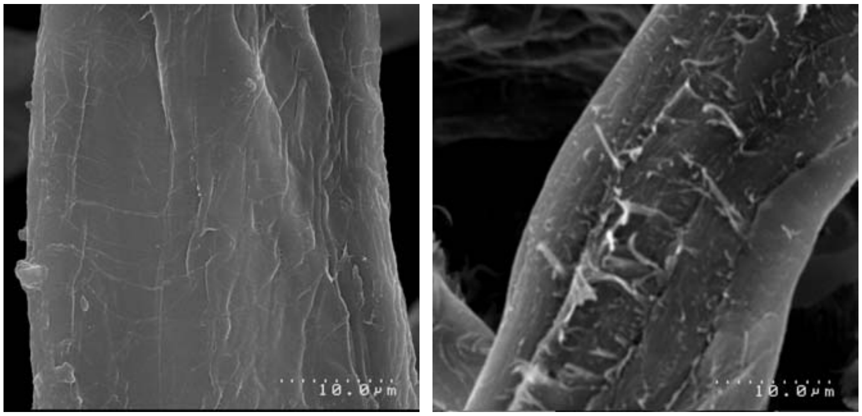
Figure 6. 34: Reduction in TS and YM of virgin and recycled composites after hygrothermal ageing.

TS and YM decreased after hygrothermal ageing for all composites (see Figure 6.32 and 6.33). The percentage reduction in TS and YM due to ageing is presented in Figure 6.34, and it can be seen that the extent of reduction in properties decreased with increased number of times the materials were recycled.



(a) Unaged (b) Aged

Figure 6. 35: SEM of virgin composites fracture surface before and after hygrothermal ageing.



(a) Unaged (b) Aged

Figure 6. 36: SEM of fibre surface before and after hygrothermal ageing.

After ageing, reductions in TS of 33% and YM of 40% were found for virgin composites compared to reductions for both TS and YM of 27% for composites recycled 8 times. This may be due to the equilibrium moisture content decreasing with increased number of times the materials were recycled, and therefore having less effect on behaviour. SEM of aged composites fracture surfaces clearly showed the loss of adhesion between fibre and matrix, characterised by the apparition of voids and fibre pull out (see Figure 6.35b) compared to better bonding for the composites fracture surface before ageing (see Figure 6.36a). Degradation of the fibres by water absorption can be seen, the fibres appear seriously degraded and the microfibrils can be clearly observed as compared to virgin fibre (see Figure 6.36).

FS and impact strength were found to increase for hygrothermal ageing (see Figure 6.37 and 6.38) which may be because water molecules act as a plasticizer in the composite material [53]. However, the extent of increase in FS and impact strength was generally found to decrease with increased number of times the materials were recycled which could be due to the reduction of equilibrium moisture content. Hardness was found to decrease for hygrothermal ageing (see Figure 6.39) expected to be due to swelling of composites by hygrothermal ageing.

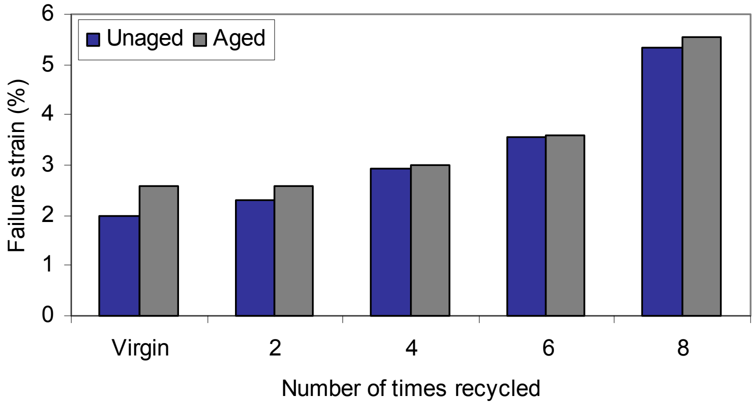


Figure 6. 37: Failure strain of virgin and recycled composites before and after hygrothermal ageing.

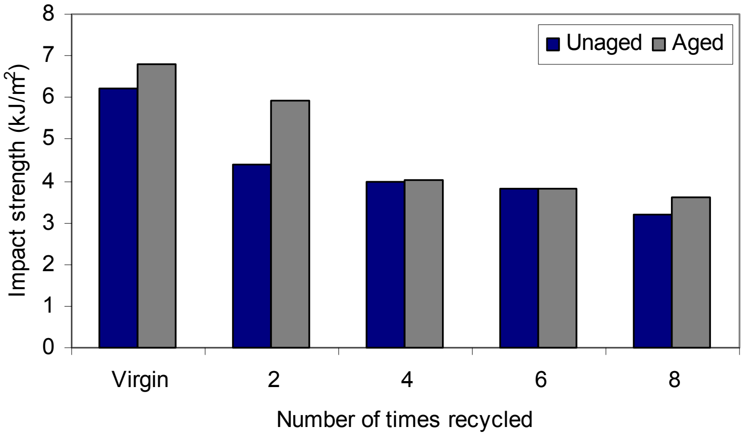


Figure 6. 38: Impact strength of virgin and recycled composites before and after hygrothermal ageing.

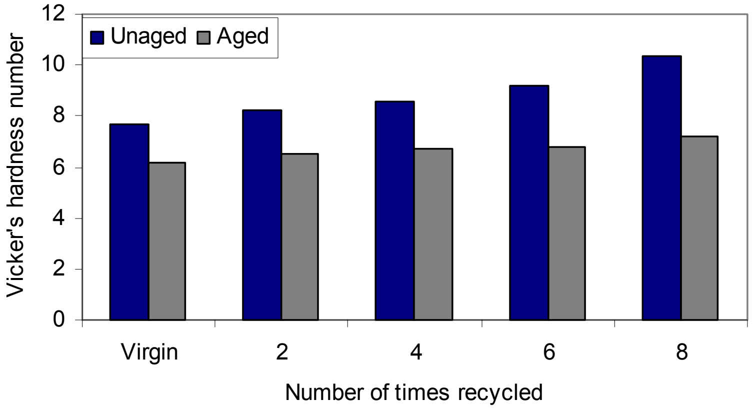


Figure 6. 39: Hardness of virgin and recycled composites before and after hygrothermal ageing.

TGA curves for virgin and recycled composites are presented in Figure 6.40 and 6.41. The positions of weight loss on the TGA trace shifted to lower temperatures after hygrothermal ageing both for virgin and recycled composites suggesting decreased thermal stability. The decrease in thermal stability could be due to the degradation of fibre and fibre matrix interfacial bonding (see Figure 6.35).

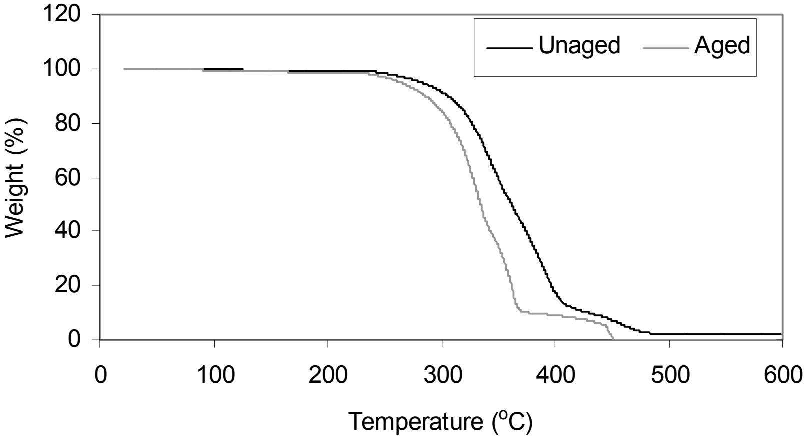


Figure 6. 40: TGA traces of virgin composites before and after hygrothermal ageing.

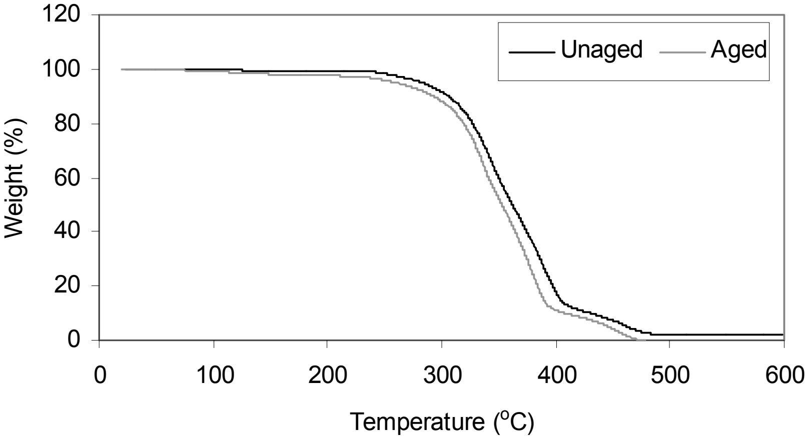


Figure 6. 41: TGA traces of composites recycled 8 times before and after hygrothermal ageing.

The DSC curves of virgin composites before and after ageing are presented in Figure 6.42 showing the reduction of T_m after hygrothermal ageing. The T_m and crystallinity of PP in virgin and recycled composites before and after hygrothermal ageing are presented in Table 6.5.

Table 6. 5: Melting point and crystallinity of PP in composites before and after hygrothermal ageing:

Number of times recycled	Before ageing		After ageing	
	T_m (°C)	I_{DSC}	T_m (°C)	I_{DSC}
Virgin composite	170.5	43.7	166.1	32.8
2 times recycled composite	168.8	44.4	166.3	33.2
4 times recycled composite	168.2	44.9	166.6	38.1
6 times recycled composite	168.1	44.9	166.2	39.7
8 times recycled composite	167.7	45.2	165.5	40.7

Both T_m and crystallinity of PP in virgin and recycled composites were found to decrease after ageing. The T_m for virgin composites reduced from 170.5°C for unaged composites to 166.1°C after ageing, and that for composites recycled 8 times reduced to 165.5°C after ageing from 167.7°C.

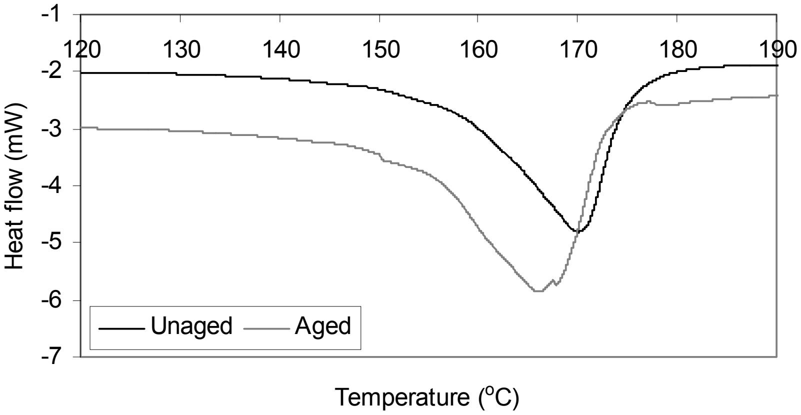


Figure 6. 42: DSC curve of virgin composites before and after hygrothermal ageing.

A reduction of crystallinity by 25% for virgin composites and that of 10% for composites recycled 8 times was found after hygrothermal ageing (see Table 6.5). This was also supported by XRD traces, where lower intensity was found for aged composites (see Figure 6.43 and 6.44) indicating lower crystallinity. The reduction of crystallinity and T_m could be due to the loss of structural integrity and debonding of the fibre from the matrix, resulting from the development of shear stress at the interface due to absorbed moisture [185]. Also, long term immersion of composites at a high temperature (50^oC) could reduce the molecular weight, resulting in a reduction of T_m.

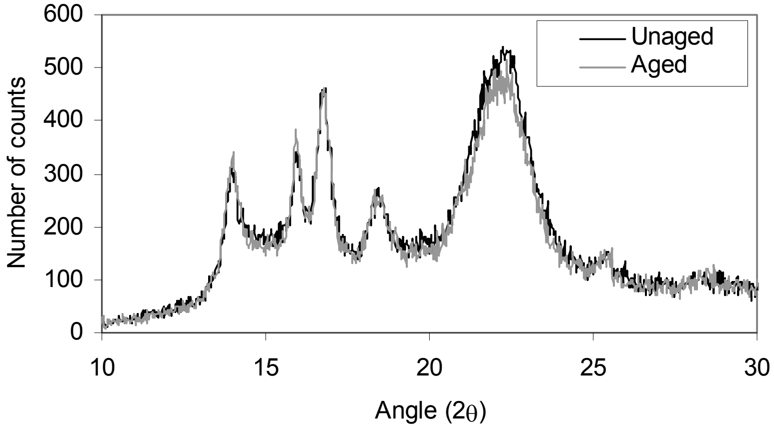


Figure 6. 43: XRD traces of virgin composites before and after hygrothermal ageing.

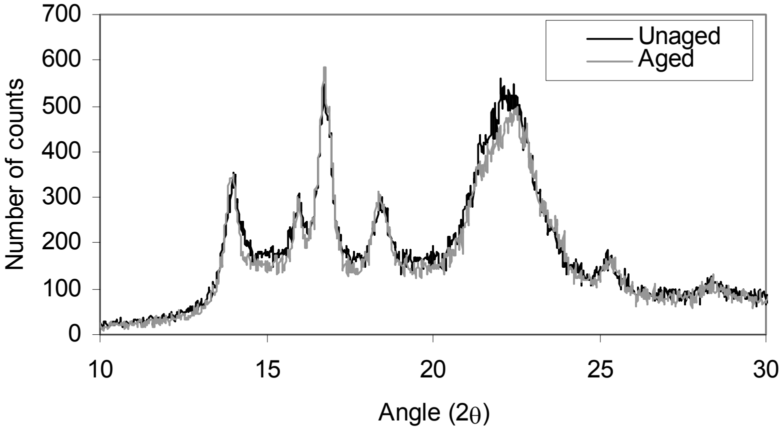


Figure 6. 44: XRD traces of composites recycled 8 times before and after hygrothermal ageing.

CHAPTER-SEVEN

SUMMARY AND CONCLUSIONS

A major challenge for thermoplastic matrix composites is the inherent poor adhesion between the hydrophilic fibre and the hydrophobic matrix. Coupling agents in wood fibre/polypropylene composites play an important role in improving the compatibility and adhesion between the polar wood fibre and non polar polypropylene matrix. For both MDF and Kraft fibre composites, TS and YM were found to increase with coupling agent. Composites with fibre content up to 60 wt% for MDF and 50 wt% for Kraft was successfully produced. Optimum mechanical properties were obtained at a content of 50 wt% fibre with 3 wt% MAPP for MDF fibre and 40 wt% fibre with 4 wt% MAPP for Kraft fibre. An increase of more than 80% for TS and 250% for YM was obtained by using 3 wt% MAPP and 50 wt% MDF fibre, compared to the unreinforced matrix. With Kraft fibre, a 65% increase in TS and 225% in YM was achieved with 40 wt% fibre and 4 wt% MAPP. It appeared that the reduction of TS at higher fibre content was due to an increase in melt viscosity resulting in limited fibre dispersion in composites.

Fibre pre-treatment increased the fibre surface charge, but damaged the fibre and decreased its crystallinity. Both TS and YM of wood fibre decreased respectively from 300 MPa and 32 GPa for virgin fibre to 220 MPa and 24 GPa after alkali treatment (with 10% NaOH). Composites with alkali treated fibres showed a reduction in TS, but showed an increase in YM. This suggests the potential to use a mild alkali treatment to improve the fibre surface for better interfacial bonding in composites whilst retaining the fibre strength.

Higher amounts of residual lignin and hemicellulose led to lower TS, FS and impact strength, although little change in YM was found for decreased hemicellulose and residual lignin content in composites. Removal of residual lignin and hemicellulose increased thermal stability of composites. Crystallinity of PP in composites was found to increase for decreased residual lignin and hemicellulose content. When composites were subjected to accelerated weathering, TS and YM were found to decrease and the extent of reduction was found to be higher for higher residual lignin composites. The reduction of mechanical properties was found to be due to degradation of lignin and PP chain scission as evaluated by increase in crystallinity of PP after weathering. Thermal stability of composites was found to decrease with weathering.

TS, YM and impact strength were found to decrease and FS increased with decreasing fibre length. Fibre pre-treatment by beating increased the TS of composites from 41 MPa for unbeaten fibre composites to 45 MPa for 5.5 min beaten fibre, and on further beating, TS was found to decrease. YM decreased with increasing beating time.

During hygrothermal aging, equilibrium moisture content and diffusion coefficient increased with increased fibre content in composites as well as with increased immersion temperature. Composites without coupling agent showed higher water uptake and diffusion coefficient than that of with coupling agent. TS and YM were found to decrease for hygrothermal ageing due to fibre damage and damage of fibre matrix interface bonding. After ageing, FS and impact strength were found to increase suspected to be due to the plasticizing effect of water.

Composite recycling was carried out 8 times by repeated pelletising and injection moulding. For 40 wt% fibre reinforced composites after being recycled 8 times, a 25% reduction in TS and only 16% reduction in YM was found suggesting great potential for recycled composites. Also for these composites, impact strength, flexural strength and flexural modulus were found to decrease with increased number of times the materials were recycled. Recycling of 50 wt% fibre composites brought about an increase in both TS and YM from 37 MPa and 4830 MPa respectively for virgin composites to 42 MPa and 6421 MPa for composites recycled 2 times, due to improved fibre dispersion followed by decreases in TS and YM upon further recycling. The reduction of TS, YM, flexural strength and flexural modulus was considered to be due to fibre damage that occurred during reprocessing as evaluated by the associated reduction of the average fibre length from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the composites recycled 8 times. The FS was found to increase with increased recycling due to shorter fibre and reduction of void content as evaluated by the increase in composites density. The thermal stability was found to increase with increased recycling due to the improvement of interfacial bonding and increased crystallinity of PP resulting from the reduction of molecular weight. TS of composites made with mixtures of virgin and recycled material were in close agreement with the Rule of Mixtures. During hygrothermal ageing, the equilibrium moisture content and diffusion coefficient was found to decrease with increased number of times the materials were recycled. After aging, a 33% reduction of TS and 40% reduction of YM was found for virgin composites, and 27% reduction of both TS and YM was found for composites recycled 8 times.

CHAPTER-EIGHT

RECOMMENDATIONS AND FUTURE WORKS

Wood-plastic composites are gaining growing acceptance for structural applications. For these applications, extrusion and injection moulding is the preferred method of production. Although hot press is commonly used for the production of long fibre composites, to retain the fibre length it can be used for wood fibre composites. Commingling can also be used for the production of wood fibre composites.

Better interfacial bonding between the fibre and the matrix is needed to get better mechanical properties of composites; addition of coupling agents is one of the most effective methods for wood fibre reinforced thermoplastic composites. However, optimum amount of coupling agents provide the highest mechanical properties. The bonding mechanism was not clearly understood; more chemical analysis (e.g. FTIR) is required to understand the bonding mechanism between the fibre and the matrix.

Mild alkali treatment is recommended to be an effective method of surface treatment for improving interfacial bonding as well as reducing lignin content, however additives (Na_2SO_3, Na_2CO_3, and NH_4OH) may increase the efficiency.

As low lignin composites provided better mechanical properties and better stability under weathering, for long term it is better to make composites with low lignin content. However, it would be useful to have comparative data of natural weathering with accelerated weathering, although it would be a long term research plan. Photo-degradation of composites is a complex process; more chemical analysis (e.g. FTIR) may be useful for better understanding the mechanism of composite degradation.

Recycling of composites subjected to actual weathering would give better understanding of the real-world performance.

Advanced modelling is needed for a better understanding of how the properties of composites change with different fibre contents. However, most of the existing models use some fitting parameter. “Modified Rule of Mixture” model can be used in this context, which consists both fibre orientation and fibre length efficiency factor (as a factor for stress transfer between the fibre and the matrix). Although it is a difficult task to determine the interfacial shear strength between wood fibre and PP, but, it would be useful to obtain better model.

As conventional methods (extrusion and injection moulding) were used for the production of virgin and recycled composites, this methods and formulation can be useful for mass production, although, it is better to go for pilot production before going for mass production.

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