The Viability of Waste Copper Chromium and Arsenic Treated Timber Reinforced Polypropylene as a Sustainable Building Material

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Abstract

The aim of this thesis was to investigate the viability of wood-plastic composites (WPCs) produced from wood flour and fibre derived from waste copper chromium and arsenic (CCA) treated timber for use as a sustainable material in the construction sector.

The research included an assessment of mechanical properties and the leaching of heavy metals from the wood-plastic composites, and the results were compared to material requirements in the building sector provided through literature and New Zealand building standards. Mechanical and chemical methods were used to prepare wood flour and fibre samples from waste CCA treated timber for use in wood-plastic composites. Composites were produced through compounding using a twin-screw extruder or a custom sigma blade compounder and then injection moulded for material testing. Composites produced using an extruder with 40 wt.% bleached fibres and 4 wt.% MAPP, increased tensile strength (TM) from 18.5 MPa for the polypropylene used for the matrix to 27.6 MPa; Young's modulus (YM) was increased from 0.84 GPa to 2.33 GPa.

Comparison of mechanical performance with commercial WPC properties suggests that waste CCA treated timber could be used as a raw material to produce WPC for semi-structural applications. The modulus (2.33 GPa, in the highest performing composites) was roughly three times lower than commonly used commercial timbers used in structural applications. The creep performance was not measured for a time frame long enough to be indicative of the 50 years required for structural application. Therefore, further research is required to investigate whether the low modulus and creep performance of the WPC is acceptable for a structural material in the construction sector.

One of the largest concerns with using waste CCA treated timber as a reinforcement material in WPC was the inclusion of heavy metals and the potential for leaching. Arsenic was considered the most toxic of the heavy metals in the CCA treated timber. Processing of the waste CCA treated timber to obtain fibre was found to reduce arsenic concentration by up to 99.94 % in the best scenario. Furthermore, arsenic in leachate from composites was found to decrease from 41.29 to 0.07 ppb when comparing wood flour composites to digested and bleached fibre composites. The concentration of copper, chromium, and arsenic in leachate from composites produced with chemically obtained fibre was found to be significantly lower than the maximum allowable drinking levels in New Zealand. Therefore, indicating the application of composites produced with wood fibre from waste CCA treated timber can be regarded as safe even in scenarios that involve human contact with the material.

A life cycle analysis study found that the use of an alkali digestion process to obtain fibre significantly increased the environmental impact compared to the processing required to obtain wood flour. In a study of a potential commercial scale process, ultrasonic treatment and hydrogen peroxide bleaching as secondary fibre treatments were the largest contributors to environmental impact in the preparation of wood fibre. Thus, the results suggest that chemical treatments should only be employed to produce wood fibre when the highest mechanical performance or lowest leaching levels are required for the application of the wood-plastic composites.

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Chapter 1

Introduction

The environment can be regarded as “the foundation and support of human existence and survival" [1]. Globally, humanity is causing environmental issues such as climate change, mass pollution, resource depletion, ocean acidification, and declining biodiversity [1, 2]. Environmental degradation has become a global concern, resulting in research into new societal, legal, and technological solutions for environmental sustainability.

The current societal norm for material consumption can be considered linear from resource extraction to waste disposal. The linear economy model is fundamentally unsustainable; the earth's natural resources are being depleted, and landfill waste is increasing. One potential solution for improving environmental sustainability is the circular economy concept. In contrast to the linear model, the circular economy concept uses a cyclic consumption of materials and products to keep materials in use for as long as possible, therefore extending the life of materials, reducing reliance on virgin materials, and decreasing mass pollution at end-of-life. The ability to draw on the circular economy model for guidance on new engineering solutions provides the potential to reduce societies' environmental impact.

The building sector is one of the most significant contributors to the arising environmental impact; globally, the construction industry consumes more than 32% of the world's resources, produces more than 25 % of the planet's solid waste, and emits about 35% of the world's greenhouse gasses [3]. The environmental impact of the building sector is no different in New Zealand. For example, the national construction and demolition industry contributes 50% of New Zealand's landfill waste [4]. Adopting ideas from the circular economy model to the building industry could see the reuse of waste materials from construction and demolition at their end-of-life as raw materials for further construction. In a long-term scenario, this could include using virgin materials and design processes that lend themselves better to circularity than the current standard. However, the transition into the circular economy could include the use of materials from current waste streams from the construction sector for further application. The circular economy concept could help mitigate waste streams, reliance on resource extraction, and the corresponding emissions of virgin material processing, therefore reducing the industries environmental impact. A circular economy also has the potential to add value to materials and products for longer periods than the linear economy standard [3].

Research for shifting to a circular economy in New Zealand's building industry has already begun. Materials science and engineering experts have considered natural fibre composites as a potential sustainable alternative material for structural and cladding in the building sector [5, 6]. Furthermore, engineering and architectural design solutions for the construction industry are being developed to improve the ease of recovery of materials for reuse. An example of this is X-Frame, which could be regarded as a leading architectural solution for introducing a circular economy to the construction sector. The design solution provides a modular building frame, produced from plywood, to provide ease of construction and deconstruction, allowing for easy recovery and reuse of standardised framing members [7]. However, incorporating innovative materials with design solutions could push environmental sustainability further.

Development in design and material technology shows promise for increased sustainability in future construction and demolition projects. However, there are still 1.8 million traditionally built dwellings in New Zealand that will require renovation and/or demolition in the future [8]. These buildings were produced before the current focus on environmental sustainability and will eventually lead to the disposal of construction materials to landfills unless the construction materials can be extracted and adapted for reuse.

A large contributor to New Zealand's landfill is timber, which makes up 20% (by weight) of construction and demolition waste [4]. Part of the reason is that treated timber is regularly used to prevent decay and increase durability; however, the treatments typically make end-of-life solutions more complex, and as a result, the timber is often sent to landfills.

Copper, chromium and arsenic (CCA) treated timbers have been produced and used extensively in the New Zealand construction industry since the mid-1950s [9]. A report in 2006 found that CCA treated timber was the most commonly produced treated timber in New Zealand; An estimated 574,750 m^2 was produced (in 2006), making up 69% of New Zealand's treated timber [10]. Copper, chromium and arsenic are used as preservatives to increase the durability of the timber, and resistance to insects, fungi and water damage [11]. Due to the low concentrations and fixation of copper, chromium, and arsenic in CCA treated timber, the potential for leaching of the metals out of the timber is low, and the treatment is regarded to have minimal environmental or societal health risk. However, the heavy metals in CCA treated timber result in a material that must be sent to leachate lined landfills at its end-of-life, due to issues with leaching in cleanfill, and the potential for emissions of toxic vapours to atmosphere from incineration [9, 12]. CCA treated timber can be regarded as a fundamentally single-use material, and the development of the treated timber for longer-lasting, more durable structures has created a significant contributor to waste in New Zealand. Adopting principles from the circular economy concept and finding a solution for the reuse of CCA treated timber would provide a means of diverting a significant portion of New Zealand's waste from landfills and potentially improving the construction industry's environmental impact.

Wood-plastic composites (WPC), a type of natural fibre composite, are commonly used in the international building industry; typical applications of WPC include 'semi-structural' applications, such as decking and fencing as an alternative to timber. In 2019 the global wood-plastic composites market was estimated to be worth USD 5.3 billion [13]. Wood-plastic composites are typically produced using waste timber and plastic as raw materials. Additionally, the application of wood-plastic composites produced with construction waste has been reported as environmentally beneficial for climate change, even when substituting timber [14]. Wood-plastic composites have also proven to be recyclable multiple times with minor losses in mechanical properties. A study in 2007 reported recycling of wood-plastic composites (50 wt.% wood fibre, 4 wt.% maleic anhydride grafted polypropylene, 46 wt.% polypropylene) 8 times with a total reduction in tensile strength of 11% [15]. The use of waste CCA treated timber as a filler or reinforcement material in wood-plastic composites in New Zealand has the potential to provide an alternative end-of-life for the treated timber. Furthermore, it could also offer a national industry for recycling waste thermoplastics. However, the potential health risks of working with the CCA treated timber and the possibility of leaching of heavy metals from CCA based wood-plastic composites have been considered as barriers to the potential end-of-life solution [11].

The literature has previously reported the leaching of heavy metals from wood-plastic composites produced using wood flour from CCA treated timber. In these studies, all leaching levels measured were compared to maximum allowable values (MAV) in drinking water [16, 17]. However, comparing leachate levels of WPC to the leachate of construction materials used in corresponding applications could better indicate the application potential. Wood-plastic composites produced using fibres from CCA treated timber have been reported, and an improvement of moisture absorption and some mechanical properties compared to using virgin timber was found. Unfortunately, the study did not include research on the tracking of heavy metals or the potential for leaching from the composites [18]. However, the chemical treatment of CCA treated timber with hydrogen peroxide for pulp production has reportedly reduced the concentration of copper, chromium, and arsenic in the resulting fibres by 95%, 100%, and 100%, respectively [19]. The reduction in heavy metal content with chemical treatment shows potential for safe to use and environmentally friendly wood-plastic composites made from waste CCA treated timber for the building sector.

Objectives

This project aims to research whether recycling CCA treated timber waste products as a reinforcement material in wood-plastic composites could provide a viable, sustainable alternative material for the building industry.

The project objectives include:

- Assess building standards and current construction materials used in industry to investigate the material properties required for structural applications.
- Produce wood flour, and wood fibres from CCA treated timber and analyse the corresponding properties.
- Produce wood-plastic composites from the CCA treated timber and undertake material testing to investigate and understand material performance.
- Complete LCA (life cycle analysis) to understand the environmental effects of producing wood-plastic composites from waste CCA treated timber.

Chapter 2

Literature Review

The following literature review focuses on the potential application of wood-plastic composites produced with waste CCA treated timber as a sustainable material for New Zealand's construction industry. This review includes background research on the material properties required for application in the construction sector, CCA treated timber, wood fibres and flour, polymers to be used as matrix materials, wood-plastic composites properties, factors affecting properties, and the environmental impacts of using wood-plastic composites in the construction sector.

2.1 Material Properties Required for the Building Sector

The structural application of wood-plastic composites (WPC) or natural fibre composites (NFC) would require material properties to meet the requirements of the New Zealand building code. The mechanical properties of wood-plastic composites are most comparable with timber and timber-based products in the building industry. For example, typical tensile strengths attained from wood-plastic composites range from 17.8 MPa to 50.2 MPa using wood flour and wood fibres, respectively [20, 21]. In comparison, the tensile strength of radiata pine (90% of New Zealand's timber [22]) ranges from 10.6 to 82.5 MPa [23, 24]. Other common structural materials in the building industry, such as steel or concrete, have very different mechanical properties. Therefore, structural requirements for timber and timber-based products were evaluated to understand the required material properties for structural applications in the building industry.

The following three New Zealand standards outline the use of wood and wood-based products in the building sector:

- NZS 3602: Timber and Wood-Based Products for the use in building [25]
- NZS 3603: Timber Structures Standard [23]
- NZS 3604: Timber-framed buildings [26]

NZS 3602 focuses on the material requirements for timber and wood-based products used in the building industry. However, the standard states that the acceptance of wood-plastic composites is outside of the scope of the standard and "shall be to the satisfaction of the territorial authority" [25]. NZS 3602 also states that components that "provide structural stability" require durability of 50 years [25].

NZS 3602 does not provide a definition of durability; however, the scope of the standard declares: "This standard gives the requirements for timber and wood-based products for particular uses in building so that they can be expected to give an acceptable performance during the life of the building" [25]. Furthermore, the Oxford dictionary defines durability as "the quality of being able to last for a long time without breaking or getting weaker" [27]. Therefore, the application of natural fibre composites in structural applications can be considered to require durability or to maintain acceptable material performance for a 50 year period.

The durability of WPC depends on several material properties due to the fibre and plastic components. ASTM D7031 and D7032 standardise evaluating mechanical and physical properties and the performance criteria for wood-plastic composite material properties in building applications. The properties outlined that could cause a decrease in physical properties over time include: temperature and moisture effects, resistance to ultraviolet (UV) light, resistance to freeze-thaw, biodeterioration, termite resistance, and creep resistance [28, 29]. For the structural application of natural fibre composites, the potential for degradation due to these properties would have to be managed over a 50 year period, either through engineering design or long term material performance.

One of the largest concerns is the resistance to creep in WPC due to the use of polymers as matrix materials. Polymers are typically very susceptible to viscoelastic behaviour, including creep and stress relaxation. The New Zealand building standards deal with creep properties in timber products by applying a factor of safety to the allowable stresses and the expected deformation of structural members. This safety factor is used to avoid tertiary creep in timber and depends on the duration of load, moisture content, and the load type (tensile, bending, compression, or shear). In the most extreme cases in the standard, the allowable stress in a member has a multiplication factor of 0.6. The expected long-term deformation is calculated using a multiplication factor of 3.0 with the expected deformation [23, 30].

The New Zealand standard shows that engineering design can be used for safe long-term structural applications even with materials prone to creep. To apply natural fibre composites in structural applications, finding the conditions of application that can avoid tertiary creep over a 50-year period would also be required. Further evaluation of other properties that affect composite durability will also have to be completed. However, the durability will likely depend on the conditions the materials are exposed to, which will be dependent on the specific application.

NZS 3603 and NZS 3604 outline requirements for structures built of timber and give characteristic mechanical properties of materials. Both standards focus on engineering design for construction, not the required material properties for application [23, 26]. For natural fibre composites to be applied in the construction industry, having mechanical properties that were comparable or better to those of currently used structural materials in the construction industry would prove the potential of the composites as structural materials. Table 2-1 summarises the mechanical properties of all structural materials approved for a 50-year durability in NZS 3602 using characteristic properties from NZS 3603 where possible. Characteristic material properties are defined by NZS 3603 as: "For strength properties, characteristic stress or strength is an estimate of the lower 5-percentile value determined with 75 % confidence, from tests on a representative sample of full-size test specimens. For stiffness properties, the characteristic value is the mean value" [23]. Table 2-1 also includes commercial wood-plastic composites used in decking applications as a reference to semi-structural applications.

Table 2-1: Characteristic properties of structural materials used in the construction industry and commercial wood-plastic composites. All properties in MPa unless stated otherwise. Data sources are provided in the material column unless stated otherwise in the material property box.

Material	Bending	Compression Parallel	Tension Parallel	Shear Parallel	Compression Perpendicular	Modulus of Elasticity (GPa)	Fatigue strength at 10^7 cycles
Radiata Pine Visually graded dry [23]	17.7-27.7	20.9-25.7	10.6-16.5	3.8	8.9	8.0-10.5	1.08 – 1.32 MPa (transverse) 21.8-26.6 MPa (longitudinal)[24]
Radiata Pine Visually graded green. Source: [23]	14.8-22.7	12.7-15.9	8.9-13.6	2.4	5.3	6.5-8.8	

Radiata Pine NZS 3618 graded dry. Source:[23]	17.7-33.9	20.9-28.6	10.6-20.3	3.8-4.1	8.9-9.4	8.0-12.0	
Radiata Pine NZS 3618 graded green. Source:[23]	14.8-26.6	12.7-17.1	8.9-15.9	2.5-2.7	5.3-5.9	6.5-9.2	
Douglas fir Visually graded dry [23]	17.7-25.1	22.1-27.1	10.6-15.0	3	8.9	8.0-10.4	0.6 -0.87 MPa (transverse) 23.1-29.8 MPa (longitudinal)[24]
Douglas fir Visually graded green. Source: [23]	14.8-22.7	14.5-18.3	8.9-13.6	2.4	4.7	6.5-8.7	
Douglas fir NZS 3618 graded dry. Source:[23]	17.7-33.0	22.1-30.1	10.6-19.8	3.0-3.2	8.9-9.7	8.0-12.0	
Douglas fir NZS 3618 graded green. Source:[23]	14.8-26.6	14.5-19.8	8.9-15.9	2.3-2.5	4.7-5.0	6.5-9.3	
Rimu Visually graded dry [23]	19.8	20.1	11.8	3.8	10.9	9.5	-
Rimu Visually graded green [23]	15	14.5	8.9	2.7	6.8	8.3	
Beech (silver) Visually graded dry [23]	23.6-36.6	24.8-31.0	14.2-21.8	3.5	7.1	9.3-10.6	0.96-2.31 MPa (transverse) 27.7-35.6 MPa (longitudinal)[24]
Beech (silver) Visually graded green [23]	20.-32.3	19.2-23.6	12.4-18.9	2.7	3.8	7.5-8.6	
Beech (red) Visually graded dry [23]	28.0-43.1	30.4-37.5	16.8-26.0	5.3	12.4	13.4-15.3	
Beech (red) Visually graded green [23]	25.1-38.1	18.3-22.4	15.0-22.7	3.8	7.7	11.3-13.0	
Beech (hard)	29.5-44.2	26.6-31.0	17.7-26.6	5	14.2	13.6-15.5	

Visually graded dry [23]							
Beech (hard) Visually graded green [23]	28.3-42.8	24.2-29.5	17.1-25.7	4.4	10.6	12.1-14.1	
Larch Visually graded dry [23]	22.7	27.1	13.6	3.5	8.9	9.6	0.6-0.99MPa (transverse) 24.1-30.7 MPa (longitudinal)[24]
Larch Visually graded green [23]	15	17.4	8.9	2.7	5.6	7.7	
Particle Board		-	-	-	-	-	
Cypress Species			-	-	-	-	
Tawa	-	-	-	-	-	-	
Matai	-	-	-	-	-	-	
	Bending	**Compression parallel**	**Tension Parallel**	**Shear Parallel**	**Compression perpendicular**	**Modulus of Elasticity (Gpa)**	**Modulus of Rigidity (Gpa)**
Structural Plywood moisture <15% [23]	22.5-57.6	16.9-43.2	13.5-34.6	4.2-6.0	8.6-20.4	9.1-16	0.45-0.8
Commercial products	**Bending**	**Compression parallel**	**Tension Parallel**	**Shear Parallel**	**Compression perpendicular**	**Modulus of Elasticity (Gpa)**	**Modulus of Rigidity (Gpa)**
LVL Nelson Pine LVL [31])	33-38	38	26-33	5.0-5.3	10	11.0-13.2	0.55-0.66
LVL (lumber worx [32])	38-48	38	26-33	5-5.3	10	11.0-13.2	0.55-0.66
WPC decking (Future wood [33])	19.17-21.26		12.45			2.08 (flexural)	

Although the mechanical performance of the materials in construction is important, the performance of a structure is also limited by applying the materials through engineering and architectural design. Design requirements for timber-framed structures are outlined throughout NZS 3603 and NZS 3604, not the required mechanical performance of materials [23, 26]. Additionally, NZS 3604 states that structural elements outside of the generic prescribed elements should be subject to specific engineering design [26]. Therefore, indicating that non-traditional materials can be used in construction. However, engineering design specific to the material properties would be required for application. NZS 3603 also includes characteristic properties and information on engineering design for properties such as pull-out strength for fasteners, indicating other material properties are important for structural application. However, new engineering and architectural design solutions are also being explored for the circular economy and could reduce reliance on properties such as fastener pull-out strength. For example, X-frame, an architectural design solution for the circular economy, improves ease of recovery and reuse of materials through a system without traditional mechanical fasteners such as nails or screws [7]. Thus, making the requirement for evaluating pull-out strength of fasteners moot. The potential for new engineering design within the construction sector could also alter the material properties required for construction. The use of natural fibre composites has the potential to increase and improve this design trend through increased variability in shapes and profiles due to increased production options compared to traditional materials.

The use of engineering design to create high quality and durable structures from materials with lower performance is possible. However, other variables should be kept in mind. For example, the usability (ease of handling and working with) of materials by tradespeople will be limited if excess volume or mass of material is required for structural application. Therefore, for structural applications, the desired mechanical properties of natural fibre composites should be at least comparable to that of traditional materials to ensure a usable product that can be directly introduced into the building sector.

2.2 CCA Treated Timber

Copper, chromium, and arsenic treated timber is used throughout New Zealand's construction industry due to the improved durability through the treatments ability to preserve wood against insects, fungi and water damage [11]. The timber is the most commonly produced treated timber in New Zealand and is regularly used in outdoor applications including, decking, garden furniture, playground equipment, landscaping, retaining walls, and fences [10, 34, 35]. "Copper is used to control fungi and marine borers, arsenic to control insects and some copper-resistant fungi, and chromium to fix the copper and arsenic in the wood" [34].

Copper, chromium and arsenic are toxic heavy metals, and all have the potential to cause harm due to exposure. Copper is the least harmful of the three heavy metals and is an essential element required as part of a normal dietary intake. The most common source of copper is through normal drinking water, and the New Zealand maximum acceptable value (MAV) in water sources is 2 mg/L [36]. Copper is toxic if exposed to people in larger quantities. The gastrointestinal tract is regarded as one of the most sensitive parts of the body, and effects such as vomiting can be induced from copper ingestion. Exposure to copper dust has also been reported to cause irritation to the lungs, causing coughing [34].

Chromium is more toxic than copper and is consumed in much lower quantities in a typical diet [34]. The MAV for chromium in New Zealand's drinking water is 0.05 mg/L [36]. Timber is treated with hexavalent chromium, which is reduced to trivalent chromium once fixed inside the timber. Doses of 4-29 mg/kg of chromium have been reported as lethal. Furthermore, hexavalent chromium is a classified human carcinogen. Trivalent chromium is considered significantly less toxic, and "it is extremely unlikely that low-level exposure would cause acute health effects" [34]. Direct skin contact with both trivalent and hexavalent chromium causes skin irritation [34].

Arsenic is the most toxic of the three heavy metals, and the New Zealand drinking water MAV is 0.01 mg/L [36]. Ingestion of exposures of 0.05 mg/kg/day "have caused vomiting, diarrhoea, abdominal pain and gastrointestinal haemorrhage, changes in liver and renal function, hypotension, tachycardia, pulmonary oedema, … difficulty breathing", and death [34]. Arsenic is classified as a human carcinogen and can cause a wide range of cancers, including, but not limited to, skin, lung, and bladder cancer [34].

In New Zealand, timber treatment is divided into hazard classes depending on the exposure, service conditions, biological hazards and typical uses of timber. CCA treatment is an acceptable treatment across all hazard classes[37]. However, it is commonly used in exterior applications, which occurs in hazard classes of H3 and higher [34, 35, 37]. NZS 3640 requires that only pinus species of timber are used to treat timber to a hazard class of H2 - H6 [37]. Pinus radiata (also known as radiata pine) is reported to make up 90% of the New Zealand forestry, with all other pinus species combined making up less than 1% of New Zealand's forestry [22]. Therefore, only CCA treated radiata pine will be considered for the rest of this study.

Copper chromium arsenic treatment is applied to timber by applying an aqueous solution of CCA under a high-pressure or vacuum process. High pressure or vacuum processes are used to improve penetration of the heavy metals into the timber, resulting in fixation of the heavy metals throughout the timber. In New Zealand, the application of copper, chromium and arsenic salts or oxides for the treatment of timber is performed to NZS 3640 [37]. The heavy metals are required to be used in proportions of 23-25 % Cu, 38-45 % Cr, and 30 -37% As [37].

The fixation of copper chromium and arsenic into the timber is achieved through a series of chemical reactions [9]. The literature appears very unclear on the exact chemistry of the fixation of preservatives into timber; however, a recent report suggests that the heavy metals are fixed in the timber in the forms of chromium(III) arsenate, chromium (III) hydroxide and wood carboxylate-copper (II) complexes [38]. Due to the fixation of the heavy metals in the timber, the leaching from the timber is suggested to be minimal and has little effect on background levels of Cu, Cr, or As in soil and water sediments [9].

Due to the heavy metals in timber, end-of-life options are limited. In New Zealand, all CCA treated timber is sent to municipal landfills that have leachate collection, treatment and disposal facilities fitted. Sending the treated timber to clean fill is avoided due to the potential of copper, chromium, and arsenic to leach into the surrounding ecosystem (Large volumes would likely leach more of the toxic heavy metals than individual pieces of timber in the construction sector). Incineration of CCA treated timber is also avoided due to the possibility of arsenic vapour emissions released into the atmosphere [9, 12]. A review on disposal technologies of CCA treated timber waste discussed the reuse of the timber in wood-based composites. The review's prognosis was that "the market is not in favour of using CCA wood in conventional wood composite manufacturing, questions about the safety of workers and environmental problems" [11]. The report also regarded the disposal method as a deferral from landfills and not avoidance. Furthermore, the report indicated further research was required to investigate "leaching, recyclability, decay resistance, emissions during processing and impacts on physical and mechanical properties" for wood polymer composites [11]. However, the deferral from landfills still adds life to the material and reduces reliance on new virgin materials and solid waste pollution.

As discussed in the introduction, research on the use of wood flour from CCA treated timber in WPC has indicated leaching levels that are higher than that of the MAV for drinking water [16, 17]. However, the use of chemical treatment to obtain wood fibres from CCA treated timber can reduce the heavy metal content in the fibre, hence potentially reducing composite leaching levels and making a composite that is safe for tradespeople to work with safe for application [19]. Studies on the use of CCA treated timber in composites also suggested many other positive effects on composite physical and mechanical performance compared to virgin timber (further discussed in Section 2.5.5).

2.3 Wood Fibre and Flour

2.3.1 Sources of Natural Fibres

Natural fibres can be extracted from plants, minerals, or animals (shown in Figure 2-1) [6, 39, 40]. As this study is on the use of CCA treated timber, plant fibres will be the focus of this literature review. Plant fibres also tend to be stiffer and stronger than animal fibres, and mineral fibres only exist within the asbestos group and are avoided due to health concerns [39, 40].

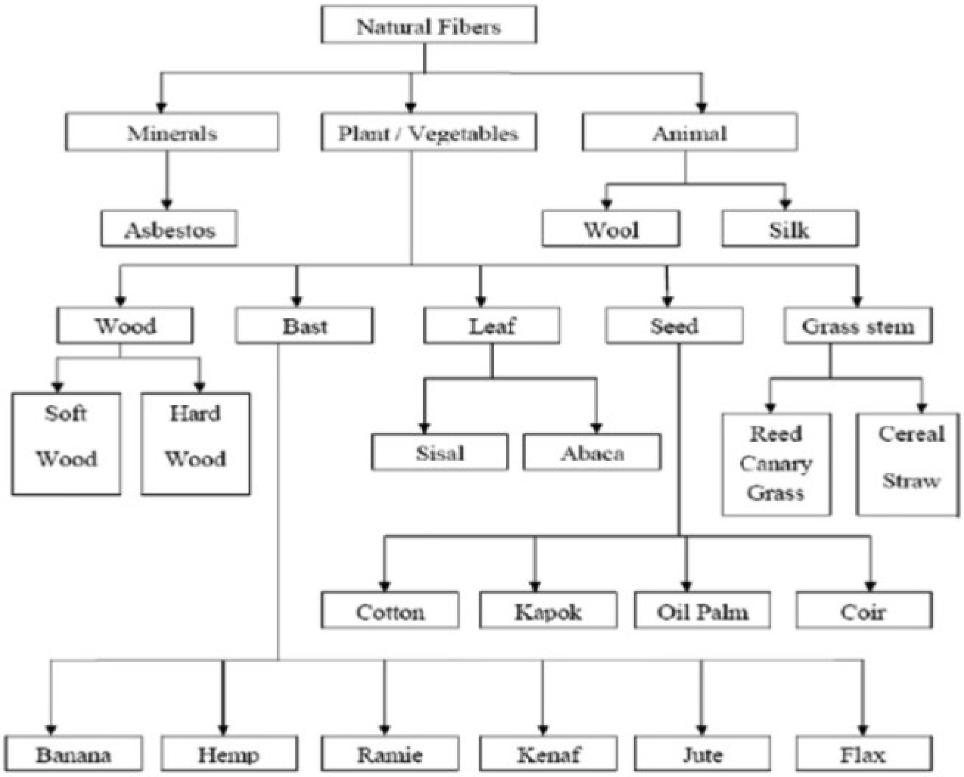


Figure 2-1: Sources of natural fibres. Image obtained from [39].

There is a large variation in the properties of plant fibres, which are typically characteristic of the source they are derived from. The properties include their natural abundance, cost, and properties that affect composite performance, such as geometry, fibre strength, stiffness, density, constituents, and crystallinity [41]. Fibre properties can also be affected by growing times, harvesting times, extraction methods, treatment and storage procedures [40]. Typical fibre properties from some natural fibres are shown in Table 2-2 (glass fibre is included for reference).

Table 2-2: Typical natural fibre properties. Data obtained from [20].

	Length (mm)	**Width (µm)**	**Density (g/cm^3)**	**Stiffness (GPa)**	**Strength (MPa)**
Flax	9-70	5-38	1.4-1.5	50-70	500-900
Hemp	5-55	10-51	1.48	30-60	300-800
Jute	2-5	10-25	1.3-1.5	20-55	200-500
Hardwood	1	15-45	1.4	10-70	90-180
Softwood	3-8	15-45	1.4	10-50	100-170
Glass	-	-	2.49	70	2700

2.3.2 Timber

Timber is one of the most abundant sources of plant fibres and is commonly used as a source of fibre in a number of industries, most notably the pulp and paper industry. Timber can be divided into two categories, including hardwoods (angiosperms) and softwoods (gymnosperms) [15]. The radiata pine primarily used for CCA treated timber in New Zealand is a softwood and, therefore, will be the focus of this study.

The basic structure of timber is composed of cellulose, lignin, hemicellulose, waxes, and other water-soluble compounds in smaller quantities, commonly referred to as extractives [6, 42]. Timber can be regarded as being made up of a number of spindle-shaped cells throughout the structure. The wall of these cells are composed of lignocellulosic natural fibres. Bundles of fibres making up the timber structure are cemented together by the middle lamella. A schematic of the timber structure and the natural fibres producing the cell wall can be seen in Figure 2-2 [43]. The natural fibres are comprised of the primary wall, secondary wall, and lumen. The primary and secondary walls consist of cellulose microfibrils held together by a matrix of lignin, hemicellulose, and extractives. The primary wall consists of randomly arranged cellulose microfibrils, whereas the secondary wall contains the bulk of the fibre and is made up of helically wound cellulose microfibrils in the direction parallel to the length of the fibre. The angle between the microfibrils and the fibre axis is individual to each fibre and is referred to as the microfibrillar angle. The secondary wall typically determines the mechanical properties of the fibre [15, 44].

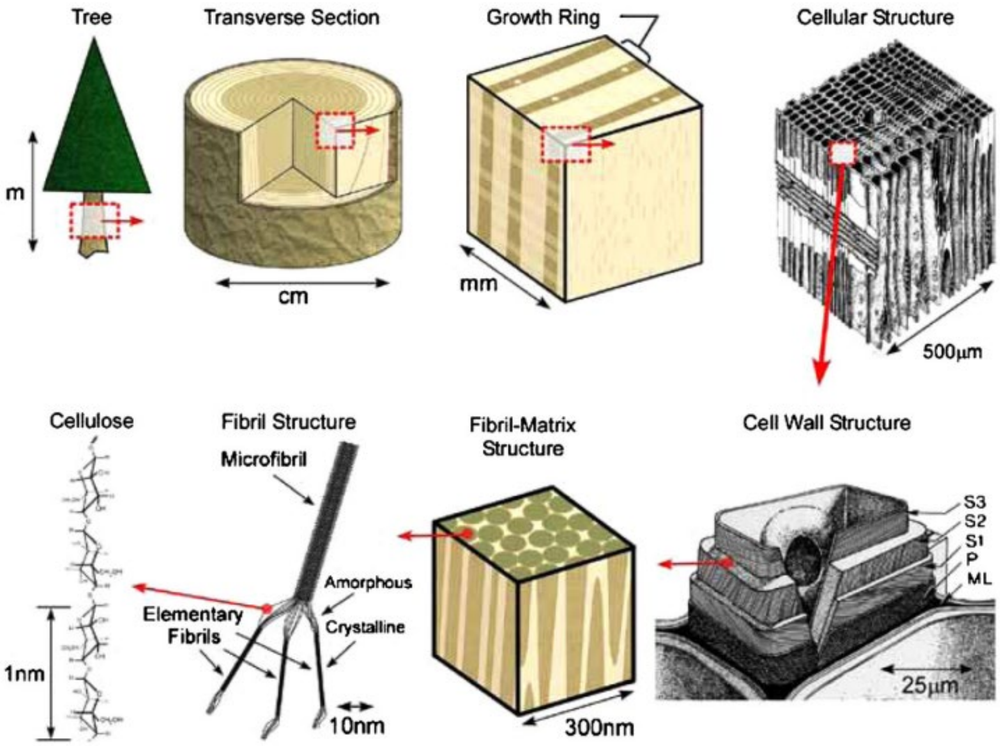


Figure 2-2: Hierarchal structure of timber. Image obtained from [43].

Cellulose is the main structural component of all plant fibres and is comprised of D-anhydroglucose molecules joined together by ß-D-glucopyranose linkages with a degree of polymerisation of roughly 8000 to 10000 in timber [6, 20, 40, 45]. Each cellulose chain is roughly 4 – 5 µm and are arranged in bundles of roughly 40 individual molecules to make cellulose microfibrils [6, 15]. Primary and secondary bonding occur in cellulose, in the form of covalent bonds, and hydrogen and van der Waal bonds, respectively. The covalent bonds occur within the cellulose structure, hydrogen bonds occur within the cellulose molecule linking the molecules together to form sheets, and van der Waal bonds link the sheets together [6]. Due to the hydroxyl functional groups, cellulose has a strong affinity to itself and water, making it highly hydrophilic. Cellulose is considered a crystalline material and is roughly 70 % crystalline in timber [6]. Highly crystalline regions of cellulose have tightly packed cellulose chains with interchain hydrogen bonding, exposing only the hydroxyl groups on the fibre surface. Whereas amorphous regions have less interchain hydrogen bonding, thus exposing more hydroxyl groups making it more prone to hydrogen bonding with water and more hydrophilic [41]. Cellulose can take place in a number of states, however, it is most commonly found in three forms including, Iα, Iβ, and II [42]. Cellulose Iα, and Iβ is commonly the natural form of cellulose [6, 42, 45]. Cellulose II is more thermodynamically stable and can be produced from cellulose I through several processes such as mercerisation (using a strong concentration of sodium hydroxide) or acid regeneration [6, 46]. TGA analysis has shown that thermal degradation of cellulose typically occurs between 315 to 400 °C [47].

Lignin is a highly complex amorphous material that consists of a three-dimensional network of phenylpropane groups. Lignin is made up of three monomer units, including p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are incorporated into the lignin structure as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units of lignin, respectively [48]. Softwood lignin is almost entirely made up of G units, whereas lignin in other plant fibres is comprised of varying ratios of the three lignin groups [6, 49]. G units of lignin are considered much more difficult to separate than S units, making the removal of lignin during fibre treatment more difficult [49]. The thermal degradation of lignin takes place over a larger temperature range than cellulose and hemicellulose, occurring from 160 to 900 °C [47].

Hemicellulose is very different from cellulose and is made up of shorter branched polymers with a degree of polymerisation of 150 to 200 [6, 20]. Hemicellulose can take different forms depending on the species; however, in softwoods, it is primarily in the form of galactoglucomannans [6]. Hemicellulose is highly hydrophilic, and thermal degradation primarily occurs between 220 to 315 °C [47, 50].

Several other constituents are known to occur in timber and herbaceous materials in significantly lower portions than cellulose, lignin, and hemicellulose. The constituents are commonly referred to as extractives and include terpenes, waxes, acids, alcohols, proteins, and inorganic materials [6].

2.3.3 Radiata pine

Radiata pine makes up 90% of the New Zealand forestry industry and is used throughout the local construction industry. Radiata pine is a species of softwood and can be expected to have fibre properties similar to those found in Table 2-2. The composition of radiata pine can be expected to vary due to a number of variables such as the age of the timber and the location within the timber. The reported average composition of dry radiata pine is displayed in Table 2-3. The lignin found in the radiata pine is reported to be primarily guaiacyl (G) units [51]. Galactoglucomannan, arabinoglucuronoxylan, and arabinogalactan can be regarded as types of hemicellulose [52].

Table 2-3: Composition of radiata pine constiuents. Data obtained from [53]

Constituent	**Composition, Percentage (%)**
lignin	26
cellulose	42
galactoglucomannan	15
arabinoglucuronoxylan	10
arabinogalactan	4
Utonic acids and others	3

2.3.4 Wood Flour

Wood flour and wood fibres can both be derived from timber and used as reinforcement methods in wood-plastic composites (a category of natural fibre composites). Wood flour is commonly used in wood-plastic composites, as it is cheap and easy to produce, and can improve some material properties. Wood flour is comprised of fine wood particles, typically small enough to pass through an 850 µm screen. There is no standardised method for the production of wood flour [21]. Wood flour only requires mechanical preparation and is still in the form of fibre bundles with all original constituents in the timber present. Wood flour is regarded as weaker than wood fibres because the forces required to break the fibres apart in their bundles are less than that of the force required to break the individual fibres [54].

2.3.5 Wood Fibres

Wood fibres can be extracted from timber through a variety of mechanical and chemical processing methods. These methods are commonly used in the pulp and paper industry. The chemical and mechanical methods used greatly affect the fibre and corresponding composite properties, which is further explored in Section 2.5.4.

Typical 'pulping' processes used in the pulp and paper industry can be split into four main categories: chemical, semi-chemical, chemical-mechanical, and mechanical. The chemical treatments rely on chemicals to separate fibres, whereas mechanical methods use physical actions. Chemical pulping produces individual fibres through the removal of soluble constituents such as lignin or hemicellulose. There are a number of potential chemical treatments to obtain individual fibre from timber. The most commonly used method for obtaining fibres from softwoods in the pulp and paper industry is the Kraft process, producing 75-80% of the virgin pulp in the United States of America. Other pulping processes include soda, sulphite, organsolv, and enzyme treatments. The soda process could be regarded as the most simple process and uses an aqueous sodium hydroxide solution to extract fibres; it is used minimally for softwoods, however, it is still used for other herbaceous species. The kraft process uses a sodium hydroxide and sodium sulphide solution, reducing the time required for pulping and increasing pulp strength compared to the soda process. Sulphite processes use "mixtures of sulphurous acid and/ or its alkali salts … to solubilise lignin" during processing [55]. The sulphite process obtains weaker pulps, requires longer treatment times, and chemical recovery is more difficult than the kraft process and is therefore used minimally. Adaptions of the sulphite process include alkaline sulphite, which uses sodium hydroxide and sodium sulphite, and produces pulp with similar quality to the kraft process. The organsolv process relies on organic solvents such as methanol, ethanol, and acetic acid, to remove lignin from the timber. As a pulping process, the organsolv process is still very experimental. However, it has advantages, including ease of chemical recovery and zero sulphur emissions [55, 56]. Enzyme treatment could be regarded as the most sustainable treatment for selectively removing lignin, hemicellulose, and other extractives to obtain cellulosic fibres [57]. However, the treatment comes at a high cost and is more complex than traditional treatments [55].

The soda process could be regarded as the simplest process due to only requiring sodium hydroxide as a solution. It has also been used for obtaining fibres from CCA treated timber for natural fibre composites, with promising composite properties [18]. Furthermore, it has been shown to give beneficial fibre and composite properties when used as a fibre treatment method for natural fibre composites (discussed further in Section 2.5.4) [40]. Therefore, due to the simplicity and the promising properties of fibres for composites, the use of sodium hydroxide for obtaining fibres was considered the most applicable to investigate the viability of using CCA treated timber for WPC through laboratory-scale testing. Furthermore, sodium sulphite could be added to potentially improve fibre processing.

Bleaching is a common practice in the pulp and paper industry and is completed using chemicals specific to the removal of lignin. Bleaching commonly consists of numerous chemicals, including oxygen, chlorine, chlorine dioxide, hypochlorite, and hydrogen peroxide [56]. Hydrogen peroxide bleaching is considered an environmentally friendly solution as it does not use any chlorine-based chemicals. Hydrogen peroxide bleaching acts through the decomposition into free radicals that react with the aromatic rings in lignin. However, a high concentration of radicals leads to poor lignin selectivity and reduced bleaching. The addition of sodium silicate to hydrogen peroxide bleaching reduces hydrogen peroxide decomposition during bleaching, therefore, improving the efficiency of the chemical process. Sodium silicate acts by forming complexes with transition metals known to catalyse hydrogen peroxide decomposition, thus, slowing down the decomposition and improving bleaching [58]. Bleaching of fibres has the potential to remove excess lignin on the surface of and within the fibres and expose more cellulose. Furthermore, a report using hydrogen peroxide as a pulping chemical found that the process was able to reduce the heavy metal content in the resulting fibres significantly. The study used electron probe microanalysis to study the distribution of the heavy metals throughout the timber and found it was primarily located in the intracellular sections. The study investigated using three different sources of waste CCA treated timber, with varying results in heavy metal content in the corresponding fibres. In the best case, 100% Cr and As and 95 % Cu was removed. In the worst case, a removal of 68%, 66%, and 95% of Cr, As, and Cu was reported [19]. The study indicates that the use of hydrogen peroxide bleaching as a secondary fibre treatment has the potential to reduce the heavy metal concentration in the corresponding fibres. The effects on fibres and resultant composite properties from the chemical treatments are investigated further in Section 2.5.4.

2.4 Matrix Materials

In composites, the matrix plays a crucial role in the performance of the material. Polymers used as matrix materials can be split into linear polymers, branched polymers, and crosslinked polymers and are typically categorised as thermoplastics (linear and branched polymers) and thermosets (crosslinked polymers).

2.4.1 Thermoplastics and Thermosets

The main difference between thermoplastics and thermosets is that the polymer chains are highly crosslinked in thermosets and minimally or not crosslinked in thermoplastics. This variance in structure leads to an array of different properties.

Thermosets typically require being chemically cured to form covalent bonds between chains, to form a highly crosslinked 3D network structure. The covalent bonds between chains restrict relative motion between chains, typically producing a material that is stiffer, stronger, and less susceptible to creep than thermoplastics [15].

Thermoplastics are made up of polymer chains that are not crosslinked together. The chains can be either branched or linear. The mechanical properties of thermoplastics are heavily influenced by their viscoelastic behaviour. When subject to loading at high strain rates, the polymers act as an elastic material. However, when subject to constant loads over time, the polymer chains are subject to sliding over one another, acting as if it were viscous. The viscoelastic properties are impacted by a number of variables, including the degree of crystallinity, the temperature in relation to the glass transition temperature T_g and the melting temperature T_m, the length of molecule chains, the amount of branching in the polymers, and the amount of entanglement [59]. Due to the viscoelastic behaviour, thermoplastics are very susceptible to time-dependent mechanical behaviour such as creep and stress relaxation [59]. The creep properties are extremely complex and determined by a number of properties that determine the polymers' ability and rate to move past each other. Below the T_g creep effects are relatively small [59].

One of the most notable limitations of matrix materials is a result of natural fibre composite processing temperatures, as natural fibres are typically susceptible to thermal degradation at approximately 200 °C. The thermal limitations require thermoplastics that can be softened or molten below 200 °C, or thermosets that can be cured below 200 °C to be used as matrix materials to allow for processing of composites without degradation.

Thermoplastics are also much easier to recycle as thermosets typically degrade rather than melt at elevated temperatures [40]. Therefore, for sustainability purposes, the use of thermoplastics could be regarded as an advantage over thermoset matrix materials due to the ease of using recycled polymers as a matrix material and the potential to recycle composites themselves.

2.4.2 Polypropylene

Polypropylene (PP) is a semi-crystalline thermoplastic used commonly throughout industries such as the automotive, packaging, and fashion industries [24]. Polypropylene can be produced through an addition polymerisation process using propene. PP is considered recyclable and downcyleable. However, the reported worldwide recycle fraction in the current supply chain is reported to be only 2.57 – 2.84 %. PP can be found as homopolymer or copolymers (including PE) which affects the material properties. Typically, a homopolymer PP has better mechanical properties compared to PE. However, this is not necessarily the case with a random copolymer. Typical mechanical properties of a random copolymer PP are shown in Table 2-4. PP has a glass transition temperature substantially below room temperature, at -24 to – 16 °C and a melting temperature of 140 to 150 °C. The maximum service temperature is reportedly 66.6 to 83.8 °C (maximum useable temperature before mechanical properties change extensively) [24].

Table 2-4: Typical mechanical properties of a random polypropylene copolymer. Properties obtained from [24].

Young's Modulus (GPa)	0.824 - 1.02
Yield Strength (MPa)	24.1 - 28.4
Tensile Strength (MPa)	26 - 50
Elongation at Yield (tensile) (%)	6.69 - 11.7
Elongation at Break (tensile) (%)	112 - 483
Flexural Modulus (GPa)	0.824 - 1.02
Flexural Strength (MPa)	31.6 - 37.5

2.5 Wood-plastic composites

2.5.1 Composites

Composite materials can be regarded as a material made up of two or more inherently different materials, adding together to produce a new material. The new material's properties are a hybrid of the original material properties. Wood-plastic composites are comprised of wood flour, or wood fibres, with a polymer matrix. The use of wood flour or fibre is used to improve the mechanical performance of the polymer matrix.

2.5.2 Method of Reinforcement

For the purpose of this study, both wood flour and fibre will be categorised as ‘reinforcement’ materials as they act to improve the mechanical properties of composites. Wood fibre composites can be regarded as short fibre composites. In short fibre composite materials, loads are transferred from the matrix to the higher strength fibres through shear stresses at the fibre-matrix interface. The ends of the fibres do not bear any of the load [40, 60, 61]. Due to this transmission of the force, the composite properties are determined by the matrix, fibres, and interfacial properties. Fibre can also be regarded as acting to 'pinch' the polymer matrix, reducing strain and increasing stiffness, especially in the fibre-matrix interface area, shown in Figure 2-3 [61].

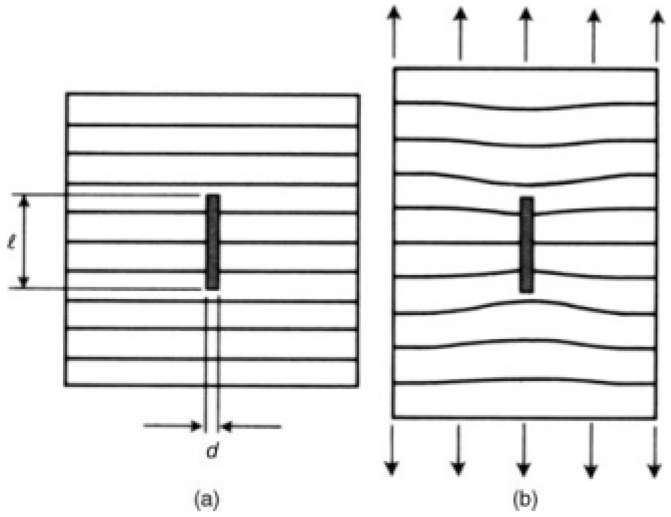


Figure 2-3: A cylindrical reinforcing fibre in a polymer matrix: A) Composite in the undeformed state, B) Composite under a tensile load. Image obtained from [61].

Due to the low aspect ratio of wood flour, the reinforcing capabilities are limited. However, the addition of wood flour does act to stiffen the material. Tensile and flexural strength are typically maintained or reduced [21]. The performance of wood flour composites has been found adequate for common applications of WPC. Furthermore, wood flour is easier and cheaper to produce, and easier to incorporate into wood-plastic composites making it more suitable for a number of applications [54].

2.5.3 Typical properties of WPC

Table 2-5 summarises common mechanical properties of wood fibre and flour reinforced PP composites (reportedly produced with 40 wt.% fibre/flour) [20]. The properties reinforce that fibres from timber do a better job of reinforcing PP than wood flour. The use of a coupling agent shows a substantial increase in mechanical performance (further discussed in Section 2.5.4). When comparing the mechanical properties to common building material in the construction sector (Table 2-1), the literature indicates that a higher strength can be attained with the composites compared to the likes of radiata pine. However, the modulus is much lower.

Table 2-5: Typical mechanical properties of wood-plastic composites produced from PP reinforced with wood flour and fibre. Data obtained from [20].

		Flexural		Tensile		
Filler type	**Coupling Agent Included**	**Max Strength (MPa)**	**Modulus (GPa)**	**Maximum Strength (MPa)**	**Modulus (GPa)**	**Elongation at Break (%)**
None	no	38.3	1.19	28.5	1.53	5.9
Wood flour	no	44.2	3.03	25.4	3.87	1.9
Wood flour	yes	53.1	3.08	32.3	4.1	1.9
Thermomechanical pulped softwood	no	48.9	3.1	29.7	3.68	2.1
Thermomechanical pulped softwood	yes	76.5	3.5	50.2	3.89	3.2

Section 2.1 suggests that the durability performance of composites can be regarded as one of the most significant properties for application, and a 50 year durability will likely be required for application as a structural component [25]. Due to the use of a thermoplastic matrix, one of the most limiting factors for durability is the susceptibility to creep [62]. The addition of natural fibres to a thermoplastic matrix has been reported to reduce the effects of creep and increase creep resistance at elevated temperatures [54, 63, 64]. However, for structural application, long term creep properties will require evaluation. Other properties that affect durability include UV resistance, biodeterioration, and termite resistance [29]. However, these properties are more dependent on the application and the exposure of the material to conditions such as the weather, ground, water. Furthermore, WPC is already commonly used in semi-structural applications (e.g.. decking and fencing) where it is exposed to weather, suggesting these properties are less of a concern than creep.

2.5.4 Factors Affecting Properties of Composites

The following section comprises some of the most influential factors affecting natural fibre composite properties.

Interfacial Strength

The interfacial strength between fibre and matrix in a composite plays a vital role in the mechanical performance of composites; force is transferred from the matrix to the fibres through the interface. Poor interfacial strength can limit the ability to transfer force. The interfacial strength of natural fibre composites and wood-plastic composites tends to be a limiting property due to the hydrophilic nature of polar cellulosic materials, naturally being repelled by typically non-polar hydrophobic polymers used as a matrix. The transmittance of force through the interface can only occur when the fibre and matrix come into contact with each other, commonly referred to as wetting of the fibre. Interfacial bonding can take many forms, including mechanical interlocking, electrostatic bonding, chemical bonding, and interdiffusion bonding. Mechanical interlocking occurs when the fibre surface is rough, resulting in increased friction to improve interfacial strength. Electrostatic bonding is possible when either the fibre or matrix is positively charged, and the other component is negatively charged, with the difference in charge causing electrostatic attraction to increase interfacial strength. Chemical bonding occurs between functional groups on fibres and in the matrix; the strength is dependent on the type of bonding that occurs. Finally, interdiffusion bonding can occur when atoms from the fibre and matrix interact with each other at the interface. For polymers, this can occur when polymeric chains from both components entangle with each other [6, 40, 41].

Fibre Length

The fibre length (and aspect ratio) is a critical variable in composite materials. In short fibre composite materials loads are transferred from the matrix to the higher strength fibres through shear stresses at the fibre/matrix interface. The ends of the fibres do not bear the load. The mechanical properties of fibres are typically higher than the matrix and the interface, therefore, if the loads in the fibre can be maximised to the point where the failure mode for the composites is through fibre failure, the composite performance will likely be maximised. However, for any short fibre composite material, a critical fibre aspect ratio defines the minimum fibre aspect ratio to attain the maximum allowable fibre stress for a given tensile load. Therefore, the fibres need to have an aspect ratio greater than the critical fibre aspect ratio (or a length greater than the critical fibre length) in order to cause the fibre to break during the tensile loading of a composite. Ideally, the fibre length would be much greater than the critical fibre length to allow maximum loading of the fibre along the majority of its length, increasing the efficiency of fibre loading. The critical fibre length, L_c, can be calculated using the following equation,

$$\frac{L_C}{d} = \frac{\sigma_f}{2\tau_i}$$

Where d is the fibre diameter (L_c/d is the critical fibre aspect ratio), σ_f is the tensile strength of the fibre, and τ_i is the interfacial strength [40, 41, 61]. Increased fibre length has also been reported to improve creep performance of natural fibre composites [54].

Thermal Stability of Fibres

The thermal stability of natural fibres is a limiting factor in producing composites. The main disadvantage is that natural fibres typically degrade at approximately 200 °C, which reduces processing options when producing composites and restricts matrix selection to polymers with a melting point below this temperature [40].

Fibre Dispersion

Fibre dispersion throughout the matrix is regarded as being closely related to fibre wetting and can significantly affect the mechanical performance of natural fibre composites. Good dispersion can be considered as separate individual fibres or particles within the matrix, whereas poor dispersion typically results in an agglomeration of fibres or particles. Good dispersion can be achieved by maximising the mixing of the matrix and fibres, which maximises the wetting of fibres, which is required for good interfacial strength. Furthermore, good dispersion helps to avoid voids or porosity within the matrix. Dispersion of fibres can be influenced by the use of additives and the methods used for compounding composites [40, 54].

Fibre Orientation

The strength and stiffness properties of composites are generally maximised when fibres are aligned parallel to the direction of the applied load and typically weaker when the fibre is perpendicular to the applied load [40, 60]. Fibre orientation is heavily influenced by the processing conditions and mould geometry used for producing short fibre reinforced composites [40, 60].

Fibre to Matrix Fractions

The ratio of fibre to matrix has a large influence on composite properties; an increase in fibre content can increase the number of fibres to transmit the load, therefore increasing strength. In contrast, a low fraction of fibres can improve the wetting and dispersion of fibres, which can improve the transmission of forces through the interface into the fibre. For composites with a reasonable interfacial strength, composite strength is reported to reach a maximum at 40-55 wt.% fibre content for injection moulded parts, whereas higher content typically reduces wetting. Maximum stiffness is reported to be at a higher fibre content of 55 – 65 wt.% [40].

Fibre Treatment and Coupling Agents

Due to the limitations of interfacial strength in natural fibre composites, significant research has been conducted into chemical and mechanical treatments of fibres to help increase the interaction of fibres and matrix. A recent review of natural fibre composites developments found that chemical treatments of fibres were more abundant in literature, and better improvements in composite properties were attained [40]. Alkali treatments and hydrogen peroxide bleaching were investigated due to their potential to obtain fibre from timber and reduce the heavy metal content in the fibre. Ultrasonic treatment was also investigated as a possible environmentally friendly secondary treatment of the fibre to improve composite properties.

Alkali treatment is commonly used with an aqueous sodium hydroxide solution to remove lignin, hemicellulose, and extractives, exposing cellulose fibres and increasing surface area and roughness for improved interfacial strength. Alkali treatments of fibres are commonly used throughout literature and have widely reported improving interfacial shear strength, tensile strength, Young's modulus, failure strain, impact strength, fracture toughness, and flexural properties of natural fibre composites [40]. Alkali treatments are known to increase the crystallinity of fibres due to the removal of lignin, hemicellulose, and extractives; however, increased levels of alkali treatment can cause degradation of the cellulose and result in the formation of an amorphous cellulose fibre [40].

Bleaching with hydrogen peroxide is commonly used in the pulp and paper industry, typically for the removal of lignin to brighten the colour of the pulp. Furthermore, it is considered an environmentally friendly process as it does not use chlorine-based chemicals [55]. The literature on the use of hydrogen peroxide for fibre treatment for NFCs is minimal; however, a few cases have shown positive results. One study focused on the effects of using hydrogen peroxide for treating kenaf fibres for use in PLA composites. When used as a reinforcing material in PLA composites, hydrogen peroxide bleaching increased the composite tensile strength from 38.5 MPa to 42.9 MPa (using 10 wt.% fibre). The report concluded that the bleaching resulted in a rougher fibre surface and, subsequently, better interfacial strength within the composites [65]. A further study found very similar results when using hydrogen peroxide to bleach oil palm empty fruit bunch fibres for use in PLA composites, with improved mechanical performance considered to be due to increased interfacial strength [66].

The environmental impact of fibre treatments is of concern due to the high chemical and energy consumption of common processes. Ultrasonic treatment of lignocellulosic biomass has shown the potential to assist with commonly used mechanical and chemical treatment processes, reducing the time of treatments and chemical consumption, therefore, potentially reducing the environmental impact [67]. However, the treatment does consume a lot of energy [67]. Ultrasonic (or ultrasound) treatments of lignocellulosic material are possibly best reviewed in a paper investigating ultrasound as a pre-treatment for biofuels [67]. In simple terms, ultrasonic treatment can be regarded as creating large localised pressure differences within a solution to enhance mechanical or chemical treatment processes [67]. Ultrasonic treatment of wood flour has been investigated as a treatment method for wood-plastic composites (maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent, and PP as a matrix). The study investigated treating wood flour with sodium hydroxide with and without ultrasonic treatment. The report found that for 1 wt.% and 3 wt.% NaOH treatments, the use of ultrasonic treatment increased lignin removal of the wood flour and increased the tensile strength and modulus of composites. The study indicated that the improvement of properties was due to the reduction of lignin and increased exposure of cellulose improving bonding ability with the MAPP coupling agent. The report also suggested some reduction in tensile strength in composites treated with higher concentrations of NaOH, most likely due to the degradation of cellulose [68]. Ultrasonic treatment also has the potential to induce fibrillation on natural fibre surfaces [69]. The potential to generate fibrillation of the fibre surface can increase the surface area of fibres and therefore increase interfacial strength within composites. This phenomenon has been shown through the use of fibre beating to induce fibrillation. Fibre beating was found to cause fibrillation of the primary cell wall, increasing surface area and therefore increasing interfacial strength. The study found an increase in up to 10% of tensile strength was possible, although with increased fibre beating, the tensile strength was reduced, likely due to a reduction in fibre length [70].

Another way to improve the interfacial strength of composites is to include a coupling agent. Maleic anhydride grafted polymers are commonly used as coupling agents as they increase the interaction between fibres and polymers. The coupling agent acts by having a functional group that can bond with the hydroxyl groups on the fibre surface and have the polymeric chain diffuse into the polymer matrix [6]. A review on natural fibre composites regarded the use of maleic anhydride grafted polymers as the most successful chemical used to improve interfacial strength [40]. Furthermore, the improvement of interaction between matrix and fibres using maleic anhydride grafted polymers has been found to improve wetting and dispersion of fibres, further improving composite performance [40].

An improvement of tensile strength can be found with the use of up to 4-8 wt.% maleic anhydride grafted polypropylene (MAPP) in wood-plastic composites [6]. A study on the use of kraft fibres from radiata pine using a PP matrix with a MAPP coupling agent found the use of 4 wt.% MAPP optimal for Young's modulus and tensile strength of composites. Furthermore, a report using alkali treated CCA treated timber fibres in a PP matrix found an increase in Young's modulus with the use of up to 4 wt.% MAPP [18].

Effects of Composite Processing

The processing of composites is commonly split into two distinct steps: compounding and manufacturing of parts. Compounding can be regarded as the step of combining the matrix and fibres into a single material. Manufacturing is then used to produce parts from the compounded natural fibre composite material. The methods used for producing composites can have a large effect on the resultant composite properties.

Extrusion is commonly used in the wood-plastic composite industry for compounding and extruding profiles [6]. Extrusion is commonly completed with single-screw or twin-screw extruders. Twin-screw extrusion has been found to give better dispersion of fibres and mechanical performance of composites than single screw extrusion [40]. Twin-screw extrusion acts through the two intermeshing screws that act to push the material through the barrel, while heating elements act to heat the barrel of the extruder to the required temperature for processing [15]. The speed and temperature of the extrusion process can affect the composites. High screw speeds can lead to effects such as air encapsulation and fibre breakage, whereas low screw speeds can lead to poor wetting and dispersion of fibres in the matrix [40].

Sigma blade mixing is a batch processing method used for compounding composites. Thermoplastics are added initially and heated until molten before adding fibres for compounding. A report on reinforcing PP composites with sisal fibres found that mixing time, speed, and temperature greatly affect composite properties. Mixing for short periods of time can lead to poor dispersion of fibres, and mixing for too long can cause fibre breakage, both leading to a reduction in mechanical performance. Rotational speeds from 30 – 50 rpm, composite performance was improved due to increased dispersion. However, increasing rotational speed increased fibre breakage. The mixing temperature was found optimal at 170 °C. At lower temperatures, fibre breakage was induced due to the high viscosity and shear stresses during mixing. At higher temperatures, thermal degradation of the fibres occurred, also causing a reduction in properties [71].

After compounding, an extra process (such as injection moulding or extruding) has to be undertaken for producing parts with specific shapes [72]. Injection moulding of thermoplastic parts is widely used and has the major advantage of being able to produce complex parts at a high production rate [73]. When injection moulding natural fibre composite materials, the fibres are orientated due to the flow of material, and the corresponding parts are anisotropic [73]. During the injection moulding process, the matrix is in a molten state and flows into the mould. The complex flow helps determine the fibre orientation in the resultant part. Converging flow results in highly aligned fibres along the direction of flow, whereas diverging flow results in fibres perpendicular to the flow. The shear acting on the flow of the polymer at the mould wall further impacts the fibre alignment. The shear along the mould wall typically aligns the fibres with the direction of the flow and forms a layer called the skin. Inside the skin layer, a core layer occurs with fibres typically orientated perpendicular to the flow. A schematic of the effects of flow in a mould on fibre orientation can be found in Figure 2-4 [74]. Residual stresses can be caused by rapid cooling of the thermoplastic matrix resulting in a premature failure of composite parts. Residual stresses can also be a result of high-pressure gradients, non-uniform temperature profiles, the orientation of polymer chains, and differences in thermal expansion coefficients between fibres and matrix [74]. Process parameters that can be altered to optimise material properties include "melt temperature, injection and screw speeds, injection pressure and the mould temperature" [74].

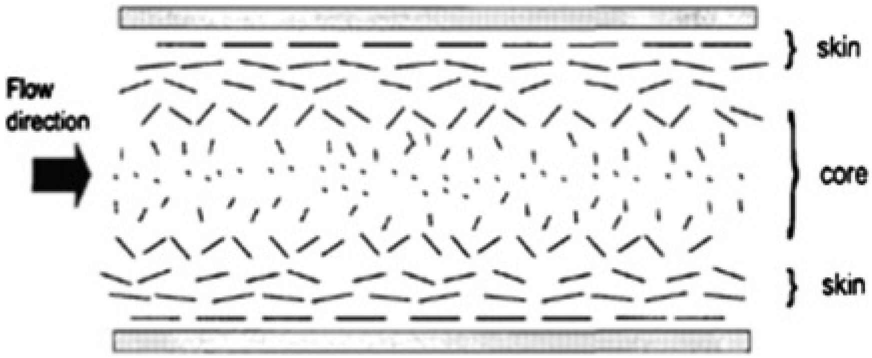


Figure 2-4: Influence of injection moulding flow on fibre orientation. Image obtained from [74].

2.5.5 Effects of CCA Heavy Metals on Composite Properties

Although the concept of using waste treated timber as reinforcement for WPC is not new, the literature is very minimal. It has also been considered potentially harmful for workers to work with and possibly hazardous in application for users and the environment due to the potential leaching of heavy metals [11].

Previous studies have explored the use of wood flour derived from CCA treated timber as a reinforcement material in wood-plastic composites. One study compared composites produced from virgin pine, recycled urea formaldehyde particle board, and recycled CCA treated timber. The composites produced with CCA treated timber gave the highest modulus of elasticity and modulus of rupture. The report suggested the improved performance was due to the increased hydrophobicity of the wood flour, and the heavy metals have the potential to increase the thermal conductivity of the wood flour, thus reducing the time taken to melt the thermoplastic during processing and improving encapsulation of the flour [16]. Both the increased hydrophobicity and increased melting rate of polymers have the potential to improve interaction with the wood flour and improve interfacial properties. The theory of increased thermal conductivity was based on research indicating CCA treated timber cell walls being covered in 1 – 5 μm deposits of copper chromium and arsenic oxides [16, 75]. Moisture absorption of CCA treated wood flour composites was reduced compared to virgin pine, and biological decay tests indicated that the use of CCA treated timber eliminated fungal decay from occurring. Furthermore, the use of CCA treated timber showed the most colour stability in composites (independent of the polymer used as a matrix) [16]. However, the report did find that leaching of arsenic from the timber was roughly 1000x greater than the allowable drinking levels when using 50 wt.% CCA treated timber flour and suggested limited applications in areas not in contact with people. Interestingly the report also indicated that the use of recycled HDPE reduced leaching compared to virgin HDPE.

More recently, another study was completed evaluating the mechanical and biological properties of wood-plastic composites produced with wood flour produced from CCA treated timber. The mechanical properties were again found to increase using CCA treated timber and was attributed to the increased interfacial properties due to the increased hydrophobicity of the wood flour due to the CCA treatment. The addition of 5 wt.% MAPE (the maximum MAPE content tested) was found to improve the properties further. The report found improved dimensional stability during moisture absorption tests with CCA treated timber wood flour compared to virgin pine and again found the best properties with 5 wt.% MAPP. Biological performance was also improved with CCA treated timber compared to virgin pine. Furthermore, the effects of wood flour content on biological performance were reduced when using CCA treated timber. Leaching of arsenic was measured and reported to be higher than acceptable drinking levels, and recommended applications were again limited. However, the report did find that the addition of MAPE reduced the leaching [17].

A recent report investigated the use of CCA treated timber fibres (obtained through a soda process) in polypropylene composites. The study mainly focused on the mechanical performance obtainable with varying fibre and MAPP (maleic anhydride grafted polypropylene) content. The study found that the use of 4 wt.% MAPP was optimal for the composites, and at 30 wt.% fibre, the properties of the composites were still increasing (30wt.% was the maximum content tested). The report also included a comparison study of virgin and CCA treated timber on the moisture absorption of composites. The results indicated that the composites produced with CCA treated timber fibres were more resistant to moisture absorption than that of the virgin wood fibre composites. The study suggested that the moisture absorption properties were improved due to the increased hydrophobicity of the fibres [18]. However, this could also be due to improved encapsulation due to increased thermal conductivity, as suggested in other studies [16]. The addition of 4 wt.% MAPP further improved moisture absorption and made a larger difference than the use of CCA treated timber [18]. The change in moisture absorption properties indicates that heavy metals are still present and affect the composite properties. Unfortunately, the study did not include any investigation into the effects of fibre treatments on the heavy metal content in the fibres or the possibility of leaching from the composites, which appear to be the biggest limitation of using waste CCA treated timber in wood-plastic composites in the other studies.

2.6 Environmental Impacts

2.6.1 Circular Economy and Life Cycle Analysis (LCA)

A recent review on the circular economy (CE) concept explained the CE model as "an economic system that replaces the 'end-of-life' concept with reducing, alternatively reusing, recycling and recovering materials in production/distribution and consumption processes. It operates at the micro level (products, companies, consumers), meso level (eco-industrial parks) and macro level (city, region, nation and beyond), with the aim to accomplish sustainable development, thus simultaneously creating environmental quality, economic prosperity and social equity, to the benefit of current and future generations" [76]. The circular economy concept's goal could be considered as a model to improve environmental sustainability by preserving natural resources and minimising waste. However, the circular economy concept also has the potential to improve other environmental issues such as reduced emissions and energy consumption from reduced processing of virgin materials [3].

Life cycle assessment (LCA) is one way of measuring the environmental impact of a product or material for a specific process. LCA can be used as a tool to measure and make decisions on the implementation of the circular economy. A review on the environmental impact of adopting a circular economy for the construction sector reported that LCA should be used to evaluate the options for circular economy solutions in order to ensure environmental benefit [3].

International standards ISO 14040 – ISO 14043 were produced as a framework for LCA during 1997-2000 and were the recommended standards for performing LCA [77, 78]. The standards have since been replaced with ISO 14040 and ISO 14044 and should be used for performing an LCA [79, 80]. ISO 14044 suggests that LCA methodology should be split into the following four categories [80]:

- Goal and scope: used to define the material or product and the purpose of the study.
- Inventory analysis: used for modelling a system according to the scope and definition of the study. The inventory analysis models the material and energy inputs and outputs to each individual process within a system and can then be used to model the material and energy flow for the entire system based on a functional unit [80].
- Impact assessment: uses the data from the inventory analysis to determine the environmental significance of the system.
- Interpretation: is the procedure of discussing and making conclusions, recommendations, or decisions from the results.

2.6.2 Circular Economy and LCA in the Construction sector

The building industry could be regarded as having one of the earth's largest environmental impacts; it is estimated that the construction sector is the world's largest consumer of raw materials and contributes more carbon emissions than any other industry [81]. Adopting the circular economy model principles in the construction and demolition industry could minimise reliance on virgin resources and solid waste pollution. Furthermore, a circular economy has the potential to reduce carbon emissions, and other environmental impacts, as a result of reduced processing and transportation of materials and resources [3].

LCA has been the primary indicator of a circular economy due to the measuring of material flows throughout a product's life cycle. The use of LCA for the building sector has been used immensely. However, the results of LCA studies vary depending on the boundary conditions used within the study, and impacts measured. A recent review paper found that environmental impact varies heavily depending on location, and industry standards and databases need to be constructed for individual countries or regions. For example, the carbon emissions of a residential building in Hong Kong range from 497-637 kg CO_2 eq./m^2 compared to 757-1022 kg CO_2 eq./m^2 in China. The report concluded that using LCA for making decisions or benchmarks for environmental impacts in the construction industry, requires data specific to individual regions [3]. The same review found that only 45 % of studies considered a cradle to grave life cycle of a building. Therefore, most studies did not cover a building's whole life cycle, making it difficult to compare the environmental impact of new solutions for a circular economy. Roughly 40 % of studies only reported one environmental impact category (primarily carbon emissions or energy consumption), and for a more comprehensive study, more environmental impact categories should be evaluated due to the complexity of the building industry and the large range of environmental impacts caused [3]. However, the study indicates that carbon emissions and energy consumption are very important impacts for sustainability and should be evaluated for comparison with other construction methods.

2.6.3 Environmental Impacts of Wood-plastic Composites for the Construction Sector

Natural fibre composites and wood-plastic composites are regularly considered environmentally friendly alternative materials for construction and automotive industries due to being produced from waste plastic or bioderived plastic and bioderived fibres or fillers. However, the production of composites requires the preparation of wood flour or fibre and plastic, as well as processing to compound and produce parts, all of which consume chemicals, solid materials, water, and electricity and produces emissions. Furthermore, the production of wood-plastic composites introduces new applications and end-of-life solutions that differ from traditional materials. All of these factors make the environmental impact of producing wood-plastic composites and using them in the construction industry much more complex than the simple notion that the use of recycled or bioderived plastic and bioderived or recycled fibres is environmentally friendly. Therefore, LCA (or other environmental impacts assessment tools) should be employed to assess and make decisions on the production and application of composites.

The environmental impact of wood-plastic composites has been studied using LCA. A New Zealand based study investigated the production of wood-plastic composites produced with virgin polypropylene reinforced with virgin wood fibres. The study found that the largest benefit to using wood-plastic composites compared with polymers was the increase in strength of composites resulting in a reduction in material required to hold the same load and hence a lower environmental impact. The report suggested a functional unit of "material service density" which refers to a volume of material required for a specific strength. The paper studied the use of 10, 20, and 30 wt.% fibre that had been attained through thermomechanical pulping. The results indicated that the addition of more fibres reduced the environmental impact, and this result was magnified when using the proposed "material service density" functional unit [82].

Additionally, other studies for LCA of wood-plastic composites have shown that the use of wood-plastic composites produced with waste materials have a reduced environmental impact than wood-plastic composites made with virgin materials [14, 83]. This includes the use of waste polymers as raw materials and waste materials being used as reinforcement [14].

A study in Finland considered the use of construction and demolition waste as raw materials for WPC. The study investigated using wood, mineral wool and plasterboard as filler materials. The study found that construction and demolition waste should be used for producing wood-plastic composites if the recovery of individual materials for reuse is not economically or technically feasible. Furthermore, the study showed that the use of construction and demolition waste as raw materials for WPC had a lower environmental impact than traditional disposal methods, including landfill and incineration. The study further concluded that the production and application of WPC produced with construction and demolition waste was environmentally beneficial (for climate change) even when substituting timber products in the construction industry [14]. The study indicated that the use of wood-plastic composites derived from the construction and demolition waste could be a viable, sustainable alternative material for the construction sector. Thus, further showing the benefits of the circular economy concept for environmental sustainability. However, the report focuses on the use of wood waste, or mineral wool and plasterboard as filler materials, which only required mechanical processing to prepare the filler materials. In comparison, chemically processed wood fibres require considerable processing and chemical and energy input to obtain fibres, and the environmental impacts are likely to be much higher. Furthermore, the report is focused on Finland's construction sector, whereas the environmental impact of processing WPC and substitution with construction materials are likely to differ in New Zealand.

Overall, adopting principles from the circular economy for the construction and demolition industry can be seen to be environmentally favourable. However, the use of LCA can improve decision-making and provide a further understanding of the environmental impact of a product or a process. The use of waste CCA treated timber as a reinforcement material for wood-plastic composites to be used in the construction industry is based on the circular economy model and has the potential to provide an environmentally friendly material. However, if fibres are used for the composite material, the environmental impact will likely be much higher due to the further processing (and corresponding energy and material consumption) required to produce fibres. Therefore, LCA should be used to understand the environmental impacts and help influence decisions on the best processing methods used for producing WPC.

Chapter 3
Materials and Methods

The following materials and methods were used to prepare and analyse wood flour and fibres and wood-plastic composites produced from waste CCA treated timber. Wood flour and fibre was produced through initial mechanical preparation and then mechanical grinding to produce wood flour and chemical treatments to obtain fibre. Wood-plastic composites were then compounded using extrusion and sigma blade compounding and then injection moulded to produce parts for testing. The wood flour, fibre and WPC then underwent material testing.

3.1 Materials

The following materials were used in the treatment of fibres, preparation of composites, and laboratory testing for all experiments.

- CCA treated timber: Radiata pine treated to an H 3.2 hazard class. Supplied as roughly 1-metre waste offcuts of 2x4" and 2x2" planks by ITM, Hamilton, New Zealand. The timber was sourced on three occasions and is referred to as batch 1, 2, and 3 throughout the processing.
- PP: Yuplene RX 3600 Polypropylene Random Copolymer, produced by SK Global Chemical.
- MAPP: AC 950P Propylene Maleic Anhydride Copolymer produced by Honeywell International Inc.
- Sodium hydroxide: NaOH, Bulk grade solid pellets, produced by Sigma-Aldrich
- Sodium sulfite: Na_2SO_3, powder, produced by Sigma-Aldrich
- Hydrogen peroxide 30%: H_2O_2, produced by Sigma-Aldrich
- Sodium Silicate Solution Extra Pure: Na_2SiO_3, produced by Millipore
- Nitric Acid 65%: HNO_3, produced by Sigma-Aldrich
Hydrochloric acid fuming 37%: HCL, produced by Sigma-Aldrich
- Type 1 water: Ultrapure (Type 1) water, prepared using Milli-Q Reference Water Purification System

3.2 Preparation of Reinforcement Material from Waste CCA Timber for Composite Production

The use of CCA treated timber waste as a reinforcement material required mechanical and chemical processes to extract wood flour and fibres. The following combination of methods was used to gather five samples of reinforcement material, including wood flour and wood fibres, to be used in wood-plastic composites (WPC). For the purpose of this study, the term ‘reinforcement’ is used to describe wood flour and fibre as they are used to improve mechanical properties. The reinforcement samples (and acronyms used) include,

- Wood flour (wood particles) (F)
- Digested fibres (D)
- Digested and ultrasonic treated fibres (DU)
- Digested and bleached fibres (DB)
- Digested, bleached, and ultrasonic treated fibres (DBU)

For reinforcement materials that underwent two or more treatments, the fibre treatment methods are listed in the order they were carried out. For example, digested, bleached, and ultrasonic treated fibres (DBU) initially underwent a digestion process, then bleaching, and finally an ultrasonic treatment.

Fibres were then oven dried, and then ‘separated’ as they were prone to ‘clumping’ together while drying. The methods also include calculations for the yield of each chemical process.

3.2.1 Preparation of CCA Timber for Mechanical and Chemical Processing

The CCA treated timber was granulated for further processing based on reports where chemical processing was used to obtain fibres from CCA treated timber [18]. The granulating process was done in the following steps.

- A band saw was used to cut along the length of the timber to give a cross-section of roughly 25x25 mm
- A Ryobi RSH 2455G Garden Shredder was used to chip the timber.

- A Moretto GR granulator with an 8mm grate was used to produce treated timber granules.
- The timber was then dried for at least 12 hours in an 80 °C oven before further processing.

3.2.2 Wood Flour Preparation

Wood flour was produced via grinding granules of timber using a Sunbeam Multigrinder to make fine wood particles. 10 g batches of dried timber granules were ground for 1-minute periods and then screened through an 850 µm sieve, the maximum size for wood flour given in ‘Functional Fillers for Plastics’ [21]. After processing 30 g of timber granules, the retained wood particles in the sieve were re-ground for another 1-minute period and re-sieved to ensure the wood flour contained all of the constituents in the timber.

3.2.3 Digestion

The primary chemical treatment used for obtaining fibres was a digestion process with a sodium hydroxide solution using a custom laboratory-scale batch digester. A screening process was undertaken to investigate the following variables.

- The solution to wood ratio.
- NaOH concentration in solution.
- Addition of Na_2SO_3 in the solution
- Digesting multiple times.

The fibres analysed and used for composite preparation were produced with the following methods. A 1:8 ratio (by weight) of dried timber granules and 10 wt.% NaOH were added to steel canisters to be used in the digester. The canisters were then loaded into the digester, as shown in Figure 3-1, and submerged in tap water.

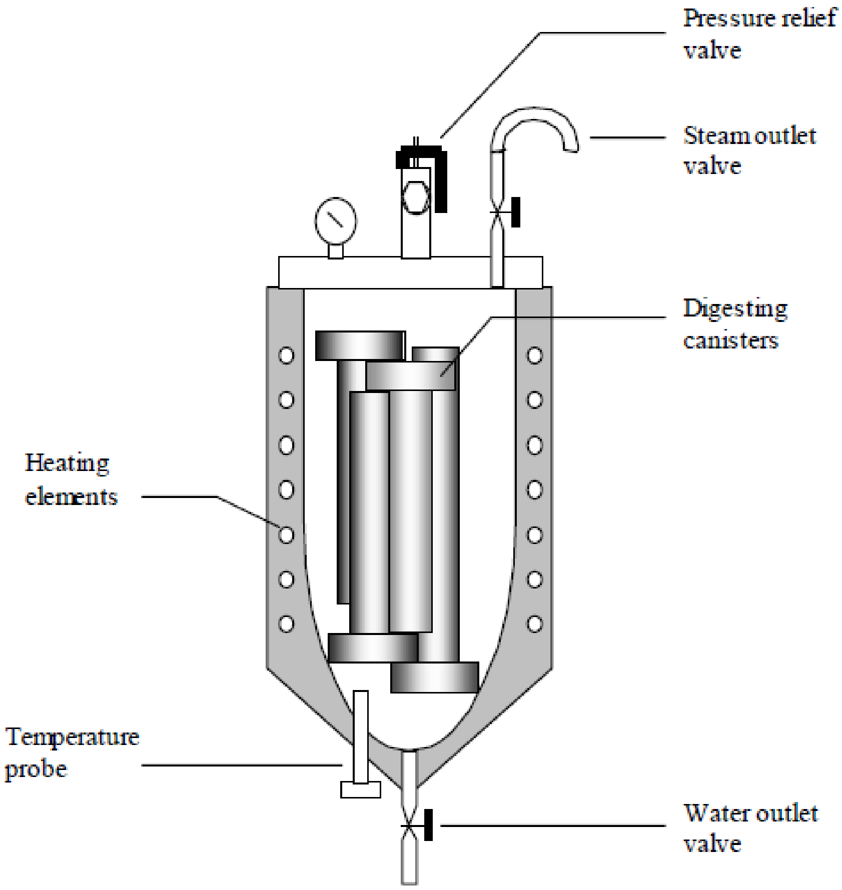


Figure 3-1: Schematic of laboratory-scale batch digester. Image obtained from [72].

The digestion was completed following the heating rate shown in Figure 3-2, based on a previous study for obtaining fibres with an alkali solution from CCA treated timber [18]. The digester was heated from room temperature to 50 °C at 30 minutes, 160 °C at 2 hours, held at 160 °C for another 2 hours, and then quenched to approximately 30 °C with tap water.

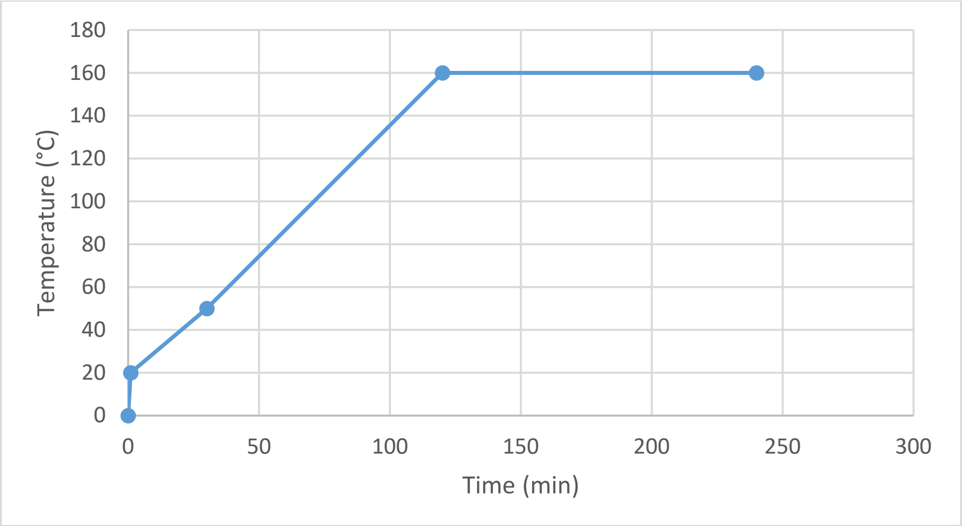


Figure 3-2: Heating rate used for digestion.

After digestion, the fibres were washed with tap water until a pH of 7 was reached to ensure the NaOH solution was removed.

3.2.4 Fibre Bleaching

Bleaching of the digested fibres was undertaken using a solution of hydrogen peroxide and sodium silicate. 25 g of oven-dry fibres and 2 L of tap water were added and mixed in a beaker creating a 1:80 ratio (by weight). A Silverson L4RT homogeniser was used to mix the fibre into the water and ensure the fibres were saturated. The mixture was then heated on a heating plate until a temperature of 70 °C was reached. 100 mL of hydrogen peroxide and 50 mL of sodium silicate were then added to start the bleaching reaction. The bleaching process was undertaken for 10 minutes on the heating plate, stirring continuously.

The fibres were then washed out with tap water until a pH of 7 was reached, ensuring the bleaching solution had been removed.

3.2.5 Ultrasonic Treatment

Ultrasonic treatment was completed with a Qsonica Q500 sonicator with a ½" probe. An ultrasonic treatment screening process was undertaken to understand the effects of sodium hydroxide in the solution, time of treatment, and the fibre to solution ratio.

Fibres used for analysis and composite production were treated using the following method. Fibres were treated in a 2wt.% NaOH aqueous solution, with a fibre to solution ratio of 1:40 (by weight); 5 g of fibre and 200 g of solution. A Silverson L4RT homogeniser was used at 3000 RPM for 2 minutes to ensure the solution saturated the fibres before treatment. The sonicator was used with 100% amplitude, a pulse time of 25 seconds on and 5 seconds off, for 5-minute periods to allow for cooling between treatment periods. The fibres were treated for a total of 20 minutes. Fibres were then washed using tap water until a pH of 7 was attained to ensure NaOH was removed.

3.2.6 Yield Calculation

The yield of each treatment was measured as the dry weight after treatment divided by the dry weight before the treatment,

$$Digestion\ yield = \frac{dry\ weight\ of\ fibres\ after\ digestion}{dry\ weight\ of\ timber\ before\ digestion} * 100\%$$

$$Bleaching\ yield = \frac{dry\ weight\ of\ fibres\ after\ bleaching}{dry\ weight\ of\ fibres\ before\ bleaching} * 100\%$$

$$Ultrasonic\ yield = \frac{dry\ weight\ of\ fibres\ after\ ultrasonic\ treatment}{dry\ weight\ of\ fibres\ before\ ultrasonic\ treatment} * 100\%$$

The total yield was found by multiplying the yield of all processes used together,

$$Total\ yield = Digestion\ yield\ * Bleaching\ yield *\ Ultrasonic\ yield$$

3.2.7 Fibre ‘Separation’ (after drying)

The fibres were prone to 'clumping' together upon drying and required ‘separating’ before composite production. The terms ‘separate’, ‘separating’, ‘separation’, and ‘separated’ in inverted commas are commonly used throughout this work to describe this physical process and not the chemical separation of fibre bundles during the digestion, bleaching, or ultrasonic fibre treatments. A Sunbeam Multigrinder was used to shear the fibres apart with blunt blades at a high rotational speed. ‘Separation’ of fibres was done using 3 g of fibre for 10 second periods. Any 'clumps' of fibre that failed to ‘separate’ repeated the process, as many times as required, until they were ‘separated’.

3.3 Fibre Analysis Methods

Analysis of the wood flour and fibres obtained from the waste CCA treated timber was completed to assess the differences in composite properties. All reinforcement samples were oven dried at 80 °C for at least 12 hours before analysis.

3.3.1 Microscopy

Microscopy was undertaken using an Olympus BX53M microscope to visually inspect fibres after processing during the screening process. Samples were prepared by mixing a small number of fibres in a drop of glycerol on a glass slide to encourage the separation of individual fibres. A second glass slide was placed on top to sandwich the fibres and promote the fibres to sit on the same plane for viewing in the microscope.

3.3.2 SEM (Scanning Electron Microscopy)

SEM was used to visually investigate wood fibre surfaces at high magnification. Fibres were mounted on aluminium stubs with carbon tape before being coated with a thin layer of platinum to make them electrically conductive using a Hitachi E-1030 Ion Sputter. The fibres were examined using a Hitachi S-4700 Field Emission Gun Scanning Electron Microscope operating at 5kV.

3.3.3 Fibre Quality Analysis

Fibre quality analysis was undertaken by Scion using a Fibre Quality Analyser - 360 (FQA-360). Triplicates of each analysis were done with a sample size of at least 10,000 fibres. The analysis was performed to provide data on fibre length, width, aspect ratio, number of bundles, and percentage of fines present after treatment. Fibre length was measured following ISO 16065-1: 2014 Determination of fibre length by automated optical analysis [84].

3.3.4 FTIR (Fourier Transform Infrared)

The effects of the fibre treatments on the chemical composition of the fibres were investigated using Fourier transform infrared (FTIR) spectroscopy. The samples were then mixed with KBr and pressed into a disk for analysis. The analyses were conducted using a PerkinElmer Spectrum 100. For each test, 32 scans were used in the spectral region of 4000-600 cm^{-1} with a resolution of 4 cm^{-1}.

3.3.5 XRD (X-Ray Diffraction)

XRD was used to measure the crystallinity index of the fibres to give insight into the amount of crystalline and amorphous material present and any potential change in the cellulose caused by the treatment. A Panalytical Empyrean X-ray diffractometer, with CuKα radiation generated at a voltage of 45 kV and a current of 40 mA was used to scan the samples between 5-60 °2θ using steps of 0.01 and 20 seconds per step. The crystallinity index of the samples, *CrI*, was calculated using the Segal peak height method [46], according to the following equation:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \; x \; 100$$

Where I_{002} represents the maximum intensity of the (002) plane reflection of the cellulose I structure at approximately $2\theta = 22.7^{\circ}$ and I_{am} is the intensity of the amorphous reflection at approximately $2\theta = 18^{\circ}$.

3.3.6 TGA (Thermogravimetric Analysis)

The thermal properties of fibres and wood flour were categorised using a Netzsch® STA449 F5 Jupiter thermogravimetric analyser (TGA). A dynamic analysis was done from 30 to 600 °C at a heating rate of 10 °C/min under argon flow of 40 mL/min. An isothermal analysis was also performed at 180 °C and 200 °C under air flow of 40 mL/min. The isothermal analysis was completed using a dynamic process to heat the samples from 30 °C to the isothermal temperature (180 °C or 200 °C) at a heating rate of 10 °C/min and then held in an isothermal state for 2 hours.

3.3.7 ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

ICP-MS analysis was performed to measure the heavy metal content in wood flour and fibres to assess changes in copper, chromium, and arsenic content with chemical and mechanical treatments.

Sample Preparation

Reinforcement samples were prepared for ICP-MS following a full sediment digestion method. A blank sample was also produced as a reference for the analysis.

Reinforcement samples were oven-dried at 80 °C for a minimum of 12 hours. Roughly 0.2 g of the sample was weighed (recorded to 4 d.p.) and placed in a clean 50 mL falcon tube. 1 mL of HNO_3 and 0.33 mL of HCl were added to the falcon tube. Type 1 water was added to ensure submersion of the samples and left to predigest in a fume hood overnight; lids were left on loosely. A digestion block was then heated to 80 °C, and the samples were heated for 1 hour.

Once the digestion was completed, type 1 water was added to each falcon tube to top up the sample to 50 ml. The samples were centrifuged for 10 minutes at 3000 RPM. Samples were then filtered using a 0.45 µm cellulose acetate, Minisart Syringe filter. 10 mL of the sample was then added to a 15 mL falcon tube for ICP-MS analysis.

Analysis

Elemental analysis was completed at the University of Waikato School of Science and School of Engineering, Mass Spectrometry Facility. The analysis was performed using an Agilent 8900 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS; Agilent Technologies, Santa Clara, California, USA) controlled by MassHunter Workstation (version 4.5). Sample introduction occurred via an SPS4 autosampler (Agilent Technologies, Santa Clara, California, USA) and PVC tubing (Pulse Instrumentation, Mequon, Wisconsin, USA). A 0.05-0.1 mL/min micromist U-Series nebuliser (Glass Expansion, Melbourne, Victoria, Australia) was attached to a quartz Scott Type spray chamber followed a quartz torch with 2.5 mm injector (Agilent Technologies, Santa Clara, California, USA). Following the plasma, sample was introduced to the rest of the instrument via a nickel sampler and skimmer cone, followed by an extraction omega lens (Agilent Technologies, Santa Clara, California, USA). The ICP-MS was optimised to maximum sensitivity daily (Table 3-1) ensuring oxides and doubly-charged were less than 2 %.

A five-point calibration curve, consisting of concentrations between 0.1 and 500 ppb was prepared for all trace elements using stock standard IV71-A (Inorganic Ventures, Christiansburg, VA, USA). A separate calibration curve, consisting of concentrations between 100 and 10,000 ppb was prepared for major elements (Ca, Si, P, S, K, Fe) using single-element standards (Inorganic Ventures, Christiansburg, VA, USA). Check standards were analysed every 20 samples and re-calibration was performed every 100 samples. Blank samples were analysed every 10 samples to ensure minimal carryover between samples. An online internal standard containing ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{193}Ir, and ^{205}Tl was used to monitor and correct for instrumental drift and matrix effects.

Table 3-1: ICP-MS Operating Conditions

ICP-MS Conditions	
Forward (reflected) power (watt) 1550	1550
Gas flows (Ar L/min):	1.05
Plasma	15
Nebulizer (carrier gas)	1.05
Makeup/Dilution gas	0.10
Sampling Depth (mm)	8.0
Detector mode	Pulse Counting
Replicates	3
Sweeps/replicate	50
Dwell time (s)	0.1-0.3

3.4 Composite Production

The production of composites was performed in two simple steps: compounding and injection moulding. Compounding was done using a twin-screw extruder or a sigma blade compounder. Injection moulding was performed to produce composite parts for material testing. All composites were produced with a random copolymer polypropylene matrix, and maleic anhydride grafted polypropylene as a coupling agent. All materials were oven dried at 80 °C for at least 12 hours before compounding and injection moulding.

3.4.1 Extrusion

Composites were produced using a Labtech LTE-20-44 Twin-screw extruder. The extruder was purged before extrusion and between different samples of composites. Extrusion was performed using a screw speed of 40 rpm and barrel temperatures ranging from 150 °C – 170 °C, Figure 3-3.

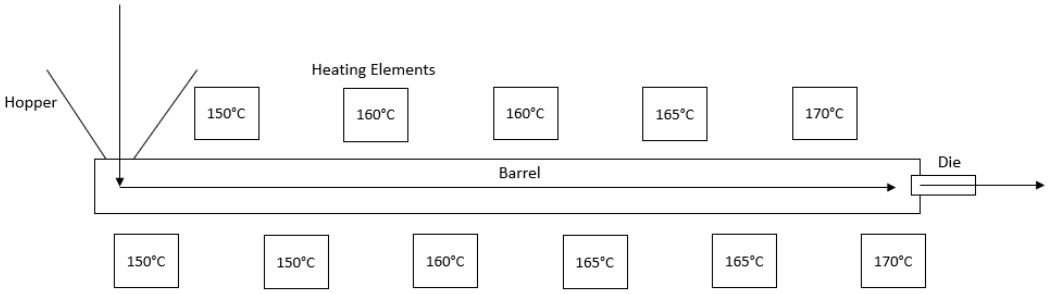


Figure 3-3:Schematic of extrusion temperature settings.

After extrusion, the composite material was granulated using a Moretto GR granulator.

3.4.2 Sigma Blade Compounding

A custom sigma blade melt compounder was used at 180 °C with a mixing speed of 40 rpm for compounding wood-plastic composites, Figure 3-4. 50 g batches of material (total mass) were used. The sigma blade compounding was performed by adding PP, then MAPP, and finally the wood flour or fibres to the mixer. After adding each material, the mixer was run until the torque and power were stable before adding the following material (roughly 3 minutes for the PP, 3 minutes for the MAPP, and 10 minutes for the wood flour of fibre), Figure 3-5.

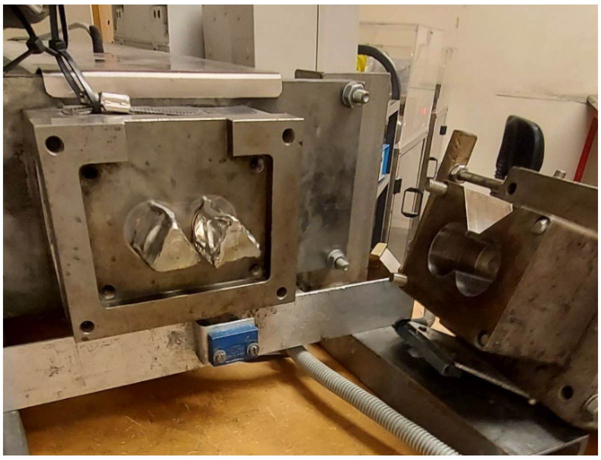


Figure 3-4: Custom laboratory-scale sigma blade mixer.

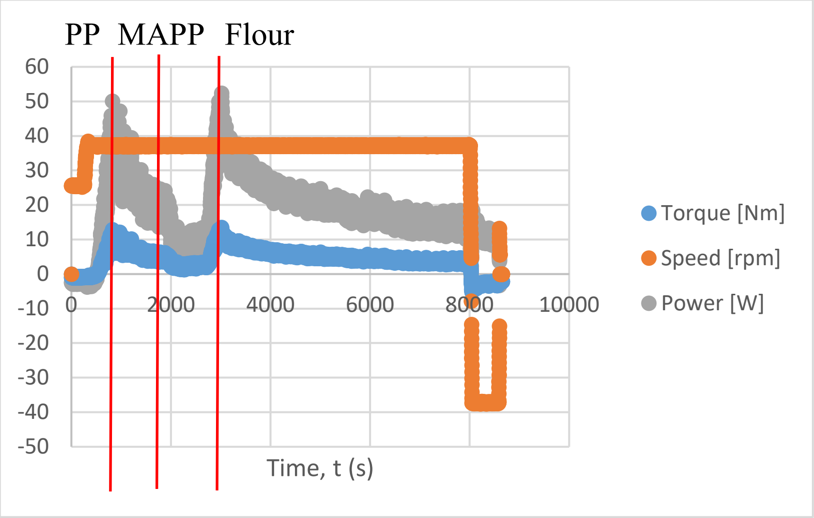


Figure 3-5: Torque, speed, and power during compounding of PP, MAPP, and wood flour using sigma blade compounder

After compounding with the sigma blade, the composite material was granulated using a Moretto GR granulator.

3.4.3 Injection moulding

The WPC granules were injection moulded using a BOY 35A Injection moulding machine, and a mould for a standardised Type 1 (ASTM 638-14 [85]) Dog-Bone, and a beam for 3 point testing (ISO 178:2019 [86]). The injection moulder was purged before use and between different WPC samples. The WPC was injection moulded with barrel temperatures ranging from 170 °C to 180 °C and 190 °C to 200 °C depending on the sample, Figure 3-6 and Figure 3-7. The temperature range used for each sample is further explained in the Results and Discussion.

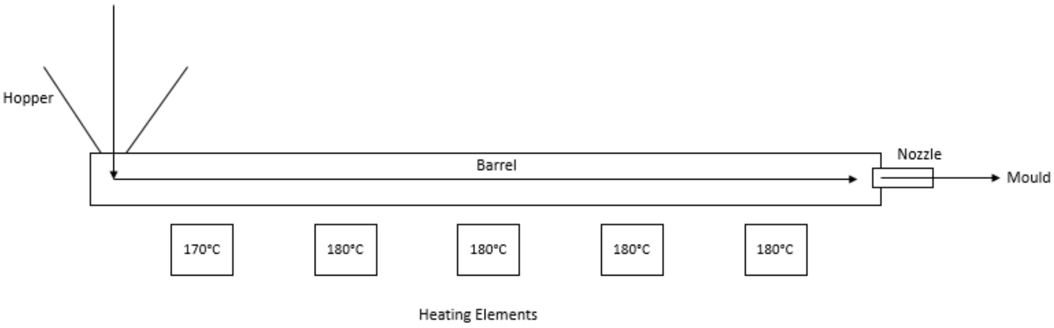


Figure 3-6: Schematic of injection moulding temperature settings (170-180 °C)

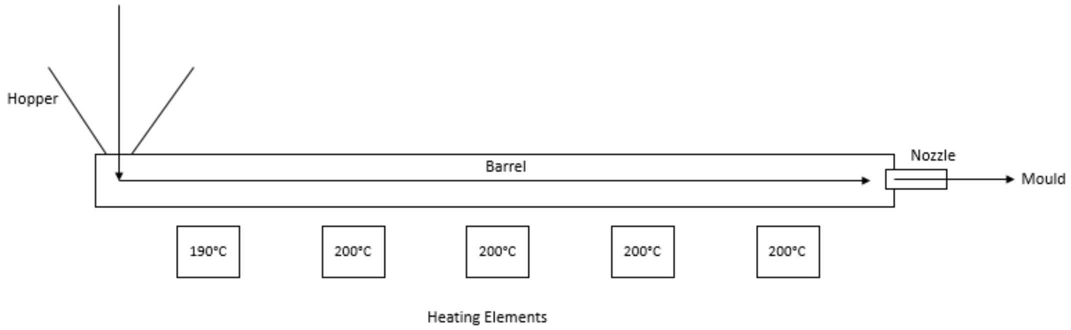


Figure 3-7: Schematic of injection moulding temperature settings (190-200 °C)

3.5 Composite Material Testing

3.5.1 Tensile Testing

Tensile testing was carried out based on ASTM 638-14: Standard Test Method for Tensile Properties of Plastics [85]. Test specimens were placed in a conditioning chamber at 23 °C ± 3 °C and 50 % ± 5 % relative humidity for at least 40 h. The specimens were then tested using an Instron 5982 Tensile Testing machine, using a 5 kN load cell operated at a speed of 5 mm/min. An Instron 2630-107 extensometer was used to measure the strain. A minimum of four composite specimens were tested per condition.

3.5.2 Flexural Testing

Flexural testing was completed based on ASTM D790-17: Standard Test for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials [87]. Test specimens were placed in a conditioning chamber at 23 °C ± 3 °C and 50 % ± 5 % relative humidity for at least 40 h. The specimens were tested using an Instron 5982 Tensile Testing machine, using a 5 kN load cell operated at a speed of 2 mm/min. A minimum of four composite samples were tested per condition.

3.5.3 SEM (Scanning Electron Microscope) Investigation of Failure Surfaces

SEM was used to investigate the failure surfaces of composites after tensile testing. Samples were mounted on aluminium stubs with carbon tape before being coated with a thin layer of platinum to make them conductive using a Quorum Q150V ES plus. The composite failure surfaces were examined using a Hitachi Regulus 8230 Field Emission Gun Scanning Electron Microscope operating at 5 kV.

3.5.4 Creep Testing

A basic creep test was undertaken to investigate the time dependent mechanical properties of composites and polypropylene. Test specimens were placed in a conditioning chamber at 23 °C ± 3 °C and 50 % ± 5 % relative humidity for at least 40 h. The specimens were tested in 3-point bending using an Instron 5982 Tensile Testing machine, using a 5 kN load cell. Creep properties were tested for polypropylene and composites at 15 and 30 % of the maximum flexural strength of the corresponding material. The test was undertaken in two steps; the specimen was initially loaded to the desired stress at a rate of 20 MPa/min and then held at the set stress for 12 hours. The ambient room temperature was measured over the same time frame as the creep test to investigate whether temperature differences could influence the test results. The ambient room temperature was measured using a Pico TC-08 logger with RS Pro K type thermocouples.

3.5.5 Moisture Absorption Testing

Moisture absorption testing was performed by submerging 3 samples of roughly 80x10x4 mm WPC in 300 mL of water. The mass of each sample was measured at varying time intervals over 15 days. Mass measurements took place at 0, 6, 24, and 48 hours and then at 4, 7, 10, 15 days.

3.5.6 Leaching Testing

Leaching analysis was completed based on AWPA E11-16 Standard Method For Accelerated Evaluation Of Preservative Leaching [88]. The leaching of heavy metals was completed by submerging 3 composite beams (roughly 80x10x4 mm) in 300 mL of distilled water. A 50 mL sample of the leachate was collected and the water replaced at set time intervals including 6, 12, 24, 48 hours and thereafter at 48 hour time intervals until 14 days was reached. The samples of leachate were then acidified by adding 0.2 mL of nitric acid, to 9.8 mL of leachate and measured for heavy metal content using ICP-MS (inductively coupled plasma mass spectrometry). A ‘blank sample’ of distilled water was also measured and subtracted from the leachate samples to find the concentration of heavy metals leached from the composite samples. The ICP-MS analysis was completed through the University of Waikato Chemistry department using the methods described in Section 3.3.7 for ICP-MS analysis.

3.6 Statistical Analysis

A statistical analysis was performed for some of the testing where a number of samples were tested. The averages of each test are displayed for the material properties. The coefficient of variance (COV) was calculated as the standard deviation divided by the average value and displayed as a percentage. Differences in fibre and composite results were tested using a statistical analysis performed using a Tukey test and analysis of variance (ANOVA) for significant ($p < 0.05$) differences. All analyses were performed using MINITAB Statistical Software.

Chapter 4

Results and Discussion

The following results and discussion section is split into three primary sections for the analysis of wood flour, fibre, and composite properties. The first section discusses the screening and development of the wood flour and fibre preparation methods. The following section focuses on characterising the wood flour and fibres used to help understand the composite behaviour. The final section investigates the mechanical and physical properties of the composites and the viability of using them in the building sector.

4.1 Screening and Visual Observations of Reinforcement Material Preparation Methods

4.1.1 Wood flour Preparation

The preparation methods used to produce wood flour were limited to the available equipment in the laboratory. It was found that a Sunbeam Multigirnder could grind the timber from granule form into wood flour. The process was slow as it could only handle 10 grams of timber at a time, and after sieving the flour, roughly one third of the timber required further grinding to refine it all to the required size. Nevertheless, the process allowed for grinding of all of the material, which ensured the entire composition of the treated timber was turned into flour for use in the composites. Thus, being true to the use of wood flour as a bulk reinforcement source from CCA treated timber where all of the timber would be ground up and used in the production of WPC.

4.1.2 Digestion Methods

The digestion process followed a heating rate as previously reported for pulping CCA treated timber and used a timber to solution ratio of 1:7 [18]. An initial trial digestion was completed using wood granules and a 10 wt.% NaOH solution. The process produced fibres that appeared to be primarily individual fibres. However, several fibre bundles were present, and the fibres were dark brown in appearance, suggesting excess lignin in the fibres.

The size of the timber pieces being digested was explored to see if larger chips of timber would obtain longer fibres, increasing the aspect ratio, and potentially provide better composite materials. For the test, mulch was used in the digestion process (timber that had not undergone the granulating step in the preparation method), and the resulting fibres were compared to those of the fibres from the timber granules. The fibres (from mulch) visually had a greater quantity and larger fibre bundles present, suggesting reduced penetration of the alkali solution resulting in less fibre separation. Furthermore, the individual fibres present did not visually appear to be longer than the fibres prepared from granules, suggesting no major advantages to using larger pieces of timber in the digestion process.

Typically, an alkaline sulphite process provides stronger pulps than a soda process (NaOH) [44, 45]. A test of adding sodium sulphite to the digestion solution to create an alkaline sulphite process was completed by adding 2 wt.% $NaSO_3$ to the 10 wt.% NaOH solution for digestion. However, visually the fibre did not appear any different (fibre bundles and fibre colour appeared unaffected), and the yield was very similar. Due to no visual changes in the fibres and requiring more chemical input into the system, the potential process was not continued. Furthermore, a commercial scale would likely require re-optimising the process due to the different scale, and equipment used, as well as potentially investigating different processes such as a kraft process. Therefore, for simplicity the soda process for digestion was continued with for investigating the viability of using waste CCA treated timber as a reinforcement material for WPC.

A trial run of fibre preparation for composite production was run using digestion with a solution of 10 wt.% NaOH. The liquor to wood ratio was also increased from 7:1 following previous reports for pulping CCA treated timber [18], to 8:1, to improve fitment of the solution and timber in the canisters of the laboratory-scale digester. Furthermore, the literature indicates a higher solution to wood ratio should improve penetration of the solution, which has potential to reduce the number of fibre bundles after digestion [56]. When comparing the fibres produced to that of the previous screening trials, the fibres were visually very similar; the fibres were dark brown, and a number of fibre bundles were present. The yield of this trial run was measured to be 33.6%. This is lower than expected from the literature, where a yield of 45- 65 % cellulosic fibres is expected for chemical pulps [18, 55, 56].

Due to the low yield obtained, testing of the digestion process was continued. The testing was focused on the effects of NaOH concentration on the fibres. Following previously reported methods for pulping CCA treated timber, a second digestion process was used with lower concentrations of NaOH in both digestion processes [18]. The first digestion was undertaken using a 2.85 wt.% NaOH solution with a 7:1 wood to liquor ratio (a 20 wt.% NaOH concentration on wood). The fibre was then washed and oven-dried at 80°C, with a resulting yield of 55.2% for the first digestion. The fibre was then digested a second time with a 2.85 wt.% NaOH solution (a 20 wt.% NaOH concentration on the initial weight of the timber). This test resulted in a yield of 37%. The fibre was visually of a lower quality than that obtained from the single digestion using a 10 wt.% NaOH solution. Fibres were visually less separated, and larger and more fibre bundles were present.

A second test was undertaken with a 5 wt.% NaOH solution and a 15 wt.% NaOH solution. The resulting fibres from the process using 5 wt.% NaOH were largely unseparated and still in the shape of the initial timber granules. The fibres from the digestion with 15 wt.% NaOH solution appeared to be lighter in colour, and smaller and fewer fibre bundles were present than the fibres from the 10 wt.% NaOH digestion process. Thus, indicating that more lignin and hemicellulose had been removed. However, fibre bundles were still present, and the yield was reduced to 25.6 %.

It appears likely that the low yield is due to factors other than just the high concentration of the sodium hydroxide solution. The issues in the digestion are likely due to a high variance in granule size, where small timber particles were potentially completely digested, and larger timber granules failed to be completely penetrated by the alkali solution and were therefore unseparated. Therefore, resulting in the low yield and the fibre bundles. This theory would agree with literature from kraft pulping, which suggests that the penetration of a solution during digestion is the same in all three directions, and therefore, the timber being digested should be separated on the basis of its thickness. However, the literature also indicates that pulp requires screening to remove fibre bundles (or shives) that have not been digested.

Due to the fibre screening results, the digestion process using 10 wt.% NaOH with a 1:8 timber to solution ratio was considered most appropriate for composite production. This decision was due to the presence of fibre bundles obtained even with higher concentrations of NaOH (15wt.%) and the potential to increase degradation of the cellulosic structure from overtreatment with higher alkali concentrations. Furthermore, secondary treatments have the potential to increase the quality of the fibres being used for composite production due to increased fibre separation through delignification and mechanical separation.

4.1.3 Ultrasonic Treatment Method

Ultrasonic treatment was investigated as a secondary treatment to improve fibre separation and delignification. Two initial tests were completed, including fibre treated in water, and fibres treated in a 2 wt.% NaOH solution. Both samples were treated for 20 minutes, with 100% amplitude, and with pulsing times of 25 seconds on and 5 seconds off. A 1: 200 ratio (by weight) of fibre to water/solution was used. It was visually evident that the ultrasonic treatment was effective for further fibre separation and lignin removal. Fewer fibre bundles were present, and the fibre appeared lighter in colour. The testing indicated increased lignin removal through visual increase of fibre separation and lightening of colour. The effects were visually greater in the test that used a sodium hydroxide solution. The ultrasonic treatment was further investigated by increasing the fibre to solution ratio. A 1:40 ratio of fibres to 2wt.% NaOH solution, resulted in fibre separation still visually increasing and the colour still appeared to lighten, suggesting delignification occurring. Microscopy also indicated fibrillation on the fibre surface, suggesting potential for increased interfacial strength in corresponding composites. Due to the reduction of NaOH required for processing fibres using a 1:40 ratio, and the limitations in the mass of fibres able to be processed with the equipment available, the 1:40 ratio was chosen for the ultrasonic treatment process.

4.1.4 Fibre Bleaching Method

The screening of the bleaching process found that after 10 minutes of bleaching, the fibres had all visually changed colour and the bleaching process seemed to be completed. The resulting fibres were significantly lighter in colour (appearing almost white), suggesting the reduction of lignin. The initial testing of the hydrogen peroxide bleaching was found to be successful, and no additional testing was completed.

4.2 Wood Flour and Fibre Analysis

For the rest of the Results and Discussion the wood flour and fibres used were produced with the processes in the Materials and Methods chapter (Chapter 3). The wood flour and fibres are also described using the following convention:

d = Digested fibres
D = Digested + ‘separated’ fibre
DU = Digested + ultrasonic treated + ‘separated’ fibre
DB = Digested + bleached + ‘separated’ fibre
DBU = Digested + bleached + ultrasonic treated + ‘separated’ fibre
F = Wood flour from the treated timber

All samples used for wood flour, and fibre analysis were produced from the first batch of timber sourced (batch 1). The term 'separated' refers to the separation process used after drying to separate 'clumps' of fibre. Wood flour was produced purely through mechanical processing and was used for testing the treated timber in FTIR, XRD, TGA, and ICP-MS experiments.

4.2.1 Scanning Electron Microscopy (SEM)

SEM was used to investigate the fibre surfaces after all processing steps and variables. Figure 4-1 (A and B) show the fibre surface of digested fibres. The images show that the separation of fibres from the wood chips has started to occur, and some single fibres are present. Figure 4-1 (A) indicates that fibre bundles are still present, and further processing could improve separation. The rough surface in Figure 4-1 (B) suggests that localised lignin and extractives remain on the surface [72]. The presence of fibre bundles further suggests lignin and extractives are present on the fibre surfaces acting to bond the cellulosic fibres together in fibre bundles [15].

Figure 4-2 (A and B) show the surface of the digested and ultrasonic treated fibres. The surfaces are visually smoother than those of the alkali pulped fibres, signifying that ultrasonic treatment has removed some of the lignin and extractives from the surface of the fibres. The images indicate that further fibre separation has occurred during the ultrasonic treatment, and fibrillation is starting to occur as small fibrils can be seen on the surface. Both fibres and cellulose fibrils within the fibres are held in place by lignin and extractives. Therefore, the potential fibre separation and fibrillation of the fibre surface indicate further removal of lignin and extractives holding the fibres and microfibrils together [15]. The potential reduction of lignin and extractives agrees with the literature where ultrasonic treatment has been found to remove lignin and extractives from wood flour [68].

Figure 4-3 (A and B) show the fibre surface of the digested and bleached fibres. The fibres in the images are seen to have a rougher surface than the digested fibre. This surface is likely a result of the removal of localised lignin and extractives from the fibre surfaces during the bleaching process, exposing the microfibrils in the fibre. This theory agrees with literature where a rougher surface was obtained from hydrogen peroxide bleaching and used to improve interfacial strength in the corresponding composites [65]. Hydrogen peroxide bleaching is also known to remove lignin content [56]. The images also imply that more fibre separation has occurred, and more individual fibres are present (compared to the digested fibre). The potential increase in fibre separation is likely the result of the removal of lignin and extractives, which naturally hold the fibres together in fibre bundles.

The digested, bleached, and ultrasonic treated fibres can be seen in Figure 4-4 (A, B and C). The use of ultrasonic treatment after bleaching the fibres shows significant fibrillation of the fibres and the exposure of microfibres and potentially nano fibres. The added fibrillation from the ultrasonic treatment increases the surface area of the fibres, suggesting a potential for more interaction and better interfacial strength between the fibres and matrix.

The fibrillation induced by the ultrasonic treatment can increase the interfacial strength through the presence of microfibrils and increased surface area. However, literature shows mechanical processing to induce fibrillation can also damage the fibres and reduce fibre length, with the potential of decreasing composite strength [15]. Figure 4-4 shows significant fibrillation induced by the ultrasonic treatment after the bleaching process, suggesting potential for the fibre strength and length to be decreased due to the ultrasonic process, and therefore, potential to reduce corresponding composite mechanical properties.

Figure 4-4 (C) indicates that the fibres tend to agglomerate after the treatment, as shown by the large group of fibres. This phenomenon has the potential to reduce the mixing of matrix and fibres during compounding, therefore reducing the wetting of fibres and reducing composite properties.

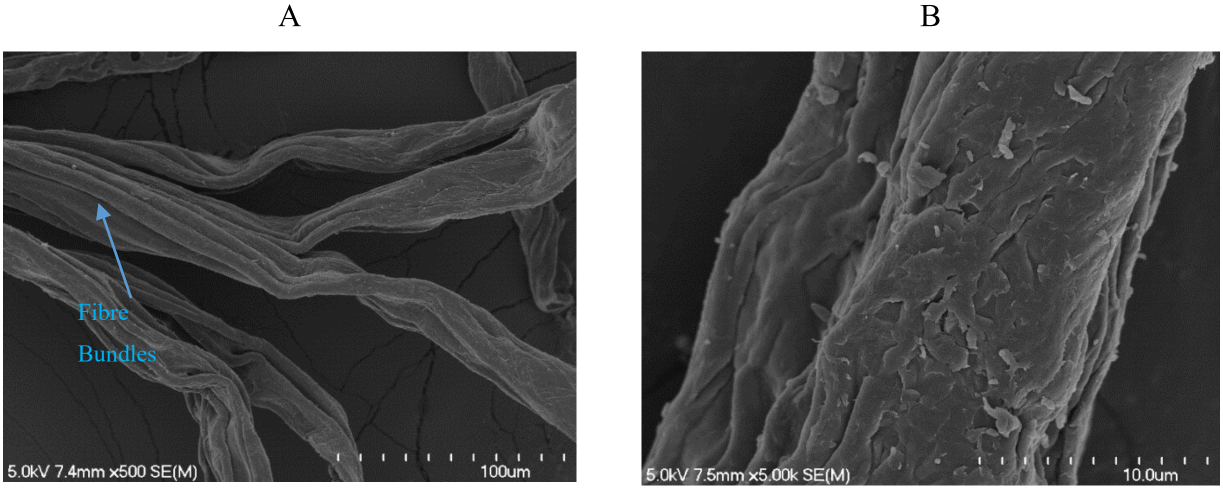


Figure 4-1: Scanning electron microscopy (SEM) of digested (D) fibre surface.

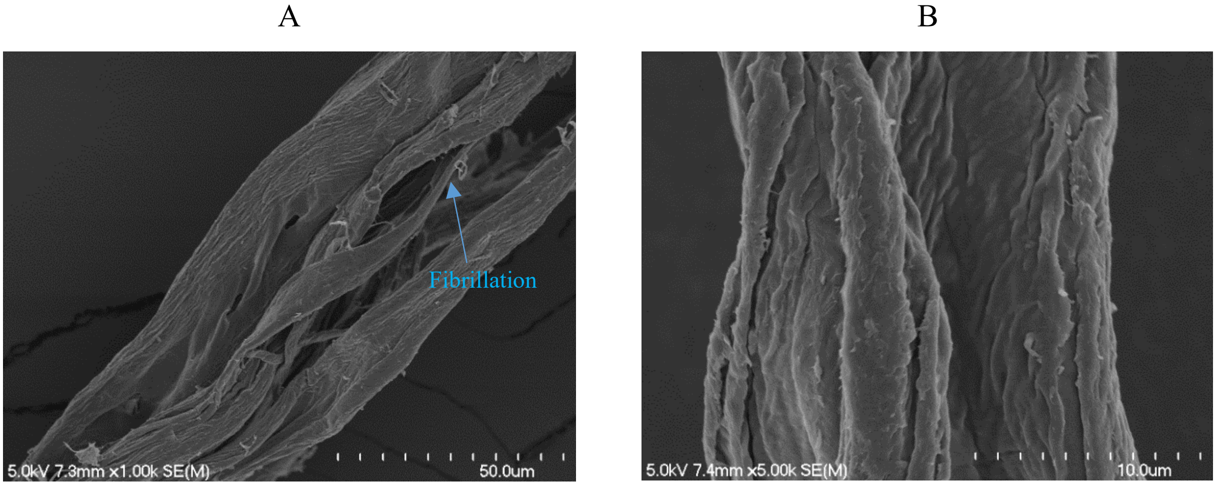


Figure 4-2: Scanning electron microscopy (SEM) of digested and ultrasonic treated (DU) fibre surface.

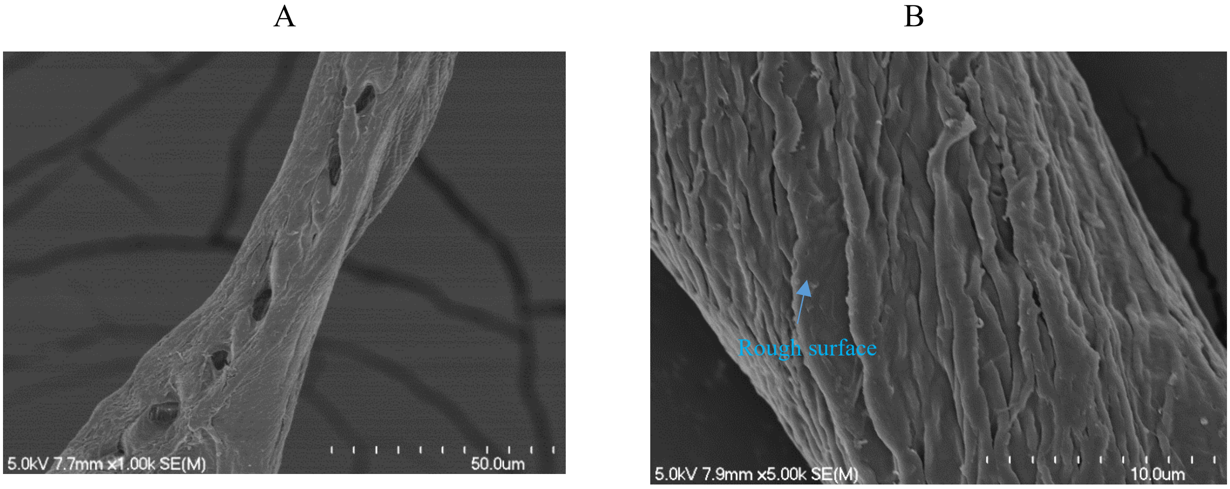


Figure 4-3: Scanning electron microscopy (SEM) of digested and bleached (DB) fibre surface.

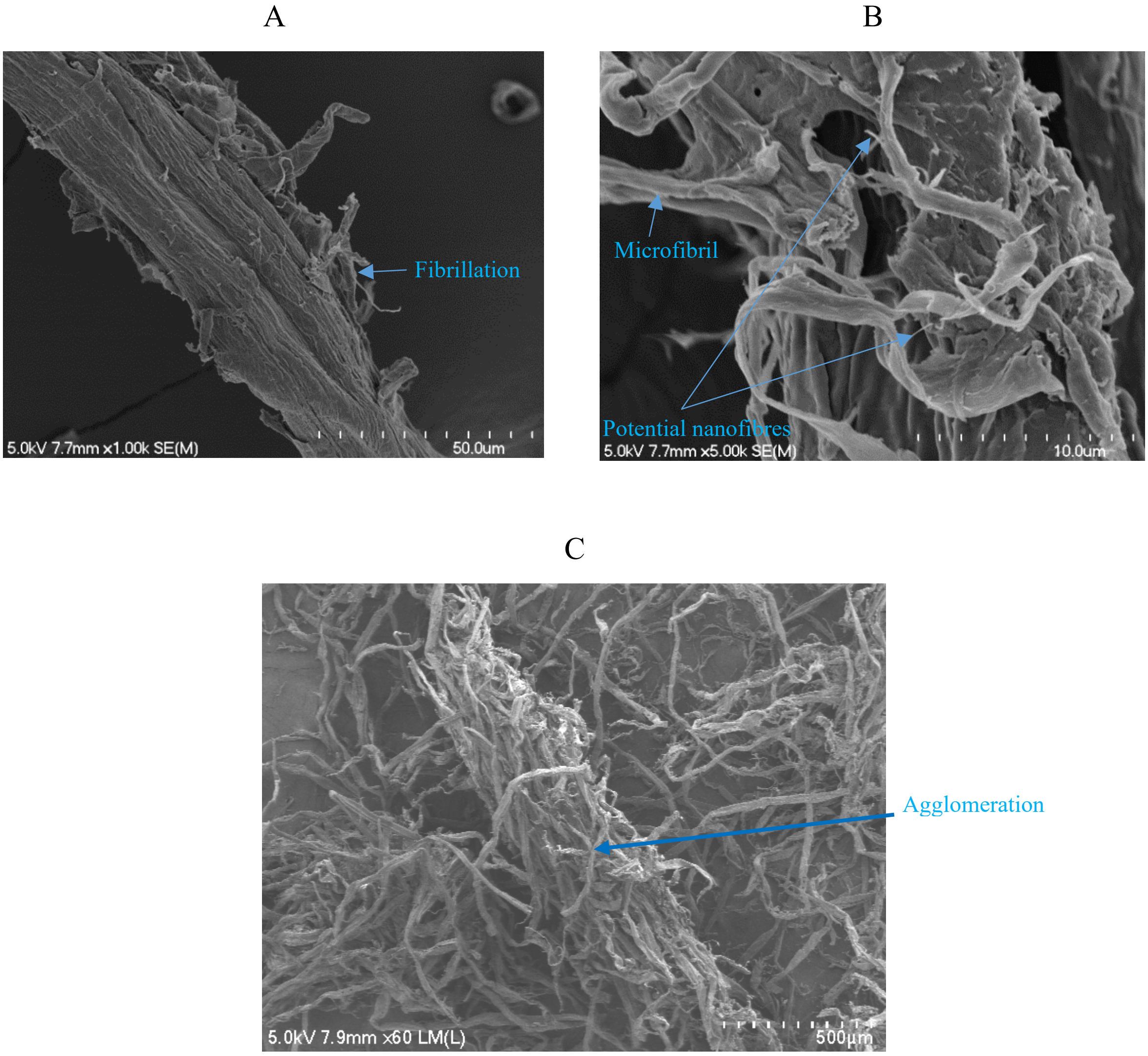


Figure 4-4: Scanning electron microscopy (SEM) of digested, bleached, and ultrasonic treated (DBU) fibre surface.

4.2.2 Fibre Quality Analysis

The results from the fibre quality analysis were used to study the fibres to geometry, including width, length, aspect ratios, number of shives (bundles), and fines. Table 4-1 summarises the information provided for all fibre processing variables. Table 8-1 (Appendix, Section 8.1) provides the complete results from the detailed analysis.

Sample d and D differ with the step of 'separating' the fibres. The results suggest that the 'separating' process using the Sunbeam Multigrinder had minimal effect on the fibre properties, and the minor differences are likely due to the selection of fibres used for analysis.

The results in Table 4-1 show that bleaching of the digested fibres reduced the diameter of the fibres without any effect on fibre length. Literature suggests that increased chemical processing results in a reduction of fibre width and the reduction in corresponding kappa number, indicating the removal of lignin [41]. Therefore, the reduction in fibre width due to the bleaching further suggests the removal of lignin and extractives from the fibre surface, reinforcing the results of the SEM. The number of bundles or shives is also seen to decrease after bleaching of fibres which further suggests the reduction of lignin and extractives in the fibres which are known to hold fibre bundles together [15].

Table 4-1 shows that ultrasonic treatment reduced the mean fibre length and had minimal effect on the fibre width, resulting in a lower aspect ratio. However, the results suggest that ultrasonic treatment (Sample DU) reduced the number of shives or fibre bundles, reinforcing the results of the SEM where more individual fibres were visually present, and separation of fibres bundles had been improved.

The ultrasonic treatment on the digested and bleached fibres was found to reduce the length of the fibres from 1.18 mm to 0.66 mm, a reduction of 44%. Furthermore, the percentage of fines, weighted by length, was increased from 1.03% to 16.66%. Although the SEM suggested the potential to increase interfacial strength due to fibrillation of the fibres, the large reduction in fibre length and increased number of fines in the fibres further suggests the potential of reducing composite properties due to reduced fibre reinforcement capability.

The analysis shows that the use of ultrasonic treatment increases the fibre width. After ultrasonic treatment, the mean fibre width of the digested fibres increased from 32.39 μm to 32.62 μm (comparing D and DU fibre) and increased the mean width of the bleached fibres from 31.47 um to 32.76 um (comparing DB and DBU fibre). The apparent increase in width is likely to be due to the additional fibrillation surrounding the fibres resulting in an apparent fibre width that is larger than the actual fibres. The SEM reinforces this idea, as the difference was larger in the width of the bleached fibres, where substantially more fibrillation was indicated. It is likely that the actual width of the fibres has been reduced due to the micro fibrils being separated from the primary wall of the cellulosic fibres and the potential removal of lignin from the fibre surface.

The results of the analysis also show that the number of shives increased with the ultrasonic treatment in the digested and bleached fibres (comparing DB and DBU fibre). The shives measured are likely a result of the agglomeration of fibres, indicated in Figure 4-4 (C) of the SEM results, being measured as shives.

Table 4-1: Summary of results from fibre quality analysis. The number of shives as a percentage of the number of fibres measured is given in parenthesis.

Sample		Number of Fibres Measured	Mean Length (mm)	Mean Width (um)	Aspect Ratio	Number of Shives	Fines (Length Weighted) (%)
Digested	**d**	35236	1.15	32.88	35.09	78.33(0.22%)	1.22
Digested + Separated	**D**	33188	1.2	32.39	36.95	85.67(0.26%)	1.01
Digested + Ultrasonic + Separated	**DU**	38719	0.94	32.62	28.80	10.33(0.026%)	2.74
Digested + Bleached + Separated	**DB**	47835	1.18	31.47	37.64	19(0.039%)	1.03
Digested + Bleached + Ultrasonic + Separated	**DBU**	36433	0.66	32.76	20.10	66.00(0.18%)	16.66

4.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Chemical and mechanical processing is often used to process natural fibres, typically to purify and obtain cellulose fibres. FTIR shows the chemical functional groups present, which can be used to identify different organic constituents. Therefore, FTIR was used to indicate changes in the constituents in the timber and fibres induced by chemical treatments. Figure 4-5 (A and B) shows the FTIR spectroscopy for all fibres samples and the wood flour.

The digestion process aimed to reduce the content of lignin, hemicellulose, and extractives, in a single step. Literature on Kraft pulping indicates that hemicellulose is originally removed at a faster rate than lignin [89]. The digestion process also appears to follow this trend; the spectra in Figure 4-5 indicates the removal of most of the hemicellulose in the digestion process, whereas residual lignin appears to remain. A clear peak in the wood flour spectra at 1726 cm^{-1} is specific to -COOH and C=O functional groups which are specifically found in hemicellulose. The spectra for all other fibres do not contain this peak, suggesting that hemicellulose has primarily been removed during the digestion process [90].

The spectra suggest a reduction of lignin in the digestion and bleaching processes. The peaks at 1511 cm^{-1} represent the functional group C=C and are assigned to aromatic rings of lignin, specifically indicating guaiacyl (G) units. The indication of G units of lignin makes sense as the lignin in soft woods such as Pinus Radiata primarily are known to primarily be composed of G units [51]. The spectra show a reduction of the 1511 cm^{-1} in the digested fibre and a further reduction in the peak after bleaching. The reduction in the size of the peak indicates partial removal of lignin from the fibre during these chemical processes. This removal of lignin is further inferred by reducing peaks at 1460 cm^{-1}, indicating the reduction of C-H functional groups assigned to lignin. However, lignin was still clearly present in all samples, shown by the small peaks still present at 1511 cm^{-1}, 1460 cm^{-1}, and the peaks remaining at 1120 cm^{-1} and 1039 cm^{-1}, which all indicate functional groups found in lignin. The presence of lignin even after bleaching is expected; Literature from the pulp and paper industry suggests bleaching of pulp can take up to seven different chemical treatments due to the difficulty of removing lignin [56, 90].

The use of ultrasonic treatment with NaOH gives no significant change in the peak, indicating little change in the constituents present in the fibres. However, the FTIR spectra used is qualitative, and the processing could have small unseen effects on the constituents present in the fibres.

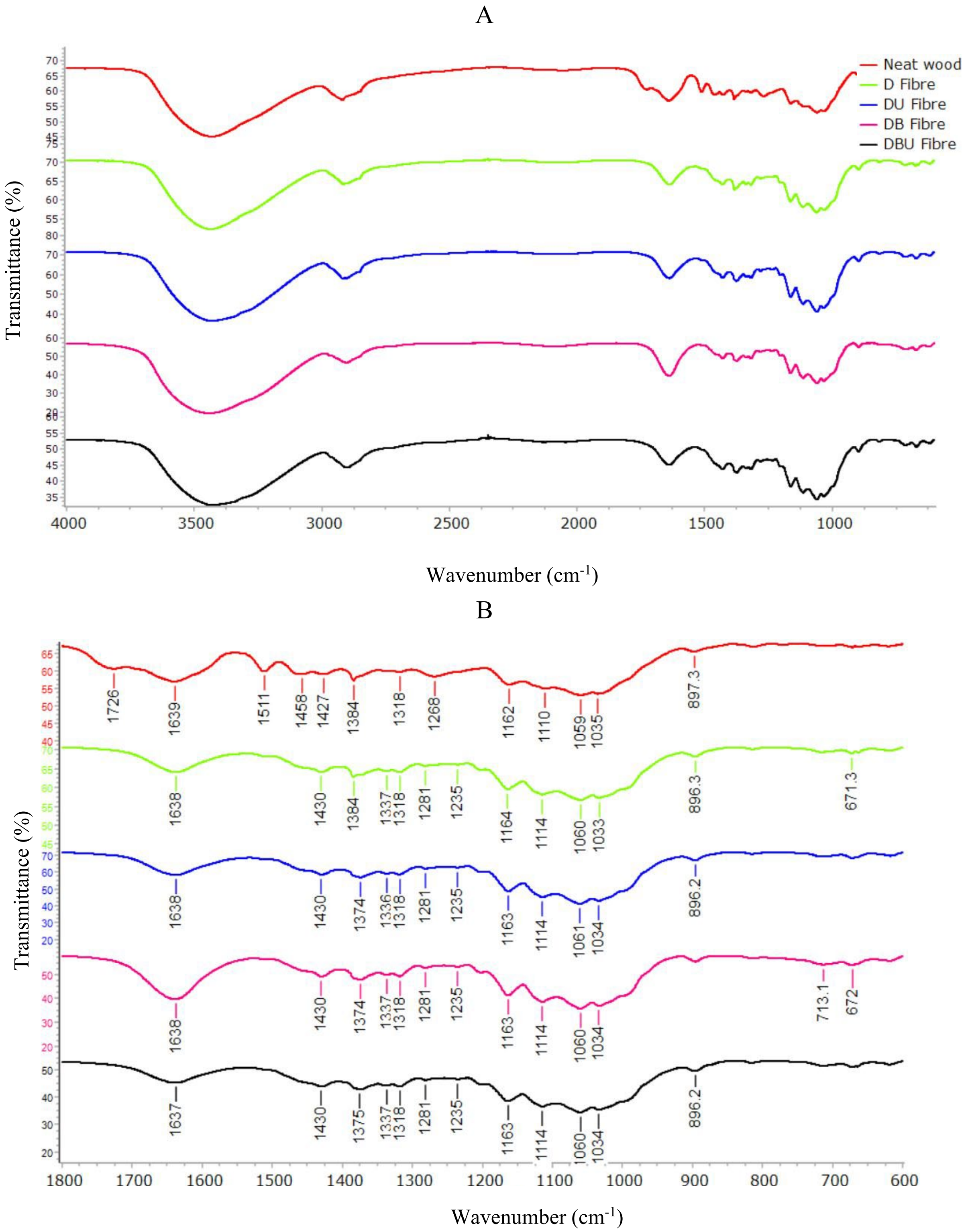


Figure 4-5: FTIR results from neat wood, and all fibre samples. Neat wood (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre). A) full spectra from FTIR analysis, B) magnification of spectra from 600 – 1800 cm^{-1}.

4.2.4 X-Ray Diffraction Analysis (XRD)

X-Ray Diffraction (XRD) was used to analyse the crystallinity of the timber and fibres. The crystallinity index of the wood flour and fibres gives further insight into the constituents in the timber, and the XRD spectra provides insight into any potential changes of the crystalline cellulose. The crystallinity index was calculated using the Segal method (Described in Section 3.3.5) using the spectra in Figure 4-6. The resulting crystallinity indices are displayed in Table 4-2. The results show that the crystallinity index increases with increasing chemical processing. The crystallinity index increased from 41.9 % to 67.2 % from the timber to the digested fibres (comparing F and D samples). Furthermore, the crystallinity index further increased to 71.5 % as a result of the hydrogen peroxide bleaching process (comparing D and DB samples). The increase in the crystallinity index was likely due to the removal of amorphous material, including lignin, hemicellulose, and other extractives. This reduction of amorphous constituents is reinforced by the SEM, Fibre quality analysis, and FTIR [72].

The results from the XRD show that the use of ultrasonic treatment after digestion also increases the crystallinity index, which is likely due to the removal of small amounts of amorphous constituents (comparing D and DU fibre). However, the crystallinity index is reduced after the ultrasonic treatment of the bleached fibres (comparing DB and DBU fibre). The spectra in Figure 4-6 shows a shoulder peak emerging at roughly 20º, most significant in the DBU fibre. The peak suggests the transformation from cellulose Iβ to cellulose II, resulting in the formation of the peak at 20º (corresponding to the 110 plane in cellulose II) and the reduction of the peak corresponding to the (002) plane. The potential transformation of small amounts of cellulose Iβ to cellulose II would explain the reduction in the calculated crystallinity index caused by the high amounts of energy in the ultrasonic treatment. This reduction also shows the limitations of the Segal method used for calculating the crystallinity index [46, 91].

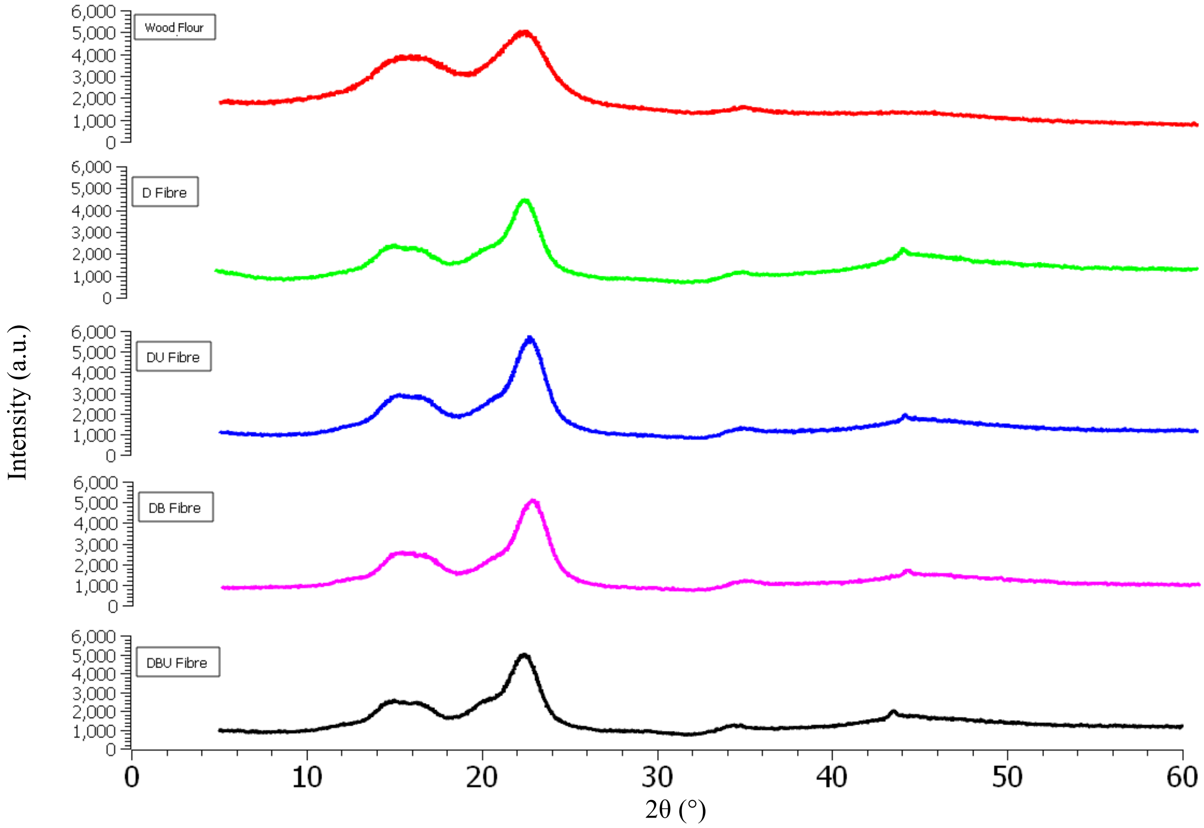


Figure 4-6: XRD results from treated timber and all fibre samples. F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

Table 4-2: Crystallinity index of timber and all fibre samples from XRD analysis. F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

	I_{002} (2θ = 22.7°)	I_{am}(2θ = 18.3°)	Crystallinity Index (%)
F	5100	2961	41.94118
D	4492	1475	67.16385
DU	5768	1760	69.48682
DB	5178	1474	71.53341
DBU	5046	1535	69.57987

4.2.5 Thermogravimetric analysis (TGA)

TGA was used to analyse the thermal degradation of the treated timber and fibres. Figure 4-7 shows the TG and DTG (1st derivative of TG) analysis for all fibres and wood flour samples. Table 4-3 summarises the mass change, onset temperature, and peak degradation temperatures for all samples. The DTG results show the first derivative of the TG results, providing peaks that represent the rate of thermal degradation. Variances in the TG and DTG for the fibre samples are likely to be due to differences in the content of cellulose, lignin, hemicellulose, and extractives. Previous studies suggest that "hemicellulose decomposes at a lower temperature range (220–315 °C) than cellulose (300–400 °C), while lignin decomposes over a broad range of temperatures (150–900 °C)" [92]. However, it has been reported that the heavy metals can affect the thermal conductivity of the material, potentially affecting the thermal degradation properties [16].

The results of the TG testing indicate an initial change in mass at approximately 100ºC in all samples suggesting the presence of water. The DTG of wood flour shows a major peak at 360 ºC, and shoulder peaks at 260.7 ºC and 326 ºC, likely indicating the lignin and hemicellulose in the timber degrading before the cellulose. The samples all indicate initial thermal degradation starts at approximately 200 ºC, most likely due to the presence of lignin which degrades at lower temperatures than the other major constituents. This is most significant in the wood flour, however, it occurs in all samples.

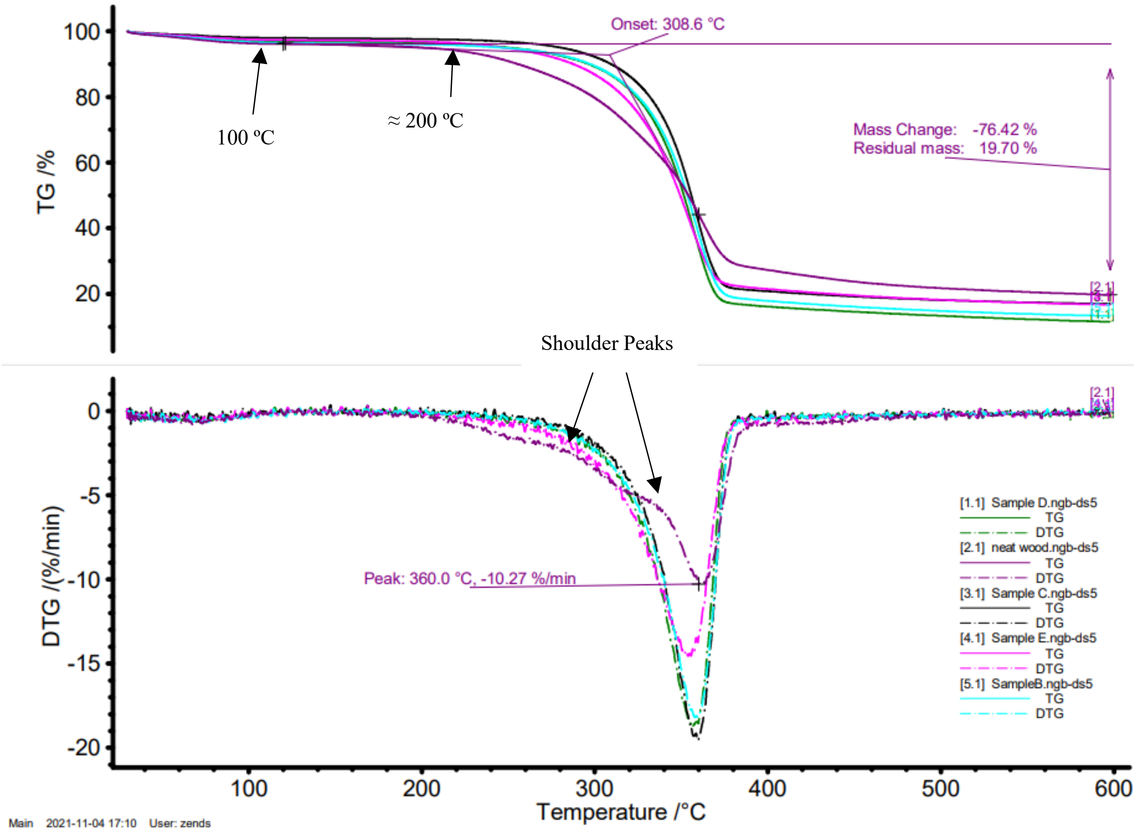


Figure 4-7: TGA results from treated timber and all fibre samples. Neat wood (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

Table 4-3: Data from TGA analysis for treated timber and all fibre samples.

Sample		**Change in Mass (%) (measured from 120°C – 600 °C)**	**Onset Temperature (°C)**	**Peak Degradation Temperature (°C)**
Digested	**D**	83.18	327.6	359.7
Digested and ultrasonic treated	**DU**	81.03	330.9	359.6
Digested and bleached	**DB**	85.41	326.6	356.5
Digested, bleached and ultrasonic treated	**DBU**	80.61	316.1	353.9
Treated timber	**F**	76.42	308.6	360

Due to the start of the thermal degradation of fibres and flour starting at roughly 200 °C (Figure 4-7), an isothermal analysis was done at 180 °C and 200 °C to understand the thermal behaviour of the fibre at these temperatures over prolonged periods of time. The analysis was performed using D, and DB fibres, as the FTIR results indicated the largest differences in constituents. The isothermal analysis results are shown in Figure 4-8 and Table 4-4. The analysis shows that both fibres are susceptible to thermal degradation at 180 °C and 200 °C at a sustained time. The thermal degradation of both fibre samples happens at a faster rate and has a larger change of mass at 200 °C. The results suggest that the fibres are likely very susceptible to small variances in conditions at these temperatures, and variable composite processing conditions could result in considerable variation in thermal degradation of fibres. Interestingly the bleached fibres seem slightly more vulnerable to thermal degradation at both temperatures. Further research would be required to provide insight into why this occurs. However, the differences could also be negligible and could be a result of only one sample being tested.

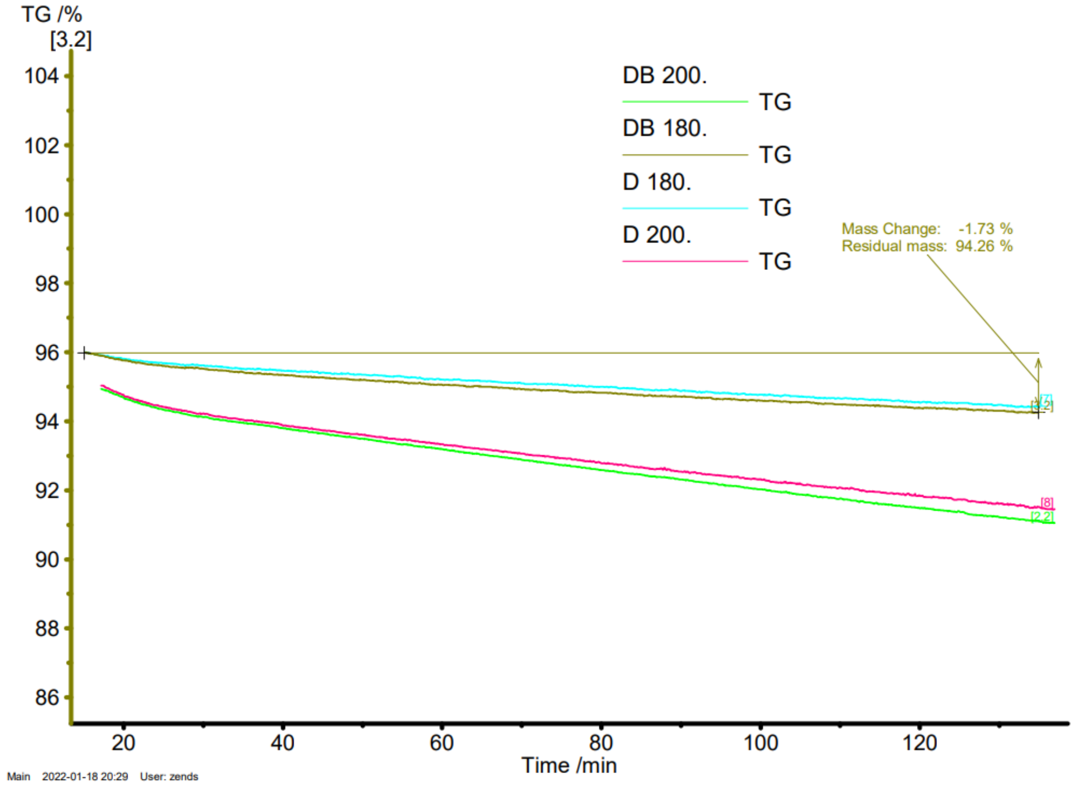


Figure 4-8: Isothermal TGA of fibres at 180 °C and 200 °C. D (digested fibre), DB (digested and bleached fibre)

Table 4-4: Mass Change Data from Isothermal TGA of fibres at 180 °C and 200 °C

Sample		**Isothermal Temperature (°C)**	**Mass Change at Isothermal Temperature (%)**
Digested	**D**	180	1.56
Digested and bleached	**DB**	180	1.73
Digested	**D**	200	3.60
Digested and bleached	**DB**	200	3.88

4.2.6 ICP-MS (Inductively Coupled Plasma Mass Spectrometry)

ICP-MS was used to analyse the heavy metal content in the reinforcement materials. The results of the analysis are shown in Table 4-5. In New Zealand, H 3.2 CCA treated timber requires the total concentration of heavy metals to be 0.37 wt.% (in the timber) as defined by NZS 3640 [37]. However, the sum of the three heavy metals in the timber adds to 0.42 wt.%, which is slightly higher than the New Zealand standard. The specific content of copper, chromium, and arsenic in the timber was measured to be 0.0839 wt.%, 0.13785wt.%, and 0.0968 wt.%, respectively, inferring proportions of 26.8% Cu, 41.2%

Cr and 32.0% As. The results fit reasonably well with the relative proportions required by NZS 3640 in the CCA treatment of 23 – 25 % Cu, 38- 45 % Cr, and 30 – 37 % As [37]. The copper concentration is the only heavy metal lying outside the expected range (1.3% higher than expected). The small differences in heavy metal content compared to the NZ standard are potentially due to variation within the timber and the small sample size of wood flour used for testing. However, the results are very similar to the New Zealand standard and can be regarded as an accurate representation of the trend in the heavy metal content in the wood flour and fibres.

Table 4-5 shows how the concentration of heavy metals changes with the treatment of the timber and fibres. The results show that the concentration of arsenic was reduced by 99.8 % from the wood flour to the digested fibres and was further reduced with further treatment. The reduction in arsenic content signifies that the fibres could potentially be used safely in wood-plastic composites for application, as arsenic is considered the most toxic of the three heavy metals [34]. The concentration of copper and chromium was also reduced after digestion, bleaching, and ultrasonic treatments. The reduction of the concentration of chromium was less than that of arsenic (Cr was reduced from 1728.5 ppm to 957.9 ppm from the treated timber to digested fibres, respectively). The concentration of copper was found to only decrease from 1126.4 ppm to 1093.6 ppm (comparing the timber and digested fibre). Bleaching with hydrogen peroxide was found to significantly reduce both copper and chromium in the fibre and further reduce the arsenic content. In contrast, ultrasonic treatment had the least effect on the heavy metal content.

The variable changes in heavy metal concentration (i.e. comparing changes in Cu, Cr, and As concentration) in the digested fibre is likely a result of how the heavy metals are fixed into the timber. The literature is very unclear on the exact chemistry of the fixation of preservatives into timber; however, a recent report suggests that the heavy metals are fixed in the timber in the forms of chromium (III) arsenate, chromium (III) hydroxide and wood carboxylate-copper (II) complexes [38]. The removal of 99.8 % of As suggests the removal of the majority of the chromium (III) arsenate in the timber during the digestion process. The potential reduction of chromium (III) arsenate in the timber would agree with the results; although, As is almost completely removed, the concentration of Cr is roughly halved, which is likely due to the chromium (III) hydroxide remaining in the fibre. Thus, the results infer that the chromium (III) arsenate is fixed primarily into the alkali soluble constituents of the timber (such as hemicellulose and lignin). However, the concentration of copper and chromium changes less, which could result from chromium (III) hydroxide and carboxylate-copper (II) complexes potentially being evenly distributed and fixed throughout all of the timber constituents (including cellulose). Although it is also possible that the interaction with the NaOH at elevated temperature and pressure has altered the chemical bonding or fixation, further analysis would be required to have an in depth understanding of the chemistry of the heavy metals during the digestion process.

When considering the yields of the digestion, ultrasonic, and bleaching processes, the mass of heavy metals in the fibres compared to the original mass of heavy metals in the timber is significantly reduced. Therefore, a significant portion of the heavy metals from the timber can be expected to be in the fibre treatment solutions after processing (digestion, bleaching, and ultrasonic treatment solutions). The presence of the heavy metals will likely alter any potential commercial-scale recovery of water, biomass, or chemicals from the solutions, and will require further research. The highly alkaline solutions used for processing may precipitate the heavy metals allowing for their removal. However, more research is required to investigate this possibility.

Table 4-5: Heavy metal concentration in fibre and timber samples. F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre). The COV is presented in parenthesis (%).

	Cu (ppm)	**Cr (ppm)**	**As (ppm)**
F	1126.4(4.57)	1728.5(5.61)	1346.0(4.97)
D	1093.6(0.91)	957.9(0.71)	1.94(1.43)
DU	986.89(3.43)	852.17(5.42)	1.30(10.8)
DB	556.53(1.99)	353.16(2.52)	1.21(3.95)
DBU	503.22(4.95)	338.76(5.70)	0.823(9.09)

4.3 Wood-plastic Composite Analysis

The wood flour and fibre were used as reinforcement materials to produce wood-plastic composites. Material testing was performed to investigate the application potential of the WPC produced with waste CCA treated timber.

Table 4-6 shows a list of all composites produced for material testing. Due to the unknown history of the timber, there is a possibility of the different batches of timber collected influencing the fibre properties and corresponding composite properties. Therefore, the timber source has been represented in three groups (batch 1, 2, and 3) for ease of comparison. The category 'Injection moulding temperature' refers to the maximum temperature used in the injection moulder barrel while producing parts for testing.

Table 4-6: List of composites produced for material testing. F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

	Reinforcement Type	**Reinforcement Content (wt.%)**	**Compounding Process Used**	**Timber Source**	**Injection Moulding Temperature**
1	F	30	Twin-Screw Extruder	1	200
2	D	30	Twin-Screw Extruder	2	200
3	DU	30	Twin-Screw Extruder	1	200
4	DB	30	Twin-Screw Extruder	1	200
5	DBU	30	Twin-Screw Extruder	1	200
6	F	30	Sigma Blade Mixer	2	200
7	D	30	Sigma Blade Mixer	2	200
8	DU	30	Sigma Blade Mixer	2	200
9	DB	30	Sigma Blade Mixer	2	200
10	DBU	30	Sigma Blade Mixer	2	200
11	D	20	Sigma Blade Mixer	3	180
12	D	30	Sigma Blade Mixer	3	180
13	D	40	Sigma Blade Mixer	3	180
14	DB	20	Sigma Blade Mixer	3	180
15	DB	30	Sigma Blade Mixer	3	180
16	DB	40	Sigma Blade Mixer	3	180
17	DB	40	Twin-Screw Extruder	3	180

4.3.1 Analysis of Composite Mechanical Properties

4.3.1.1 Effects of Wood Flour and Fibre Processing Methods and Compounding Methods on Composite Mechanical Properties

Composites were initially produced with 30 wt.% fibres, 4 wt.% MAPP, and 66 wt.% PP using a twin-screw extruder and sigma blade for compounding. The composites were injection moulded at temperatures ranging from 190 to 200°C. The tensile properties of the composites are displayed in Table 4-7. The tensile properties of the PP used for the matrix material were also evaluated and included as a reference.

The polypropylene was injection moulded (without undertaking either compounding method) and was tensile tested up to approximately 1500% strain without failure. Therefore, the properties reported for PP in this study were obtained by testing PP to a maximum strain of 20% for comparison with composites. The maximum tensile strength (TS) of the PP was found to be 18.49 MPa, which is substantially lower than the expected strength of PP (26 – 50 MPa [24]). The lower tensile properties are likely due to being a random copolymer, with unknown amounts of PE included. Furthermore, the low tensile properties of the PP are likely to have affected the composite strength properties that are determined by the matrix, fibre, and interface properties.

Tensile Properties of 30 wt.% Extruded Composites

Table 4-7 shows the tensile properties of the composites produced using the twin-screw extruder and 30 wt.% reinforcement. Overall, the results are very similar for all composites produced with fibres. A higher tensile strength was attained in the fibre composites than wood composites flour. The highest TS obtained was from the composites produced with DU fibres, and the highest young's modulus (YM) was from the composites produced using D fibre.

The results of extruded composites shown in Table 4-7 show that the bleaching process reduced the average TS and YM of corresponding composites. When comparing composites produced with D and DB fibres, the average TS was reduced from 26.74 MPa to 25.37 MPa, and the YM from 1928.92 MPa, to 1896.13 MPa.

The ultrasonic treatment had similar effects for both the digested and digested and bleached fibres. The inclusion of an ultrasonic treatment was found to increase the average TS and decrease the YM for composites in both cases (comparing D and DU fibre composites and DB and DBU fibre composites). The increase in TS is likely due to the increase in the surface area caused by the fibrillation from the ultrasonic treatment shown in the results of the SEM of fibre surfaces (Figure 4-2 and Figure 4-4). The increase in fibre surface area has the potential to increase interfacial strength and therefore improve composite TS. Furthermore, the reduction in YM is likely a result of the decrease in fibre length induced by the ultrasonic treatment which was shown in the fibre quality analysis (Table 4-1). The reduction in length is likely to have reduced fibre reinforcement efficiency as the length of fibre that the load is transferred to is reduced [70]. However, the results from the tensile testing of the fibre composites are all very similar. The COV and the results of the Anova test indicate that the differences in TS and YM of the fibre composites are statistically insignificant.

Tensile Properties of 30 wt.% Sigma Blade Composites

Due to the small variation between composite properties using the twin-screw extruder, the composites were reproduced with the sigma blade compounder to further investigate the influence of the fibre treatments used. The results of tensile testing of the sigma blade compounded composites are shown in Table 4-7. After injection moulding, the composites were observed to be visually darker than the composites produced with the extruder, possibly suggesting thermal degradation of the fibres had occurred during processing.

The overall results show that the TS and failure strain were reduced, and the YM was increased when using the sigma blade to produce composites compared to the extruder. However, the statistical tests indicate more significant variance between composites produced using the sigma blade with the different reinforcement types, thus, giving more indication on the effects of the wood flour and fibre processing on composite properties.

Unlike the extruded composites, the TS increased as a result of the bleaching of the fibres. Comparing the tensile properties of D and DB fibre composites, the TS increased from 20.96 MPa to 24.31 MPa. Furthermore, the YM increased from 1978.64 MPa to 2292 MPa.

The use of the ultrasonic treatment also had a different effect on the composite performance compared to the extruded composites. The ultrasonic treatment of the digested fibres increased composites TS from 20.96 MPa to 21.25 MPa and increased YM from 1878.64 MPa to 2081.79 MPa (comparing D and DU fibre composites). However, ultrasonic treatment of the digested and bleached fibres reduced both the composites TS and YM and increased the failure strain (comparing DB and DBU fibre composites).

The increased TS due to ultrasonic treatment of the digested fibre (DU) is again likely attributed to increased interfacial strength caused by the fibrillation shown in the SEM, Figure 4-2 (A). Interestingly, the YM of the DU fibre composites was greater than that of the D fibre composites, possibly suggesting better compatibility of the fibres with the matrix and coupling agent due to increased interfacial surface and possibly more exposure to cellulose hydroxyl groups on the fibre surface. Thus, the improved interface possibly has a greater effect on the mechanical properties than the reduction in length (shown in Section 4.2.2 from the fibre quality analysis). However, the statistical analysis indicates that the TS and YM of the D and DU fibre composites are not statistically significantly different.

The reduction in TS between the DB and DBU fibre composites suggests that the potential fibre damage or reduction in fibre length caused by the ultrasonic treatment (Figure 4-4 and Table 4-1) has reduced the reinforcement capability of the fibre, outweighing the potential increase from improved interfacial strength. This would agree with the literature, which found increased fibrillation induced by fibre beating, initially increased tensile strength due to improved interfacial strength, and then reduced TS likely due to the reduced fibre length [70]. The fibre analysis and the composite analysis results indicate that the ultrasonic treatment after bleaching has damaged the fibres and reduced reinforcing capabilities. To attain better performance of the composites, investigating the use of ultrasonic treatment before bleaching or with reduced time, amplitude, or sodium hydroxide concentration could be explored to lessen the effects of the treatment. Although the TS and YM were reduced, the statistical analysis results indicate that the differences are statistically insignificant.

The DBU fibre composites were also potentially affected by the agglomeration of fibres after treatment, shown in Figure 4-4 **(**C). The agglomeration of fibres could have reduced the mixing of the matrix and the fibres. Furthermore, it is expected that the sigma blade has reduced shear forces and pressure (compared to the extruder), which could potentially reduce mixing and wetting of the fibres and potentially increase the effects of the agglomeration.

Table 4-7: Mechanical properties of 30 wt.% F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre)composites produced using the sigma blade compounder (sigma) and extruder. The COV is presented in parenthesis (%). Means that share a letter (A, B, C, D, E, or F), suggest that the differences are statistically insignificant.

Composite	Number of Samples Tested	Timber Source	Tensile Strength (MPA)	Failure Strain (%)	Young's Modulus (MPA)
PP - REFERENCE	2	N/A	18.49(0.03)^{F}	N/A	835.3(2.95)^{C}
PP F - Extruded	5	1	24.36(1.21)^{BC}	6.31(19.7)	1899(6.33)^{B}
PP D - Extruded	5	2	26.74(1.48)^{A}	5.26(11.3)	1928(1.50)^{AB}
PP DU - Extruded	5	1	26.88(1.53)^{A}	5.74(17.3)	1880(7.16)^{B}
PP DB - Extruded	5	1	25.37(2.84)^{AB}	5.28(7.35)	1896(6.04)^{B}
PP DBU - Extruded	5	1	25.69(2.87)^{AB}	6.19(15.1)	1883(7.02)^{B}
PP F - sigma	4	2	22.35(1.22)^{DE}	3.68(16.9)	1976(7.71)^{AB}
PP D - sigma	4	2	20.96(4.36)^{E}	2.23(20.3)	1978(13.5)^{AB}
PP DU - sigma	4	2	21.25(4.55)^{E}	2.06(10.5)	2082(6.19)^{AB}
PP DB – sigma	4	2	24.31(2.19)^{BC}	2.46(11.9)	2292(5.45)^{A}
PP DBU - sigma	4	2	23.04(3.04)^{CD}	2.69(29.5)	2113(9.45)^{AB}

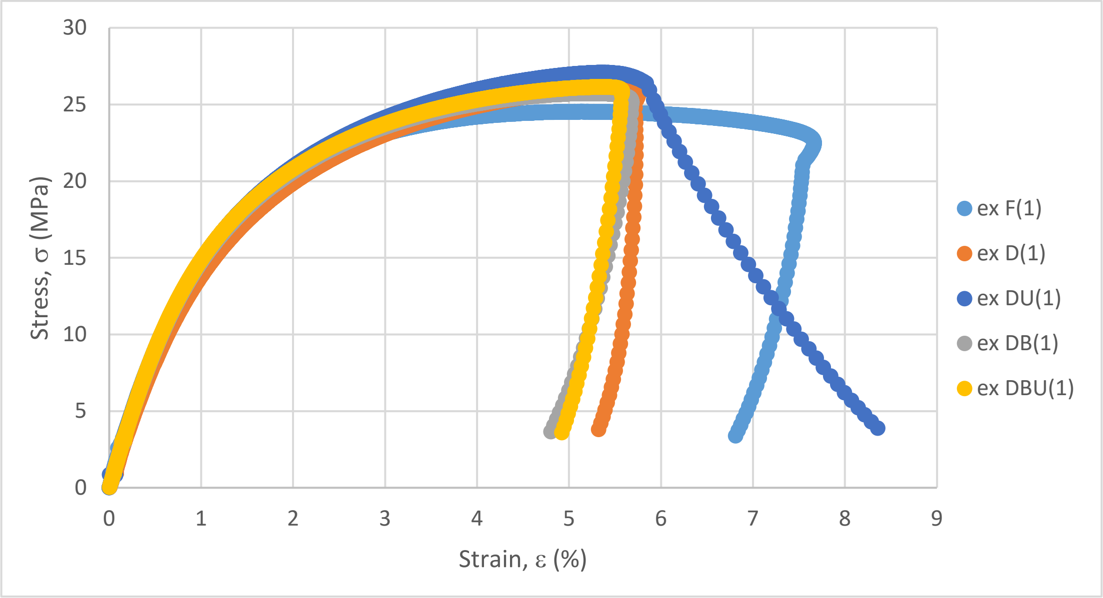
Comparison of Mechanical Properties from Different Compounding Methods

The results in Table 4-7 summarise the tensile data from the composites compounded with the extruder and the sigma blade melt compounder. Overall, it can be seen that all composites have increased mechanical performance than the virgin PP. The mechanical performance appears to be improved using fibres compared to wood flour composites for the extruded composites. However, the composites compounded with the sigma blade show a reduction in strength in the D fibre composites and the DU fibre composites compared to the wood flour composites.

The variance in composite properties from the two different compounding methods could be due to a number of different variables. The extruder is likely to apply greater shear forces and pressure during compounding than the sigma blade. The possible increased shear has the potential to damage the fibre and reduce the fibre length during compounding. The potential reduction in fibre length could explain the reduction in YM attained from the extruded composites compared to the sigma blade composites. The fibre quality analysis (Section 4.2.2) indicated that the ultrasonic treatment caused a significant reduction in fibre length. However, a reduction in fibre length due to extrusion could reduce the variances in fibre length induced by fibre treatment in corresponding composites. Therefore, potentially minimising the fibre length induced differences in composite strength and modulus in the extruded composites. Thus, potentially explaining why the ultrasonic treatment of fibre resulted in a slight increase in TS of the extruded composites (induced by increased interfacial strength), but the ultrasonic treatment of the bleached fibres slightly reduced the TS of the sigma blade composites (due to significantly reduced fibre length).

The stress-strain curves of the composites produced with the extruder and sigma blade were also relatively different. Figure 4-9 (A and B) comprise typical stress-strain curves of the composites made with both compounding methods. The graphs show that more plastic deformation occurs in the extruded composites than the sigma blade compounded composites before failure. Furthermore, the sigma blade compounded composites have a failure strain at the maximum tensile strength, whereas the extruded composites fail after the tensile stress plateaus and then decline. This failure of the composites at a lower failure strain and before the stress plateaus suggests the WPC compounded with the sigma blade could be more prone to unexpected failure, reducing the structural application potential. The graphs also further reinforce the effects of the different fibres in the wood-plastic composites compounded with the sigma blade. It can be seen that the various reinforcements have significantly different stress-strain curves, whereas using the extruder, all fibres follow roughly the same curve.

A



B

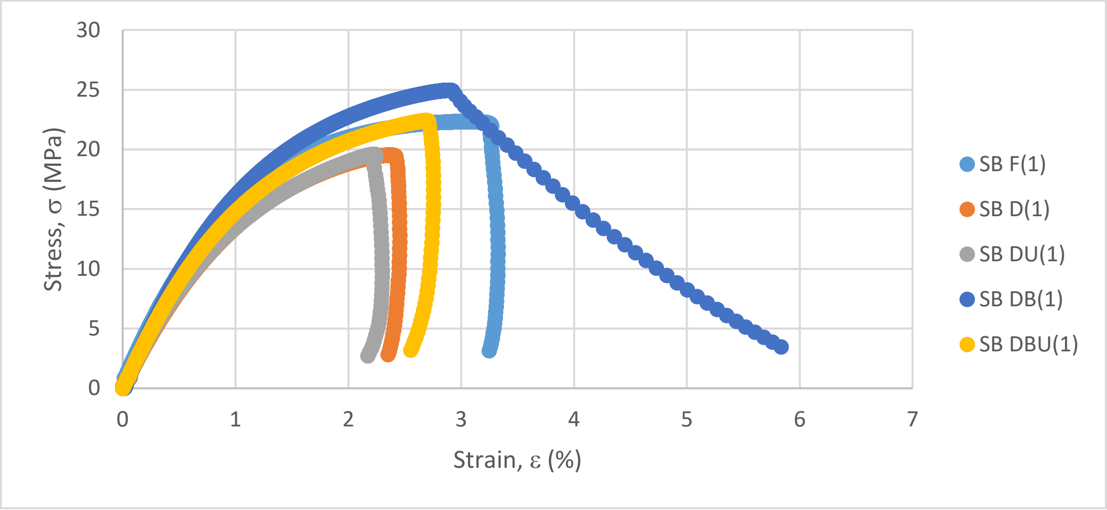


Figure 4-9: Typical stress-strain curve for A) Extruded, and B) Sigma blade compounded composites with 30wt.% F (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

SEM of Failure Surfaces of Extruded Composites to Investigate Effects of Fibre Preparation

Due to the increased variability in composite properties using the sigma blade, the composites were analysed further to understand the effects of the different fibre treatments. SEM (scanning electron microscopy) was used for analysing the failure surface after tensile testing of composites produced with the sigma blade.

Figure 4-10 (A and B) shows the failure surface of a composite produced with wood flour. Figure 4-10 (A) shows minimal porosity compared to the composites produced with fibres (example seen in Figure 4-12). The minimal porosity seen is possibly due to the ease of processing with wood flour compared to fibres [54].

The failure surfaces of all composites produced with fibres (D, DU, DB, and DBU) indicate a homogenous failure surface (except for large voids pointed out), suggesting good dispersion of fibres and good mixing during processing. The indicated homogeneity is expected from the sigma blade compounding due to the ability to monitor the torque and power input during the compounding process and mixing until the torque and power are stable due to a consistent viscosity and a homogenous mixture.

Figure 4-11 (A and B) shows the failure surface of a composite produced with digested fibres. Figure 4-11 (A) shows a number of small holes across the failure surface, indicating fibre pull-out across the surface. Figure 4-11 (B) suggests relatively poor wetting through the partial contact between fibre and matrix. Comparing the digested fibre composites and the wood flour composites (Figure 4-11 (A) and Figure 4-10 (A)), the failure surface of the wood flour composites suggest that the matrix goes through more plastic deformation, as shown by the large ductile regions of the plastic matrix. In comparison, the failure surface of the digested fibre composites indicates less plastic deformation and a more brittle failure mode of the composite.

Figure 4-12 (A and B) displays a typical composite failure surface of composites produced with DU fibres. Figure 4-12 (A) also shows many small holes in the failure surface indicating fibre pull-out. Figure 4-12 (B and C) suggests improved wetting and interface with the ultrasonic treatment compared to the digested fibre composites. This improvement is shown by the fibres being in direct contact with the matrix material. However, the failure of the plastic around the fibre in Figure 4-12 (C) and the minimal matrix material still attached to the fibre surface indicates that the composite is failing at the interface between the matrix and fibre, and the interfacial strength could be improved. Figure 4-12 (A) indicates large amounts of porosity shown by the large holes in the centre of the composite material. Furthermore, the area around the holes shows smooth sections of plastic, indicating that the matrix has not failed here and the surface already existed before tensile testing (Figure 4-12 (B)). The porosity suggests large stress concentrations in the composite material, which likely reduced the composite strength.

The DB fibre composite, shown in Figure 4-13 (A, B and C), gave the best tensile strength and Young's Modulus of all of the sigma blade compounded composites (Table 4-7). Figure 4-13 (A) shows a large void (likely porosity) in the centre of the composite, which would likely have reduced the tensile strength of the composite due to acting as a stress concentration in the sample. Therefore, if the porosity could be reduced, the tensile strength would likely be improved further. Figure 4-13 (B and C) shows the matrix material is still largely attached to the fibres on the failure surface, unlike the D and DU fibre composites. The matrix material still attached to the fibre indicates that the bleaching process has potentially improved the interfacial strength of composites, as the interface is more intact after tensile testing, and the failure appears more dependent on the limitations of the matrix. The inferred improvement in interfacial strength is likely the reason for attaining the highest TS out of the sigma blade compounded composites. However, Figure 4-13 (B) indicates that fibre wetting is still a possible limitation with some fibres; the large fibre in the centre is not in contact with the matrix and is likely an example of fibre pull-out.

Figure 4-14 (A, B, C, and D) show the failure surface of the composites produced with DBU fibres. Figure 4-14 (A and B) shows that the composite failure surface primarily looks very similar to that of the bleached fibre composites. Figure 4-14 (B) indicates good fibre wetting in the composites. The PP matrix stays attached to the fibres after tensile testing suggesting an improved interfacial strength than the fibres without the bleaching step. Fibre pull-out is still apparent in Figure 4-14 (A and B), suggesting the interface could be improved. Figure 4-14 (C and D) shows that some regions of the failure surface appear different from the other composites. Figure 4-14 (C) suggests that the region potentially exhibits fibre pull-out, shown by the hole in the centre that fits the dimensions of the diameter of a fibre (32.76 mm, Section 4.2.2). However, the figure also shows regions or boundaries between the matrix material with a much smaller width than the fibres; Figure 4-14 (D) shows that these regions are roughly 1-2 µm wide. The small width indicates the regions could be caused by an agglomeration of microfibrils that have not been separated during compounding. The potential for the regions to be a result of microfibrils is reinforced by the tendency of the fibres to group together in the DBU fibres, as visually seen in the SEM (Figure 4-4). However, the effects of the regions on the composite properties are unknown.

The porosity indicated in the DU and DB composite failure surfaces is expected to be typical across all fibre composites produced with the sigma blade; visually, small holes could be seen in all composite failure surfaces. More analysis would be required to fully understand the porosity and the influence of the fibre treatment. However, focusing on reducing porosity for the potential to improve composite results was considered more important than understanding the details of the porosity.

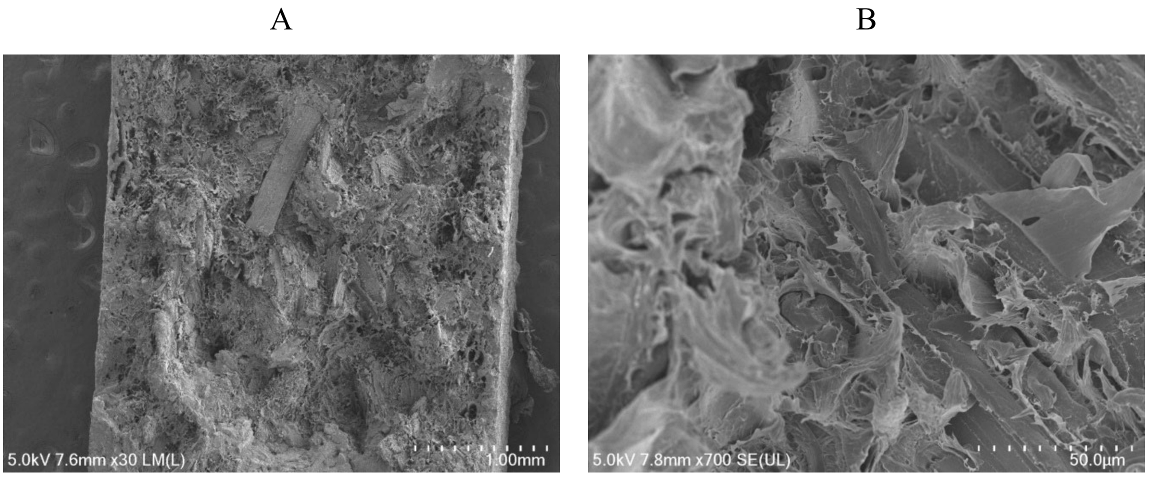


Figure 4-10: Scanning electron microscopy (SEM) of a typical sigma blade compounded 30 wt.% F (wood flour) composite tensile test failure surface.

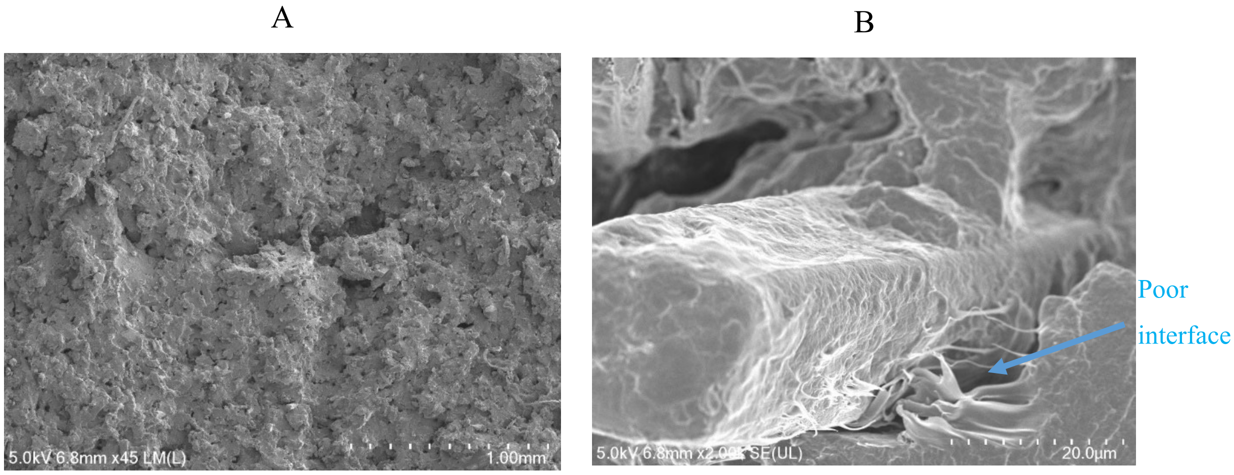


Figure 4-11: Scanning electron microscopy (SEM) of a typical sigma blade compounded 30 wt.% D (digested) fibre composite tensile test failure surface.

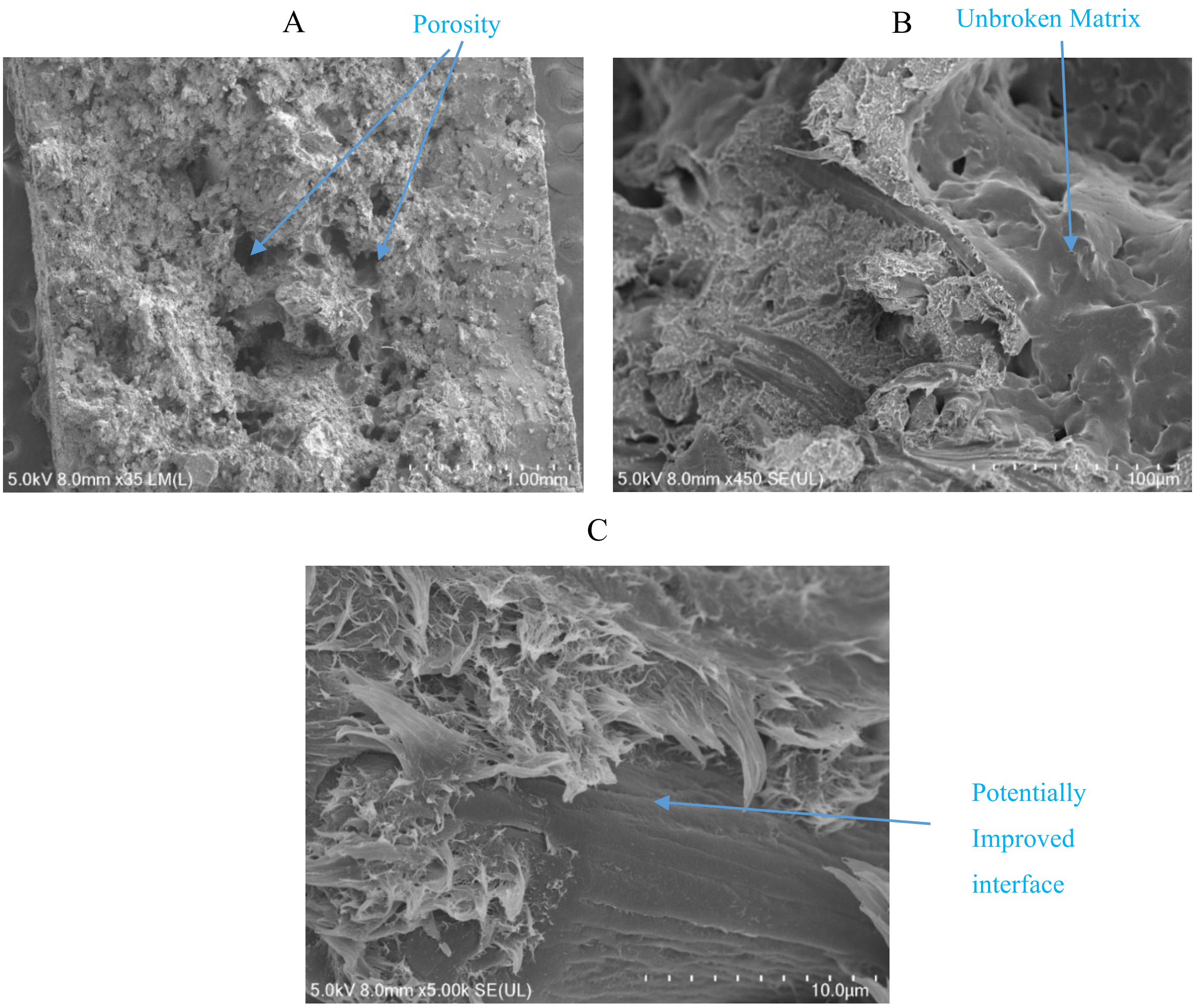
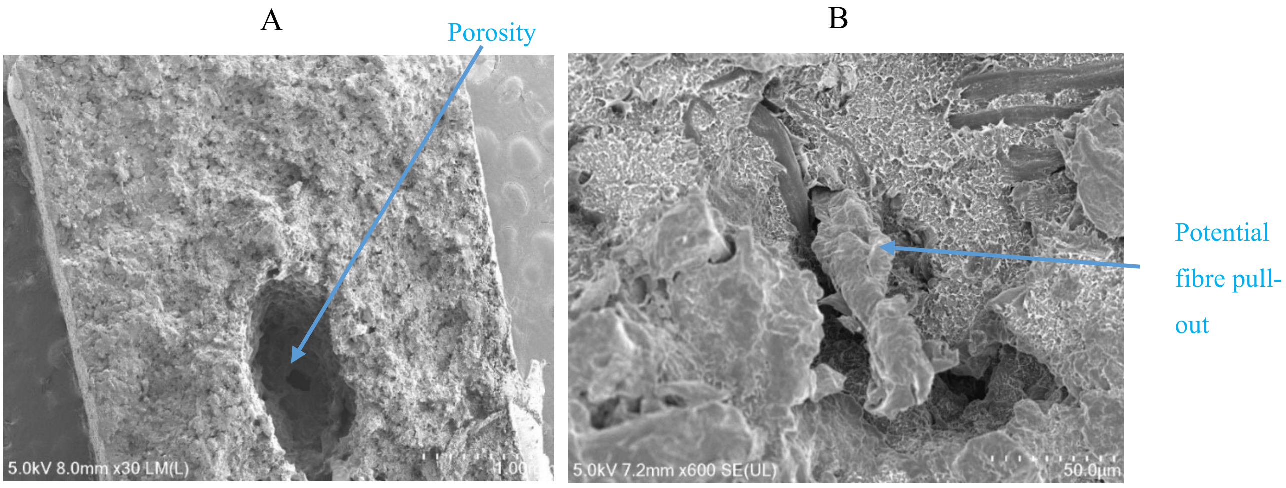
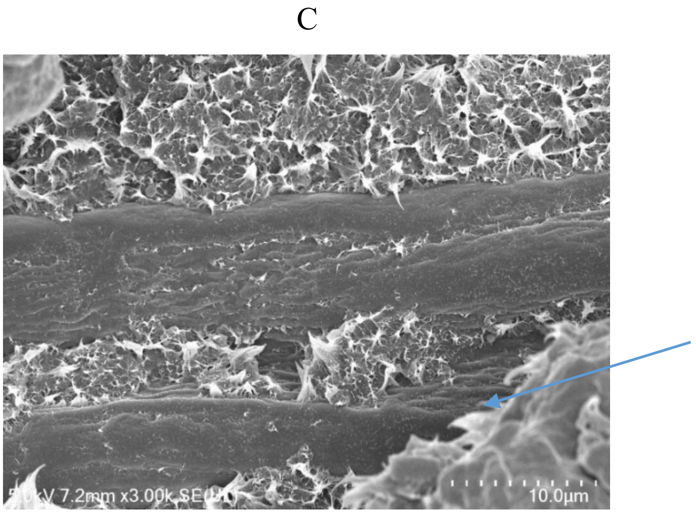


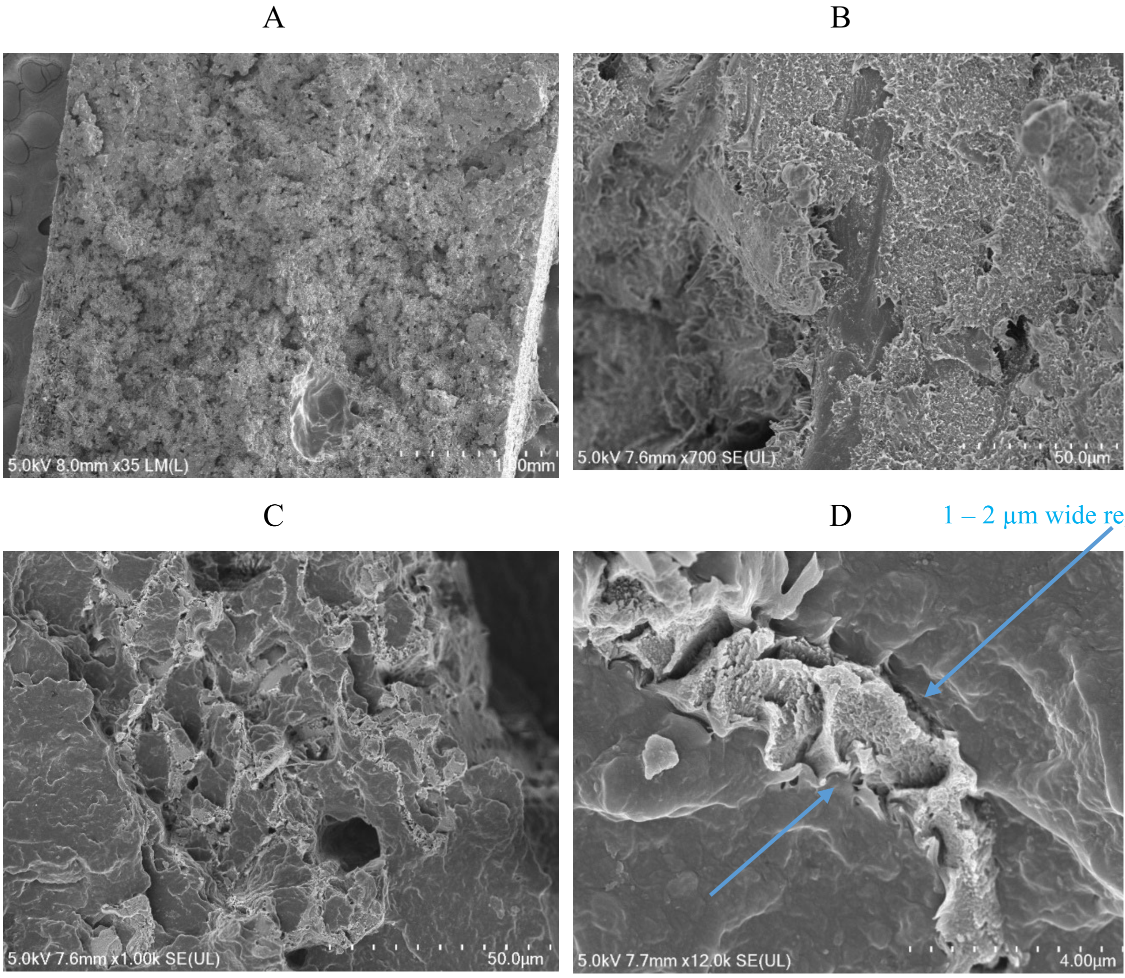
Figure 4-12: Scanning electron microscopy (SEM) of a typical sigma blade compounded 30 wt.% DU (digested and ultrasonic treated) fibre composite tensile test failure surface.





Polymer failure, still attached to fibre surface

Figure 4-13: Scanning electron microscopy (SEM) of a typical sigma blade compounded 30 wt.% DB (digested and bleached) fibre composite tensile test failure surface.



1 – 2 μm wide region

Figure 4-14: Scanning electron microscopy (SEM) of a typical sigma blade compounded 30 wt.% DBU (digested, bleached, and ultrasonic treated) fibre composite tensile test failure surface.

SEM to Investigate Differences Between Composites Produced with Extruder and Sigma Blade Compounder

Due to the large variation in properties seen between the composites produced with the extruder and sigma blade, SEM was used to investigate the failure surfaces to evaluate the difference in properties.

Figure 4-15 (A and B) and Figure 4-16 (A and B) compare the composite failure surfaces of the digested fibre composites produced with both the extruder and the sigma blade. The images show that the failure surface of the extruded composite is much less homogenous than that of the composites produced using the sigma blade, likely due to the extended time the composite material spent in the sigma blade ensuring homogeneity.

One of the largest differences between the composite failure surfaces is the ductility apparent in the failure surface of the extruded composites compared to the more brittle failure surface of the sigma blade compounded composites. The failure surface of the extruded composites shows large amounts of ductile deformation of the polymer matrix across the failure surface (compared to the sigma blade composites). This ductility in the extruded composites is also shown in the mechanical properties of the composites, where the sigma blade composites failure strain is much lower than the extruded composites. Figure 4-16 (A) shows the matrix 'tongues' from plastic deformation are of the same magnitude (if not bigger) of the fibres within the composite. The mode of failure of the matrix (i.e. ductile or brittle) is dependent on the fracture speed (significantly affected by the loading rate of the matrix) and the temperature of the sample. High loading rates and low temperatures can lead to brittle failures, whereas slow loading rates or high temperatures can lead to ductile failures [60]. Therefore, the matrix failure (or crack propagation of the matrix) in the extruded composites must have occurred at a slower rate than in the sigma blade composites. The reduced rate of failure in the extruded composites could be due to a number of reasons. The potential for increased shear and pressure in the extruder could have increased fibre wetting while also reducing fibre length. The combination of properties induced by the extruder has the potential to increase interfacial strength (due to improved wetting, while also potentially reducing the load carried by the fibre (due to reduced length). The potential for both improved interface and reduced load in the fibre could have reduced the chance of sudden failure of the composites due to fibre pull-out and reduced the potential for fibre or interface failure causing a sudden high load on the matrix. The resultant properties of the extruded composites include a matrix that is loaded at a slower rate resulting in more ductility of the composites. The reduced Young's modulus of the extruded composites reinforces this theory as it is likely due to a reduction in fibre length [70]. The failure surface of the sigma blade composites also indicates significant fibre pull-out, which is a sign of poor interfacial strength. However, due to the ductility seen in the extruded composites, it is difficult to observe whether fibre pull-out occurs in the extruded composites.

The extruded composites failure surface seen in Figure 4-15 (A) shows that there is potentially porosity which was also seen in the sigma blade composites (Figure 4-12 (A) and Figure 4-13 (B)). The porosity in the composites produced with both compounding techniques implies that the porosity could result from the high temperatures the composite material is exposed to during injection moulding.

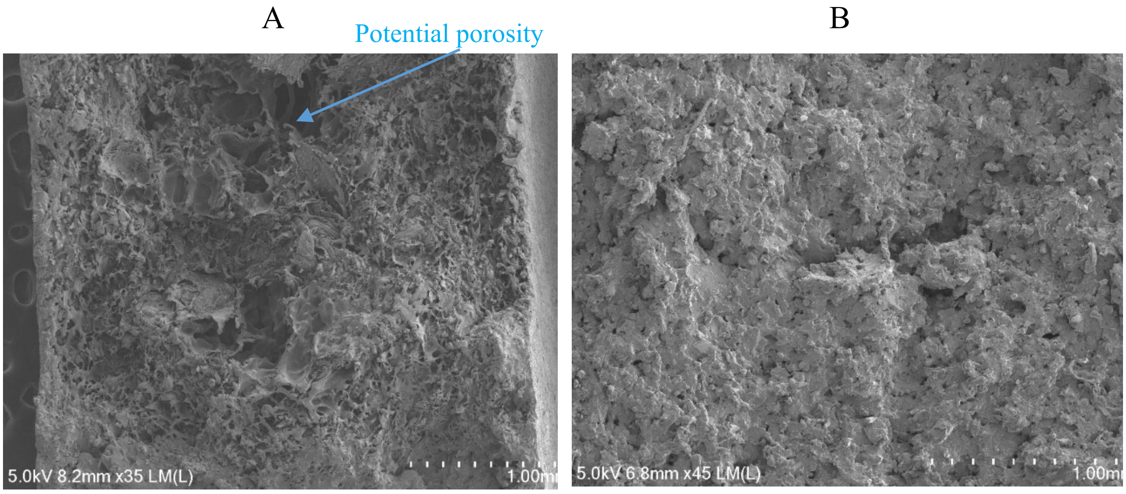


Figure 4-15: Low magnification scanning electron microscopy of digested fibre composite failure surfaces produced with: A) Extruder B) Sigma blade.

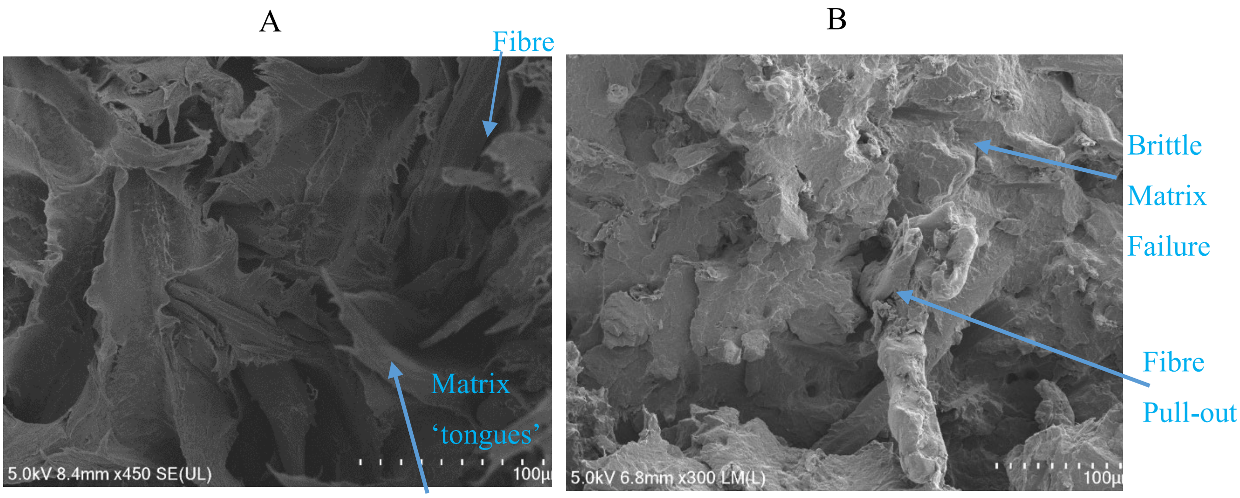


Figure 4-16: High magnification scanning electron microscopy of digested fibre composite failure surfaces produced with: A) Extruder B) Sigma blade.

Tensile Properties with Varying Injection Moulding Temperatures

Through the use of SEM, observations were made indicating large voids and porosity in the composites injection moulded at 200 °C. The visual colour change comparing the extruded and sigma blade composites suggests that thermal degradation could occur during processing, which has the potential to have caused porosity. Thermal degradation of the fibres has the potential to produce gasses that could have built up and created the voids seen in the composite failure surfaces. Furthermore, the interface and the fibre strength could have been affected due to the decomposition of the fibres.

The wood flour and fibre analysis results indicated that the largest differences in the constituents within the reinforcement occurred as a result of the digestion and bleaching processes (and not the ultrasonic treatment). The previous results from tensile testing of the sigma blade composites further indicated that these chemical processes led to the largest differences in the mechanical properties in the corresponding composites. Due to the differences in constituents and mechanical properties of composites, the D and DB fibre composites were used to evaluate whether porosity could be reduced.

The isothermal TGA of the D and DB fibres indicate that the degradation of both fibres occurs at both 180 °C and 200 °C (Figure 4-8 and Table 4-4). However, the degradation was seen to be substantially quicker and resulted in a larger change in mass at the higher temperature. The variance in mass change between temperatures suggests that small variations in temperature or conditions in this temperature range could have a large effect on the thermal stability of the fibres.

Due to the porosity shown in the composites and the reduced thermal stability of the fibres at 200 °C indicated through the isothermal TGA, the D and DB fibre composites were reproduced using a reduced temperature range in the injection moulder barrel (Figure 3-6). The composites were tensile tested, and the properties in Table 4-8 were attained. Visually, the composites were lighter in colour than those produced with the higher injection moulding temperature. Furthermore, the composite failure surface was investigated using SEM and suggest porosity was reduced compared to previous tests, Figure 4-17 (A and B).

Interestingly the reduction in temperature used for injection moulding resulted in lower TS and failure strain of the composites, as shown in Table 4-8. The reduction is potentially due to the reduction in temperature during injection moulding resulting in an increase in viscosity of the matrix and reducing fibre wetting during the process. The differences in the properties were much larger in the D fibre composites than the DB fibre composites. The variance between fibres suggests that the bleaching process used to expose more cellulose has improved the interaction between the fibre and matrix, therefore resulting in increased interfacial strength and mechanical performance. The statistical analysis further suggests that the reduction in temperature resulted in a statistically significant difference in composite TS using the digested fibres, whereas there was not a significant difference in the composites produced using the DB fibres. The composites produced at 180 did use a different source of timber, which could have a slight effect on composite performance. However, the DB fibre composites indicate that any potential impact is minor as the differences in properties are significantly insignificant.

Table 4-8: Tensile properties of composites with varying injection moulding temperatures. Composites produced with 30 wt.% D (digested) and DB (digested and bleached) fibre using the sigma blade compounder. The COV is presented in parenthesis (%). Means that share a letter (A, B, C, or D), suggest that the differences are statistically insignificant.

Composite Sample	Number of Samples tested	Timber source	Tensile Strength (MPa)	Failure Strain (%)	Young's Modulus (MPa)
PP - REFERENCE	2	N/A	18.49(0.03)^{C}	N/A	835(2.95)^{B}
PP D (180)	4	3	16.00(3.24)^{D}	1.00(3.24)	2303(7.24)^{A}
PP D (200)	4	2	20.96(4.36)^{B}	2.23(20.3)	1978(13.5)^{A}
PP DB (180)	4	3	23.18(1.94)^{A}	1.82(5.33)	2368(2.92)^{A}
PP DB (200)	4	2	24.31(2.19)^{A}	2.46(11.9)	2292(5.45)^{A}

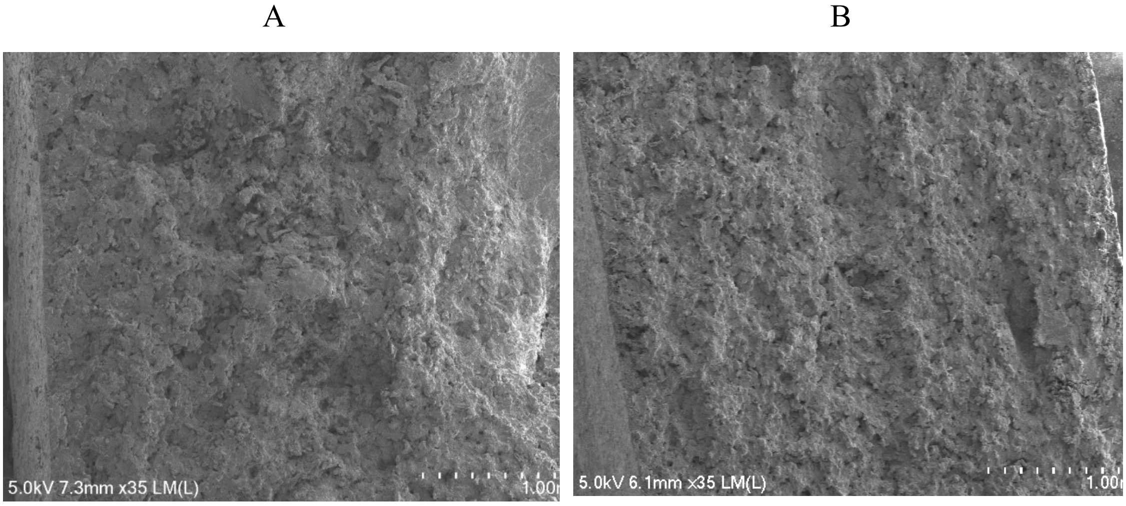


Figure 4-17: Composites produced using the sigma blade and injection moulded at a maximum temperature of 180°C. A) D (digested) fibre composites. B) DB (digested and bleached) fibre composites.

4.3.1.2 Effects of Fibre Content on Composite Mechanical Performance

The effects of fibre content were investigated using D and DB fibres, compounded with the sigma blade. The fibre content was studied to improve understanding of the effects of the fibres on the corresponding composite properties. D and DB fibres were chosen due to the large difference shown in the tensile properties with 30 wt.% fibre using the sigma blade and the variance in properties using reduced injection moulding temperatures. The composites were produced using the sigma blade with 20, 30, and 40 wt.% fibres and 4 wt.% MAPP for all samples. The injection moulding was completed at 180 °C. Tabl 4-9 shows the variation in tensile and flexural properties of the composites.

The TS and failure strain were found to decrease with increasing fibre content for the D fibre composites. Maximum TS was attained using 20 wt.% fibre (Table 4-9). Literature suggests that natural fibre composite strength should reach a maximum of 40-55 wt.% fibre; a reduction in strength at higher fibre content is typically caused by poor fibre wetting [40]. The decrease in tensile strength with increasing fibre content in the digested fibre composites indicates poor compatibility between fibres and matrix, resulting in poor wetting of the fibres. The reduction in tensile strength after reducing the injection moulding temperature (Table 4-8) reinforces the possibility of poor compatibility.

The DB fibres were also used to investigate varying fibre content. Differing from the digested fibre composites, the maximum TS was attained using 30 wt.% fibre (Table 4-9). The increase in tensile strength from 20 to 30 wt.% fibre reinforces the possibility of improved compatibility between the bleached fibres and the matrix. The alteration of compatibility is likely a result of reduced lignin, hemicellulose, and extractives from the fibre surface, thus exposing more cellulose, potentially improving interaction with MAPP, and resulting in a rougher fibre surface for improved interfacial properties. The differences in fibre properties were indicated in the SEM, FTIR, XRD, and fibre quality analysis (Section 4.2). However, the reduced tensile strength at 40 wt.% suggests that the compatibility could be improved, or other issues are potentially arising due to the processing conditions.

Table 4-9: Mechanical properties of composites produced with varying fibre content. Including D (digested fibre), and DB (digested and bleached fibre). The COV is presented in parenthesis (%).

Composite	Timber Source	Tensile Strength (MPa)	Tensile Failure Strain (%)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Failure Strain (%)	Flexural Modulus (MPa)
PP D (20 wt.%)	3	24.53(1.66)	5.01(18.8)	1666(5.50)	34.91(3.98)	11.4(15.3)	1219(5.69)
PP D (30 wt.%)	3	16.00(3.24)	1.00(3.24)	2303(7.24)	28.54(6.17)	2.14(16.2)	1863(11.8)
PP D (40 wt.%)	3	8.54(23.76)	0.42(23.8)	2624(19.3)	11.88(50.9)	0.85(7.89)	1845(32.8)
PP DB (20 wt.%)	3	22.10(1.92)	4.06(18.5)	1589(9.93)	32.79(2.02)	10.6(19.4)	1134(3.91)
PP DB (30 wt.%)	3	23.18(1.94)	1.82(5.33)	2368(2.92)	36.88(2.06)	3.10(7.05)	1974(2.55)
PP DB (40 wt.%)	3	15.76(18.8)	0.77(18.8)	2987(6.93)	24.53(19.5)	1.43(41.8)	2438(8.51)

The results of the fibre content testing show that the 20 wt.% digested fibre composites have a higher tensile strength than the 20 wt.% digested and bleached fibre composites (24.53 MPa and 22.1 MPa, respectively, Table 4-9). The higher TS indicates that wetting is good in both the D and DB fibre composites at 20 wt.% fibre content. The reduction in tensile strength using the DB fibre composites suggests that the bleaching process, which was used to remove lignin and other constituents from the fibres, has potentially decreased the fibre strength resulting in reduced reinforcement capability. The potential reduction in fibre strength could be a result of reduced lignin and cementing constituents holding the microfibrils in the fibres together or possible degradation of the cellulose. However, the increase in composite strength with 30 wt.% fibre using the bleached fibres indicates that the compatibility of the bleached fibres with the matrix is better and has the potential to give the best mechanical performance due to being able to increase fibre content.

For both D and DB fibre composites, the YM increased, and the failure strain decreased with increasing fibre content, as expected from the literature. The change in properties can be affiliated with the typically high modulus and brittleness of natural fibre [15].

The flexural properties of the composites produced with the sigma blade using digested fibres and bleached fibres were also analysed using a 3-point bending test. The general trend of the flexural properties were the same as tensile properties. However, the flexural strength of the 30 wt.% DB fibre composites was higher than the 20 wt.% D fibre composites. Thus, the flexural properties further indicate that although the strength of the DB fibres may be lower than the D fibres, the DB fibres have the potential to attain better mechanical performance due to the potential to increase mechanical properties through increasing fibre content.

Increasing Fibre Content with the Extruder

Comparing the results of the composites produced with the extruder and the sigma blade in Table 4-7, the tensile strength of the extruded composites was substantially higher than the composites prepared with the sigma blade. The failure strain was much higher, with the extruded composites suggesting more 'useable' properties in application. Furthermore, the interface was potentially better with composite produced with the extruder. Due to the increase of TS and failure strain, and possible improvements of wetting and interface, the extruder was used to produce composites with the bleached fibres that appeared optimal for compatibility with the matrix. Furthermore, the bleached fibres had the lowest heavy metal content, likely giving an advantage as a commercially viable product. The composites were produced using 40wt.% fibre, 4 wt.% MAPP, and 56 wt.% PP, to provide a better understanding of the mechanical performance attainable. A summary of the tensile strength of all DB fibre composites can be seen in Figure 4-18 to show how fibre content and processing affect TS. Table 4-10 summarises the tensile and flexural properties of the 40 wt.% DB fibre composites.

Table 4-10 shows that the resulting average tensile strength was found to be 27.61 MPa, and the average flexural strength was 45.19 MPa, the highest strength properties attained from any composites tested during this study. The modulus increased compared to the composites extruded with 30 wt.% bleached fibres (Table 4-7), and a modulus of 2.33 GPa was attained. The failure strain was 3.75 %, which is substantially higher than the failure strain of the composites prepared using 30 or 40 wt.% fibres in the sigma blade. Due to the high YM and failure strain attained from the extruded 40 wt.% DB fibre composites the composites could be regarded as having the most useable mechanical properties.

The results from the extruded composites using 40 wt.% fibres suggest that the wetting of the fibres using the extruder is still good with the increased fibre content, therefore providing good interfacial strength and increased mechanical performance. Although the bleached fibres did not give the best mechanical performance in the composites produced with 30wt.% with the extruder, the results of the composite testing indicate an improvement of compatibility with the matrix and coupling agent leading to the ability to increase fibre content and maximise composite properties.

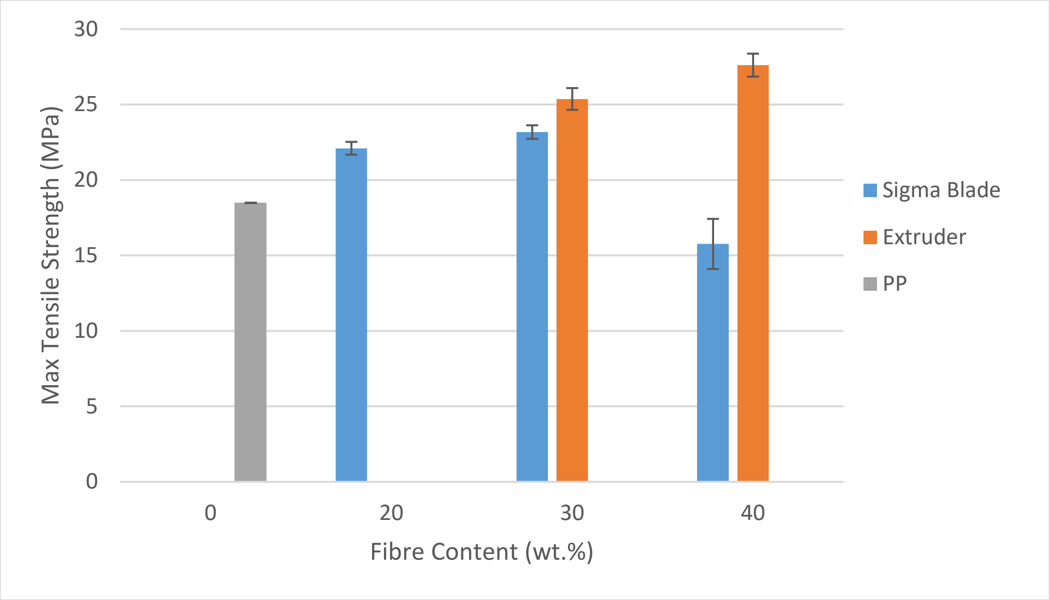


Figure 4-18: Tensile strength with varying fibre content. Including sigma blade compounded composites, extruded composites, and virgin PP (0% fibre content).

Table 4-10: Summary of 40 wt.% bleached fibre extruded composite properties. The COV is presented in parenthesis (%).

Tensile strength (MPa)	Young's Modulus (MPa)	Tensile Failure Strain (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Failure Strain (%)
27.61(2.75)	2334.99(5.79)	3.75(12.76)	45.19(1.88)	2097.73(4.70)	6.07(4.01)

When comparing the mechanical properties of the extruded 40 wt.% DB fibre composites (Table 4-10), with the characteristic properties of common structural materials in the construction industry (Table 2-1, Section 2.1), it can be seen that the composite tensile flexural strength are higher than all of the common timbers from NZS 3603 (Radiata Pine, Douglas Fir, Rimu, Beech, and Larch). The composite strength properties are similar to the commercial LVL and roughly twice as high as the commercial WPC. However, the commercial timber strengths are an estimate of the lower 5 percentile value, and the average strength values could be significantly higher.

The Young's modulus of the extruded 40 wt.% DB fibre composite was found to be approximately 2.3 GPa, and the flexural modulus was approximately 2.1 GPa, whereas the elastic modulus of radiata pine was in the range of 6.5 – 12 GPa (green and dry, Table 2-1, Section 2.1), roughly three times higher than the composite. The lower stiffness of the composite indicates that the composites would be difficult to be used as a direct replacement in structural applications as deflection would be at least three times greater if the same stress was applied to a WPC member. However, this could be overcome with engineering design to reduce the stress in the material. Furthermore, the use of wood-plastic composites also allows for varying profiles and shapes through different production methods, which further has the potential to improve the engineering design of structures for the lower mechanical properties.

The tensile and flexural properties of the extruded 40 wt.% DB fibre composite was higher than that of commercial WPC (Table 2-1, Section 2.1). The commercial WPC is used in decking applications, which shows that the use of WPC produced with wood fibres from CCA treated timber could be suitable in this type of application. Furthermore, all of the composites produced from CCA treated timber using the extruder and 30 wt.% reinforcement (Table 4-7) meet the tensile strength of the commercial WPC and are similar in elastic modulus. To completely understand the application potential as a WPC material, the flexural properties of the 30 wt.% extruded composites should be tested and compared with the required properties of ASTM D 6662: Standard Standard Specification for Polyolefin-Based Plastic Lumber Decking Boards [93]. However, the properties of the 40 wt.% D fibre composites produced with the sigma blade were the lowest properties attained in the study, and the flexural properties appear useable as a decking material as per the standard. Therefore, it is likely that all composites produced would meet the flexural properties required.

4.3.1.3 Creep

Creep testing was undertaken over a 12 hour period to understand the influence of the introduction of fibres to PP on the viscoelastic behaviour. The 40 wt.% DB fibre composites from the twin-screw extruder were used for the study due to having the most appropriate mechanical properties for the construction sector. PP was used as a comparison. The composite and PP were tested at 15 and 30 % of their specific flexural strength. The PP flexural strength was 23.56 MPa, and the DB composites flexural strength was 45.19 MPa. The resultant flexural strain was measured over a 12-hour period and shown in Figure 4-19. The temperature during testing was also measured and displayed in Figure 4-20.

Figure 4-19 shows that for tests at both 15 and 30 % of the flexural strength, PP has a higher flexural strain than the composites, even though the applied stress was lower. Furthermore, the results indicate that the creep rate is higher in the PP than the DB fibre composites in both tests. Both the differences in strain and creep rate between PP and composites appear to be more pronounced in the 30% strength tests than the 15% tests.

Figure 4-19 also shows that the creep curve for the DB fibre composites follows a smooth line that is potentially starting to plateau in both 15 and 30% tests over a 12-hour period. However, the PP curve for the 30 % test has an initial plateau at roughly 15000 seconds before starting to accelerate again later in the test. This curvature is potentially indicative of the PP sample reaching a tertiary creep phase as the creep rate starts to accelerate at the end of the test. However, it is also possible that it is due to other factors, such as the complex semi-crystalline structure of PP. The data suggests that using the DB fibres is useful for reducing the strain in the composites and the creep rate in the material. Furthermore, it is possible that the introduction of wood fibres has increased the time taken to induce tertiary stress, which is important for structural application in the building section, where tertiary creep should be avoided [23, 30].

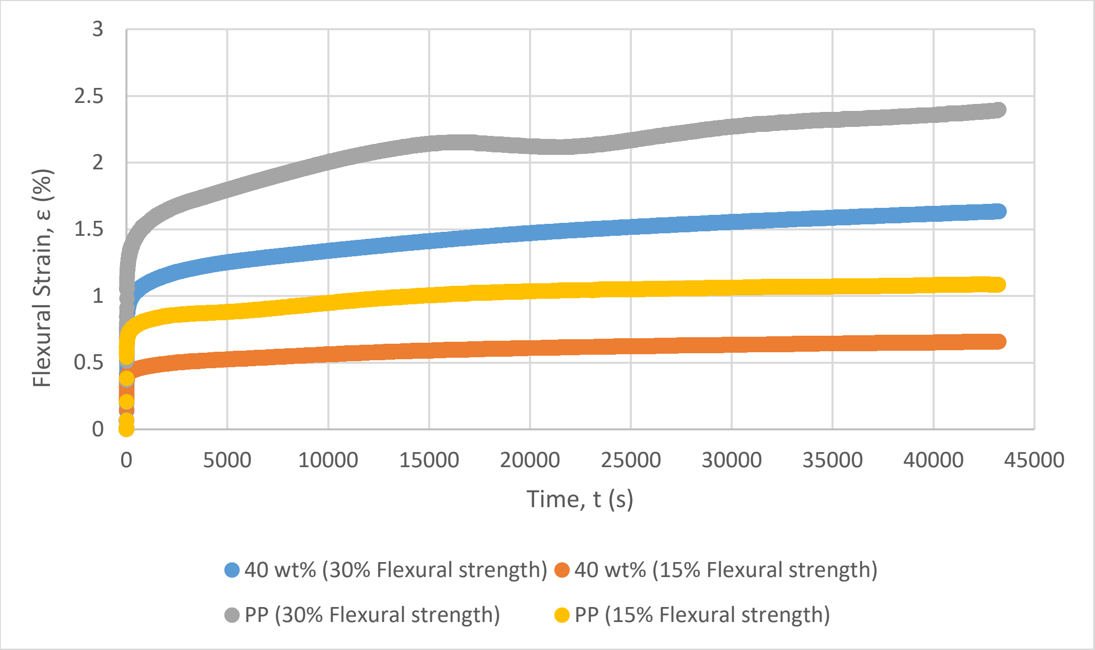


Figure 4-19: Creep testing of polypropylene (PP) and 40 wt.% DB (digested and bleached) fibre composites.

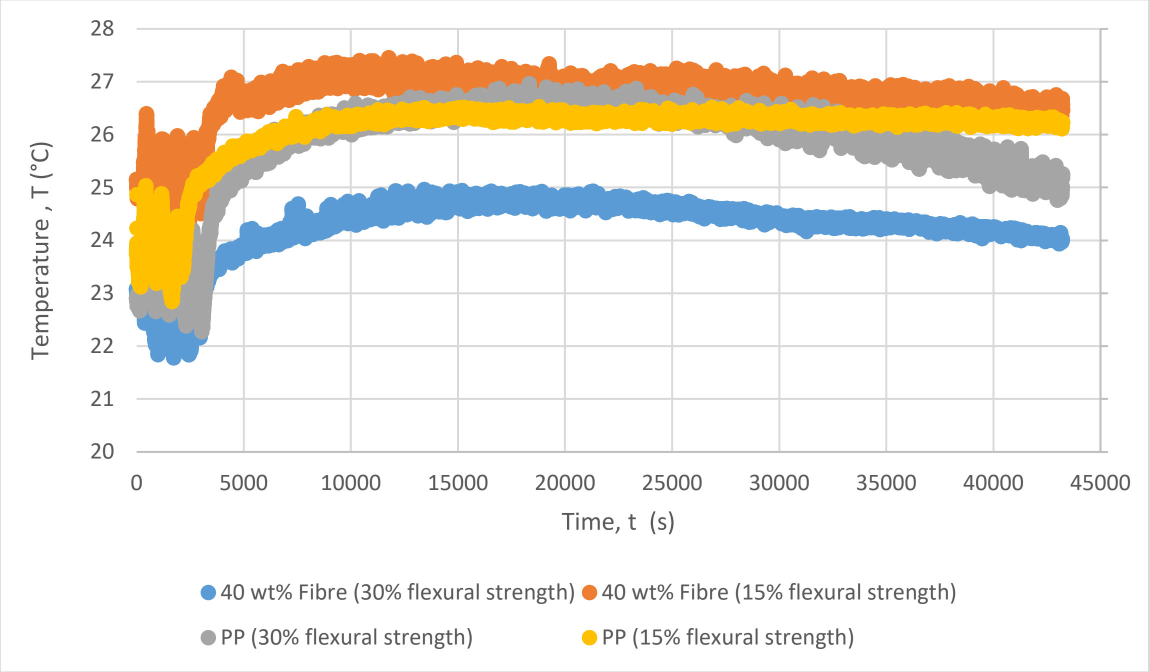


Figure 4-20: Ambient room temperature during creep testing of polypropylene (PP) and 40 wt.% DB (digested and bleached) fibre composites.

The data is very limited for several reasons. Firstly, the data is based on only 1 sample per condition, which does not give any allowance for variance in conditions or within samples. The testing was not performed in a controlled environment, and therefore the samples were exposed to different temperatures, as shown in Figure 4-20. The variances in temperatures may have affected the test results due to the susceptibility of polymers to variance in temperature. However, it is unlikely that the small differences in the temperature during testing affected the trends found in the results. The temperature difference is most pronounced in the 30% test of the DB fibre composites. However, the test result still fits within the trends of the data. Furthermore, the trends of the data make sense as the creep rate is increased with higher applied stresses for both samples, as expected.

The testing gives insight into the improvement of creep properties when fibres are added to polymers to alter properties. However, to understand long term application potential, more testing is required, and the results from this study should not be used to assess the effects of creep on the potential for structural application. The New Zealand standards require durability for 50 years for structural applications, and therefore, further research is required to understand creep performance in this time frame and whether tertiary creep can be avoided [25].

4.3.2 Analysis of Composite Physical Properties

The results from the fibre analysis indicated that the digestion and bleaching processes had the largest impacts on constituents present in the fibres and the content of the heavy metals (suggested by FTIR, Section 4.2.3, and ICP-MS, Section 4.2.6). The testing of composites produced with the sigma blade further indicated that the properties varied more when comparing digested (D) fibre and digested and bleached (DB) fibre than the implementation of ultrasonic treatment on the fibre. Due to the large difference in constituents, heavy metal content, and composite properties, leaching from wood flour (F), D fibre, and DB fibre composites was investigated. The wood flour composites were used to assess minimal processing and maximum heavy metal content. The use of extrusion was considered most comparable to potential commercial production, and therefore the 30 wt.% extruded composites used in the mechanical testing were used for the study. The leaching properties were considered to be most heavily impacted by the heavy metal content of the reinforcement material used. However, moisture absorption was also considered to have a large influence due to being a mechanism for leaching. Thus, moisture absorption and leaching of the composites were studied to investigate the application potential as safe, low leaching composites.

4.3.2.1 Moisture Absorption

The composites produced with 30 wt.% F, D, and DB reinforcement using the extruder, were tested for their moisture absorption over 15 days. A PP sample was also measured as a reference. The moisture absorption was studied through the change in mass as a percentage, shown in Figure 4-21 and Table 4-11. The testing shows that the moisture absorption over 15 days is greater for all composites than PP, as expected due to the hydrophilic nature of the reinforcement materials. The digested fibre composites were found to have the largest mass change over 15 days. This large change in mass is potentially due to having the worst interfacial properties (indicated by the mechanical testing), allowing for more moisture to be absorbed. The wood flour and bleached fibre composites had a similar mass change over 15 days, likely due to having a better interface than the digested fibre composites. The COV (shown in Table 4-11) suggests that moisture absorption is statistically similar for all composites.

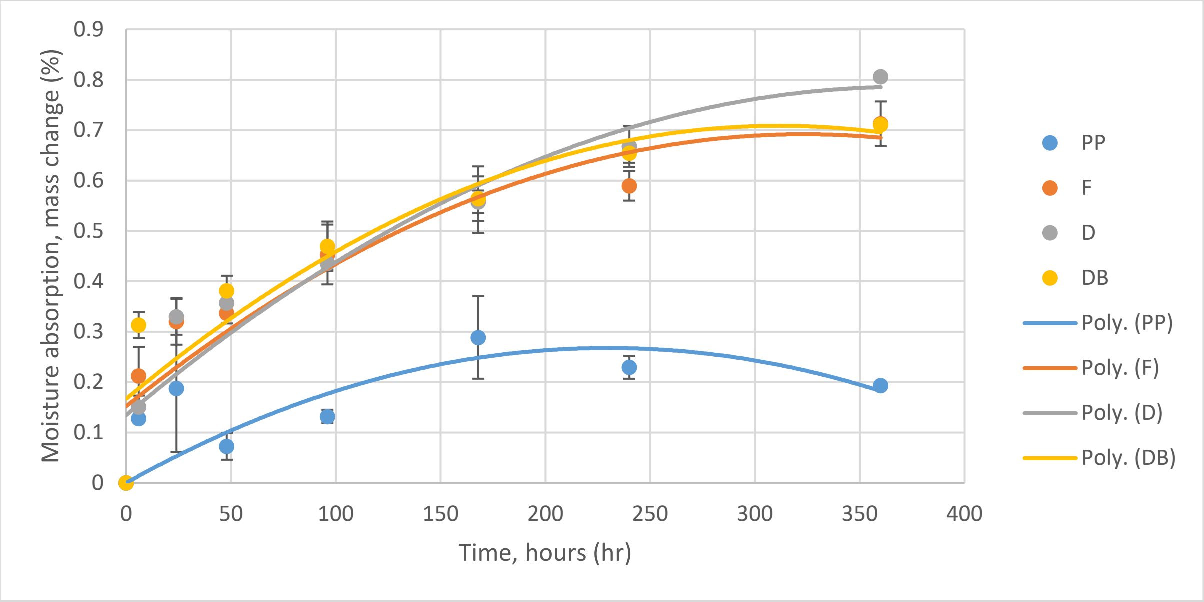


Figure 4-21: Moisture absorption measured as mass change (percentage) of polypropylene (PP) and 30 wt.% F (wood flour), D (digested fibre), and DB (digested and bleached fibre) extruded composites.

Table 4-11: Total moisture absorption measured (over 15 days) as mass change (percentage) of polypropylene (PP) and 30 wt.% F (wood flour), D (digested fibre), and DB (digested and bleached fibre) extruded composites. The COV is presented in parenthesis (%).

Composite Type	PP	F	D	DB
Moisture Absorption (%)	0.289(28.4)	0.712(6.23)	0.806(0.81)	0.711(15.5)

4.3.2.2 Leaching

Figure 4-22 (A, B, and C) show the cumulative leaching of copper, chromium, and arsenic from 30 wt.% wood flour (F), digested fibre (D), and digested and bleached fibre (DB) extruded and injection moulded composites over a 14-day period (cumulative leaching values after 14 days are summarised in Table 4-12). The experimentation took place by measuring only one sample of leachate per composite material at each time interval, and the accuracy of the results could be increased through testing replicates. Furthermore, although the results of all of the testing were above the quantitative limit of the ICP-MS experimentation, some of the results indicate extremely low levels of heavy metals (especially the leaching of As from D and DB fibre composites), and the results of samples with very low levels of leaching are potentially susceptible to errors in the methods undertaken or contamination. However, the results shown in the figures give a clear trend in leaching properties between samples.

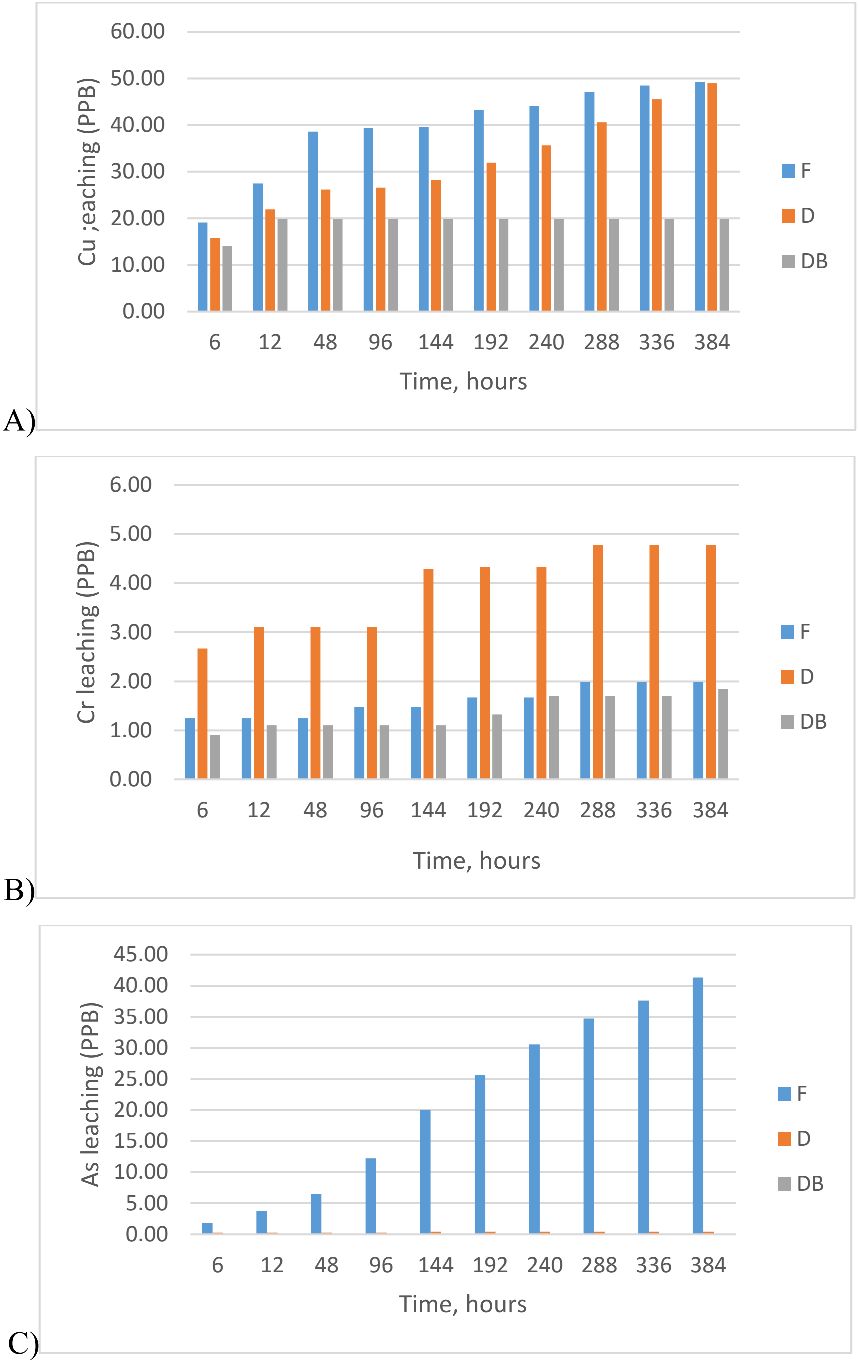


Figure 4-22: Cumulative leaching of A) copper, B) chromium, and C) arsenic, from 30 wt.% (wood flour), D (digested fibre), and DB (digested and bleached fibre) extruded composites.

Table 4-12: Summary of cumulative leaching (total over 14 days) of copper, chromium, and arsenic, from 30 wt.% F (wood flour), D (digested fibre), and DB (digested and bleached fibre) extruded composites.

	Cu (ppb)	Cr (ppb)	As (ppb)
F	49.22	1.98	41.29
D	48.96	4.78	0.42
DB	19.84	1.84	0.07

The recorded leaching values of the wood flour composites were lower than other studies, likely due to the low content of wood flour in the composites allowing for better encapsulation in the matrix, therefore, restricting water penetrating the composites and reducing the ability of the heavy metals to leach out [16, 17].

The results shown in Figure 4-22 and Table 4-12 show that the leaching of copper is higher from all materials than the leaching of chromium and arsenic. This is interesting as the content of chromium in both the wood flour and digested fibres is higher than the other heavy metals, shown in Table 4-5. The arsenic leaching from the wood flour was also significantly higher than the chromium leaching.

The leaching of copper and arsenic appears to be directly related to the heavy metal content in the flour and fibres. The concentration and leaching of copper were very similar for wood flour and digested fibres, and the concentration and leaching of copper were much lower for the digested and bleached fibres. The properties were very similar for arsenic; the wood flour has a high concentration of arsenic and leaches the most, whereas the D and DB fibres have very low concentrations of arsenic, and the corresponding leaching was also minimal.

Differing from the copper and arsenic leaching properties, the leaching of chromium does not appear to directly relate to the content in the wood flour and fibres. The wood flour has the highest chromium content, whereas the digested fibres appear to leach the most over a two-week period. The digested fibre composites were seen to absorb the most moisture, which has the potential to allow for more chromium to leach out of the composites. However, the leaching of chromium from the DB fibre composites suggest that there was further reasoning; leaching and moisture absorption of the wood flour composites and the digested and bleached fibre composites appeared to be very similar, however, the content of chromium in the DB fibres in approximately 5 times less that that of the wood flour (353.16 ppm compared to 1728.5 ppm). Therefore, it is likely that the fixation of chromium into the composites was altered with the digestion process due to the high temperature, and pressure in the alkali solution. This could be a result of residual chromium (III) arsenate, which is expected to have been primarily removed, now being more susceptible to leaching, or an alteration in the fixation of chromium (III) hydroxide. However, it should be noted that the leaching was all measured to be in the same magnitude of ppb, and it is possible that small amounts of contamination could have caused the differences in results.

The maximum acceptable values (MAV) for the heavy metals in New Zealand's drinking water are 2000, 50, and 10 ppb for Cu, Cr, and As, respectively [36]. The leaching from composites produced with D and DB fibres both meet these standards, as seen in Table 4-12. Therefore, even if there were small amounts of contamination or error in the measurements, the samples are still below the MAV for safe drinking water.

The literature on using WPC produced with waste CCA treated timber indicated that one of the largest concerns was the heavy metal content and the potential for leaching when in application. Furthermore, the two studies that investigated leaching from WPC showed leachate levels that were significantly higher than the MAV for safe drinking water and used this as a justification for their concerns. However, the results of this study suggest that the use of chemical processing to obtain wood fibres from CCA treated timber has the potential to be used in the wood-plastic composite materials with leachate levels significantly lower than the MAV of drinking water. Therefore, the leaching test results indicate the potential for safe usage and application of composites produced with wood fibres from waste CCA treated timber, even when in contact with people.

Chapter 5

Life Cycle Analysis (LCA)

LCA was used to investigate the environmental impact of using waste CCA treated timber as a raw material for WPC production. An attributional gate to gate LCA study was performed to compare the different processing methods of waste CCA treated timber to produce reinforcement material for WPC. The processes studied include mechanical and chemical processing methods to obtain wood flour and fibre. The study was completed based on ISO 14040 and ISO 14044 and evaluated global warming potential, resource depletion, solid waste produced, energy consumption, and water consumption [79, 80].

5.1 Goal and Scope

The aim of this thesis aim is to investigate the viability of using waste CCA treated timber as a reinforcement material in wood-plastic composites to be used as a sustainable building material in the construction sector. Therefore, understanding the environmental effects of processing the timber for use in WPC is required.

Previous research has indicated that the production and application of wood-plastic composites produced from construction and demolition waste can be beneficial for the environment, even when comparing the application to timber [14]. However, the study focused on using construction and demolition waste has only required the use of mechanical preparation. In comparison, the environmental impact caused by the use of chemical treatments is likely to be significantly larger.

As part of this study, wood flour and fibres extracted through mechanical and chemical processes from waste CCA treated timber were compared for fibre properties, composite mechanical performance, and the effects on the heavy metal content in fibre and leaching from composites. To further evaluate the use of the wood flour and fibre obtained from CCA treated timber, the environmental impact of the processing was also considered. Therefore, the goal of this LCA study was to investigate the environmental 'cost' of the varying preparation methods used for producing WPC from waste CCA treated timber. The LCA results should be used to influence decision making on the viability of using reinforcement materials derived from waste CCA treated timber as a reinforcement material for WPC for increased sustainability in the building sector.

The environmental study aims to research the use of waste CCA treated timber as a reinforcement material in wood-plastic composites. As part of this process, a number of reinforcement preparation methods were performed to understand the effects on the composite properties and evaluate the best method of producing fibres or wood flour for use in composite materials. For the purpose of this study, the term 'reinforcement' encompasses both wood flour and fibre as materials used to improve mechanical performance in a polymer matrix. The reinforcement materials studied were split into five categories, including the following:

- Wood Flour (F)
- Digested Fibres (D)
- Digested and ultrasonic treated fibres (DU)
- Digested and bleached fibres (DB)
- Digested, ultrasonic treated, and bleached fibres (DBU)

The methods used for preparing reinforcement materials were explained in-depth in the Materials and Methods (Chapter 3)

The study was based on data obtained from the laboratory when producing composites from waste CCA treated timber. The laboratory-scale study was also modified to use data based on assumptions, calculations, and literature to investigate the differences when wood flour and fibre was produced on an 'ideal' commercial scale. The modified data was compared to a commercial pulping process, commonly used for attaining fibre in the form of pulp from timber, to understand the accuracy of the study. Furthermore, the data was compared to the production and disposal of waste CCA treated timber.

The environmental study focused on the equivalent carbon dioxide emissions from the process to evaluate global warming potential (GWP) and the energy consumption, as these appeared to be the focus of most LCA studies for the construction sector [3]. Resource depletion, solid waste produced, and water consumption were also assessed as they were considered essential indicators for the circular economy.

Functional Unit

The functional unit is the reference to which inputs and outputs to the system are normalised. The goal of the study was to evaluate the environmental impacts of using waste CCA treated timber as a reinforcement material for the construction industry. Therefore, two functional units were studied, including the use of one tonne of waste CCA treated timber as an input, and secondly, the production of one tonne of reinforcement material as an output.

System Boundaries

The concept of using waste CCA treated timber as a reinforcement material in wood-plastic composites was based on incorporating ideas from a circular economy to reuse the timber at the end of its life. Furthermore, the production of WPC has the potential to use waste plastics from the construction sector as a matrix material. The goal was to have the end product take the place of currently used commercial building materials, such as CCA treated timber itself. Figure 5-1 shows this concept as the raw materials for producing WPC are primarily end-of-life materials from the construction sector. The system boundaries for this study are based on a gate to gate system for the preparation of reinforcement material from the waste treated timber for WPC production, as seen in the orange box in Figure 5-1.

The system used for the study was based on the laboratory methods used for processing waste CCA treated timber as a raw material to produce wood flour or fibre. All samples required some initial mechanical preparation where the timber was mulched, granulated, and dried before further treatments were completed to obtain wood flour and fibre. The wood flour was produced by grinding the timber granules until they fit through an 850 μm sieve. In contrast, the wood fibres undertook a digestion process to separate the fibres chemically. Secondary fibre treatments were also investigated for improved composite properties, including hydrogen peroxide bleaching and ultrasonic treatment. The system boundaries for the environmental study included the laboratory-based processes, the production of electricity and chemicals, and wastewater treatment.

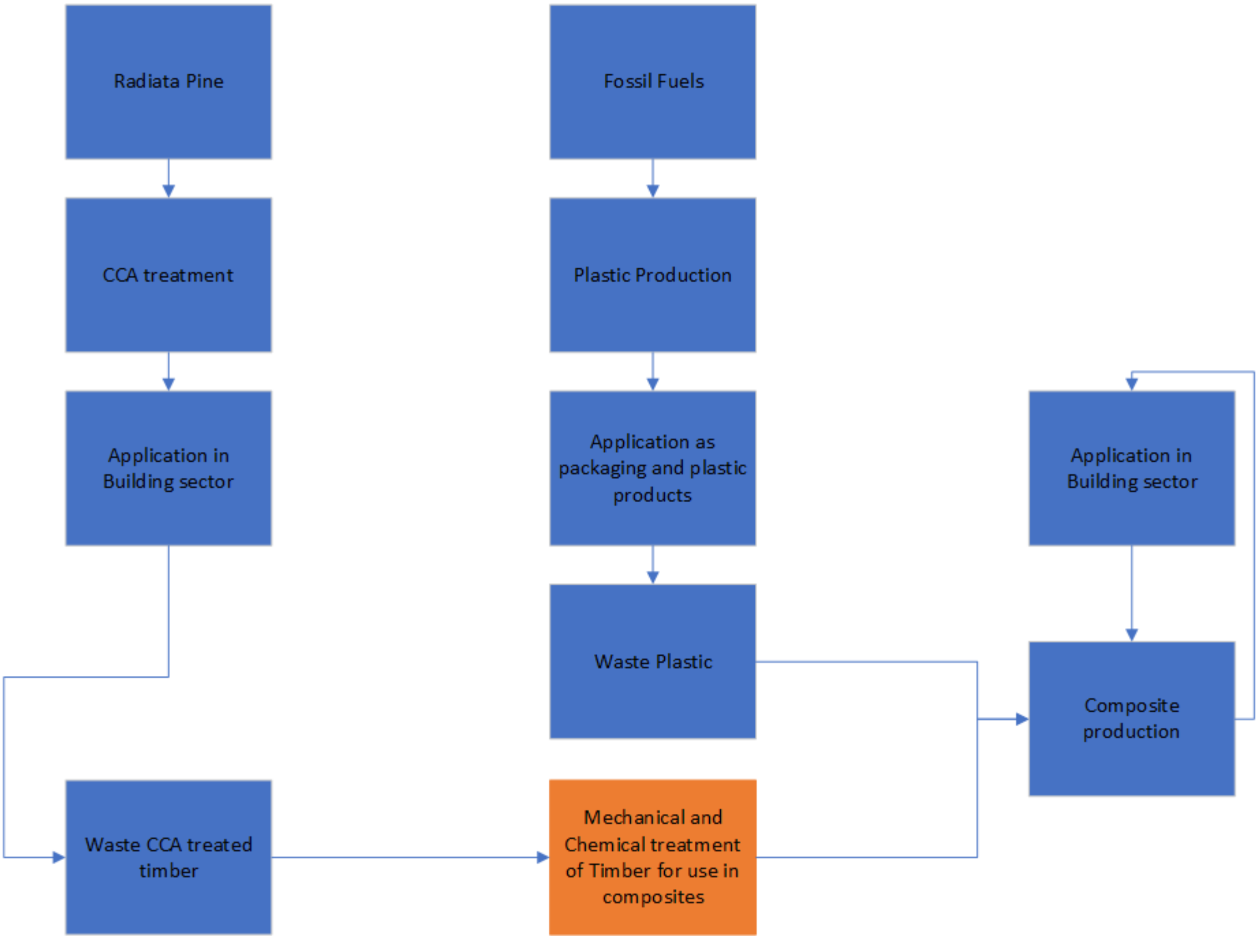


Figure 5-1: Simple circular economy concept for using waste CCA treated timber and waste plastic for producing WPC for the construction sector. (Orange process to be studied)

Figure 5-2 shows an example of the system boundaries for the laboratory scale system used to produce DBU fibres from waste CCA treated timber (this was the most complex method used for producing fibres). The model for the processing of DBU fibre also gives an indication for the energy, water, and chemical consumption, for the D, DU, and DB fibre as the processing uses the same methods with a different combination of secondary fibre treatments. The orange boxes indicate the processes included in the environmental study, and the blue boxes indicate the flow of materials and energy. The methods used were based on the material processing at a laboratory scale, described in Materials and Methods (Chapter 3).

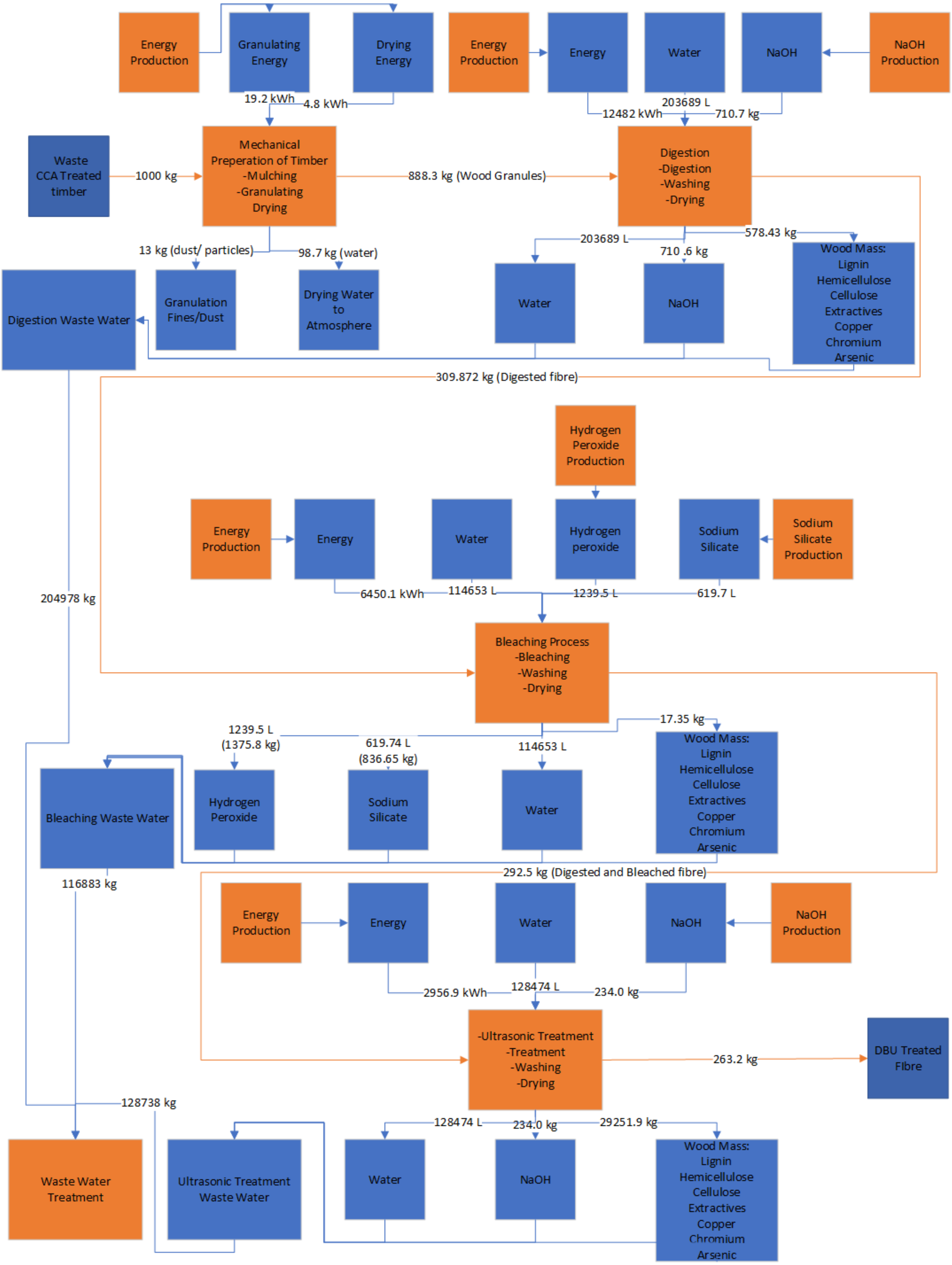


Figure 5-2: System boundaries of the digested bleached and ultrasonic treated (DBU) fibre process. (Orange boxes are processes accounted for in study, blue boxes are material flows between processes).

5.2 Inventory Analysis

Data Collection

The life cycle inventory (LCI) produced for the study was based on the preparation methods used in the laboratory. An LCI was created for the processes highlighted in orange in Figure 5-2, using the materials and energy in blue as inputs and outputs. The data required for the LCI processes not completed in the lab were based on data found in literature.

The energy used in the laboratory was measured using a Hioki PW3365 – 20 clamp-on power logger for three-phase systems and a PowerTech plus MS6108 mains power meter for single-phase equipment. Water consumption was measured to the nearest 500 mL. The mass for chemical consumption was based on the methods used for reinforcement preparation in Materials and Methods (Chapter 3), measured to the nearest gram or millilitre.

The production of chemicals and energy and wastewater treatment was based on data found in literature. The emissions from electrical energy consumption were found by comparing the average energy consumption to the average CO_2 equivalent emissions from electrical energy in New Zealand in 2020. The kg CO_2 eq. emissions per kWh of energy consumed based on the data was found to be 0.123 kg CO_2 eq./kWh. Both sets of data were sourced from the Ministry of Business, Innovation, and Employment [94, 95]. For the production of electricity, only energy consumption and carbon emissions were considered as these were the main focuses of the study [3]. LCI data for NaOH consumption for the digestion and ultrasonic process was directly based on an LCI study of sodium hydroxide production in Malaysia [96]. Hydrogen peroxide and sodium silicate LCI data were also based on literature and were modified for the concentrations of the chemicals used in the laboratory [97, 98]. The life cycle inventory data for wastewater treatment used a data set for the treatment of wastewater in Victoria, Australia [99]. Comparison data for commercial pulping was obtained from Oji Fibre solutions, and data for producing and disposing of CCA treated timber was obtained from literature [100, 101].

Allocation Procedures

The processing described in the system boundaries was based on the production of wood flour and fibre for use as reinforcement material in wood-plastic composites. The data was used to produce an LCI for each reinforcement type studied. The LCI was then used to evaluate the global warming potential (kg CO_2 eq.), resource depletion of fossil fuels and minerals (kg), solid waste produced (kg), energy consumption (kWh), and water consumption (L) for each process. The waste CCA treated timber was treated as a raw material and was considered not to contribute to any of the environmental impacts. The global warming potential (GWP) was calculated from the emissions to air from the chemical production and water treatment and the CO_2 equivalent emissions from the electrical energy consumption during processing. Resource depletion, solid waste produced, and water consumption were calculated from the chemical production data, the wastewater treatment data, and the fibre processing data. Energy consumption was based on the electrical and fossil fuel energy consumed in all processes. Several materials produced during processing have the potential to be used for other products or purposes. Materials include the extraction of heavy metals or lignin from the chemical treatment solutions for reuse (heavy metals) or incineration for energy (lignin or biomass). However, this study did not investigate these possibilities, and all environmental impacts were allocated to the production of the reinforcement material.

Inventory

An LCI was completed for each process in the study and used with the functional unit to develop an LCI for the entire system for each reinforcement type. An example of the life cycle inventory can be seen for the DBU fibres in the appendix (Table 8-2, Section 8.2). The data in the LCI for the DBU fibres directly relates to the system shown in Figure 5-2 and is split into categories based on the mechanical and chemical processes used in the system.

Assumptions

The environmental study of the production of reinforcement material required a number of assumptions. Firstly, the system treated the waste CCA treated timber as a raw material with no environmental impact. This was done to dissociate the production (growth, harvesting and treatment) and application of the timber with the reuse of it as a material for wood-plastic composites. Therefore, the input of the material was not considered to have any environmental impact so that the processing could be compared to typical end-of-life disposal methods.

The system boundaries excluded transportation from contributing to the environmental impact. The transportation of timber was excluded as the timber would require transportation to landfill if it were not used as a raw material for WPC. Thus, the diversion from the landfill would likely have roughly the same environmental impact for transportation depending on the location of the landfill and proposed processing facilities. The transportation of chemicals was also excluded in the study. The expected mass and volume of chemicals used in processing was expected to be relatively low (compared to the transportation of timber), and therefore a comparatively low environmental impact for the transportation of the chemicals was expected.

Water consumption was measured to the nearest 500 mL for washing and quenching water used in the laboratory experiments. Although this was a minimal amount of water, when the measurements are extrapolated out for a study for one tonne of material being processed, this could make a substantial difference in the results for water consumption.

The drying process was based on the material drying in an 80 °C oven for at least 12 hours. The energy input required for an oven in the laboratory was measured over a week and averaged for 12 hours to find the energy required. The process was considered to be non-dependent on the mass of fibre or timber being dried as the oven can fit significantly more material than was used for the drying in the laboratory process. However, this assumption is very limited due to the maximum volume of the oven and the reduced drying potential when the oven's contents are increased.

The LCI for wastewater treatment was based on the production of one tonne of clean water and not on the input volume or mass of water. Therefore, the study assumed that one tonne of water output required one tonne of water input (masses are balanced). The other material inputs (chemicals, heavy metals, and biomass) were expected to be output as sludge. However, the high concentrations of heavy metals disposed of (especially arsenic) would likely require all of the sludge to be disposed of to landfill, which is not the case in the LCI used for the study [102]. Furthermore, the LCI was based on typical wastewater processing in Victoria.

The ideal scenario (or commercial scale scenario) used a number of assumptions to calculate energy inputs and modify chemical and water consumption to process timber to obtain fibre.

Firstly, the yield of the digestion process was assumed to be improved based on literature for chemical pulping timber. The yield for the laboratory scale digestion process was found to be 33.6 %. In comparison, the yield for a kraft process is reported to be between 65-70% for brown papers and 47-50% for bleachable pulp [55]. The yield for the ideal scenario for the digestion of the CCA treated timber was therefore assumed to be 50 % as it was used for bleaching and the concentration of NaOH in the process could be regarded as relatively high.

In the laboratory processes, the timber and fibre were dried after each processing step to ensure a consistent moisture content during processing. However, for the ideal scenario, drying was assumed to only be completed once for each reinforcement type (e.g. the DBU fibres only undertook a drying step once after all fibre treatment steps had occurred). Drying energy was calculated assuming that the fibres were suspended in a 1:1 ratio (by mass) of water and fibre after washing. Therefore, the same mass of water as fibre required removing through drying. Drying was calculated using the energy required to heat water to 100 °C plus the heat required to turn the water to steam, using the following two equations,

$$E = mC_p\Delta T$$

$$E = mL$$

Where E is energy, m is the mass of water being heated, C_p is the specific heat of water at constant pressure (4.186 kJ/kg*K), (assuming drying would take place at atmospheric pressure), ΔT is the change in temperature during processing (assuming heated from room temperature, 25 °C, to boiling temperature at atmospheric pressure, 100 °C, ΔT = 75 K), and L is the latent heat of vaporisation (2260 kJ/kg). The energy required for drying the fibres was found as the sum of the energy required to heat the water to 100 °C and the energy required to convert the water to steam. Furthermore, it was assumed that 11-21% of the energy could be recovered in an ideal scenario at a commercial scale [103]. Thus, the energy consumption used in the LCA calculations used 85% of the energy calculated (15 % recovery). The energy required to heat the fibres and surroundings was assumed negligible. Furthermore, heat transfer out of the system while heating was assumed negligible. Similar assumptions were made for heating the solution for both the digestion and bleaching chemical treatments.

The digestion energy was calculated as the energy required to heat the digestion solution to 160 °C. The energy calculations were approximated using the assumption that only water was being heated, and the fibres and NaOH did not affect the specific heat of the solution. Furthermore, the heating energy required to heat the digester, canisters, and processing water was assumed negligible, and it was assumed there was no thermal energy losses during the digestion processes. The pressure in the system was measured to be approximately 650 KPa (above atmospheric pressure), where the boiling point of water is 167.6 °C. Thus, the solution is expected to be liquid at 160 °C. Therefore, the energy consumption was calculated as the energy required to heat water from room temperature (25 °C) to 160 °C, in a constant volume process. The energy was calculated using the following equation,

$$E = mC_v\Delta T$$

Where E is energy, m is the mass of water being heated, C_v is the specific heat of water at constant volume, and ΔT is the change in temperatureΔT is the change in temperature (assuming heated from room temperature, 25 °C, to 160 °C, therefore ΔT = 135 K). The specific heat of water with constant volume changes with temperature (4.13 kJ/kg*K at 25 °C and 3.47 kJ/kg*K at 160 °C) and, therefore, the average was used. It was also assumed that 11-21% of the energy could be recovered [103]. Thus, 85% of the calculated energy was used (15 % recovery).

The bleaching energy was calculated very similarly. The bleaching process was done open to the atmosphere and required heating to 70 °C. The solution was assumed to have the specific heat of water. The calculations assumed only the solution was heated, ignoring the fibre and surroundings. The following equation was used to calculate the energy to heat the water to 70 °C from room temperature,

$$E = mC_p\Delta T$$

Where E is energy, m is the mass of water being heated, C_p is the specific heat of water at constant pressure (4.186 kJ/kg*K), (assuming drying would take place at atmospheric pressure), ΔT is the change in temperature (assuming heated from room temperature, 25 °C, to 70 °C, therefore ΔT = 45 K). It was also assumed that 11-21% of the energy could be recovered. Hence, 85% of the calculated energy was used (15% recovery) [103].

The energy used for the ultrasonic treatment was based on the measurements in the laboratory. However, due to the temperature increase of the solution, the energy consumption was modified to assume that 11-21% of the thermal energy induced into the system could be recovered [103]. The solution was assumed to reach an average temperature of 60 °C during the treatment. The thermal energy induced into the system was calculated as,

$$E = mC_p\Delta T$$

Where E is energy, m is the mass of water being heated, C_p is the specific heat of water at constant pressure (4.186 kJ/kg*K), (assuming drying would take place at atmospheric pressure), and ΔT is the change in temperature (assuming heated from room temperature, 25 °C, to 60 °C, therefore ΔT = 35 K). Assuming 11 – 21% of the thermal energy could be recovered, 15% of the thermal energy calculated was subtracted from the measured energy for the ultrasonic treatment [103].

Chemical recovery was assumed possible for the digestion and ultrasonic treatment of the fibres. A recovery of 97 % of the NaOH was assumed based on literature for chemical recovery in the pulp and paper industry (using a kraft process) [104]. However, this assumption did not include any extra processing required, which would likely require further energy and possible chemical input to recover the chemicals. Furthermore, this assumption relies on the heavy metals in the solution not affecting the recovery process. This assumption is potentially possible as the sodium hydroxide solution (used for the digestion and ultrasonic treatments) could be used to precipitate the heavy metals after the treatment (through hydroxide precipitation). However, further assessment would be required to understand this potential process [17]. The recovery of the bleaching chemicals was not considered as hydrogen peroxide is expected to decompose into oxygen and water.

The literature suggests that roughly only 5-8 % of water is consumed during the processing of pulp, and approximately 95 % of water is returned to streams and water networks after-treatment of the water [105]. Freshwater consumption is expected in

European mills to span from 9 to 90 m^3 per tonne of pulp, with the most water-intensive scenarios being for bleached kraft pulp [105]. However, typical bleaching processes use a number of steps involving different chemicals, whereas our process only uses one step for hydrogen peroxide bleaching, and therefore a lower water consumption could be expected [56]. The measured water consumption for the digestion process in the lab was found to be 203 m^3. Therefore, it was assumed that the freshwater consumption in an ideal scenario could be reduced to 10% of the measured water consumption (20.3 m^3) with the rest of the water being reused within the processing, thus fitting the typical water consumption of a European mill. This assumption was continued throughout the study for the bleaching and ultrasonic treatments. All freshwater consumed was assumed to be treated through the wastewater treatment plant and returned to the environment, and the 5-8% of water consumption was considered negligible. Therefore, the water consumption evaluated in the environmental study can all be expected to be returned to natural water networks after processing.

Environmental Impacts Measured

The primary environmental impact categories investigated were GWP (kg CO_2 eq) and energy consumption (kWh), as the literature on LCA and circular economy in the construction sector suggested these were the two primary indicators focused on [3]. Other indicators studied included resource depletion (kg), solid waste emissions (kg), and water consumption (L), as they were considered important indicators for the circular economy.

Energy consumption was categorised into fossil fuel consumption and electrical energy consumption. Using the LCI energy consumption, resource depletion, solid waste, and water consumption were measured. Global warming potential (GWP) was calculated through the use of characterisation factors for the emissions to air from the data in the LCI. Emissions considered included CO, CO_2, CH_4, N_2O, NMVC, H_2, SO_x, NO_x. Global warming potential was calculated in kg CO_2 eq. using classifications and characterisation factors attained from IPCC (Intergovernmental Panel for Climate Change) where possible (for CO, CO_2, CH_4, N_2O, NMVC, and H_2), and life cycle initiative for the characterisation factors of all other contributors to global warming potential [106, 107]. GWP characterisation factors used for the LCA are shown in Table 5-1.

Table 5-1: Global warming potential (GWP) carbon dioxide equivalent characterisation factors used in LCA study.

Emissions	Characterisation Factor	Emissions	Characterisation Factor
CO	1.9	**NMVC**	3.4
CO_2	1	**H_2**	5.8
CH_4	25	**SO_x**	-38
N_2O	298	**NO_x**	-28

5.3 Environmental Impact Assessment and Interpretation

Laboratory Scale Analysis

The data collected in the lab was used to produce an LCI for the system and study the environmental impacts based on one tonne of waste CCA treated timber used for each reinforcement type. Table 5-2 shows the environmental impact and yield for each reinforcement type. The contributions to resource depletion, solid waste, energy consumption, and water consumption for the DBU fibre can be seen in the LCI (Table 8-2, Section 8.2). Figure 5-2 further shows the contributions of each processing step to the electrical energy consumption for the DBU fibres.

Table 5-2: Environmental impacts calculated based on laboratory data for one tonne of waste CCA treated timber consumed. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

	F	D	DU	DB	DBU
Reinforcement material obtained (kg)	888.3	309.9	278.9	292.5	263.3
Global warming potential, GWP (kg co2 eq)	18.8	2196.9	2884.6	3397.0	4046.2
Resource depletion (kg)	0	94.0	128.9	822.0	854.9
Solid waste (kg)	0	2.4	3.2	118.5	119.3
Electrical energy consumption (kWh)	152.9	12937.0	16148.0	19967.1	22999.0
Fossil fuel energy consumption (kWh)	0	715	972	2440	2680
Water consumption (L)	0	203,689	339,785	493,477	621,951

The global warming potential and energy consumption were further broken down to understand the individual contributors throughout the process. The results are shown in Figure 5-3 and Figure 5-4.

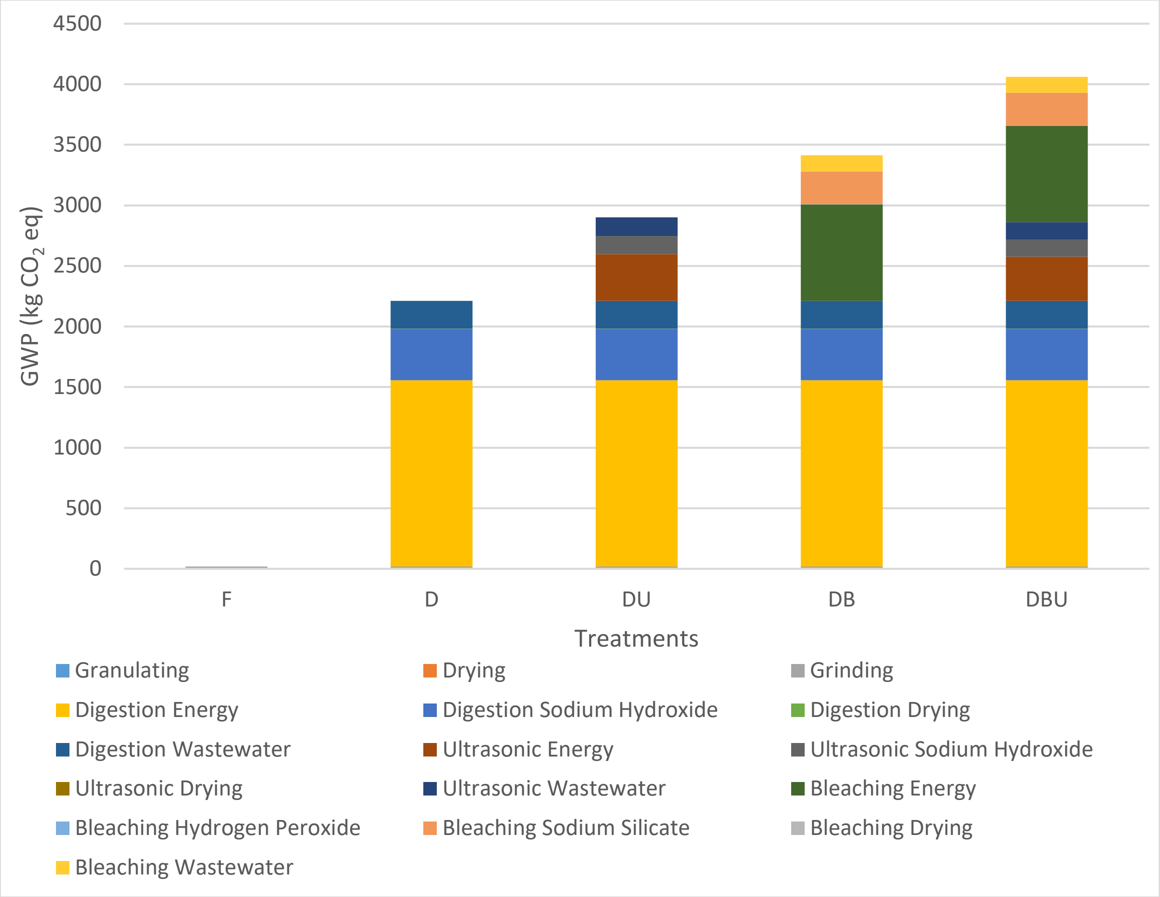


Figure 5-3: Global warming potential (GWP) for the consumption of one tonne of waste CCA treated timber on a laboratory scale. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

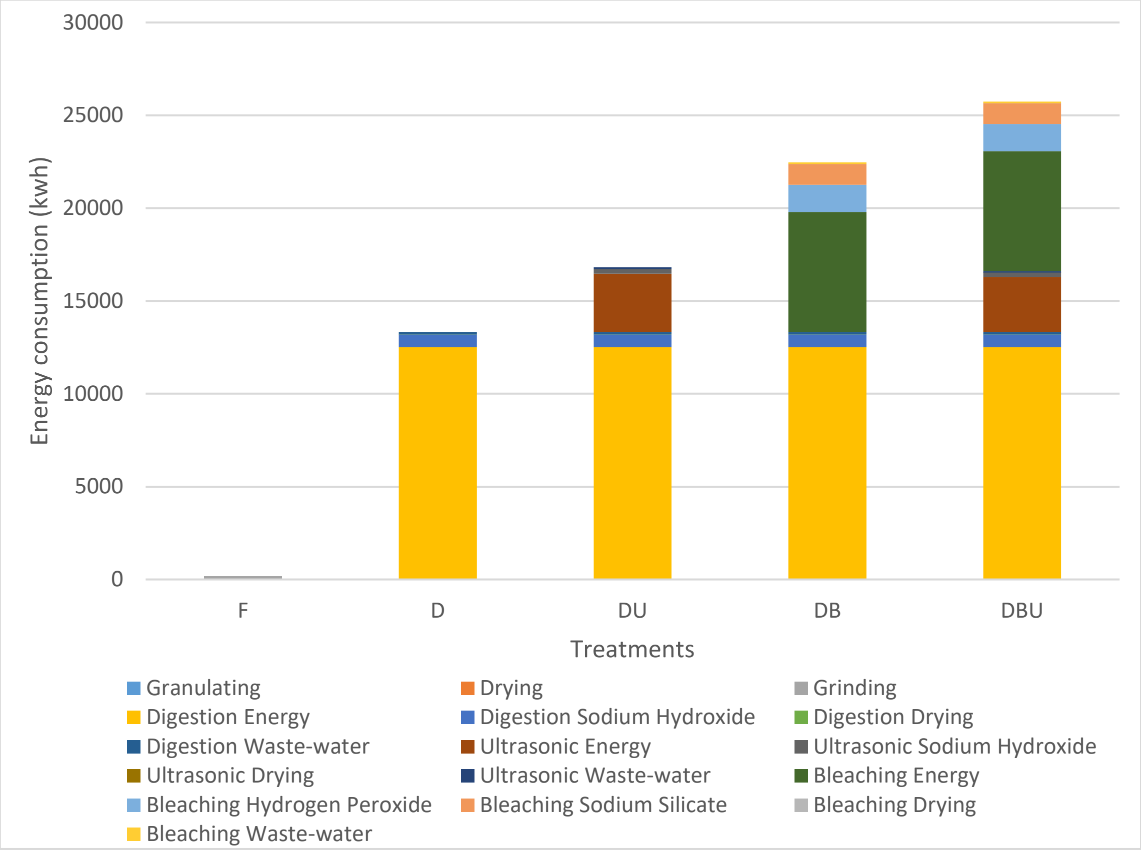


Figure 5-4: Energy consumption (electrical and fossil fuel) for the consumption of one tonne of waste CCA treated timber on a laboratory scale. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

The figures indicate that the largest contributor to global warming potential was a result of the energy consumption during processing for all of the chemical processes. Both figures appear closely related, as the digestion process consumed the most energy and produced the most carbon dioxide equivalent emissions. The bleaching and ultrasonic processes are the next largest consumers of energy, and the bleaching and ultrasonic treatment energy and chemical production are the next largest contributors to GWP (Following the digestion energy). The drying energy appears negligible from the graphs. However, due to the assumptions made about the drying, the actual energy required for drying the fibre was likely to be significantly higher and produce more CO_2 eq. emissions. Overall, wood flour processing has a lower environmental impact than all of the chemical processes. The digested fibres have the second-lowest impact as all other reinforcement types have other treatments used as well. Comparing the DU and DB fibres in Table 5-2, the DB fibres appear to have a greater environmental impact in all categories. DBU fibres have the largest environmental impact due to the most processing required.

Ideal (Commercial Scale) Analysis

Due to the limitations of the reinforcement processing in the laboratory, the environmental impact is expected to be much larger than if the process was performed on a commercial scale. Therefore, the environmental impact was recalculated as if the processing was completed in an ideal scenario. The environmental impact results are shown in Table 5-3. The equivalent environmental impacts for the disposal of waste CCA treated timber are included in the table (data sourced from [101]). However, the CCA treated timber data was based on annual impact and not the total, and therefore, it is difficult to draw direct comparisons. The updated yield of reinforcement material is also included.

Table 5-3: Impacts calculated based on an ideal scenario for one tonne of waste CCA treated timber consumed. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

	F	D	DU	DB	DBU	LANDFILL OF CCA TREATED TIMBER
Reinforcement material obtained (kg)	888.3	444.2	399.7	419.3	377.3	0
Global warming potential, GWP (kg co2 eq)	27.0	192.1	756.5	807.7	1,352.9	16.6
Resource depletion (kg)	0	88.3	90.2	1,119.5	1,121.3	-
Solid waste (kg)	0	0.1	0.1	166.5	166.5	1000
Electrical energy consumption (kWh)	218.7	1,108.6	5,469.6	3,418.5	7,534.8	-
Fossil fuel energy consumption (kWh)	0	23.2	35.8	2,480	2,490	1.67E-04
Water consumption (L)	0	20,369	39,876	319,808	338,223	78.7

The data was also used to break down the global warming potential and energy consumption based on each process and displayed in Figure 5-5 and Figure 5-6 below. Commercial data for pulping was attained from Oji Fibre and used as a reference [100]. The commercial pulping data used in the figures was based on the Tasman mill only, because it only uses virgin wood as an input (no recycled pulp). However, the exact details of the pulping process and possible bleaching processes are unknown [100]. The GWP graph also contains the production and landfill of CCA treated timber. The data used for waste CCA treated timber was based on the annual environmental impact from the production and disposal of a CCA guard rail post in the USA and was extrapolated to give insight on the environmental impact for one tonne of timber [101]. The data was also based on the annual impact of the timber and not the impact over the lifetime of the timber, therefore, making direct comparisons difficult.

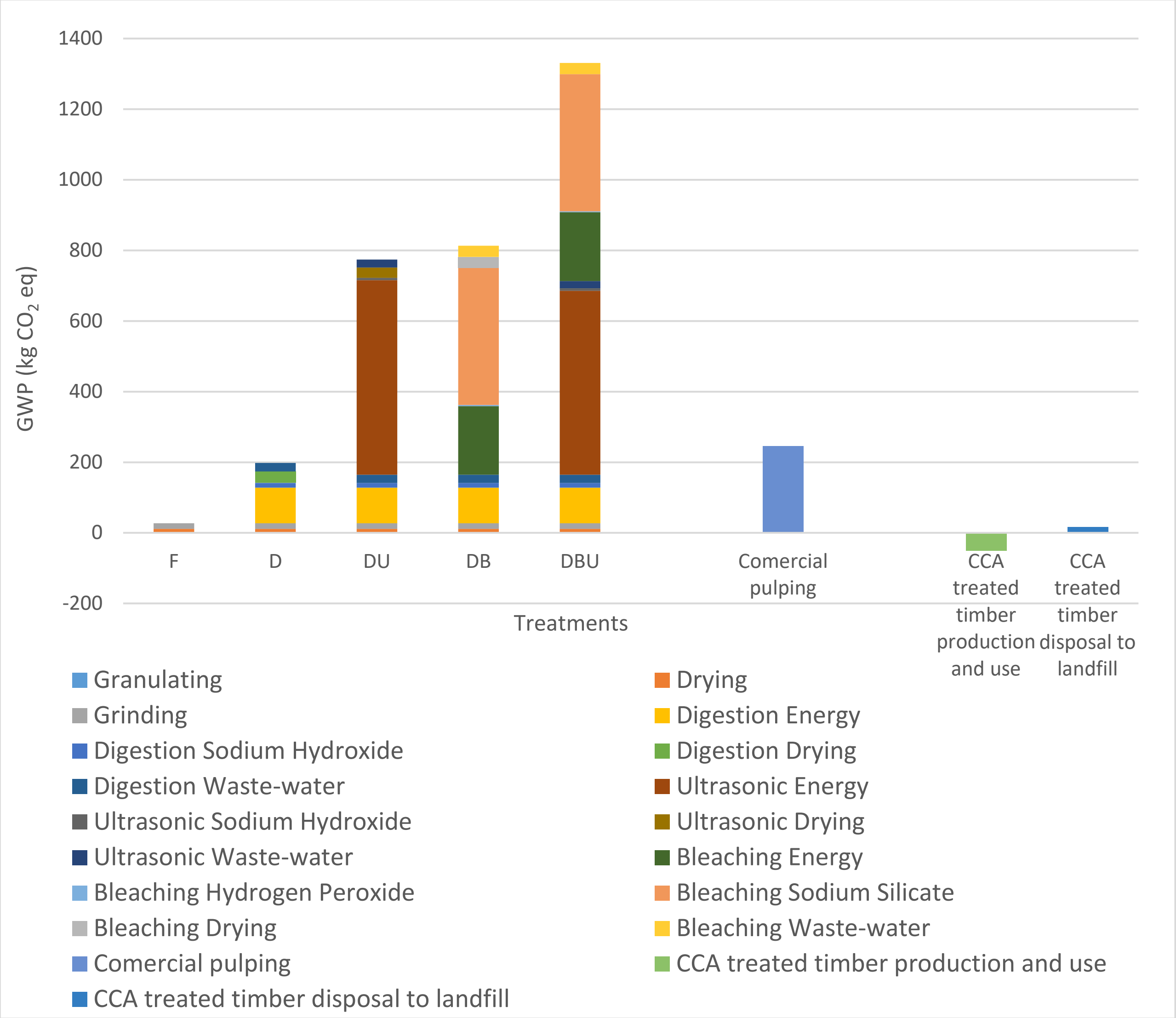


Figure 5-5: Global warming potential, GWP (kg CO2 eq.) for one tonne of timber input into the system in an ideal scenario. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

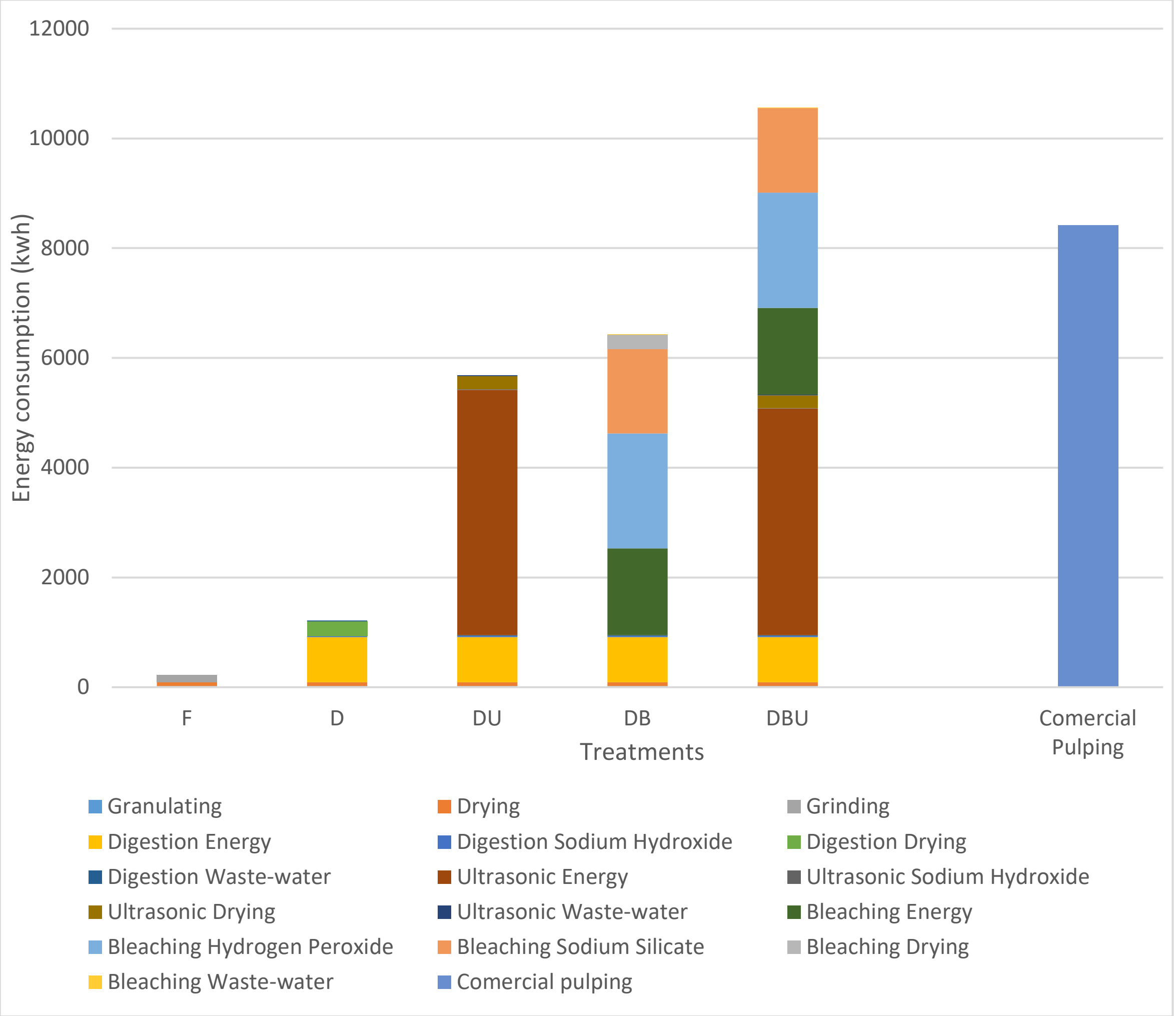


Figure 5-6: Energy consumption (electrical and fossil fuel) for one tonne of timber input into the system in an ideal scenario. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

Figure 5-5, Figure 5-6, and Table 5-3 show that the calculated environmental impact of wood flour is significantly lower than any of the chemical treatments. The GWP is a mere 14% of the digested fibre processing, and the electrical energy consumption is roughly 20% of the digested fibres (both in an ideal scenario, based on data in Table 5-3).

The results of the laboratory-scale process study suggested that the digestion process was one of the largest contributors to the environmental impact in all chemical processes. However, this was primarily due to the electrical energy consumption, which was significantly reduced when investigating an ideal scenario. Figure 5-5 suggests that the digestion process now contributes less than 1/3rd of the carbon equivalent emissions in the DU and DB fibre processes in an ideal scenario.

The energy consumption and GWP of DU and DB fibres are very similar, with the DB fibres having a slightly higher GWP and energy consumption. However, the results in Table 5-3 indicate that the resource depletion, solid waste produced, fossil fuel consumption, and water use are significantly higher for the DB fibres, suggesting that the DU fibres could be substantially better for a circular economy.

In the laboratory-scale testing, the DU fibre impacts were largely influenced by the digestion energy. However, in the ideal scenario, the results indicate that ultrasonic treatment energy would be the largest contributor to GWP and the largest consumer of energy in the process. This difference in the energy contribution is primarily due to the large amount of energy required for ultrasonic treatment, without any indication of significant reductions when processing is completed at a commercial scale.

The digestion energy was also the largest contributor to environmental impact for the DB fibres when based on a laboratory scale. However, the results of the ideal scenario shown in Figure 5-5 suggest that the production of chemicals required for the bleaching of fibres would be the largest contributor to GWP at a commercial scale. This difference in GWP contribution is largely due to the large amount of sodium silicate required and the assumption that it cannot be recovered after the treatment. Interestingly, sodium silicate contributes to the GWP more than hydrogen peroxide, even though twice as much hydrogen peroxide is consumed than sodium silicate.

The digested, bleached, and ultrasonic treated fibres have the largest environmental impact across all categories due to requiring all three chemical processing methods.

Ideal Scenario Producing One Tonne of Reinforcement Material

The environmental impact assessment was reproduced for the production of one tonne of reinforcement material to understand the differences when a set amount of reinforcement material is required for producing WPC. Table 5-4 summarises the data and includes the amount of CCA treated timber diverted from landfills to produce one tonne of reinforcement material.

Table 5-4: Impacts calculated based on ideal scenario using assumptions, for one tonne of reinforcement produced . F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

	F	**D**	**DU**	**DB**	**DBU**
CCA treated timber diverted from landfill (kg)	1125.7	2251.5	2501.7	2385.1	2650.1
Global warming potential, GWP (kg CO_2 eq.)	30.3	393.5	1953.7	1479.1	2873.6
Resource depletion (kg)	0	190.6	215.8	1915.3	2071.8
Solid waste (kg)	0	0.153	0.258	276.8	297.9
Electrical energy consumption (kWh)	246.2	2424.5	13809.9	6235.1	16418.5
Fossil fuel energy consumption (kWh)	0	50.0	86.9	4135.6	4480.1
Water consumption (l)	0	43958.8	97256.2	544133.3	629615.9

Figure 5-7 and Figure 5-8 show the contribution of each processing step to the GWP and energy consumption. The results differ from that of the previous studies due to the yield of each process affecting how much energy and material consumption is required to produce a set amount of material.

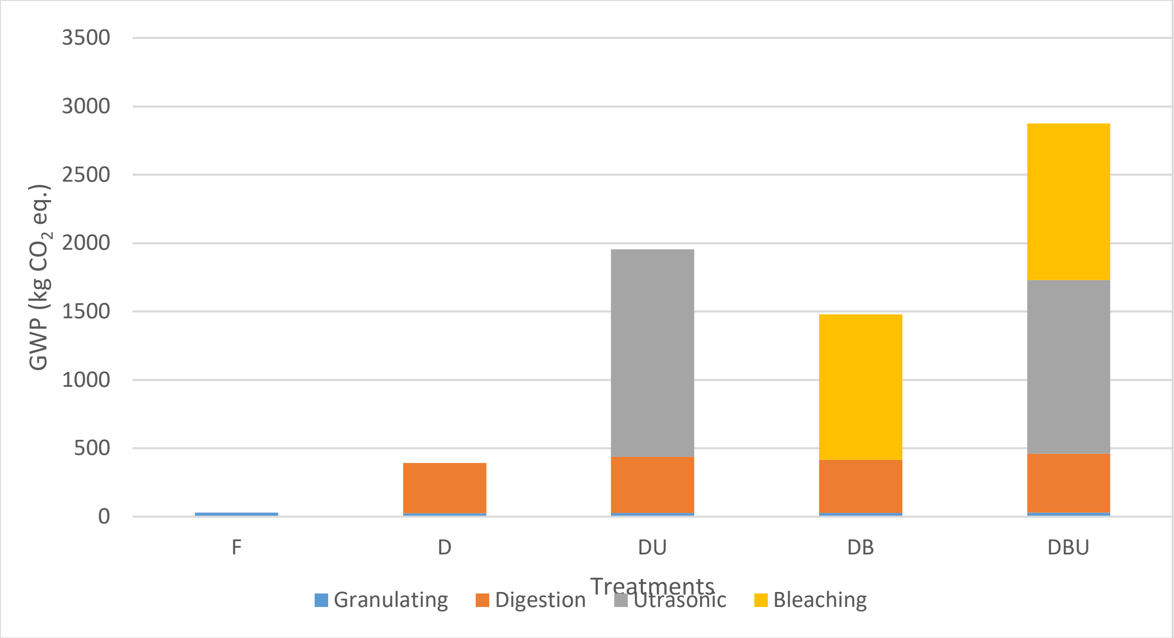


Figure 5-7: Global warming potential (GWP) for one tonne of reinforcement material produced in an ideal scenario. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

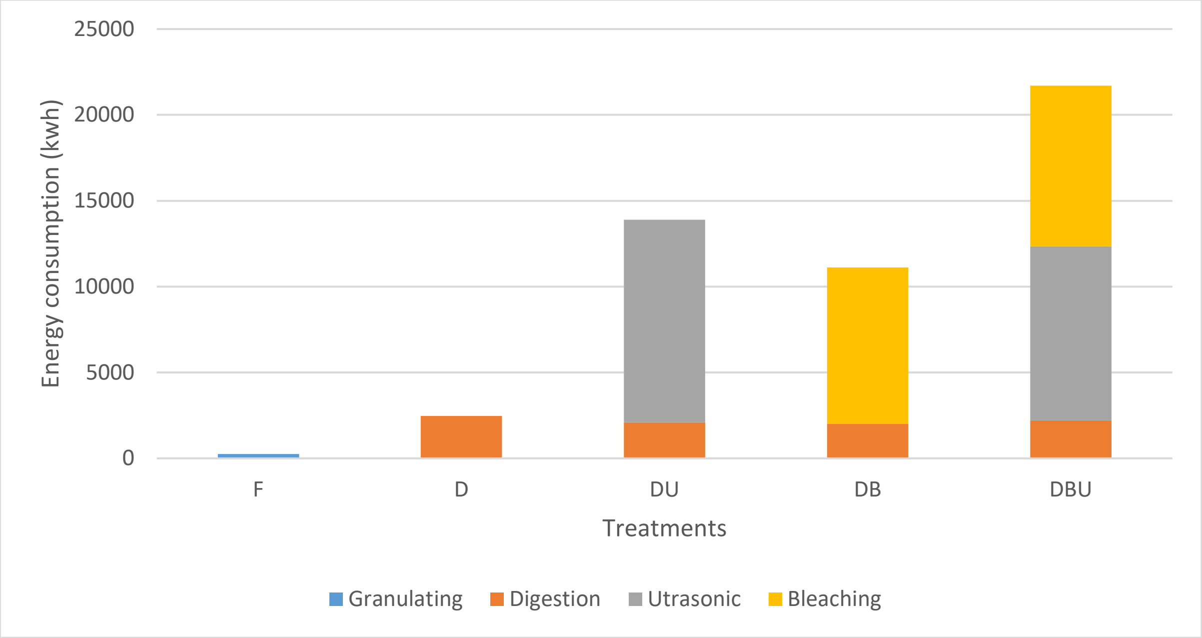


Figure 5-8: Energy consumption (electrical and fossil fuel) for the production of one tonne of reinforcement material in an ideal scenario. F, (wood flour), D (digested fibre), DU (digested and ultrasonic treated fibre), DB (digested and bleached fibre), and DBU (digested, bleached and ultrasonic treated fibre).

Table 5-4, Figure 5-7, and Figure 5-8 show that the environmental impact results primarily reflect the previous studies using the other functional unit. However, differing from the earlier studies, the GWP and the energy consumption of the DB fibres is lower than the DU fibres. This change in results is likely due to the yield of the ultrasonic process being lower than that of the bleaching process, therefore requiring more material and energy input into the system to produce the same amount of fibre.

Comparison of Results (Laboratory-Scale, Commercial, and Functional Unit)

The environmental impact of producing wood flour and fibre was evaluated to improve decision making for the viability of waste CCA treated timber as a reinforcement material for WPC to be used in the construction sector. The results were split into categories, including the consumption of one tonne of waste CCA treated timer based on laboratory processes, the consumption of one tonne based on a commercial process, and the production of one tonne of reinforcement material based on a commercial operation. Overall, all three analyses show that chemical treatments had a much larger environmental impact than the production of wood flour, which used mechanical methods.

The results suggest that the proposed commercial-scale process has a much lower environmental impact than the laboratory-scale process. Furthermore, the largest contributors to environmental impact appear to change from the laboratory-scale process to the commercial-scale process. In the laboratory-scale process, the largest contributor to GWP and energy consumption for all chemical processes was the digestion energy, followed by the bleaching energy and ultrasonic energy. In the proposed commercial-scale processes, shown in Figure 5-4, the largest contributors to GWP appear to be the energy consumption for ultrasonic energy followed by the production chemicals for bleaching.

The results for consuming one tonne of waste CCA treated timber were compared to producing one tonne of reinforcement material, both using the proposed commercial process. The most significant difference in the study is that the yield of every process is very different, which affects the amount of material and energy input into a system to produce the required mass of reinforcement material. The significance of the yield is shown by the differences in GWP of the DU and DB fibres. The DU fibres had a lower GWP than the DB fibre for the consumption of one tonne of waste timber, whereas the DB fibres have a lower GWP for producing one tonne of reinforcement material. However, the yields for both bleaching and ultrasonic treatments were based on the laboratory scale process and could change in a commercial process, possibly affecting the results.

The results of the ideal scenarios suggest that the use of bleaching and ultrasonic treatments have a larger environmental impact than the primary fibre treatment of digestion. However, the study shows that the primary contributor to the impact in the ultrasonic treatment is the high energy input for the treatment, and the primary contributor in the bleaching process is the consumption of sodium silicate. These categories were changed minimally from the laboratory process to the ideal process, and further research could help reduce the environmental impact. For example, sodium silicate could potentially be removed or reduced in processing, and the use of more hydrogen peroxide or different processing conditions could possibly provide similar fibre properties and reduce the environmental impact.

The goal of this study was to incorporate the idea from the circular economy to reuse waste material for the production of new materials in the construction sector, thus, minimising waste streams and reliance on virgin material. The study of preparing one tonne of reinforcement material for WPC shows the solid waste produced is greatest for treatments that include a bleaching step. However, when comparing the solid waste produced from the wood flour and fibre processing methods and the CCA treated timber diverted from landfill, all of the processing methods can be considered to reduce waste to landfill. The reduction in landfill waste is shown best by the DBU fibres, which produced the most solid waste destined for landfill in the ideal scenario for producing one tonne of fibre (297.9 kg of solid waste, Table 5-4). However, the process diverted 2650.1 kg of waste CCA treated timber from landfill as reinforcement material (Table 5-4). Therefore, the study indicates that WPC production from waste CCA treated timer reduces landfill waste in all cases considered. Furthermore, the production of WPC has the potential to use waste plastic as a matrix material, which could divert more material from landfills.

Table 5-4 shows that the preparation of one tonne of F, D, and DU reinforcement materials consumed roughly 0, 190, and 215 kg of the earth's resources, respectively. Assuming a scenario where 30 wt.% reinforcement composites are produced from the reinforcement material, this would be the resource depletion from the reinforcement material of approximately 3.3 tonnes of WPC. A maximum of 215 kg of resources consumed is much lower than the equivalent mass of treated timber if used in the same application (roughly 3.3 tonnes of timber). However, the results focus on non-renewable resources such as minerals and fossil fuels, whereas wood can be considered a renewable material. Further investigation would be required to understand the difference between the non-renewables used to produce treated timber and the non-renewables consumed for the processing of waste treated timber for producing WPC.

Resource depletion of DB and DBU fibres, in Table 5-4, is approximately 2000 kg for both, which is significantly higher than the other reinforcement types. The resource consumption is likely due to the consumption of hydrogen peroxide and sodium silicate in the bleaching process and the inability to recover the chemicals to reduce the environmental impact of chemical production.

Overall the results suggest that mechanical processing is better for the environmental impact than chemical processing for producing WPC reinforcement from waste treated timber. However, for some applications, the use of chemical treatments could be required to alter the properties of the composites (e.g. reducing leaching of heavy metals or improving mechanical performance). The results of the chemical treatments show that using a single digestion process is significantly better for the environmental impact than using secondary treatments. If secondary treatments are required, ultrasonic treatment and bleaching result in similar GWP and energy consumption (both impact categories depend on the functional unit of the study). However, resource depletion, waste production, fossil fuel use, and water consumption are much larger for bleached fibres than ultrasonic treated fibres. Thus, indicating that for the circular economy, ultrasonic treatment is better than bleaching as a secondary fibre treatment. Although, when comparing the fibre and composite properties, the use of ultrasonic treatment had minimal effect on the heavy metals and constituents of the fibres and mechanical properties of the corresponding composites. Therefore, due to the large environmental impact induced, the ultrasonic treatment should not be considered unless further composite performance can be attained with further research. In comparison, the bleaching of fibres had a large influence on fibre and composite properties. Hence, even with the greater environmental impact, the fibres should potentially still be considered for some applications.

Comparison of Results with Literature

The data attained from the study is complicated to compare to other LCA studies due to the assumptions made for the study and the lack of literature on using LCA to investigate the use of waste CCA treated timber as a reinforcement material in wood-plastic composites.

The results of the LCA study for an ideal scenario (Figure 5-5) indicate that the GWP of the digested fibres is comparable to Oji Fibre's commercial pulping process (192.1 kg CO2 eq. and 245 kg CO_2 eq. respectively for one tonne of timber consumed). However, the energy consumption in the commercial pulping process was substantially higher than that of the digested fibres (8422 kWh and 192.1 kWh respectively for one tonne of timber consumed) [100]. Comparing the results indicates that the assumptions made to produce the ideal scenario give indicative results of the same magnitude of an actual commercial scale pulping process (especially for the GWP). However, an actual commercial process is much more complex than the laboratory process that the ideal commercial process was based on, which is likely the reason for the variance in results. First of all, the commercial pulping used by Oji fibre used a kraft pulping process and not a soda process. This processing will require different chemicals and varying energy and water consumption to produce the pulp. Processes such as recycling and reusing chemicals and water for the pulping process are also likely to require more energy input into the system. This extra input was not accounted for in the assumptions made for the ideal scenario. Furthermore, commercial pulping often relies on further processes such as the incineration of 'black liquor' to produce more energy for processing, which would also affect environmental impacts such as the carbon emissions of energy consumption.

The LCA study focused on the production of reinforcement material for producing WPC rather than the whole WPC production process, making the results difficult to compare with literature on the production of WPC. However, assuming WPC can be produced with 50 wt.% reinforcement material (In the typical range of flour/fibre to matrix ratios used for commercial WPC), the production of one tonne of WPC would require 500 kg of reinforcement material. Therefore, using this assumption, the carbon emissions contributed by wood flour and fibre processing for WPC production could be considered and compared to the production of WPC in literature. The kg CO_2 eq. emissions per kg of WPC produced (kg CO_2 eq./ kg_{wpc}) were calculated using the emissions of 500 grams of reinforcement based on the results in Table 5-4. The results are as follows,

- F = 0.015 kg CO_2 eq./ kg_{wpc}
- D = 0.197 kg CO_2 eq./ kg_{wpc}
- DU = 0.977 kg CO_2 eq./ kg_{wpc}
- DB = 0.739 kg CO_2 eq./ kg_{wpc}
- DBU = 1.44 kg CO_2 eq./ kg_{wpc}

Literature on producing WPC from polypropylene and wood fibres (through thermo-mechanical pulping) suggests that polypropylene is the primary contributor to the environmental impact and the wood fibres have a minimal effect. However, this study used virgin PP and timber, whereas recycled materials could alter the results [82]. Another report focusing on producing WPC with construction and demolition waste (using mechanical preparation of reinforcement) found that the GWP of the production of WPC was 0.4-0.5 kg CO_2 eq./ kg_{wpc}, which is lower than the ideal scenario for the emissions from DU, DB, and DBU fibres alone [14]. Furthermore, the processing of the D fibre emits almost half of these emissions and could be regarded as a primary source of the emissions, unlike the study using thermomechanical pulped timber [82]. Comparing the results of the LCA study with these two reports suggests that the chemical processing to attain fibres, even in an ideal scenario, has a significant impact on the GWP of corresponding composites. Thus, the literature on the environmental benefits of using construction and demolition waste to produce WPC does not necessarily relate to the use of CCA treated timber after chemical processing.

The study on producing WPC from construction and demolition waste also investigated substituting plastics, timber and aluminium with the WPC produced. The study found that the substitution of plastic and aluminium (based on weight) in the construction industry could reduce carbon equivalent emissions by approximately 1.8 kg CO_2 eq./ kg_{wpc} and 2.1 kg CO_2 eq./ kg_{wpc}, respectively [14]. These values suggest that the application of WPC produced using chemically prepared fibres could still be beneficial for the environment when replacing plastic or aluminium materials. However, this report is based on the construction sector in Finland, and to completely understand the environmental impacts of the application and substitution of materials in New Zealand, further research would be required.

The idea for this research was based on the diversion of waste CCA treated timber from landfills to produce more materials to be used in the construction sector, thus also reducing reliance on virgin materials. Therefore, the best comparison could be considered to be the life cycle of CCA treated timber with the use WPC produced from waste CCA treated timber to be used in the construction sector. When comparing the impacts of these scenarios in Table 5-3 and Figure 5-5, the only reinforcement material with comparable GWP is the use of wood flour. In every category except solid waste produced, the disposal of waste CCA treated timber appears to be more environmentally friendly than the chemical processing of fibres for WPC. However, the data used for the impacts of CCA treated timber were based on annual impact, and the impact for the life cycle is likely to be significantly higher. Furthermore, the LCA study produced only investigated the processing of the timber to create reinforcement material and not the full life cycle of WPC produced from waste CCA treated timber. The WPC produced from the treated timber is expected to be recyclable up to 8 times, which has the potential to improve the sustainability of the WPC significantly. Recycling could likely be done through a simple process of granulating the WPC and the reproducing parts for the construction sector (through processes such as extrusion). Assuming recycling of the WPC could be performed eight times, the environmental impact of producing and recycling the WPC should be compared to the production, application, and disposal of 8 times the mass of WPC worth of CCA treated timber [15].

Data Quality Assessment

The following section assesses the quality of the data and assumptions used for the environmental study.

The system boundaries for the study did not include the transportation of timber or chemicals. The transportation of timber was ignored due to the disposal of timber to landfills would also require transportation, with the only differences being based on the location of disposal or processing. The literature on producing WPC from polypropylene and timber fibres in New Zealand also found that the transportation of fibres and PP did not have a significant effect on the environmental impact of the WPC production (transporting PP from Australia and fibres from Rotorua to Auckland) [82]. Therefore, the actual contributions of carbon emissions from transportation are expected to be minimal, and the assumption to ignore transportation of the chemicals and timber will likely not have majorly affected the LCA results.

The data for the life cycle of CCA treated timber used as a comparison did consider emissions for transportation to construction sites and disposal at the end of life. The emissions made up 14% of the carbon emissions for the total life cycle of CCA treated timber. However, the study was based in the USA, where travelling distances could be assumed to be larger than in New Zealand [101]. Therefore the assumptions used for each LCA study are not directly comparable. However, the transportation used in the system boundaries is not the largest difference in the environmental studies (annual impacts vs total impact is likely to make a much larger difference). To attain a direct comparison, research specific to New Zealand on the environmental impact of the whole life cycle of CCA treated timbers would be required. Therefore, the literature used for comparing the results to the life cycle of waste CCA treated timber could be regarded as dissatisfactory.

The LCI data for the chemicals used were based on literature from around the world. The sodium hydroxide data was obtained from literature based in Malaysia published in 2013 [96]. It is unlikely that the time frame has a large effect on the process as it was produced in the last decade. However, the location of the chemical production is likely to have a large effect on the resources consumed and emissions produced. Thus, depending on where the sodium hydroxide used in processing is produced relative to Malaysia, the LCI could be significantly different. The LCI obtained from the literature for hydrogen peroxide production was reported in 2007, based on data from eight different producers. Due to the data being collected from several sources, the data can be regarded as very accurate. However, if the hydrogen peroxide used was produced outside of Europe, the LCI for the hydrogen peroxide production could be affected. The data is unlikely to be significantly affected by the date of the report. A report produced in 1997 in Europe was used for the sodium silicate LCI. The sodium silicate production is more likely to have changed since 1997 (e.g. the energy sources are likely to be more environmentally friendly). The material and energy inputs and emissions are also expected to be affected by production location. Overall, the sodium hydroxide and hydrogen peroxide data are likely relevant to today's productions. In contrast, more recent data for sodium silicate production could improve the study. Location based variables such as the energy grid emissions, transportation and infrastructure required could have an effect on the LCI of the chemicals. The data is likely representative of the actual chemical productions. However, the accuracy of the study could be improved by using details for the actual production of the chemicals used in processing.

The emissions from electrical energy consumption in New Zealand only included the carbon equivalent emissions used to calculate GWP, as energy consumption and GWP were considered a priority for the study. The production of electrical energy is likely to produce other emissions and cause other environmental impacts, which could affect the results. The CO_2 equivalent emissions were on average energy consumption and emissions for the entire power grid in New Zealand. However, the emissions would likely change depending on locations in New Zealand depending on the primary source of electrical energy production (e.g. hydro vs wind vs geothermal). Furthermore, incineration of biomass is potentially an option during processing to produce more energy which would further change the energy emissions. The data used can be regarded as very relevant for the study due to being a concept for WPC production without a set location. If a commercial process was performed, energy consumption should be assessed using specific site data to evaluate the environmental impact.

The laboratory-based study investigated the treatment of one tonne of waste CCA treated for use as reinforcement material in WPC. However, the data obtained from the study is not indicative of the processing on a commercial scale. The digestion yield was very low, the energy consumption was extremely inefficient, chemicals were not recovered, and water was not reused. These issues in the laboratory scale process were accounted for with several assumptions to produce data based on calculations instead of using the data measured from the laboratory. The results of this study are expected to be more representative of an actual commercial process. There are still several variances compared to an expected commercial process. Firstly, the recovery of sodium hydroxide was based on the recovery of chemicals in a kraft process, and the chemical recovery of sodium hydroxide is likely to be different. Commercial processing of waste CCA treated timber would likely use a kraft process, however, the study does not accurately represent a kraft process as the different operating conditions and chemical consumptions required would result in different environmental impacts. Judging by the differences between the ideal scenario studied and the data from Oji fibre, the results are likely indicative of the environmental impact and are relevant for the comparison study of processing methods used. Therefore, the accuracy of the study could be improved for an actual commercial-scale process.

The energy calculations used for the ideal commercial process were based on extremely basic assumptions to make an ideal scenario. In retrospect, the actual energy consumption for fibre processing could be considerably different. The energy calculations were all based on an ideal scenario for heating the solution, assuming the solution had the thermal properties of water. Although the thermal properties are unlikely to be substantially different from water, heating the solution in all systems (digestion, bleaching, ultrasonic, drying) would require heating the timber or fibre and the solution surroundings. Furthermore, some thermal loss would be expected, and more energy would be needed to maintain temperatures over time. In a commercial scale process, agitation of timber/fibre solutions and fibres while drying would be expected, requiring more energy input.

The processing of waste CCA treated timber for reinforcement material for WPC would require consumables for processing, and energy and material input to produce and run the processing infrastructure, both of which were not accounted for in this study.

Overall, the environmental study can be considered representative of the environmental impacts of producing reinforcement material and can be used to give insight into the differences between processing procedures, the hotspots of the system, and the potential environmental 'cost' of producing WPC from waste CCA treated timber. However, the study results should not be considered as the actual environmental impacts of the processes or be used for direct comparison with literature due to the many assumptions made and the limitations of the data used. Further research should be conducted to understand better the true environmental impact of producing WPC from waste CCA treated timber and using the WPC to substitute other materials in the construction sector. Studies should also include data from New Zealand's construction sector to analyse the potential as a construction material. Furthermore, environmental indicators such as acidification potential, eutrophication potential, ecotoxicity, and human toxicity should be considered. These indicators are likely to be very important for WPC produced with waste CCA treated timber due to heavy metals in the timber, fibre, waste, and emissions.

Chapter 6

Conclusions

6.1 Reinforcement and Composite Results

This dissertation completed a study of the viability of production and application of wood-plastic composites produced with waste CCA treated timber as an alternative sustainable building material. Mechanical and chemical methods were used to prepare wood flour and fibre samples from waste CCA treated timber for use in wood-plastic composites. Wood flour was primarily used as a low cost and low environmental impact reference sample for fibres obtained through more complex chemical methods to be compared. The wood flour and fibre were characterised, and the mechanical and physical properties of the composites were assessed and compared to the material properties required for application in the building sector.

An alkali digestion process (using 10 wt.% sodium hydroxide aqueous solution) was used to obtain digested (D) fibres from the timber. The fibre analysis indicated that the digestion process reduced the composition of non-cellulose constituents and obtained primarily individual fibres. However, residual lignin and several fibre bundles were present. The heavy metal analysis indicated that the digestion process reduced the content of arsenic by 99.8 %, slightly reduced the chromium concentration, and minimally affected the copper concentration in the fibre obtained from the digestion. The D fibres improved composite properties compared to the wood flour in the extruded composites. However, the sigma blade compounded composites indicated a reduction in tensile strength, likely due to poor compatibility between fibres and matrix, resulting in a poor interface.

Bleaching of the digested fibre (to obtain digested and bleached (DB) fibre) was completed with hydrogen peroxide to remove residual lignin from the fibres and potentially reduce the heavy metal content. The fibre analysis indicated that the bleaching reduced the residual lignin content and resulted in a rougher fibre surface than the digested fibres. The use of ICP-MS to analyse the heavy metal content indicated that bleaching further reduced the concentration of arsenic to 0.09 % of the concentration in the treated timber. Additionally, the bleaching reduced the concentration of copper and chromium in the fibre by 50.6 % and 79.5 %, respectively, compared to the initial concentration in the timber. The SEM and mechanical testing of the DB fibre composites indicated that the bleaching process improved compatibility between the fibre and matrix, allowing for an improved interface, and increased mechanical performance of composites. The reduction of lignin in the fibres and the increase in roughness of the fibre surface is likely the reason for improved compatibility and interfacial strength. However, the composite mechanical properties did indicate that the individual fibre strength may have been reduced.

Ultrasonic treatment was completed as a potentially environmentally friendly fibre treatment, with the potential to reduce lignin and hemicellulose content in the fibre and induce fibrillation to increase composite interfacial strength. The fibre analysis indicated that the treatment had the least effect on the constituents in the fibre. However, XRD and the ICP-MS analysis did indicate some change in the fibre composition. Fibrillation was induced into the fibre, indicating the potential for the increased interfacial strength in composites due to the increased surface area of the fibres. However, the fibre quality analysis showed that fibre length was reduced. The mechanical performance of composites produced with digested and ultrasonic treated fibres (DU) and the digested, bleached, and ultrasonic treated fibres (DBU) indicated that ultrasonic treatment as a secondary fibre treatment could improve composite mechanical performance. However, the mechanical properties of the sigma blade compounded composites suggested that bleaching as a secondary treatment had a greater effect on composite performance. Furthermore, the DBU fibre composites produced with the sigma blade compounder implied that the ultrasonic treatment could also decrease mechanical performance, likely due to the reduction in fibre length.

The mechanical properties of WPC produced using any of the fibre treatments completed in this study appears to be acceptable for semi-structural applications such as decking. The highest mechanical properties in the study were achieved by 40 wt.% DB fibre composites produced with the twin-screw extruder. The composites achieved a TS of 27.6 MPa, a YM of 2.33 GPa, a flexural strength of 45.2 MPa, and a flexural modulus of 2.10 GPa. However, the use of the composites as a structural material appears limited due to the low modulus of the composites compared to traditional building materials. The research conducted into creep performance only indicated that the creep properties were improved compared to virgin PP. The study did not investigate the effects of creep on the potential structural application of WPC components. Further research will be required to see if a structural application is viable and the low modulus and the creep behaviour of the composites can be accounted for through engineering design. The use of a higher-performing matrix material could help improve the composite properties and improve structural application potential.

The potential for leaching of heavy metals was expected to be one of the largest limitations of composites produced with waste CCA treated timber. However, the leaching test results indicated that the chemical treatments used to obtain fibre for composites also significantly reduced the leaching of copper, chromium, and arsenic from the corresponding composites. The results for all composites were significantly lower than previously reported results in the literature for WPC produced with wood flour. Furthermore, the concentration of copper, chromium, and arsenic in the leachate from the D and DB fibre composites was considerably lower than the maximum allowable values in New Zealand's drinking water. The results of the leachate study with D and DB fibres suggests that the leachate from the composites is potentially safe to drink, and the potential for societal or environmental harm due to the leaching of toxic heavy metals is minimal. Thus, the results indicate that the wood fibres produced in this study could safely be used as a reinforcement material in WPC applied within human contact in New Zealand's construction sector. The leaching of the WPC produced with wood flour is likely lower than the leachate of CCA treated timber itself due to the encapsulation of the wood flour in a PP matrix. Therefore, it is likely that the wood flour composites are also useable in applications that do not require contact with people. However, further research would be required to reinforce the application potential.

6.2 Life Cycle Analysis Results

The final step of this dissertation completed an attributional gate to gate life cycle analysis study to investigate and compare the environmental impact of the processing methods used to produce WPC from waste CCA treated timber. The study compared the mechanical and chemical methods used for wood flour and fibre processing. The results of the study indicated that for environmental sustainability, the use of wood flour is significantly better than wood fibre at both a laboratory scale and a commercial scale. The results from the study of a potential commercial-scale process found that the use of bleaching or ultrasonic treatment as a secondary fibre treatment significantly increased the carbon emissions and energy consumption required for processing the fibre. Furthermore, bleaching as a secondary treatment substantially increased the waste to landfill and the resource depletion of fibre processing. The results of the LCA also indicate that chemically processing waste CCA treated timber to produce WPC is likely to result in a higher environmental impact than WPC in other studies. Therefore, further research is required to understand whether alkali digestion, ultrasonic treatment, or hydrogen peroxide bleaching can be used in the production of WPC to improve the sustainability of the building sector.

From the results of the environmental study, different reinforcement types should be considered for different applications. The use of wood flour has by far the lowest environmental impact and is likely the cheapest and easiest to process. However, the mechanical performance and the potential for leaching is likely to limit its potential application. Therefore, the use of wood flour is recommended for applications such as fence posts, where high mechanical performance is not required, and leaching is likely not an issue as the material is not in direct human contact. Due to the significantly higher environmental impact, the use of wood fibres from CCA treated timber should only be considered when maximum mechanical performance or minimum leaching is required.

Chapter 7

Future Work Recommendations

The results of this thesis showed the potential for the use of wood flour and fibre derived from waste CCA treated timber to be used as a reinforcement material for New Zealand's building sector. The following section outlines recommendations for future work for improving the properties and application potential of WPC produced from waste CCA treated timber as a sustainable building material in New Zealand.

The study investigated a soda treatment (using an aqueous sodium hydroxide solution) to obtain fibres from the waste CCA treated timber. However, other processes are likely more applicable for a commercial process or to improve sustainability. A kraft process is likely to be more efficient and provide improved fibre strength. At the same time, an enzyme treatment or an organasolv process has the potential to be more environmentally friendly.

The digestion and bleaching processes used to obtain fibres from waste CCA treated timber should be optimised to maximise the fibre and composite properties. For example, the results of the study indicated that the fibres were prone to thermal degradation. Improved fibre processing has the potential to alter the fibre constituents and alter the thermal properties of the fibre.

The study focused on wood flour and fibre processing and the characterisation of the wood flour, fibre and corresponding composites. The chemical processing of waste CCA treated timber was found to reduce the heavy metal content in the corresponding fibre. However, the processing also resulted in the inclusion of copper, chromium, and arsenic in the solutions used for the digestion, bleaching, and ultrasonic treatment. Further research is recommended to understand whether the heavy metals in these solutions can be recovered and if commonly used commercial processes such as chemical recovery or incineration of the 'black liquor' can be completed. The outcomes of this study will likely have a large influence on the commercial viability and sustainability of processing waste CCA treated timber for use in WPC.

The idea to use waste CCA treated timber for wood-plastic composites is based on the circular economy concept. However, the research used virgin polypropylene as a matrix material for the composites. Virgin PP was used to focus on the wood flour and fibre obtained from the waste CCA treated timber. The use of recycled or bioderived polymers as a matrix material could significantly improve composite sustainability. Furthermore, the PP used in the study was found to have very low mechanical performance, and altering the source of the polymer for the matrix and using a polymer with improved mechanical performance also has the potential to increase the resultant composite performance.

The study investigated the material property requirements for the application of wood-plastic composites in the building sector. Reviewing building standards indicated that the only fixed requirement for a material to be used in a structural application was a durability of 50 years. Creep was outlined as one of the largest issues for WPC to meet the required durability of 50 years in structural applications. The creep testing investigated the advantages of using natural fibres as a reinforcement material in polymers. However, further research is recommended to understand the long term creep properties of wood-plastic composites. Additionally, the potential for using stresses low enough to avoid tertiary stress over a 50-year period should be investigated for potential application. Other durability properties should also be considered for application, however, these properties are likely to be affected by the conditions the materials are exposed to, which will be dependent on the specific application (e.g. outdoors or internal).

LCA was completed to give insight into the environmental impacts of producing WPC from waste CCA treated timber through mechanical and chemical processing of fibre. However, to completely understand the potential of improved sustainability in the building sector, a life cycle assessment should be completed for the entire cradle to grave life cycle of the composites. The results of the LCA should also be compared to current building materials in New Zealand using local data to understand the environmental impact completely.

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Chapter 8

Appendix

8.1 Fibre Quality Analysis

Table 8-1: Fibre quality analysis complete data set for all fibre samples.

Number of replicates	3	**Digested fibre (not 'separated')**		3	**Digested Fibre 'separated'**	
Number of fibres measured	35236			33188		
	Mean	Std. dev.	± 95%	Mean	Std. dev.	± 95%
Fines						
arithmetic, %	9.90	0.22	0.25	8.98	0.33	0.37
weighted, %	1.22	0.05	0.05	1.01	0.03	0.04
Fibre length						
mean, mm	1.15	0.01	0.01	1.20	0.01	0.01
Length weighted, mm	1.61	0.01	0.01	1.59	0.01	0.01
Weight weighted, mm	1.99	0.00	0.01	1.94	0.01	0.01
Fibre width, µm	32.88	0.09	0.10	32.39	0.07	0.08
Aspect ratio	35.09	0.32	0.36	36.95	0.25	0.29
Num. shives	78.33	8.33	9.42	85.67	5.77	6.53
Shive length, mm	2.47	0.05	0.06	2.34	0.10	0.12
Shive width, µm	203.58	5.61	6.35	220.81	12.02	13.60
Shives/metre	5.79	0.70	0.79	6.47	0.50	0.57
Number of replicates	**3**	**Digested and Ultrasonic Treated Fibre 'separated'**		**3**	**Digested and Bleached Fibre 'separated'**	
Number of fibres measured	38719			47835		
	Mean	Std. dev.	± 95%	Mean	Std. dev.	± 95%
Fines						
arithmetic, %	17.21	0.23	0.26	9.30	0.89	1.00
weighted, %	2.74	0.05	0.05	1.03	0.12	0.13
Fibre length						
mean, mm	0.94	0.00	0.00	1.18	0.01	0.01
Length weighted, mm	1.37	0.01	0.01	1.57	0.01	0.01
Weight weighted, mm	1.78	0.02	0.02	1.90	0.01	0.01
Fibre width, µm	32.62	0.07	0.07	31.47	0.14	0.16
Aspect ratio	28.80	0.15	0.17	37.64	0.18	0.21
Num. shives	10.33	1.53	1.73	19.00	5.20	5.88
Shive length, mm	2.22	0.35	0.39	1.78	0.12	0.13

Shive width, µm	188.08	7.61	8.61	222.35	14.25	16.13
Shives/metre	0.85	0.14	0.16	1.01	0.29	0.32
Number of replicates	**3**	**Digested, Bleached and, Ultrasonic Treated Fibre 'separated'**				
Number of fibres measured	36433					
	Mean	Std. dev.	± 95%			
Fines						
arithmetic, %	52.54	0.41	0.46			
weighted, %	16.66	0.23	0.26			
Fibre length						
mean, mm	0.66	0.00	0.00			
Length weighted, mm	1.05	0.01	0.01			
Weight weighted, mm	1.52	0.03	0.03			
Fibre width, µm	32.76	0.18	0.21			
Aspect ratio	20.10	0.15	0.17			
Num. shives	66.00	12.29	13.91			
Shive length, mm	1.67	0.06	0.07			
Shive width, µm	214.30	19.06	21.57			
Shives/metre	8.25	1.52	1.72			

8.2 Life cycle Inventory

Table 8-2: Life Cycle Inventory (LCI) for processing digested, bleached, and ultrasonic treated fibre.

Digested, bleached, and ultrasonic treated fibre

Material/ Energy Flow	**Type/Source/Destination**	**Quantity**	**Unit**
	Inputs		
Waste CCA treated Timber	Raw material	1000	kg
	Granulating		
Electrical Energy	NZ Energy grid	19.2	kWh
Drying Energy	NZ Energy grid	4.79571429	kWh
	Digestion		
Timber Granules	Granulating Process		
Water for Solution	Water	6404.02326	L
Water for Digester	Water	21691.0465	L
Quenching Water	Water	41316.2791	L
Water for Washing	Water	134277.907	L
Sodium Hydroxide	Sodium Hydroxide Production	710.64	kg
Electrical Energy	NZ Energy Grid	12477.5163	kWh
Drying Electrical Energy	NZ Energy Grid	4.79571429	kWh
	Sodium Hydroxide Production		
Al Reserves	Raw Materials/Fuels	0.02807028	kg
Cu Reserves	Raw Materials/Fuels	0.00472576	kg
Pb Reserves	Raw Materials/Fuels	0.00017126	kg
U Reserves	Raw Materials/Fuels	6.6587E-06	kg
Zn Reserves	Raw Materials/Fuels	0.00095936	kg
Coal (Coke)	Raw Materials/Fuels	0.00381614	kg
Coal (Combustion)	Raw Materials/Fuels	77.45976	kg
Crude Oil	Raw Materials/Fuels	4.7044368	kg
Limestone	Raw Materials/Fuels	1.5207696	kg
Natural Gas	Raw Materials/Fuels	0.05038438	kg
Oil Reserves	Raw Materials/Fuels	3.9156264	kg
Silica Sand	Raw Materials/Fuels	0.00138575	kg
	Wastewater Treatment		
Aluminium Sulphate	Materials/Fuels	0.64592769	kg
Diesel	Mechanical	43.414179	MJ
Electricity, At Wind Power Plant	Electricity/Heat	2.71338619	MJ
Electricity, Biogas	Electricity/Heat	134.919026	MJ
Electricity	Electricity Country Mix/Low Voltage	293.045708	MJ
Heat, Liquefied Petroleum Gas	Electricity/Heat	10.8535447	MJ

Heat, Natural Gas,	Electricity/Heat	32.5606342	MJ
Iron (III) Chloride, 40% In H_2O	Materials/Fuels	3.26817439	kg
Iron Sulphate, At Plant	Materials/Fuels	2.39004725	kg
Operation, Van, Petrol	Road/Operations	3.92355642	km
Sewer Grid, Class 3	Electricity/Heat	4.4685E-05	km

	Bleaching		
Fibre	Digestion	309.872093	kg
Bleaching Solution Water	Water	24789.7674	L
Washing Water	Water	89862.907	L
Energy (Heating)	NZ Energy Grid	6445.33953	kWh
Hydrogen Peroxide	Hydrogen Peroxide Production	1239.48837	L
Sodium Silicate	Sodium Silicate Production	619.744186	L
Drying Energy	NZ Energy Grid		kWh

	Hydrogen Peroxide Production		
Hydrogen	Raw Materials	602.614457	m^3
Aluminium Oxide	Raw Materials	7.93304785	kg
Quinone	Raw Materials	0.52831952	kg
Quinone And Solvents	Raw Materials	1.03187407	kg
Solvents, Aromatic	Raw Materials	0.81724426	kg
Solvents Unspecified	Raw Materials	1.19697392	kg
Sodium Hydroxide	Raw Materials	0.52831952	kg
Inorganic Chemicals	Raw Materials	0.43751461	kg
Chemicals Unspecified	Raw Materials	0.12382489	kg
Air	Raw Materials	177.441065	kg
Nitrogen	Raw Materials	41.9683822	kg
Oxygen	Raw Materials	24.2118932	kg
Water (Processing)	Water	1.58495857	m^3
Water (Cooling)	Water	140.334873	m^3

	Sodium Silicate Production		
Rock Salt	Raw Materials	198.287152	kg
Sand	Raw Materials	240.119885	kg
Limestone	Raw Materials	158.964384	kg
Washed Sand	Intermediates for Na-Silicate Prod	240.119885	kg
Soda	Intermediates for Na-Silicate Prod	124.661543	kg
Water for Steam Prod	Auxil. Materials for Na-Silicate Prod	96.2152849	m^3
Compressed Air	Auxil. Materials for Na-Silicate Prod	7.02789907	Nm^3
Additives	Auxil. Materials for Na-Silicate Prod	0.58565826	kg

	Wastewater Treatment		

Aluminium Sulphate	Materials/Fuels	0.36832018	kg
Diesel	Mechanical	24.7555853	MJ
Electricity, At Wind Power Plant	Electricity/Heat	1.54722408	MJ
Electricity, Biogas	Electricity/Heat	76.9333786	MJ
Electricity	Electricity Country Mix/Low Voltage	167.100201	MJ
Heat, Liquefied Petroleum Gas	Electricity/Heat	6.18889633	MJ
Heat, Natural Gas,	Electricity/Heat	18.566689	MJ
Iron (III) Chloride, 40% In H2O	Materials/Fuels	1.8635748	kg
Iron Sulphate, At Plant	Materials/Fuels	1.36285011	kg
Operation, Van, Petrol	Road/Operations	2.23728602	km
Sewer Grid, Class 3	Electricity/Heat	2.548E-05	km

Ultrasonic Treatment

Fibre	Bleaching	292.519256	kg
Water for Solution	Water	11466.7548	L
Water for Washing	Water	117007.702	L
Sodium Hydroxide	Sodium Hydroxide Production	234.015405	kg
Energy	NZ Energy Grid	2952.10433	kWh
Drying Energy	NZ Energy Grid		kWh

Sodium Hydroxide Production

Al Reserves	Raw Materials/Fuels	0.00979196	kg
Cu Reserves	Raw Materials/Fuels	0.00164852	kg
Pb Reserves	Raw Materials/Fuels	5.9743E-05	kg
U Reserves	Raw Materials/Fuels	2.3228E-06	kg
Zn Reserves	Raw Materials/Fuels	0.00033466	kg
Coal (Coke)	Raw Materials/Fuels	0.00133121	kg
Coal (Combustion)	Raw Materials/Fuels	27.0208465	kg
Crude Oil	Raw Materials/Fuels	1.6410826	kg
Limestone	Raw Materials/Fuels	0.53050102	kg
Natural Gas	Raw Materials/Fuels	0.01757595	kg
Oil Reserves	Raw Materials/Fuels	1.36591619	kg
Silica Sand	Raw Materials/Fuels	0.0004834	kg

Wastewater Treatment

Aluminium Sulphate	Materials/Fuels	0.40484871	kg
Diesel	Mechanical	27.2107459	MJ
Electricity, At Wind Power Plant	Electricity/Heat	1.70067162	MJ
Electricity, Biogas	Electricity/Heat	84.5633253	MJ
Electricity	Electricity Country Mix/Low Voltage	183.672535	MJ
Heat, Liquefied Petroleum Gas	Electricity/Heat	6.80268647	MJ

Heat, Natural Gas,	Electricity/Heat	20.4080594	MJ
Iron (III) Chloride, 40% In H2O	Materials/Fuels	2.04839674	kg
Iron Sulphate, At Plant	Materials/Fuels	1.49801217	kg
Operation, Van, Petrol	Road/Operations	2.45917116	km
Sewer Grid, Class 3	Electricity/Heat	2.8007E-05	km

	<u>Outputs</u>		
	Granulating		
Timber Granules	Digestion	888.3	kg
Fines/Dust	Emissions to Air	13	kg
Water	Atmosphere	98.7	kg
	Digestion		
Fibre	Bleaching	309.872093	kg
Sodium Hydroxide	Wastewater Treatment	710.64	kg
Timber Solubles	Wastewater Treatment	578.427907	kg
Waste Water	Wastewater Treatment	140681.93	L
Clean Water	Wastewater Treatment	63007.3256	L
	Sodium Hydroxide Production		
CO_2	Emissions to Air	444.15	kg
As	Emissions to Air	6.4597E-06	kg
CH_4	Emissions to Air	0.00294916	kg
Cd	Emissions to Air	5.3369E-07	kg
Cr	Emissions to Air	1.1726E-05	kg
Hg	Emissions to Air	7.817E-06	kg
N_2O	Emissions to Air	0.0195426	kg
NMHC	Emissions to Air	0.00471865	kg
NO_x	Emissions to Air	0.87479784	kg
Ni	Emissions to Air	1.3218E-05	kg
PM10	Emissions to Air	0.00350346	kg
Pb	Emissions to Air	3.0913E-05	kg
SO_2	Emissions to Air	0.00603333	kg
SO_x	Emissions to Air	0.04661798	kg
Dust	Emissions to Air	0.00217456	kg
Hydrocarbons	Emissions to Air	0.02686219	kg
As	Emissions to Water	2.7857E-07	kg
BOD	Emissions to Water	0.04306478	kg
Cd	Emissions to Water	4.1857E-08	kg
Cr	Emissions to Water	8.3856E-07	kg
Hg	Emissions to Water	2.7857E-08	kg
Industrial Waste Landfill (Unspecified)	Industrial Waste	2.3522184	kg
Low-Level Radioactive Waste	Industrial Waste	4.6547E-06	kg

Plastic Wastes (Landfill)	Industrial Waste	3.5035E-06	kg
Rubbles (Landfill)	Industrial Waste	6.9643E-06	kg
Slag (Landfill)	Industrial Waste	0.00902513	kg
Sludge (Landfill)	Industrial Waste	3.3542E-05	kg
Wastewater Treatment			
Ammonia, As N	Emissions to Water/Ocean	0.84755691	kg
Bod5, Biological Oxygen Demand	Emissions to Water/Ocean	1.24626821	kg
Boron	Elementary Flows/Emission to Water/Ocean	0.03836911	kg
Chlorine	Emissions to Water/Ocean	0.00986569	kg
Cod, Chemical Oxygen Demand	Emissions to Water/Ocean	2.79590434	kg
Dinitrogen Monoxide	Elementary Flows/Emission to Air/High Population Density	0.21690219	kg
Fluoride	Elementary Flows/Emission to Water/Ocean	0.21687795	kg
Methane, Biogenic	Elementary Flows/Emission to Air/High Population Density	6.6885553	kg
Nitrogen, Total	Emissions to Water/Ocean	2.79865253	kg
Phosphorus, Total	Emissions to Water/Ocean	1.15700141	kg
Suspended Solids, Unspecified	Emissions to Water/Ocean	1.56603439	kg
Water	Emissions to Water/Ocean	204.978324	t
Bleaching			
Fibre	Ultrasonic Treatment	292.519256	kg
Water	Wastewater Treatment	114652.674	L
Hydrogen Peroxide	Wastewater Treatment	1239.48837	L
Sodium Silicate	Wastewater Treatment	619.744186	L
Timber Extractives	Wastewater Treatment	17.3528372	kg
Hydrogen Peroxide Production			
Waste to Landfill	Solid Waste	2.3279079	kg
Filter Residues	Solid Waste	0.03656962	kg
Waste Unspecified	Solid Waste	73.254804	kg
Aromatic Hydrocarbons	Emissions to Air	0.1056639	kg
NMVOC	Emissions to Air	0.43751461	kg
Hydrogen	Emissions to Air	0.03161662	kg
Dust, Particles	Emissions to Air	0.00011392	kg
Bod	Emissions to Water	0.21462981	kg
Cod	Emissions to Water	0.7759693	kg
Toc	Emissions to Water	0.24764978	kg
Nitrate	Emissions to Water	0.16757635	kg
Phosphate	Emissions to Water	0.01031874	kg
Suspended Solids	Emissions to Water	0.12465039	kg
Chloride	Emissions to Water	0.31368972	kg

Hydrogen Peroxide	Emissions to Water	0.49529955	kg
Other Emissions	Emissions to Water	0.00030956	kg
Sodium Silicate Production			
Mineral Waste	Solid Waste	39.4900995	kg
Filter Residues	Solid Waste	0.75298919	kg
Inert Chemicals	Solid Waste	0.2509964	kg
Ammonia	Emissions to Air	0.07387661	kg
Carbon Dioxide Fossil	Emissions to Air	355.300457	kg
Carbon Monoxide	Emissions to Air	1.17633644	kg
Dust, Particles	Emissions to Air	1.21649586	kg
Methane	Emissions to Air	0.25685298	kg
Nitrogen Oxides	Emissions to Air	1.19139622	kg
NMHC	Emissions to Air	0.35139495	kg
Sulfur Oxides	Emissions to Air	1.601357	kg
Ammonium	Emissions to Water	0.03798412	kg
BOD As G O2	Emissions to Water	0.00011713	kg
Chlorides	Emissions to Water	116.600375	kg
COD As G O2	Emissions to Water	0.00133865	kg
Inorg. Salts and Acids	Emissions to Water	0.07146118	kg
Metals	Emissions to Water	0.00962153	kg
Suspended Solids	Emissions to Water	8.95555139	kg
Wastewater Treatment			
Ammonia, As N	Emissions to Water/Ocean	0.48329297	kg
Bod5, Biological Oxygen Demand	Emissions to Water/Ocean	0.71064569	kg
Boron	Elementary Flows/Emission to Water/Ocean	0.02187879	kg
Chlorine	Emissions to Water/Ocean	0.00562561	kg
Cod, Chemical Oxygen Demand	Emissions to Water/Ocean	1.59427749	kg
Dinitrogen Monoxide	Elementary Flows/Emission to Air/High Population Density	0.12368173	kg
Fluoride	Elementary Flows/Emission to Water/Ocean	0.1236679	kg
Methane, Biogenic	Elementary Flows/Emission to Air/High Population Density	3.81394064	kg
Nitrogen, Total	Emissions to Water/Ocean	1.59584456	kg
Phosphorus, Total	Emissions to Water/Ocean	0.65974407	kg
Suspended Solids, Unspecified	Emissions to Water/Ocean	0.89298241	kg
Water	Emissions to Water/Ocean	116.882514	t
Ultrasonic Treatment			
Fibre	Product	263.26733	kg
Timber Extractives	Wastewater Treatment	29.2519256	kg
Water	Wastewater Treatment	128474.457	L

Sodium Hydroxide	Wastewater Treatment	234.015405	kg
	Sodium Hydroxide Production		
CO_2	Emissions to Air	146.259628	kg
As	Emissions to Air	2.1272E-06	kg
CH_4	Emissions to Air	0.00097116	kg
Cd	Emissions to Air	1.7575E-07	kg
Cr	Emissions to Air	3.8613E-06	kg
Hg	Emissions to Air	2.5742E-06	kg
N_2O	Emissions to Air	0.00643542	kg
NMHC	Emissions to Air	0.00155386	kg
NO_x	Emissions to Air	0.28807296	kg
Ni	Emissions to Air	4.3527E-06	kg
PM10	Emissions to Air	0.0011537	kg
Pb	Emissions to Air	1.018E-05	kg
SO_2	Emissions to Air	0.00198679	kg
SO_x	Emissions to Air	0.01535141	kg
Dust	Emissions to Air	0.00071609	kg
Hydrocarbons	Emissions to Air	0.00884578	kg
As	Emissions to Water	9.1734E-08	kg
BOD	Emissions to Water	0.01418133	kg
Cd	Emissions to Water	1.3784E-08	kg
Cr	Emissions to Water	2.7614E-07	kg
Hg	Emissions to Water	9.1734E-09	kg
Industrial Waste Landfill (Unspecified)	Industrial Waste	0.77459099	kg
Low-Level Radioactive Waste	Industrial Waste	1.5328E-06	kg
Plastic Wastes (Landfill)	Industrial Waste	1.1537E-06	kg
Rubbles (Landfill)	Industrial Waste	2.2934E-06	kg
Slag (Landfill)	Industrial Waste	0.002972	kg
Sludge (Landfill)	Industrial Waste	1.1046E-05	kg
	Wastewater Treatment		
Ammonia, As N	Emissions to Water/Ocean	0.53122404	kg
Bod5, Biological Oxygen Demand	Emissions to Water/Ocean	0.7811247	kg
Boron	Elementary Flows/Emission to Water/Ocean	0.02404864	kg
Chlorine	Emissions to Water/Ocean	0.00618353	kg
Cod, Chemical Oxygen Demand	Emissions to Water/Ocean	1.7523916	kg
Dinitrogen Monoxide	Elementary Flows/Emission to Air/High Population Density	0.13594799	kg
Fluoride	Elementary Flows/Emission to Water/Ocean	0.1359328	kg
Methane, Biogenic	Elementary Flows/Emission to Air/High Population Density	4.19219211	kg
Nitrogen, Total	Emissions to Water/Ocean	1.75411408	kg

Phosphorus, Total	Emissions to Water/Ocean	0.72517487	kg
Suspended Solids, Unspecified	Emissions to Water/Ocean	0.98154485	kg
Water	Emissions to Water/Ocean	128.474457	t