

**PULTRUSION MANUFACTURING, MATERIALS TESTING, AND LIFE
CYCLE ASSESSMENT OF THERMOPLASTIC GFRP COMPOSITES**

by

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Abstract

This thesis pertains to the development of novel thermoplastic (TP) polymer-based glass fibre-reinforced polymer (GFRP) composites in a pultrusion manufacturing method.

Thermosetting (TS) -based composites have a limited ability to absorb impacting energy and deform in the transversal direction. The idea that TP polymer is a suitable alternative to conventional TS polymer in pultrusion manufacturing processes has been tried by the composite community before. For the first time, however, this thesis assessed the plausibility of this shift via a holistic research approach combining: TP-integrated GFRP manufacturing via pultrusion, mechanical and environmental property characterization of pultruded composites, and a novel life cycle framework (LCF) to estimate/analyze economic and environmental impact from ideation to end-of-life of pultruded TP vs TS -based GFRP.

The novel TP composites were found to be manufacturable with comparable mechanical properties to TS counterparts, similar energy and environmental impacts, and up to 25% less expensive to manufacture.

Dedication

For my grandfather, Ronald McGrath,
who introduced me to computers and taught me how to work with my hands.

For my high school physics professor, Mark Murchison,
who encouraged me to study engineering.

And for Steve Jobs,
who inspired me to want to make the world a better place.

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Most importantly, I would like to thank my parents, Mark and Brenda Mackin, for the life they've given me. Throughout my life, my family (living and dead), friends, and friends who are like family have supported me more than one could hope, especially Donald Warner. Without their love, guidance, criticism, and encouragement, I would not be the person I am today.

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Chapter 1 Introduction

In engineering design, selecting the best material for the application at hand is an important consideration. The desire to use lighter, stronger, and environmentally resilient components has led to the advent of new materials over time: composites.

Composite materials continue to find their way into more and more areas of industrial relevance. The term 'composite' refers to a body made of multiple distinct constituents, when merged together creates a new material with new properties. Composites allow the use of existing materials in new means, providing improved mechanical properties in ways that traditional materials are not able to do. A commonly known industrial-based composite is concrete, which is a mix of cement and rock aggregate. Modern examples of composite use include car body panelling which uses glass or carbon fibres and polymer moulded into the desired shape, bike frames made of carbon fibre reinforcements for weight reduction, and so forth. Composite materials offer significant environmental and economic benefits in our daily life. For example, reducing the weight of vehicles drastically reduces the amount of fuel required for travelling, thus reducing the greenhouse gas (GHG) emissions on a per-kilometer basis. One way to achieve the economic benefits is by replacing metallic reinforcements, such as steel, with composite rebars, avoiding dangerous rust and corrosion which costs the world nearly \$2.2 trillion annually [1]. Since modern composites do not contain metallic components, the risk of oxidation and corrosion is eliminated, bringing additional economic savings. With simple benefits like these, using composites in place of traditional materials, such as steel and other alloys, makes environmental and economic sense.

1.1 Motivation

The most important social issue the world faces today is arguably that of climate change and how it will affect the future of our planet. As such, environmental-impact considerations are often high on the list when making engineering decisions. With the Paris Agreement under the United Nations Framework Convention on Climate Change, nearly 200 countries/parties aim to “prevent a global temperature increase above 1.5 degrees Celsius relative to pre-industrial levels” [2]. One way of achieving this is by reducing or eliminating GHG emissions wherever possible.

In 2017, the transportation, heavy industry, and waste sectors combined accounted for 40% of all GHG emissions in Canada, as shown in Table 1.1 [3]. More specifically, these sectors include mining, cement, iron, and steel production, as well as light manufacturing and construction. Metals processing is a large polluter, which means that the everyday items we interact with come at an environmental cost. Reducing our reliance on metals can come with many potential improvements; one way of reducing the necessity of metal production is by integrating new types of materials instead.

Table 1.1: GHG emissions from various industries in Canada, 2017 (megatonnes of CO₂ equivalent) [3]

Year	Oil & Gas	Transportation	Buildings	Electricity	Heavy Industry	Agriculture	Waste/Other
2017	195	174	85	74	73	72	42

1.2 Opportunity

Modern composites are primarily composed of two constituents: fibre reinforcement and resin matrix. Fibres are typically made from glass or carbon, and the resin matrix is made from either a thermosetting (TS) or a thermoplastic (TP) polymer. The composite materials manufacturing method that was the focus of this study is an impregnation-based pultrusion technology, which is a continuous, energy-efficient process. The process involves pulling resin-soaked fibres through a heated die with the help of a series of pulleys at the exit of the die [4]. Pultruded shapes are typically prismatic, and up until now, due to viscosity requirements, TS polymers have been used in impregnation-based processes, such as pultrusion.

There now exists a poly(methyl methacrylate) (or PMMA) -based TP polymer that has been designed for impregnation-based processes with a low viscosity, with the potential to offer a recyclable alternative to existing TS pultruded components. With minimal research available on pultruded GFRPs of low-viscosity TP polymers, this opens up a door to explore the potential benefits of these new materials over existing TS materials.

Research is just emerging on the possibility of a PMMA-based, low-viscosity, TP polymer designed with pultrusion applications in mind. As part of this research, this thesis focused on the manufacturing and reliability assessment of the new TP polymer-based pultruded composite materials in a number of areas, as well as the formation and adoption of a novel composite materials life cycle analysis (LCA) framework.

The author acknowledges that the work pursued through and presented in this thesis is novel in nature, and therefore further research with additional and more compelling manufacturing and field data are needed to substantially validate results presented in this study. It is, however, important to note that in the void of any comparative LCA pertaining to traditional TS-based and the novel TP-based composite materials, the author believes that this research promises to be a cornerstone when it comes to the acceptance of transitioning from TS- to TP-based advanced composites. The study thus brings two sides of the reliability together: mechanical/environmental performance, and the cost/environmental analysis of the material life cycle (hence, the LCA). The approach thus required the adoption of a combination of experimental and empirical research methodologies to support the two sides, respectively. The conviction is that by embracing and advancing such an unconventional approach, a comprehensive economic/environmental case can be put forward before composite materials stakeholders: designers, end-users (industry), and next-generation researchers.

1.3 Hypothesis and Research Objectives

With a lack of understanding in pultrusion composite manufacturing with low-viscous TP polymer, this gives an opportunity for research into the design, manufacturing, and reliability testing of these pultruded glass fibre-reinforced polymer (GFRP) materials. Therefore, based on the benefits of TP composites discussed in Chapter 2, the following research hypothesis was adopted:

Pultruded TP composite materials are competitive with existing TS materials in three key areas: mechanical properties, environmental resilience, and economics.

In order to test the hypothesis, questions needing answered were as follows:

1. Could the new TP polymer integrated GFRP materials be manufactured in a lab-scale pultrusion process with required initiators (or the ‘process recipe’ development)?
2. Would these new materials provide superior mechanical and environmental properties than those currently available with TS polymer integrated GFRP materials?
3. Was it viable to replace TS polymer with TP polymer when manufacturing GFRP composites from energy, environment, and cost perspectives?

These questions led directly into the research objectives, which were to:

1. Develop and test a pultrusion-based manufacturing process using novel TP PMMA polymer and manufacture pultruded TP rebars with the use of an in-house pultrusion machine;
2. Perform mechanical and environmental testing on the produced TP GFRPs to determine their mechanical and environmental properties and compare them with those of the existing TS GFRPs; and
3. Develop an LCA on both TP and TS pultruded GFRPs to analyze their effectiveness in areas of energy usage, environmental impact, and economics.

These objectives were upheld as the three pillars of this research and more critically had served the purpose of adopting a combined experimental and empirical research methodology, further discussed in Chapter 3.

1.4 Scope

As suggested, the primary technology used in the experimental part of this research was the UNB's Nanocomposites and Mechanics Laboratory (NCM Lab) custom-designed pultrusion machinery. The manufacturing of the GFRPs was accomplished by using the novel, low-viscous PMMA TP polymer for producing a $\varnothing 9.5$ mm prismatic rebar. While the manufactured specimens featured a $\varnothing 9.5$ mm shape, it is worth noting that one of the desired use cases for this new material was the development of composite-based interlocking sheet piling for marine applications. Therefore, the mechanical loading and environmental degradation performance of these TP rebars were compared to those of existing TS-based GFRP rebars of the same shape and manufacturing process through a variety of testing conditions, including 3-point flexural bending before and after heat/UV/water exposure in a Weather-Ometer[®] chamber, cold weather, and 31-day immersion in high pH (12.6) corrosion solution. The LCA was accomplished for both the new TP and existing TS GFRP rebars manufactured from the in-house impregnation-based pultrusion process for comparisons, considering the common inputs and outputs between the two composites from the raw materials production stage to end-of-life.

Chapter 2 Literature Review

2.1 Composites

There are countless types of composites, with different manufacturing processes that can be used depending on the desired component. While concrete is a common example of a composite material, modern composites are composed of two main constituents: fibre reinforcement and surrounding resin matrix. This fibre and matrix combination allows novel materials to be made to take on many different shapes.

In the world of manufacturing, there are a number of manufacturing processes available for producing various types of components. This includes casting processes, bulk deformation processes such as extrusion or rolling, machining, and various forms of welding [5]. One process used to produce composites is known as pultrusion.

2.2 What is Pultrusion?

With numerous manufacturing methods available, one of the most economical procedures with a low-energy impact is pultrusion. In order to understand pultrusion, it may be useful to first understand extrusion.

Extrusion involves forcing or pushing material through a die to produce a component, similar to how pasta is made [5]. In a similar way, pultrusion is a continuous process that involves pulling material through a die with the help of a series of pulleys at the exit of a

die [4]. Due to its continuous nature, this makes pultrusion a highly automated process allowing for high production rates.

The types of components produced from pultrusion are typically prismatic in nature, where the size and shape of the part is the same throughout its length, like a piece of pasta. This can include I beam sections, hollow tubing, and pultruded rebar, which was the focus of this study.

2.3 Types of Pultrusion

There are different subsets of pultrusion which are beneficial for different types of components. The pultrusion process relevant to this research involved the use of continuous, unidirectional glass fibre rovings and an open resin bath impregnation process [4]. A roving is a cylindrical spool of reinforcement fibre, which is typically stored on a creel, a structure used for organizing and storing rovings of fibre in composite manufacturing. The individual strands of glass in each roving are uninterrupted and unbroken throughout the entire spool. The open resin bath impregnation set-up means that the resin and glass are combined at room temperature and pressure for as long as the fibres are submerged in the resin mixture. Other forms of pultrusion also use sheets or mats of material for prepreg applications, as well as cases where an injection chamber is used for resin delivery as opposed to using an open resin bath, as shown in Figure 2.1 below [4].

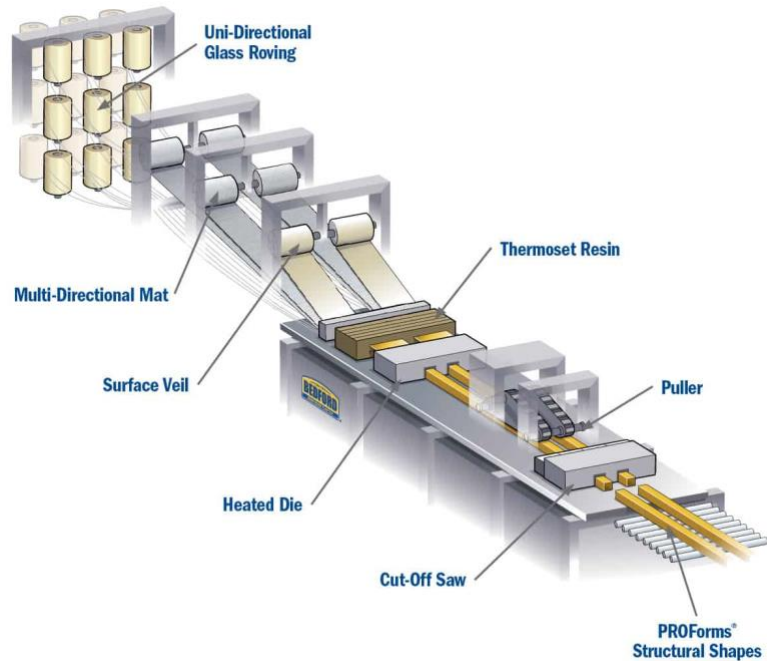


Figure 2.1: Industrial pultrusion machine [6]

2.3.1 Impregnation-based Pultrusion

In impregnation-based pultrusion, the pultruded product starts off in its raw components. Dry, continuous glass fibre rovings pass through a guide plate to ensure even separation of the glass. These dry fibres then pass through a resin bath, where a pre-mixed blend of resin, initiator, lubricant, and additives is sitting [7]. Upon passing through the resin bath, the dry rovings are now soaked or “impregnated” with the resin mixture. This wetted product then passes through a second series of guide plates to redirect and reform the material into the direction and shape of the heated die. The wet product enters a heated die, where the wet resin-fibre matter is heated until cured or solidified. The final product exits the heated die in the shape defined by the inside cavity. The continuous movement

of the glass fibres and pultruded product throughout the entire process is driven by a series of pulleys at the end of the pultrusion machine [7]. This process is described further in section 3.1.3 and is what is typically used with TS resins.

2.4 Fibre

The fibre in a composite material acts as the reinforcement, providing rigidity and strength to the component. This fibre constituent can take many forms, including long continuous fibres in collections called rovings, woven mats that are delivered in sheets, and short fibres [4]. These fibre reinforcements are available in a number of different material types, the most common of which are glass and carbon fibres; however, additional materials such as basalt and wood-based fibres are also available [7].

Composite components are typically referred to as fibre-reinforced polymer (FRP). When using glass or carbon fibres, this abbreviation can be written as GFRP or CFRP, respectively.

2.5 Matrix

Often, the matrix of a modern composite is an organic-based material that surrounds and interfaces with the fibre constituent. There are two main types of polymers used as part of the matrix in FRP composites: TP and TS [7]. These polymers are generally in a powder or liquid resin form and can be mixed with the reinforcing fibres in a number of ways. In some cases, the sheets of fibre come with the polymer already integrated into the woven mat (known as ‘prepreg’), at which point heat is applied to the sheet to solidify the

composite into its desired shape. Heat-sensitive resin can also be brushed onto dry sheets of fibre and layered with additional reinforcement. In continuous processes, the fibre material can mix with the matrix by passing through a bath of resin, typically a TS polymer [7].

2.5.1 Thermoset Polymers

TS polymers have been the standard in large-scale industrial composite manufacturing and research as they tend to be economically cheaper than TP polymers. This class of plastics, typically in the form of powder or liquid resin, cures with heat in a permanent polymerization process. From a chemistry standpoint, TS polymers solidify via a cross-linking reaction in the polymer matrix, as shown in Figure 2.2 [4]. Since this process cannot be undone, TS polymers are not thermoformable and do not melt with

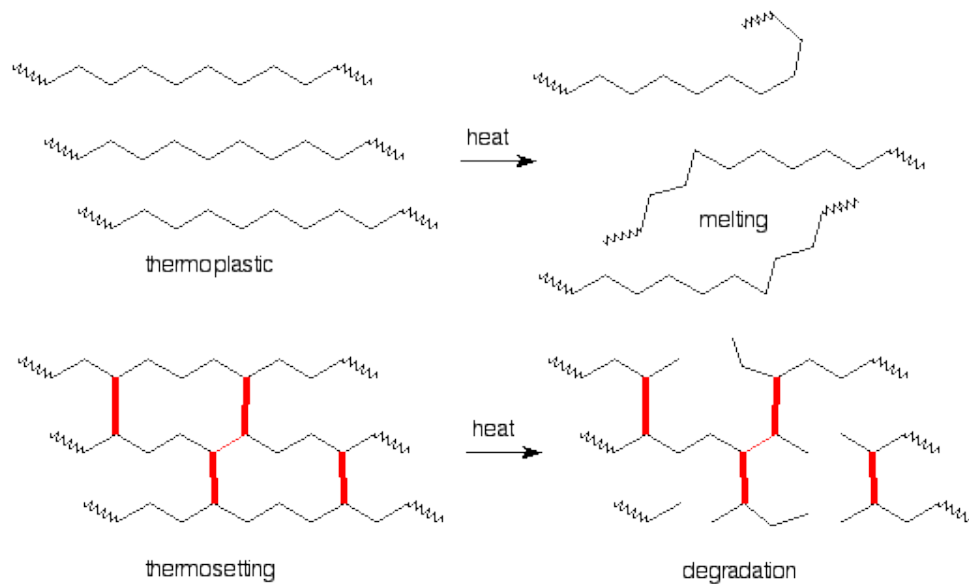


Figure 2.2: TP polymer chains and TS polymer cross-linking [8]

applied heat after the polymerization stage, which makes these particular polymers beneficial for use in high-heat applications [9]. This also means these plastics are not recyclable and cannot be post-processed.

Examples of TS polymers are vinyl-ester, polyester, epoxy, silicone, and polyurethanes which are used in powder or liquid resin forms to create products such as FRPs, protective coatings, synthetic fibres, circuit boards, and car parts via processes including extrusion and injection moulding [10].

2.5.2 Thermoplastic Polymers

TP polymers are generally much more viscous than the TS variety, making them a non-ideal solution for continuous composite manufacturing processes. As such, there has been less research in this area, and TP polymers are rather typically used in prepreg applications, where the semi-solid polymer matrix is already integrated into a woven fibre sheet upon delivery. These plastics cure with applied heat via the formation of molecular chains, as shown in Figure 2.2 above [4]. This polymerization process is completely reversible, contrary to that of TS polymers. TP polymers are therefore thermoformable, in that their shape can be modified after the polymerization process has occurred, under the appropriate thermal and pressure loading [4]. TP polymers typically have high-impact resistance and high strength properties while also offering improved surface finishes and chemical resistance [9].

Examples of TP polymers include PMMA (acrylic), acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), nylon, polycarbonate (PC), and polyvinyl chloride (PVC) [10]. These are again used in solid or quasi-liquid forms to produce components such as plexiglass, toys, clothing, 3D-printed components, prosthetics, and public infrastructure such as sewer pipes [10]. Of these, PMMA possesses glass-like properties while providing 10 times greater resistance to impact [11].

As a strong but light plastic, PMMA has better scratch resistance than polycarbonate and generally has good chemical resistance [11]. Since PMMA is transparent and does not absorb much light, this results in an immunity to UV light and other weathering effects [12]. Therefore, PMMAs are suitable for outdoor applications where a combination of mechanical and environmental properties are important, making them an ideal choice for GFRP components [11].

2.5.3 Recyclability

Since TP polymers are thermoformable with applied heat, this means the polymer can be recycled after its design life has passed. This can be achieved by subjecting the plastic to high heat in a pyrolysis process, or undergoing depolymerization by exposing the plastic to molten lead, after which the plastic can be used in other components [13]. TS polymers do not have this advantage due to their irreversible polymerization process. Additional research on the recycling of TP polymers is ongoing [14].

2.5.4 Environmental Resistance

Environmental resistance of composites is an important quality to consider when choosing the right resin for the matrix constituent of the material. By subjecting materials to accelerated weathering tests, including UV light and corrosive solutions, evaluations can be made to determine immunity to certain conditions. This is particularly useful if the composite materials are subjected to sunlight and seawater, as would be the exposure conditions for interlocking sheet piling for marine applications.

Based on the information provided by Industrial Specialties Mfg. [15], it was found that TP polymers like PMMA and TS polymers like vinyl-ester generally have excellent resistance to calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH), and potassium hydroxide (KOH). These resistances are valid when the composites are exposed to these solutions at room temperature in concentrations of 10%, 50%, and 30%, respectively. These compounds are typically included in corrosive caustic bath solutions, used to simulate accelerated corrosion environments. However, since the resistance properties of these polymers are high, such a caustic bath solution may not have much effect on the properties of a composite, meaning these types of composites are expected to deal well with corrosive environments.

2.6 Matrix Additives

In composite production, it is common for additives or fillers to be combined with the designed matrix. Supplements to the resin matrix can provide improved resistance

properties for UV and flame exposure, improved conductivity, improved bonding, and cost reductions due to less resin being used in the manufacturing process [1]. These additional ingredients are added to the fibre or matrix prior to or during the manufacturing process, depending on the constituent.

2.6.1 Fillers and Additives

Examples of fillers and additives include biochar, calcium carbonate (CaCO_3), kaolin, aluminum oxide (Al_2O_3), and alumina trihydrate (ATH) [1]. Biochar material is the solid particles left over from subjecting biomass such as wood chips to a pyrolysis process [16]. Biochar as an additive also has the potential to provide improved mechanical properties to composites [16][17][18]. The proportion of filler to resin (PPHR, or parts per hundred resin) can vary; however, some resins with a ‘high filler content’ can contain upwards of 50 PPHR of filler [19]. One example of the continued research in fillers for polymeric composites is the study of nano-fillers acting as reinforcements. It was found that the reinforcement effect from incorporating nano-scale fillers over micro-fillers, at the same weight percentage, proved to be better due to the increase in the contact surface area with the nano-fillers [20][21]. The highly researched and publicized graphene is an example of these nano-fillers, which provide improved electrical properties to the composite in addition to enhanced mechanical characteristics [22].

2.6.2 Initiators

In order to accelerate and control the polymerization process to produce solid components with the respective polymer, initiators are generally required. In the case of off-the-shelf epoxies, for example, the hardener resin acts as an initiator. These particular additives are typically organic peroxides (OPs), causing free radicals to begin the addition of monomers to the polymer chains in the presence of heat [1][4]. These create cross-links in TS polymers or long polymer chains in TP polymers, which solidifies the plastic and provides strength [1].

Different initiators are designed for different types of resins, heating profiles, and rates of polymerization [23]. The polymerization of the plastic used undergoes a transition from monomer to polymer, which is known as the conversion of the polymer [24]. In many cases, a combination of different OPs is used in resin preparation in order to control the degree and rate of polymerization, as using only one initiator would result in a conversion efficiency below 100% [23]. These combinations of OPs will typically feature initiators with slow, medium, and fast conversion rates in order to account for this [23].

Using too much initiator in resin preparation, however, can be detrimental to the conversion of the polymer. An excess of an initiator acting at the beginning of the polymerization process may result in a “large amount of shorter, lower molecular weight chains” [23]. Since the mechanical properties of a polymer like PMMA are dependent on the quantity and length of the polymer chains, shorter chains may cause a decrease in

mechanical performance. In cases where excessive quantities of initiator are used, the polymerization process may even be pre-emptively terminated [23].

Inhibitors also exist to reduce the rate of polymerization or to prevent a resin from solidifying at room temperatures [1]. These inhibitors are sometimes included in the off-the-shelf resin in order to prolong the usable life of the resin.

2.6.3 Coupling Agents

Another composite additive that can be useful in certain manufacturing processes is a coupling agent. When considering the bonding characteristics between the matrix and fibre components in a composite, there is usually room for improvement. While initiators contribute to the strength of the composite when polymerizing the resin matrix, the interface between the polymer and fibre is not escalated. Since the polymer constituent is an organic compound, chemical bonding between the organic surface of the matrix and the inorganic surface of the glass fibre is not typically strong [25]. As such, surface modifiers such as coupling agents are used to facilitate improved bonding between these two constituents. Coupling agents act as an interface, like a puzzle piece, between the organic and inorganic materials; one side of the compound bonds with the glass, while the other side bonds with the polymer. This improved bonding leads to increased strength properties, as well as the potential for improved microstructure qualities. There are two main implementation methods of coupling agents in pultrusion manufacturing processes: precoating and in-situ. The precoating process passes the glass fibres through a diluted

bath of the coupling agent, after which the fibres are dried prior to the pultrusion process. In-situ, on the other hand, incorporates the coupling agent directly into the resin matrix during pultrusion manufacturing, usually at a higher additive ratio compared to the precoating process. Due to the complexity of the precoating process, this option is less cost effective but more efficient in terms of the amount of the coupling agent used [25].

2.7 Mechanical Properties

When considering the study of mechanical properties for a material, a common starting point is a tensile test. With a tensile test, the testing material is machined or formed into a dog bone-shaped specimen, the ends of each side of the dog bone are placed within the grips of a materials testing system, with a pulling force applied axially to the specimen until failure. For unidirectional composites, many tensile tests have been completed in the past, results for which are found in Figure 2.3. In these tests, the majority of the tensile strength is attributed to the glass fibres used in the composite that are aligned axially with the specimen. As these tests have been completed many times in the past, performing these tests again may not introduce many new results.

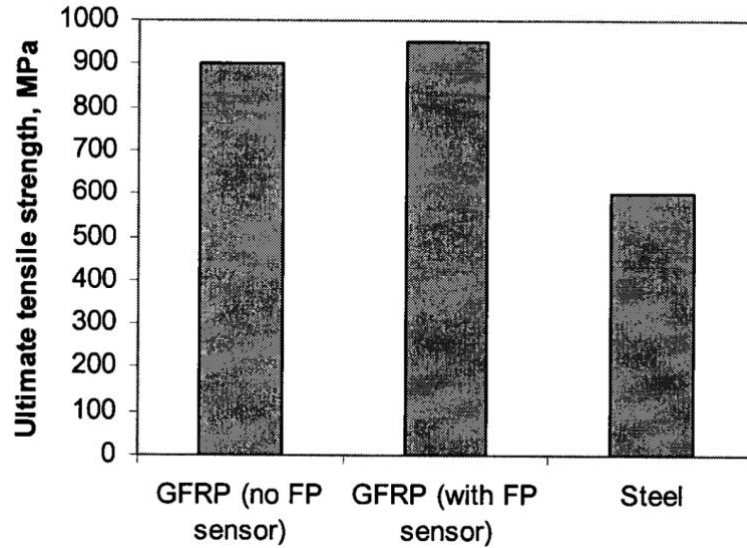


Figure 2.3: Bar graph showing ultimate tensile strength of GFRP composites and steel [26]

With a unidirectional composite material, however, creating these dog bone specimens proves to be difficult. Machining out dog bones from a flat sheet of composite material with unidirectional fibres, for example, would result in stress concentrations at the ends of the dog bone [27]. This becomes even more complicated with round pultruded specimens. If a significant gripping force is required, the clamped ends of the dog bones also have the potential to fail before the tensile test has completed [27]. There are some alternative methods for other approaches to these tensile tests; one method would be to sand-coat the ends of a specimen and place each end of the specimen into an expanding mortar cement contained within steel tubing [16]. In this case, the combination of the sand-coated ends within the cement and steel tubing would act as the ‘grips’ of the test, with the steel tubing connected to a material testing system via shear pins, for example [16]. This introduces another potential issue, however, in that the specimens may not be perfectly mounted within the steel tubing, causing alignment issues; these alignment

issues could result in the specimen not undergoing a perfect tensile setup, but rather an unintended combination of both tensile and sheer loadings. If manufacturing defects like roving knots are present, there is also the potential for sections of the composite material to fail before others. With these difficulties in tensile testing, “It is debatable whether one should even attempt a tensile test on a unidirectional composite” [27].

In the case of a component like interlocking sheet piling in marine applications, the typical loading configuration would not be represented by a tensile test. A bending or flexural test may be more appropriate, as the sheet piles would incur stress and impact from waves and boats, for example, resulting in flexural stress and strain on the materials between their respective supports. It is unlikely that the sheet piles would undergo any significant amount of tensile stress over the lifetime of the material.

In a thesis from Wallace, the flexural properties of various TS GFRP biocomposites were determined via a 3-point flexural bending test, a graphical representation of which can be found in Figure 2.4 below [16]. The flexural strength of the control TS GFRP (without added biochar) was found to be 735 MPa, with the addition of biochar resulting in greater flexural strength to as high as 980 MPa, as alluded to previously [16].

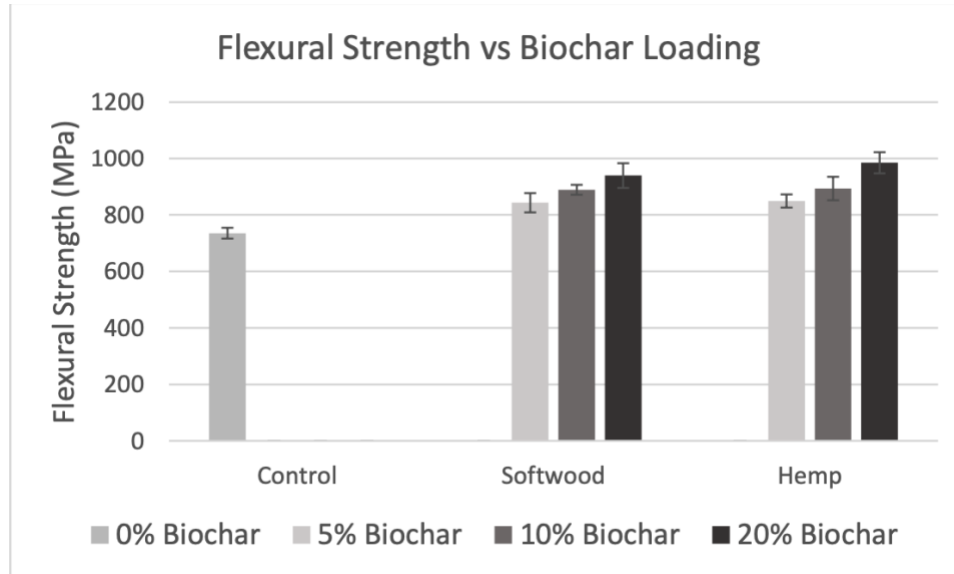


Figure 2.4: Flexural strengths of various TS bio-composites [16]

2.8 Composite Life Cycle Analysis

In an LCA for a product or material, energy usage, environmental impact, and cost are all considerations that are typically made. As such, the existing data found in literature is divided accordingly below.

2.8.1 Energy Required

When considering how much energy is required to produce a composite material, there are several different areas to analyze. Energy is required to produce the e-glass reinforcing fibres used, the specific resin matrix, OP initiators, and for manufacturing the composites via pultrusion manufacturing. In some manufacturing cases, a combination of fuel and electricity is required, whereas other processes may only require electricity.

2.8.1.1 Raw Materials Production

In an LCA paper on sustainable composites titled “Environmental analysis of innovative sustainable composites with potential use in aviation sector – A life cycle assessment review” from Bachmann et al., a collection of primary energy and GHG emission data is given for multiple raw materials used in the production of composites. For epoxy resin, a TS polymer, a required energy for manufacturing range of 76 – 137 MJ/kg is given across four different sources [28]. Similarly, PMMA was found to require 116 – 207.3 MJ/kg to produce, higher than that of the TS resins found [29]. Bachmann et al. also collected a series of references for energy usage data for glass fibre manufacturing, a range for which is given as 10.3 – 45.6 MJ/kg when taking all five sources into account [28].

OP initiators are required in composite manufacturing to facilitate the polymerization of the polymer matrix in the presence of heat. There are many different initiators available for use, each designed for different subsets of resins and conditions. Unfortunately, details on the energy required for producing OPs was not available at the time of writing.

2.8.1.2 Pultrusion Manufacturing

The energy required for pultrusion is for heating and pulling; to heat the different heating zones along the die to a constant temperature before the process begins, and to drive a series of pulleys to pull the wetted and cured material through the die. Based on currently available data from literature, it was found that the typical on-site energy intensity for a

pultrusion process is 1333 BTU/lb of material pultruded [30][31]. Converted into SI units, this is 3.101 MJ/kg.

2.8.1.3 Recycling

To fully consider the energy requirements of a material, it is beneficial to understand the energy impact after the design life of the composite. The energy, environmental impact, and cost required to recycle composite materials shed light on the economic feasibility of GFRP materials as opposed to considering only using brand new raw materials.

In TS recycling, despite the inability to thermoform or melt the material without the degradation of the complex cross-linked chains in a TS polymer-based composite, there exists many methods to partially recycle these materials. This includes extracting raw materials from the composite or creating a variation of new resources from the material at the end of its life cycle. There has been much topic of debate about the recyclability of TS composite materials and much research has gone into trying to find an optimal solution with high yields [32]. This is difficult not only due to the lack of thermoforming abilities in TS composites, but also due to the lack of proper economic markets for these recycled materials and the resources extracted from them [32]. Below are some of the energy demands and yields of conventionally practiced TS composite recycling processes following methods of energy recovery, mechanical recycling, pyrolysis, and fluidized bed processing.

The energy recovery recycling process takes TS composite material at the end of its usable life and converts it into usable heat, electricity, or fuel through a variety of combustion processes [32]. It was determined that “mixing scrap composites at 10% loading [by weight] with municipal solid waste has been shown to be a practical way to dispose of scrap composite materials if landfill is prohibited” [32]. Dumping composite materials into landfills, even where accepted, poses environmental risks and hazards, and should be avoided whenever possible.

The calorific value of a material is the amount of energy dissipated into the surroundings during the complete combustion of that material. This is an important value that indicates the potential energy production possible via the combustion of a certain material. The calorific value for typical TS polymers (using vinyl-ester resin) was found to be 30,000 KJ/kg when incinerated for energy recovery, resulting in an energy gain [32]. Since composite materials are only partially constituted of the polymer matrix by weight, the percentage of which varies from material to material, this calorific value would not be perfectly reflective of the entire composite. The industry standard glass and carbon fibres used for composite materials are mostly incombustible at conventional incineration temperatures, however, therefore having negligible calorific values and a minimal impact on the energy produced [32].

Similarly, the fillers and additives used in manufacturing composite materials are also mostly incombustible or tend to absorb the heat released, which can diminish the overall calorific value that can add to the combustion energy; however, these are again mostly

negligible [32]. For instance, if aluminum trihydrate was used as a filler in a particular TS composite material, this would result in an estimated energy draw of 1000 KJ/kg, which means that even at as high of a concentration of 1:1 with the polymer, the overall calorific value would only decrease by 3.3% [32]. Similarly, if calcium carbonate was used at the high concentration rate of 1:1, it only has an energy draw of 1800 KJ/kg, meaning the overall calorific value has the potential to only drop by a value of 6% [32]. This gives a strong basis for the successful incineration of TS composites for energy recovery.

Mechanical recycling of TS composite materials is easily described as the grinding or shredding of the end-of-life composite product into a mixture of fine powder or granular chunks of small glass fibres and resin matrix [32]. This is a very promising method of recycling, especially for materials that are clean, uncontaminated, and of a known origin like the scraps and cut-offs from manufacturing processes. In a large-scale study of mechanically grinding typical TS composite materials, a specific energy model was created and applied to determine the power required for the machinery used. It was found that the average power draw was 2748W for a typical, small scale machine used within industry for the shredding of composite waste [33].

Using this information, a comprehensive model was adapted to find the additional specific energy required per kg of composite material processed. It was observed by Shuaib and Mativenga that the specific energy required per kg of material processed decreases with an increase in production rate [33]. This is inherently logical, as the

increased speed of the machine accompanies an increased ability to process more waste material without a large power increase.

The application of the specific energy model used in the study was extended to a larger, more heavily used industrial granulator to better predict the specific energy demands that would coincide with large scale recycling plants. For the purposes of the work done by Shuaib and Mativenga, they extended the model to a Wittmann ML2201 granulator [33]. They then estimated the total specific energy demand per kg of material processed to be 1.93 MJ/kg down to 0.17 MJ/kg for a recycling rate as it increases from 10 kg/h to 150 kg/h, respectively [33]. This specific energy demand is significantly lower in comparison to other recycling processes, giving mechanical recycling a very low energy draw and thus making it a very viable economic option [33]. From this study, it was found that recovering products from GFRP composite waste requires much less energy (0.17 – 1.93 MJ/kg) compared to production of virgin glass fibres (10.3 – 45.6 MJ/kg) [28].

Another recycling process, pyrolysis, is high-temperature heating in the absence of oxygen and has been around for a long time for use in industry for coal or wood applications [32]. Over the past 20 – 30 years, several advancements have led to pyrolysis being further developed for use with polymeric materials, like TS and TP composites [34]. Due to the organic nature of the cross-linked polymer chains in TS polymers, the resin polymer matrix is decomposed into smaller chains as it is exposed to this kind of environment. This breaks down the chains into low molecular weight products in the form of solids, liquids, or gases. These have the potential to be used as fuel or chemical

sources. The inorganic materials, such as fibres and calcium carbonate, remain chemically unmodified through the pyrolysis process and can be recycled and reused for future products [34]. Due to the heating requirements of the pyrolysis process, naturally it is most cost effective for use in large scale applications [34]. It was found that the typical range of specific energy demands for recycling via pyrolysis is 3 – 30 MJ/kg [33]. Again, this is due to the high, sustained heat required for the pyrolysis process to take place. The large variation in energy demand can be accounted for the inconsistencies within large scale heating operations.

The fluidized bed process for recycling is an application of a high-heat air stream used to separate the resin matrix of the composite material from the inorganic elements, such as the reinforcing fibres and fillers. Typical operation is at 450 – 550 °C, where a bed of silica sand is fluidized to a velocity of 0.4 – 1.0 m/s [32]. Due to the high heat impacts of the silica sand on the matrix, the polymer volatilizes and oxidizes, thereby decomposing and releasing the fibres and fillers of the material [33]. The polymer resin from the matrix is then subjected to a combustion chamber, where the incineration of the material can provide energy recovery as noted previously. The fibres and fillers can then be collected for recycling or reuse which is further discussed in Appendix A. In an experiment testing the viability of the fluidized bed process for use in industry, the annual electricity and fuel costs were calculated, thus determining the energy usage of a fluidized bed reactor [35]. Estimated for a processing rate of 1 tonne of composite material per hour, running over the course of 6000 hours per year of operation, it was calculated that \$350,045

worth of electricity and \$103,704 worth of methane gas would be required to run the process each year [35].

With the recycling of TP composites, on the other hand, a PhD thesis from Cousins presented information for different recycling opportunities available for TP wind turbine blades [29]. This information can be extrapolated down to the scale of GFRP rebars, if desired. TP composites have more repurposing opportunities available compared to their TS counterparts. TP materials do share some of the same recycling methods as TS composites, however, including mechanical grinding and pyrolysis. Since TP composites are thermoformable, this means existing material can be re-shaped into something new.

The mechanical grinding process for TP composites is the same process as described for TS composites previously. The advantages here are that the process is mature in the industry and relatively simple; however, the reduction in fibre length limits future applications of the material [29]. Potential uses include using the ground material in injection moulding processes, bulk moulding compounds (BMC), and sheet moulding compounds (SMC), allowing the old material to be used as a reinforcement in new products [29]. It was estimated that the energy demand for grinding PMMA-based TP composites is 0.29 MJ/kg [29].

Pyrolysis for TP materials again follows the same procedure as that for TS materials previously. Like grinding, this process is mature in industry; unlike grinding, however, pyrolysis maintains the length of the fibres from the material, expanding the range of

potential reuses [29]. This comes at a loss of the polymer matrix from the material, as well as a degradation of the mechanical properties of the recovered fibres [29]. When pyrolyzing PMMA, the process can be designed such that the monomer from the resin can be recovered for future use, providing more use cases than when using TS polymers, such as vinyl-ester [29]. Similar to the energy recovery process described for TS materials, the combustion of PMMA can also be used to drive processes like pyrolysis or heating kilns by sacrificing part of the polymer since it has a high embedded energy and heat of combustion [29]. The energy demand for the pyrolysis of TP composites was estimated at 1 MJ/kg [29].

There are a number of different types of dissolution processes for recycling plastics. This recycling method is appealing because it allows the individual components of the composite to be recovered with very little material loss and low impacts on the mechanical properties of the components [29]. During dissolution, the composite material is subjected to a polymer-dependent solvent. This solvent would dissolve all of the polymer resin away from the glass fibres and respective fillers in the composite, turning it into a “slurry” mixture of solvent and polymer [36]. From here, the glass fibres can be removed with minimal change in mechanical properties for future reuse, any fillers can be filtered out, and the slurry mixture can be dealt with separately [29] [36]. This includes distillation and evaporation techniques, which are further discussed in Appendix A. For the distillation and evaporation types of dissolution for PMMA composites, the expected energy consumption was found to be 20.0 MJ/kg and 4.0 MJ/kg, respectively [29].

2.8.2 Environmental Impact

The consideration of environmental impact is arguably the most important part of an LCA. The release of carbon dioxide due to some manufacturing processes has long lasting effects in our atmosphere and environment, some of which can be alleviated with recycling.

2.8.2.1 Raw Material Production

It was found that the production of raw materials is a large contributor to GHG emissions in composite materials.

For TS resins, data was again used for existing epoxies from Bachmann et al. [28]. The range of GHG emissions for epoxy resin production was given at 4.7 – 8.1 kg CO₂eq/kg resin based on data from 2 sources [28]. In contrast, a base CO₂eq/kg output of 5900000 mg CO₂eq/kg PMMA produced was found in literature [37]. This is equal to 5.9 kg CO₂eq/kg, which is within the range of the data given for epoxies above. Bachmann et al. also collected references for GHG output of glass fibre production. In this case, a range of 1.6 – 2.6 kg CO₂eq/kg glass was estimated across 3 different sources [28].

As mentioned in section 2.8.1.1, the details on the energy required for OP production were not available. In addition, unfortunately specifics on the CO₂ output from producing OPs was also not available at the time of writing.

2.8.2.2 Pultrusion Manufacturing

As discussed earlier in this thesis, the pultrusion manufacturing process is a highly automated procedure allowing for high rates of production due to its continuous nature. This helps pultrusion be a rather efficient process, meaning GHG emissions are relatively low.

Since the pultrusion process only requires electricity to heat the die and power the motors for the pulleys, there are no effective emissions due to pultrusion at the time of manufacturing. Instead, the emissions are present at the time of energy production, which would be dependent on the amount of energy used and the average GHG output due to energy production at the grid level.

2.8.2.3 Recycling

During the recycling phases, the processes involved all rely heavily on electrical energy to operate. Therefore, average GHG emissions for recycling typically depends on energy consumption for the respective process.

For energy recovery, the CO₂ emissions from burning TS resins was found in literature, with an average CO₂ output from incinerating vinyl-ester resin measured to be 1.87 kg CO₂/kg resin [38]. For fluidized bed processes, however, the equivalent emissions from the methane used can be determined by using a molar ratio of the complete combustion

of the methane gas into CO₂. As noted, no direct GHG emissions data was available for the other recycling processes concerning TS composites.

There also was no direct data for emissions from TP composite recycling, and so information from energy usage may be used to extrapolate what the equivalent environmental footprint would be for each recycling process.

2.8.3 Cost

Cost estimations were available for most of the raw materials required for composite manufacturing. The manufacturing and recycling processes themselves, however, had less information available, as these processes can vary widely and are dependent on the energy required, the unit price of that energy, as well as shape and size of the composite material. For energy consumption in New Brunswick, Canada, power pricing from NB Power is given as \$0.1345/kWh [39].

2.8.3.1 Raw Materials

As discussed throughout, the three main raw materials of GFRP composites are the respective resin used, glass fibres, and OP initiators. Since the resin types are different for the two composite types considered, each has their own associated cost. It was found that the TS resin had a higher unit cost than the TP resin, priced at \$7.47/kg vs. \$3.29/kg, respectively [40][29]. This was interesting, given that TS composites are typically seen as being more economical than TP counterparts. The Pulstrand 4100 (4800TEX) glass fibre

rovings from Owens Corning are estimated to cost \$2.14/kg [40]. Finally, for OPs, each initiator considered was found to have a different unit cost, which can be found in the overall cost structure in Table 2.1 below.

2.9 Summary

As mentioned in this literature review, there are countless different types of composites that can be manufactured, featuring different resins, fibres, and manufacturing processes.

While pultruded composites have been made for quite some time, these have almost exclusively used TS polymers due to viscosity complexities with TP polymers.

Therefore, there is a gap in the current state of composite research for pultruded TP GFRP composite materials. With the existence of a novel TP PMMA resin designed for pultrusion processes, the doors have been opened into researching whether TP composite materials are competitive with existing TS materials in areas like mechanical properties, environmental resilience, and economics, thus achieving the objectives in this study.

Table 2.1: Cost of raw materials for GFRP composites (unit pricing)

Cost	Thermosetting (\$/kg)	Thermoplastic (\$/kg)
Resin	7.47 [40]	3.29 [29]
Glass	2.14 [40]	2.14 [40]
OPs	<ul style="list-style-type: none"> • NOROX 500-750MS = 23.2 [41] • NOROX TBPB = 17.4 [41] • NOROX Pulcat AMB = 59.29 [42] 	<ul style="list-style-type: none"> • Perkadox 16 = 48.51 [40] • NOROX TBPB = 17.4 [41]

Chapter 3 Methodology

The three pillars of this research (pultrusion manufacturing, mechanical/environmental testing, and LCA) required their own set of specific methods for completing the objectives. As such, this chapter will be divided into three subsections.

3.1 Composite Manufacturing

3.1.1 Materials

The components used in this pultrusion process started out as raw materials. The new PMMA TP polymer was acquired in a liquid form with the requirement to store the polymer at room temperature, not exceeding 50°C, such that the polymer remains in a liquid state. A collection of OP initiators was combined with the TP resin to accelerate the free radical polymerization process [43]. These included NOROX TBPB (tert-butyl peroxybenzoate) and NOROX 500-75OMS (75OMS) from United Initiators, and Perkadox 16 from AkzoNobel. The glass rovings used in the pultrusion process were the Pulstrand 4100 E-glass product from Owens Corning Canada (Mississauga, ON), which are a continuous, unidirectional roving designed for pultrusion. The rovings are of 4800 TEX size with a glass density of 4.8 g/m. The liquid lubricant used in the pultrusion process is known as 190-TG from Technick Products (Montreal, QC). During the experimental process, additives were also used, including Kaolin, aluminum oxide, and methyl methacrylate (MMA), to determine if combining these with the PMMA resin would improve mechanical and bonding properties. A collection of these raw materials is shown in Figure 3.1 below.



Figure 3.1: Materials used for pultrusion manufacturing. From left to right: lubricant, resin, glass fibre roving, initiators, and fillers.

3.1.2 Resin Preparation and Mixing

Prior to pultrusion manufacturing, the PMMA polymer, a proprietary combination of OP initiators, lubricant, and any additives were first measured out according to the design of experiments (DoE) being used and were all added to a paint mixing bucket. The components were then blended using a glass stir stick until mixed well such that no clumps were present in the mixture. In the event adequate mixing was not achieved using a stir stick, a $\varnothing 2$ " paint mixer attached to a drill or drill press was used to gain better mixing results. Once the polymer had been prepared, it was then poured into the resin bath of the pultrusion machine.

3.1.3 Pultrusion Manufacturing

The pultrusion machine used for this research was an in-house, custom-designed and -built machine. This machine was designed for TS composite production; however, this same set-up was also used for TP production with modifications. The pultrusion set-up is shown both pictorially and schematically in Figure 3.2 - Figure 3.4 below.

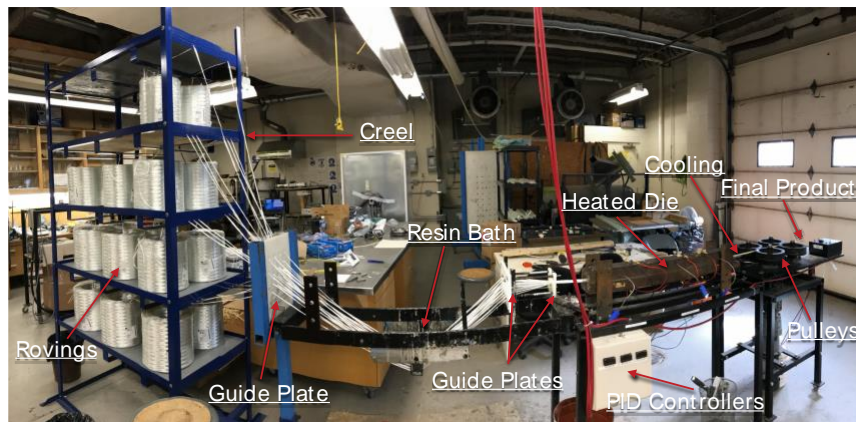


Figure 3.2: Side view of pultrusion set-up



Figure 3.3: Top view of pultrusion set-up

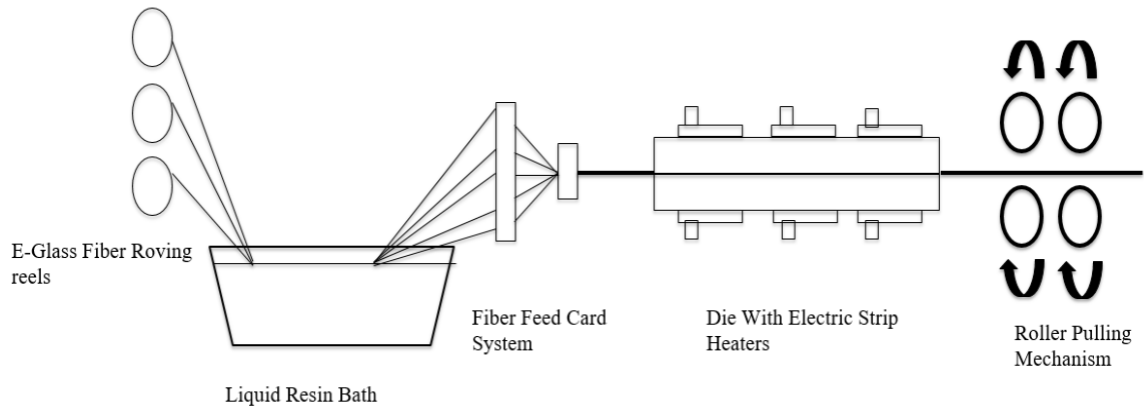


Figure 3.4: Pultrusion diagram [16]

The creel on the left, shown in Figure 3.2, marks the beginning of the pultrusion machine, storing the dry, continuous E-glass fibre rovings. These rovings pass through individual holes in a guide plate before entering a resin bath where the TP polymer is soaked and impregnated into the dry fibres. The wetted fibres then pass through a series of guide plates until the wetted product is in the shape of the inside of the die, in this case a rebar. This non-polymerized product then enters the heated die, which is 90 cm in length. The die is heated from the top and the bottom using three pairs of electric strip heaters, and the temperature for each pair is adjusted via PID controllers that take input from a series of T type thermocouples which are inserted into the midsection of the die. While the resin and fibres are passing through the heated die, pulleys at the end of the process are pulling the product. These pulleys feature a circular hole passthrough such that the shape of the rebars is retained as much as possible. The pulleys are controlled via a dial and switch system which allows the pulling speed to be adapted or turned off on the fly in case of manufacturing defects or emergency. In a typical TS set-up, the rebars are completely

solid upon exit. With TP polymers, however, the rebars are still slightly pliable to the touch due to the thermoformable nature of the resin. As such, a cooling section/die is commonly installed to allow the pultruded product to solidify completely. Incorporating a cooling die was not ideal for this particular machine, and so the composite rebars were actively and continually cooled upon exiting the heated die with convective heat transfer via a hair dryer on a cool setting, acting as the cooling section for this pultrusion process. This allowed the TP GFRPs adequate cooling time to reach room temperature, thus shifting away from its thermoformable state. Finally, the solid rebars were manually cut with a saw to their desired length (typically 1 m) during the continuous process and each rebar was labelled with a unique identifier. This set-up is shown in Figure 3.2 and Figure 3.3, with a schematic representation shown in Figure 3.4, above.

The composite materials produced via the pultrusion manufacturing process were $\varnothing 9.5$ mm rebars that use continuous, unidirectional glass fibres as reinforcements, examples of which are given in Figure 3.5. These produced composite materials were $\sim 75\%$ glass, by volume.



Figure 3.5: Lab-manufactured and -tested TP (top) and TS (bottom) GFRP specimens

3.1.4 Design of Experiments

During the composite manufacturing experimentation phase of the research, a total of 17 experimental manufacturing formulas were developed and attempted. These formulas, or ‘recipes’, tested the quantitative and qualitative effects on the manufactured GFRPs from varying the conditions of initiators, additives, heating, and pulling speed. Each recipe was designed based on the data acquired from previous experiments until an acceptable formula was developed. For the sake of brevity, an overview of these recipes is described in Chapter 4 of this thesis.

3.1.5 Microstructural and Porosity Analysis

For analyzing the microstructural qualities and porosity presence estimation in the developed GFRP materials, 3D optical profilometry was used in conjunction with ImageJ software analysis. This allowed for the comparisons between the developed recipes to be made throughout the experimental phase of production. The goal was to determine the percentage of porosities in the cross-section of the analyzed specimens, providing insight to the bonding properties of the tested materials, in turn ensuring the developed materials did not exceed an acceptable porosity percentage of 5%, as per the average represented figure in the closest standard with ASTM E2109 [44]. Composite materials development was therefore continued until an acceptable material within this 5% porosity range was manufacturable.

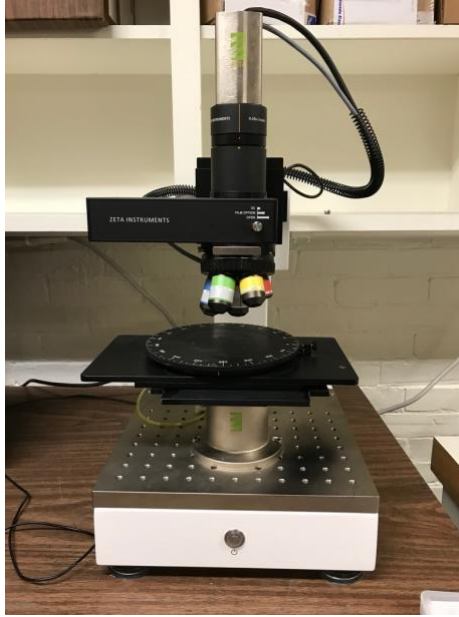


Figure 3.6: Zeta Optical Profiler from Zeta Instruments

3D microstructure images were captured using a Zeta Instruments Optical Profiler, as shown in Figure 3.6 above, which interfaces with the Zeta 3D software package for displaying and collecting data.

Within ImageJ, the captured microstructural images from optical profiler were imported and the colour of each image was split into three separate channels: red, green, and blue. The colour channel with the most contrast was selected, at which point the black and white threshold on the image was adjusted such that the porosities in each image were classified as being white, whereas the remainder of the composite material was classified as black. Once completed, a script was used to determine the area percentage of white in each image, providing an estimated value of the porosity percentage within the cross-section of the respective composite.

3.2 Mechanical and Environmental Testing of Pultruded GFRP

To gain knowledge and understanding of how the novel TP pultruded GFRP composites compare to the existing TS composites, a comprehensive reliability testing plan was developed. As per suggestions from the ASTM D790 standard, five rebars from each experimental formula underwent a series of heat/UV/water exposure tests in a Weather-Ometer chamber, cold weather exposure tests in a laboratory freezer, and 31-day immersion testing in high pH (12.6) corrosive caustic bath solution [45]. After each of these environmental exposure procedures were performed, the composite materials were then subjected to a 3-point flexural bending test.

3.2.1 Environmental Testing

The experimental materials under investigation were identified for testing purposes as TS# (thermosetting polymer) and TP# (thermoplastic polymer). One batch of each composite material was independently subjected to each of the exposure conditions listed in Table 3.1: heat/UV/water testing as described by the ASTM D2565 standard [46], cold environment, and corrosive caustic bath immersion. A final group of specimens was used as a control group that incurred no environmental experimentation. This resulted in effectively 4 material treatment groups for environmental testing. With 2 different materials under consideration, and 5 specimens per material per group (5 specimens each for flexural testing), this resulted in 40 required specimens in total for the purposes of these environmental tests. An overview of the specimens required from these tests is given in Table 3.2 below. From these specimens, a total of 6.6 m of pultruded GFRP

product was required for each material type to complete all of the environmental experiments outlined.

Table 3.1: Summary of environmental testing procedures [46] [47]

Exposure Test	Environment	Apparatus	Duration
Heat/UV/ Water [46]	Light: 47°C air temperature, 50% relative humidity, 0.35 W/(m ² nm) irradiance, periodic water spray Dark: 38°C air temperature, 95% relative humidity, no water spray	Atlas Ci4400 Weather-Ometer	24 hours per cycle: Light: 18 hours, alternating 102 minutes of light, followed by 18 minutes of light and front spray (9 repeats), Dark: 6 hours 3 cycles, 72 hours of exposure time
Cold	-38°C	Revco ULT2500-Series Upright Laboratory Freezer	72 hours of continuous exposure time
Corrosion [47]	A caustic bath solution (pH 12.6) with a composition of 118.5 g of Ca(OH) ₂ , 0.9 g of NaOH, and 4.2 g of KOH in 1 litre of tap water, with enough solution to completely submerge all rebars.	Custom built corrosion chamber made out of PVC piping.	1 month (31 days)

Table 3.2: Required specimens for environmental testing comparisons prior to flexural testing

Specimen Type	Control	Heat/UV/ Water	Cold Environment	Corrosion
Thermoplastic (TP#)	5 x 33 cm rebars	5 x 33 cm rebars	5 x 33 cm rebars	5 x 33 cm rebars
Thermosetting (TS#)	5 x 33 cm rebars	5 x 33 cm rebars	5 x 33 cm rebars	5 x 33 cm rebars

Environmental testing was important to perform on composites to gain knowledge of how prolonged exposure to sustained weathering cycles impacted the mechanical performance of the GFRP in question. Each of these exposures was performed separately to determine the uncoupled environment effect on each material type. As presented in Table 3.2, five specimens of each recipe were subjected to the respective environment prior to flexural testing. Each rebar was dip-coated in LePage Professional Speed Set™ epoxy resin to protect the cut faces of each rebar prior to exposure, as per the ASTM D7705 Standard [47], in order to better reflect the true exposure scenarios for the GFRP. GFRP rebars are typically dip-coated to prevent moisture from entering through the face cuts on either end of the rebar. Representative as-is test samples (prior to being dip-coated) are shown in Figure 3.7.



Figure 3.7: Unexposed GFRP rebar samples

3.2.1.1 Heat, UV, and Water Exposure Testing

The heat/UV/water exposure testing was performed at the UNB Wood Science and Technology Centre (WSTC) located at the Hugh John Flemming Forestry Centre in Fredericton, NB. In order for the rebars to be mounted into the testing apparatus, each specimen had two holes of 3/32” in diameter drilled through the cross-section of the rebars at opposite ends of the specimen. This was done in order to accommodate two steel mounting wires that were placed through each specimen during mounting.

The ASTM D2565 designation titled ‘Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications’ [46] was followed for these exposure tests. In order to simulate the environments required, these tests took place within an Atlas Ci4400 Weather-Ometer, with each operating parameter (irradiance, internal chamber temperature, rack temperature, relative humidity, etc.) specified (as per the ASTM D2565 Standard). All respective specimens from the two material groups were exposed to this environment during the same testing procedure, lasting three full cycles (24 hours each) as defined by the ‘2A’ cycle number from the standard, for a total of 72 hours of exposure time [46]. After each full cycle was completed, the Weather-Ometer was opened and the GFRP composites were inspected to ensure the rebars were still secured within the chamber. The Weather-Ometer apparatus is shown in Figure 3.8. Once the three cycles of exposure from ASTM D2565 were completed, the composite specimens were dismantled from the internal exposure space and the steel mounting wires were removed.



Figure 3.8: Atlas Ci4400 Weather-Ometer at WSTC

3.2.1.2 Cold Environment Testing

The cold environment testing was also conducted at the UNB WSTC in Fredericton, NB. The specimens were placed in a Revco ULT2500-Series Upright Laboratory Freezer, as shown in Figure 3.9 below, at a controlled temperature of -38°C with no thermal ramping. At this temperature, humidity and moisture could not be controlled as any moisture content would freeze almost instantly. All GFRP composites were placed into the freezer in a circular bundle wrapped in paper towel and stored in this environment for a continuous period of 72 hours. Once this testing was completed, the rebars were removed from the freezer and adequate time was allowed for the rebars to return to room temperature before each post-testing specimen was subjected to a 3-point bend test.



Figure 3.9: Revco ULT2500-Series Upright Laboratory Freezer

3.2.1.3 Corrosion Testing

It is possible for corrosive environments to negatively affect the mechanical performance of composites. To examine how each GFRP material deals with harsh environments, the GFRP composites were subjected to a caustic bath solution for an extended period of time. This testing was performed in UNB's NCM Lab. The caustic bath solution was produced using the recommended alkaline solution from the ASTM D7705 Standard titled "Standard Test Method for Alkali Resistance of Fibre Reinforced Polymer (FRP) Matrix Composite Bars used in Concrete Construction" [47]. As described in section 8.7 of the standard, "the suggested composition of alkaline solution consists of 118.5 g of $\text{Ca}(\text{OH})_2$, 0.9 g of NaOH, and 4.2 g of KOH in 1 litre (33.8 fl. oz.) of tap water" [47]. An

adequate amount of this solution with a pH of 12.6 was made to fully submerge all GFRP specimens for the duration of the test, which lasted for a period of 31 days.

In order to contain the caustic bath solution and sample testing, a testing chamber was custom-designed and -manufactured using PVC piping. This chamber was comprised of 4" diameter PVC pipe, with end caps attached to either end. The bottom end cap was secured in place with contact cement, and the top end cap was cut and sanded down to facilitate easy removal. Plastic wrap was placed between the open top of the cylinder and the top end cap to minimize the evaporative moisture loss. Inside the cylinder, a custom guide plate with precut holes was press-fit to keep all samples separated during submersion. This cylinder is shown in Figure 3.10.



Figure 3.10: Caustic bath corrosion chamber

Once each of the hydroxide components to the caustic bath were measured out, the solution was mixed in an unused 20-gallon paint bucket at first by hand, and then finally with the use of a paint mixer attached to a drill press. Each of the GFRP composite rebars were then placed into the guide plate holes within the empty cylinder, after which the caustic bath solution was carefully poured into the cylinder, completely submerging each rebar. The plastic film and the top end cap were then placed on the top of the cylinder, and all composites remained in this caustic solution for the entirety of the 31-day period. Once the one-month submersion period was completed, the rebars were removed one at a time from the caustic bath using a pair of metal tongs. The composites then went through a cleaning process to remove any residual liquid or solids from the caustic bath solution and were allowed to dry.

After all of the environmental testing was completed, flexural analyses (as described in section 3.2.2) were resumed to gain further knowledge on how subjecting GFRP rebars to these environments affected their mechanical properties compared to those of the standard GFRP control rebars. The results from these testing procedures are found in Chapter 4.

3.2.2 3-point Flexural Testing

As noted in section 2.7, there is debate over whether conducting tensile testing on unidirectional composites is advisable considering the associated difficulties [27]. For the case where the newly developed TP composite material is used to manufacture

interlocking sheet piling for marine applications, the typical loading configuration would be better represented by a bending or flexural test; the sheet piles would incur stress and impact from waves and boats, for example, resulting in flexural stress and strain on the materials between their respective supports. Therefore, to determine the mechanical properties of the tested materials such as Young's modulus, stress-strain relationships, load, and deflection qualities, flexural testing in the form of a 3-point bending test was performed according to the ASTM D790 Standard [45]. Whereas the majority of the tensile strength in unidirectional composites comes from the reinforcing fibres, there is little effect dependent on the polymer matrix used. In a flexural test, however, the combination of both tensile and compressive qualities are assessed resulting in a more holistic evaluation of the material in question [16].

The manufactured and environmentally exposed GFRP rebars were cut to 33 cm in length and placed horizontally within the supports of an Instron SATEC Model T10000 Materials Testing System, which was modified to support a 3-point bending test set-up, as shown in Figure 3.11. This system was controlled via the Instron Partner™ Materials Testing Software, which recorded deflection values in mm, force applied in Newtons, as well as the time in seconds at which each data point was collected. This data was saved as a .csv file for each rebar tested, after which all of the datasets were imported into MATLAB where force-displacement and stress-strain curves were produced, as well as the calculations for the Young's modulus and maximum force, stress, and deflection values of each rebar.



Figure 3.11: Instron SATEC Model T10000 Materials Testing System

These bending tests have provided the mechanical properties for each rebar, allowing comparisons to be made from the TS and TP pultruded GFRPs. These tests also allowed for comparisons to be made between recipe differences for the novel thermoplastic rebars.

3.2.2.1 Flexural Calculations

The ASTM D790 Standard was followed for performing the flexural property calculations, which is designed for determining the flexural characteristics of FRP materials in a 3-point bending test setup [45]. The calculations used to determine the

flexural stress (or flexural strength), flexural strain, and Young's modulus are outlined in Equation 1 – Equation 3 below.

$$\sigma_f = \frac{FL}{\pi R^3} \quad \text{Equation 1 [45]}$$

$$\epsilon_f = \frac{6Dd}{L^2} \quad \text{Equation 2 [45]}$$

In Equation 1 and Equation 2, 'F' is the load applied in Newtons, 'L' is the span between the two supports of the 3-point bending test in mm, 'D' is the deflection measured in mm, 'd' is the original diameter of the circular rebar tested in mm, and 'R' is the original radius of the rebar in mm [45].

$$E = \frac{\sigma_{f2} - \sigma_{f1}}{\epsilon_{f2} - \epsilon_{f1}} \quad \text{Equation 3}$$

To determine the Young's modulus, the difference in stress was divided by the difference in strain when taking two data points from a straight-line path of the stress-strain curve, as shown in Equation 3. The average of the Young's moduli from the specimens tested for each material, as well as the maximum load, displacement, and stress values were plotted on separate bar graphs for the experimental formulas tested, including their respective standard deviations, as shown in Chapter 4.

3.2.3 Statistical Design

In order to compare the mechanical differences between the two materials subjected to the four environmental exposure conditions, a statistical design was implemented. This was represented by a 2x4 factorial design, since there are two factors involved: one factor

with 2 levels (material type), and one factor with 4 levels (exposure type) [48]. The metric considered for comparison was the flexural strength (or maximum flexural stress) of the composites, as calculated by the 3-point flexural bending tests conducted.

The calculated data (see in Appendix B) was imported into Minitab, where a general linear model was used to analyze this design. The model implemented was as follows:

$$y_{ijk} = \mu + \tau_i + \gamma_j + \tau\gamma_{ij} + \epsilon_{ijk} \quad \text{Equation 4}$$

where the variables in the model represent:

- y_{ijk} = measured flexural strength for the i 'th material, j 'th environmental exposure, and k 'th replicate.
- μ = population mean for all pultruded GFRP specimens
- τ_i = material type factor at the i 'th level, 2 levels (TP and TS)
- γ_j = environmental treatment group factor at the j 'th level, 4 levels (control, corrosion, cold, UV)
- $\tau\gamma_{ij}$ = interaction between the material type and environmental treatment group factors at the i 'th and j 'th levels
- ϵ_{ijk} = random error associated with the k 'th sample for the respective group material type and environmental treatment group

The population mean is the mean of every possible GFRP specimen as produced by the in-house pultrusion machine at the NCM lab. Since it is impossible to manufacture and

test every possible piece of composite material, this value is impossible to know. In this model, both the material type and environmental treatment group factors are fixed effects, in that the influence of each of these factors on the final flexural strength is not random, but rather can be estimated to some extent through testing. The error, however, is always random, since there will always be slight variations or noise in any statistical test that are out of control of the observer.

Prior to performing the statistical analysis using the general linear model according to Equation 4, a number of assumptions must be checked: the data is normal, the samples were independent of one another, the samples were collected randomly, and that there is constant variance. For the tests performed, a confidence interval (CI) of 95% and a significance level of $\alpha = 0.05$ were chosen [48]. Results from this analysis are given in Chapter 4.

3.3 Composite Life Cycle Analysis

An LCA of a material or product can be viewed in many different ways [49]. Generally speaking, looking at the material in question from birth to death is important to ensure all respective contributions are taken into account. Therefore, a life cycle framework (LCF) was developed to consider how the individual stages of the life cycle, each having their own inputs and outputs, participate to complete the overall life cycle of a composite material. These stages, shown in Figure 3.12, are: 1) raw materials production; 2) composite manufacturing; 3) useable life; and 4) reuse and recycling.

The life of a composite material begins during the raw materials production stage. Here is where glass fibre, resin, and other material constituents are produced. Each process in this stage of the life cycle requires energy, money, and respective precursor matters, which all act as inputs for this stage. Concerning the precursor matters stage, the relevant outputs are the raw materials themselves, so are the equivalent carbon footprint from each process. An overview of this life cycle flowchart is shown schematically in Figure 3.12.

Once the raw materials have been produced, these materials are then brought together to produce the novel composite materials. Here, the previously manufactured raw materials, energy, and monetary costs all act as inputs for this stage. Energy and money are required for the composite manufacturing process to function, and raw materials are combined to produce the new composite. As expected, the outputs from this stage are the newly manufactured composite material and a carbon footprint derivative of the manufacturing process.

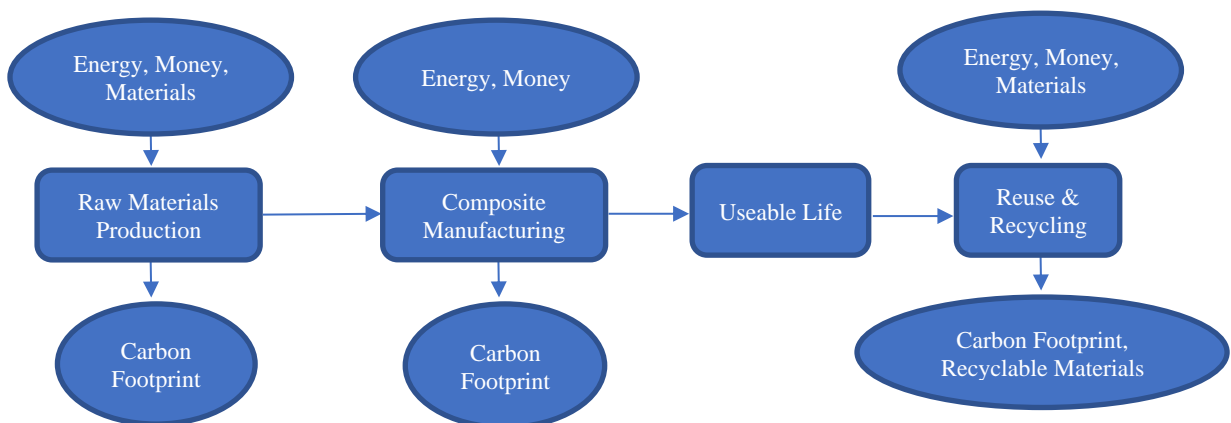


Figure 3.12: LCF of the individual life cycle stages, used in the current study

With the composite materials manufactured, they can now live out their intended use in the useable life stage. During the design life of the material, it was assumed that there is typically no energy or money required to maintain the material, and thus no carbon footprint as a result. This is dependent on the material and situation; considering every possible scenario of composite use, however, is beyond the scope of this analysis.

After the material has performed its service over its usable life, the composite material is ideally reused or recycled, further extending the actual life of the material. The available recycling or reuse processes in this stage of the life cycle will vary depending on the material type, size, shape, etc., and are further discussed in Appendix A. What are generally common amongst any recycling process, however, are the inputs of: end-of-life composite material, energy, money, and consumable materials required for further processing. These components can be quantified on a case-by-case basis. The outputs of recycling processes are also generally similar; this includes reusable material of some sort and a carbon footprint from the processes used.

With the inputs and outputs from each stage of the material life cycle outlined, the LCF was defined. Since each process of the various life cycle stages for a composite material is very different, it was crucial to establish a baseline on which all processes could be compared in an equal and objective manner. This was especially important since multiple material types were compared in this analysis.

The common components from each process in each stage of the composite material life cycle were consolidated to just three areas of focus: energy usage, environmental impact, and economics. Energy and money acted as the common inputs in this regard, whereas the carbon footprint was seen as the common output.

The processes implemented in each stage of the life cycle require energy and money to operate. While the processes implemented may vary between stages and material types, their energy and costs could be reduced to base units (Joules and dollars, respectively). From all processes throughout the life cycle, there is some form of carbon footprint associated. The energy required to power these processes is almost never 100% renewable in today's landscape, whether that is from electricity production or some other means of energy, thus resulting in some amount of CO₂ being released into the atmosphere. This was increasingly important to consider as the environmental impact of all engineering operations around the world must be ethically monitored and adjusted in order to reduce the negative effects of climate change. This also makes the recycling aspect of composites crucial to further reducing these effects, with details on various recycling options provided in Appendix A.

Therefore, these two common inputs and one output became the areas of interest or components for this LCA. The generalized LCF of how these components interact within each process is shown in Figure 3.13. Since this analysis studied the differences between two material types, TS and TP composites, it made sense to analyze each material side by side according to each component of the LCA. Thus, each section of the LCA focussed

on a particular LCA component: energy use, carbon footprint, and cost. Within each section, every process from each stage of the material life cycle was analyzed according to that particular LCA component, providing direct comparisons between the two material types, as desired, thus achieving the objectives straight out.

In some cases, most notably with OPs, some LCA data was not available. For the sake of simplicity, it was assumed that the LCA impact of OP initiators was the same with both polymer types since supporting data was not available. Composite materials can often contain fillers in the polymer matrix, however, these were neglected from this analysis.

In order to simplify comparisons, all metrics were converted into SI units, currency was converted to Canadian Dollars, and all calculation results related to the LCA were rounded and truncated to 4 significant figures. This may affect the totals presented in the respective tables.

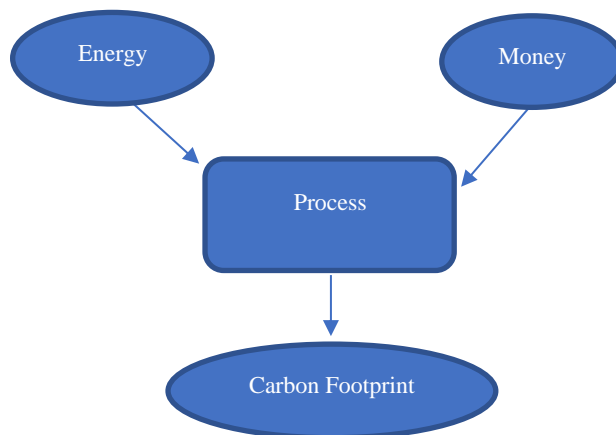


Figure 3.13: Generalized LCF describing the components required for a generic process in composite manufacturing



Figure 3.14: Jerricans of TP (left) and TS (right) resins

3.3.1 Materials and Processes Considered

Finally, the composite materials considered under this analysis were the same pultruded $\varnothing 9.5$ mm rebars as described in section 3.1.1. Two resin types for the composites produced were reviewed: TS vinyl-ester, and the novel TP PMMA. In cases where data for vinyl-ester resin was lacking, said data for epoxy resins was used, due to similarities. Jerricans of the resins used are shown in Figure 3.14 above.

3.4 Summary

The methods for composite materials development were designed to allow a novel TP GFRP composite material to be manufactured in a lab setting for further testing. This

testing was then conducted to determine the mechanical and environmental properties of the developed TP materials and compare them to existing TS GFRP materials. Finally, with the LCA, the impacts of both TP and TS composite materials were investigated in terms of energy requirements, GHG emissions, and economics.

The combined experimental and empirical research methodologies outlined above enabled the three pillars of this research to stand on their own before coming together in Chapter 4.

Chapter 4 Results and Discussion

4.1 Composite Manufacturing

As discussed in section 3.1, the composite manufacturing stage of the research was completed according to a series of experimental designs in order to develop a manufacturable material with acceptable microstructure qualities. For the sake of brevity, a reduced overview of the experimental formulas or recipes developed is provided in Table 4.1.

Table 4.1: Summary of recipes developed

Recipe	#2	#8	#17
Fibre	22 Rovings of "Flexstrand 700" glass fibre.	22 Rovings of "Flexstrand 700" glass fibre.	20 Rovings of Owens Corning Pulstrand 4100 glass fibre.
Resin	(1000 mL) @ 100 pphr	(1000 mL) @ 100 pphr	(1000 mL) @ 100 pphr
Lubricant	Technick Products 190-TG	Technick Products 190-TG	Technick Products 190-TG
Initiators and Additives	Perkadox 16	- MMA, - NOROX TBPB (tert-butyl peroxybenzoate), - NOROX 500-75OMS, - Perkadox 16	- NOROX TBPB, - Perkadox 16
Heating	Heater #1: 110 °C, Heater #2: 110 °C, Heater #3: 80 °C, Setpoint +/-: 1 °C	Heater #1: 100 °C, Heater #2: 100 °C, Heater #3: 65 °C, Setpoint +/-: 1 °C	Heater #1: 110 °C, Heater #2: 110 °C, Heater #3: 110 °C, Setpoint +/-: 1 °C, Cooled with hair dryer upon exit.
Pulling Speed	0.3 m/min, Dial Reading: 40	0.055 m/min, Dial Reading: 15	0.15 m/min, Dial Reading: 22.5

With Recipe #2, minimum amounts of initiator were used, and the wetted glass fibres were pulled at a speed of 0.3 m/min. When material exited the heated die, however, the pultruded product was not solid. This was attributed to a combination of not enough initiator and too high of a pulling speed. To correct for this, more initiator and a slower pulling speed were then used in subsequent experiments.

In Recipe #8, three initiators were used for polymerization, and the proportion of initiator with respect to the resin was drastically increased. As noted in Chapter 2, this increase and diversification of initiators was chosen to control the rate and degree of polymerization. In previous experiments, cross sections of the pultruded material were found to have large porosities when viewed under a microscope. It was hypothesized that perhaps these porosities could be due to a lack of resin impregnation in the fibre which could be related to the viscosity of the resin used. Therefore, MMA was used as a diluent in this experiment with the goal of decreasing the viscosity of the resin to potentially improve the impregnation of the resin into the fibre rovings. The pultrusion machine pulled at a much slower speed of 0.055 m/min, which allowed a solid product to exit the die. This solid product was analyzed with 3D optical profilometry, which still showed porosities in the cross section of the material (shown as the dark areas in Figure 4.1). Since these porosities were still present, the conclusion was made that diluting the resin with MMA did not achieve its intended goal and was therefore omitted from future experiments. Porosities were an issue throughout development, which led to researching different methods for increasing bonding within composite materials.

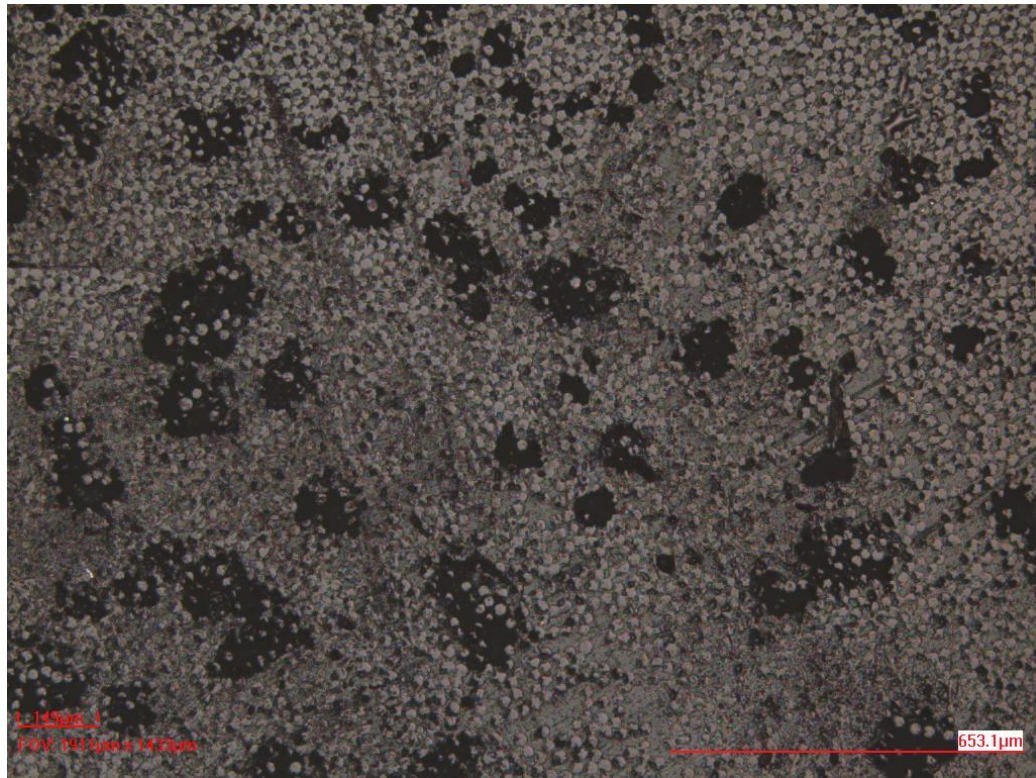


Figure 4.1: Microstructure of a cross section of a rebar from Recipe #8, 5x magnification

With the microstructure captured for Recipe #8, ImageJ photo analysis was conducted as per section 3.1.5. It was estimated from the analysis that the porosity area percentage was 13.5%, which is far above the 5% goal throughout the composite manufacturing stage and leaves room for improvement. The high contrast image in Figure 4.2 below is the black and white conversion of the image in Figure 4.1 previously.

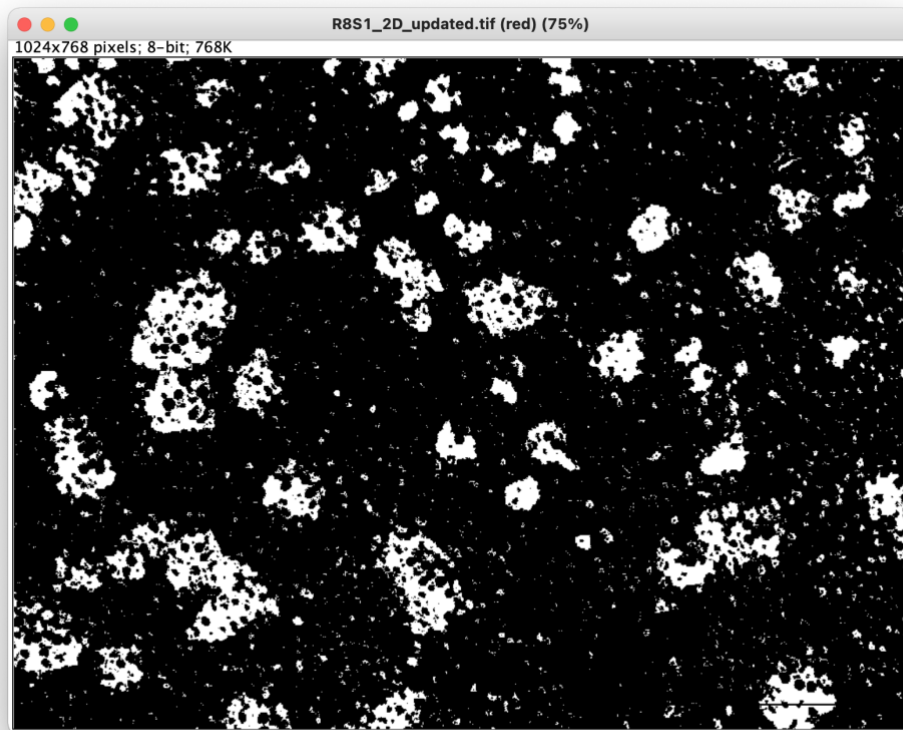


Figure 4.2: Microstructure image for Recipe #8 converted to black and white.

The final experimental formula designed, Recipe #17, uses less initiator than in Recipe #8 previously, while pulling at a faster rate of 0.15 m/min. This lower amount of initiator used was designed to be more efficient in the way initiator is used in the manufacturing process. As mentioned in Chapter 2, the solution to a lack of polymerization in composite manufacturing does not always mean to add more initiator; it is possible to add too much initiator to the resin, which may result in a peroxide oversaturation within the resin, thus reducing the effectiveness of the polymerization process [23]. Using more initiator than what is necessary also results in a waste of consumable materials and subsequently

increased costs. For a TP polymer, this could mean an increase in the number of shorter polymer chains, as opposed to the desired longer polymer chains that give the TP its strength [23]. This experimental formula also used a slightly higher glass percentage than previous recipes, bringing the estimated glass percentage in the composite to 75% by volume, with the intention of helping decrease porosity levels and increase compaction on the cross section of the material. Testing the manufacturing process at a higher pulling speed was an attempt to gain some time efficiencies in the process; the faster the pulling speed, the more material a manufacturing plant can produce in a given day. In industry, pulling speeds vary depending on the size and profile of the pultruded component, however, for a similar $\varnothing 9.5$ mm profile to the composites manufactured in this study, a pulling speed range between 250-300 mm/min would be typical [40]. The solid material from this experimental design was cooled upon exiting the heated die with a hair dryer to prevent shape distortions as the pultruded rebars passed through the pulleys, as referenced in section 3.1.3.

The material was also analyzed using 3D optical profilometry show in Figure 4.3, which exhibited a lower proportion of porosities than other recipes. After converting this image to black and white in Figure 4.4, the porosity area percentage was estimated at 5.2%, which is a close approximation to the porosity density goal of 5%. The combination of fewer porosities, less initiator used, and a faster pulling speed resulted in a material suitable for further testing.

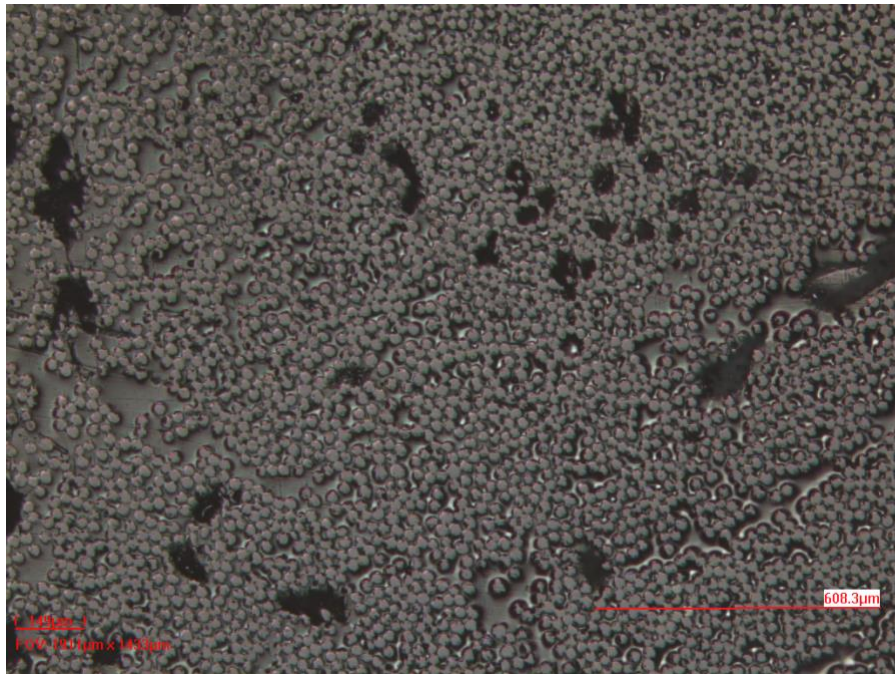


Figure 4.3: Microstructure of a cross section of a rebar from Recipe #17, 5x magnification

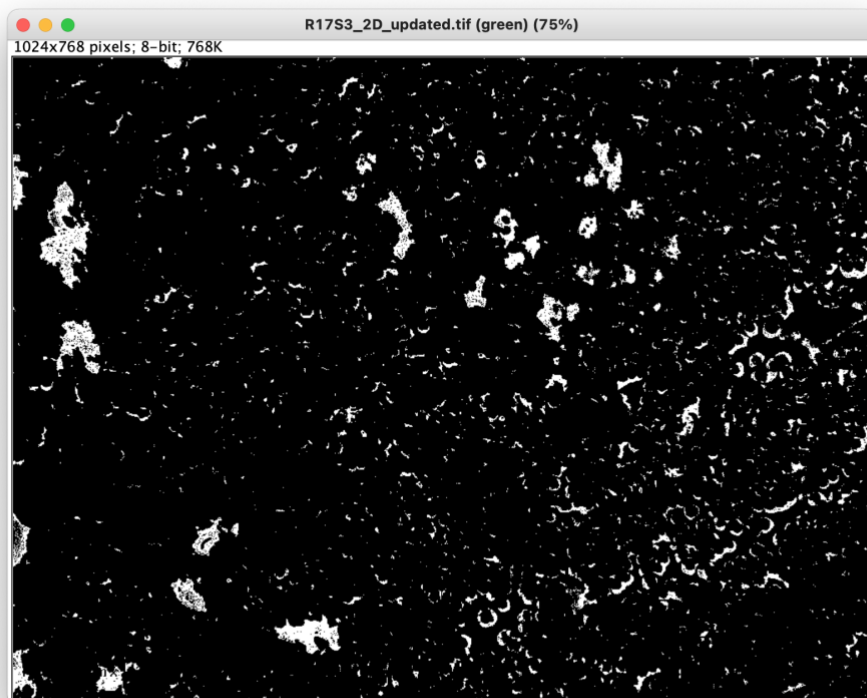


Figure 4.4: Microstructure image for Recipe #17 converted to black and white.

Once the initial phase of composite manufacturing experimentation was complete, the TP experimental formula was adapted to determine if incorporating fillers into TP polymer resins improved mechanical properties in the produced composites. Three experiments containing fillers were conducted and the manufactured specimens were compared to control TP and TS rebars.

GFRP rebars were produced using aluminum oxide (Al_2O_3) as a filler at 20% and 30% by weight, as well as kaolin (obtained from Composites One, Montreal, QC) at 20% by weight. Each of the rebars produced contained the same percentage of glass fibre, estimated to be 75% by volume. Two control rebars were also produced, one using the novel PMMA-based TP, and the other using a vinyl-ester TS resin, for a total of 5 rebars under investigation. All TP experiments used the same chemical percentages, meaning the same percentages of resin, lubricant, initiators, and glass were used to determine the difference between the various fillers and percentages used. The TS rebars also used the same glass fibres, however, the chemistry, heating, and pulling set-up was adjusted for the vinyl-ester polymer composition. These experiments are outlined in Table 4.2 below.

Table 4.2: Experiments developed for filler exploration

Recipe	Resin	Initiators	Additives	Heating	Pulling Speed
Al₂O₃ – 30 %	PMMA	- NOROX TBPB, - NOROX 500-75OMS, - Perkadox 16	Aluminum Oxide @ 30 % by weight	Heater #1: 110 °C Heater #2: 110 °C Heater #3: 110 °C	0.15 m/min
Al₂O₃ – 20 %	PMMA	- NOROX TBPB, - NOROX 500-75OMS, - Perkadox 16	Aluminum Oxide @ 20 % by weight	Heater #1: 110 °C Heater #2: 110 °C Heater #3: 110 °C	0.15 m/min
Kaolin – 20 %	PMMA	- NOROX TBPB, - NOROX 500-75OMS, - Perkadox 16	Kaolin @ 20 % by weight	Heater #1: 110 °C Heater #2: 110 °C Heater #3: 110 °C	0.15 m/min
Thermoplastic	PMMA	- NOROX TBPB, - NOROX 500-75OMS, - Perkadox 16	None	Heater #1: 110 °C Heater #2: 110 °C Heater #3: 110 °C	0.15 m/min
Thermoset	Vinyl-Ester	- NOROX TBPB, - NOROX 500-75OMS, - NOROX PULCAT AMB	None	Heater #1: 120 °C Heater #2: 150 °C Heater #3: 150 °C	0.33 m/min

After the GFRP rebars based on the recipes above were manufactured, 5 x 33cm specimens from each experiment group were subjected to a 3-point flexural bending test, as described in section 3.2.2. The raw data from these tests was imported into MATLAB where further calculations were performed. In order to draw comparisons between the materials in question, the maximum flexural stress (or flexural strength) of each specimen was determined. With 5 specimens per material type tested, the average flexural strength measure was plotted along with their respective standard deviations, which can be found in Figure 4.5.

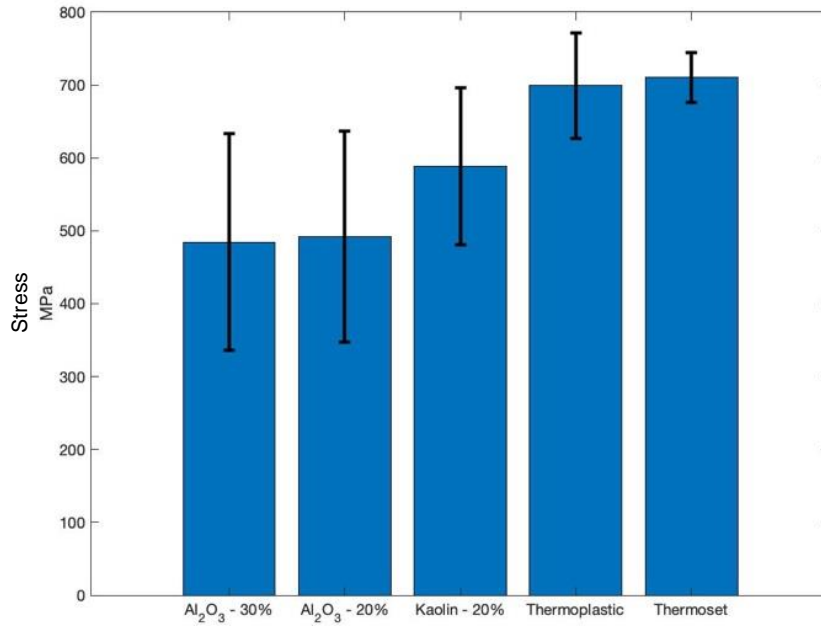


Figure 4.5: The average range of the maximum stress value for all 5 experiments

These bar graphs are also summarized numerically in Table 4.3 below, featuring the average values for each metric calculated.

Table 4.3: Average values of flexural strength for each of the 5 experimental materials tested

Experiment	Flexural Strength (MPa)
Al ₂ O ₃ – 30 %	484.69
Al ₂ O ₃ – 20 %	492.20
Kaolin – 20 %	588.52
Thermoplastic	699.14
Thermoset	710.26

With the materials containing Al_2O_3 , both the 20% and 30% cases performed similarly during flexural testing. Both materials, however, had a flexural strength ~30% lower than the TP materials during testing. With the kaolin samples, the average flexural strength was also found to be 15.8% lower than the standard TP specimens. When comparing only the control rebars, the TP samples, on average, had a flexural strength 1.6% lower than the TS counterparts, meaning the samples are comparable. Overall, these tests indicated that the fillers tested did not provide improved mechanical properties, but rather the opposite; using these particular fillers during the manufacturing process of the composite material resulted in reduced flexural strengths when compared to materials that did not contain any filler in the polymer matrix.

The hypothesized reasoning behind this result is that during pultrusion manufacturing, there was a surplus of glass fibre strands that became separated from the resin-soaked, unpolymerized composite material. These short strands of wet fibre did not end up being integrated into the composite, and so the manufactured specimens would have had a lower content of glass, thus reducing the strength properties of the composites. As for how the glass fibre were separated, it was hypothesized that the coarse microstructure of each of the fillers combined with friction during the pultrusion process resulted in the fibres being cut; assuming this effect was applied to all fibres equally, it would also be expected that the fibres that were not cut still incurred an abrasive effect from the fillers, thus reducing their individual strength properties. With the continuous fibres seemingly damaged, it would be expected that the composite material would have impacted mechanical properties.

Given the potential complications and adverse effects associated with some fillers, and that the developed TP material showed promise in having comparable mechanical properties to those of existing TS materials, the composite manufacturing phase of the research was concluded with the final standout experimental formula (Recipe #17) selected for further mechanical and environmental testing.

4.2 Mechanical and Environmental Testing

With the progression of the experimental designs described above, the best TP formula with Recipe #17 was tested against existing pultruded TS GFRPs developed previously using the same pultrusion machine. These experimental formulas are outlined in Table 4.4.

Table 4.4: DoE formulas developed for materials analysis [16]

DoE	Thermoplastic	Thermosetting
Fibre	20 Rovings of Owens Corning Pulstrand 4100 glass fibre.	19 Rovings of Owens Corning Pulstrand 4100 glass fibre.
Resin	(1000 mL) @ 100 pphr	Reichhold DION 31038-00 (1400 mL) @ 100 pphr
Lubricant	Technick Products 190-TG	Technick Products 190-TG (14 mL) @ 1 pphr
Initiators and Additives	- NOROX TBPB, - Perkadox 16	- NOROX PULCAT AMB - NOROX TBPB - NOROX 500-75OMS
Heating	110 °C, 110 °C, 110 °C Setpoint +/-: 1 °C, Cooled with hair dryer upon exit.	120 °C, 150 °C, 150 °C Setpoint +/-: 1 °C
Pulling Speed	0.15 m/min, Dial Reading: 22.5	0.33 m/min Dial Reading: 40

Environmental exposure procedures were performed on the samples as described in Table 3.2, after which flexural testing was conducted on the specimens according to section 3.2. With the collected flexural strength data (see Appendix B) imported into Minitab, the statistical analysis based on a general linear model was implemented. Prior to analyzing the collected data, a number of conditions were checked:

- **Normality:** In order to check for normality, a normal probability plot with a 95% CI was created in Minitab:

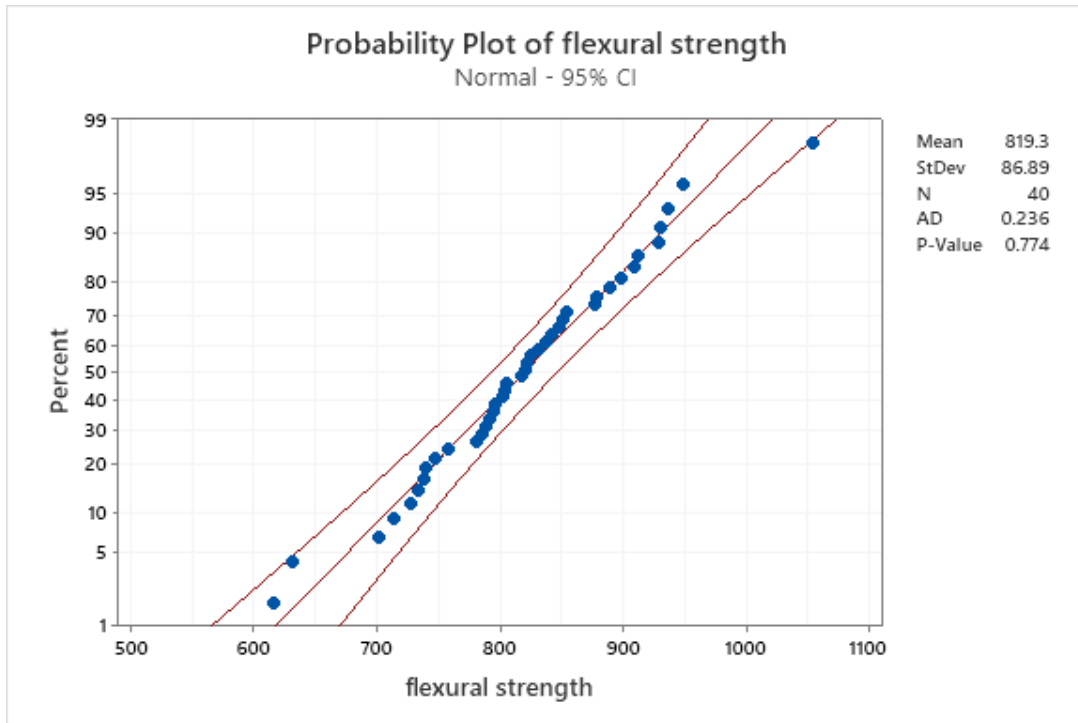


Figure 4.6: Probability plot for flexural strength data within 95% CI bands

From Figure 4.6, we can see that the collected flexural strength data for all specimens falls within the 95% CI bands, showing that the data seems to have some normality associated with it. This is also shown by the p-value determined from this test of 0.774. Since the null hypothesis for this ‘Anderson-Darling Test’ is that the data follows a normal distribution, and since the p-value determined is greater than 0.1, it cannot be concluded that the data does not follow a normal distribution, thus failing to reject the null hypothesis [50]. Therefore, by contradiction, this test rather shows that there is evidence of some normality in the data.

- **Equal variances:** In order to check for the equal variance assumption, a Levene test was performed in Minitab, the results from which are shown in Figure 4.7:

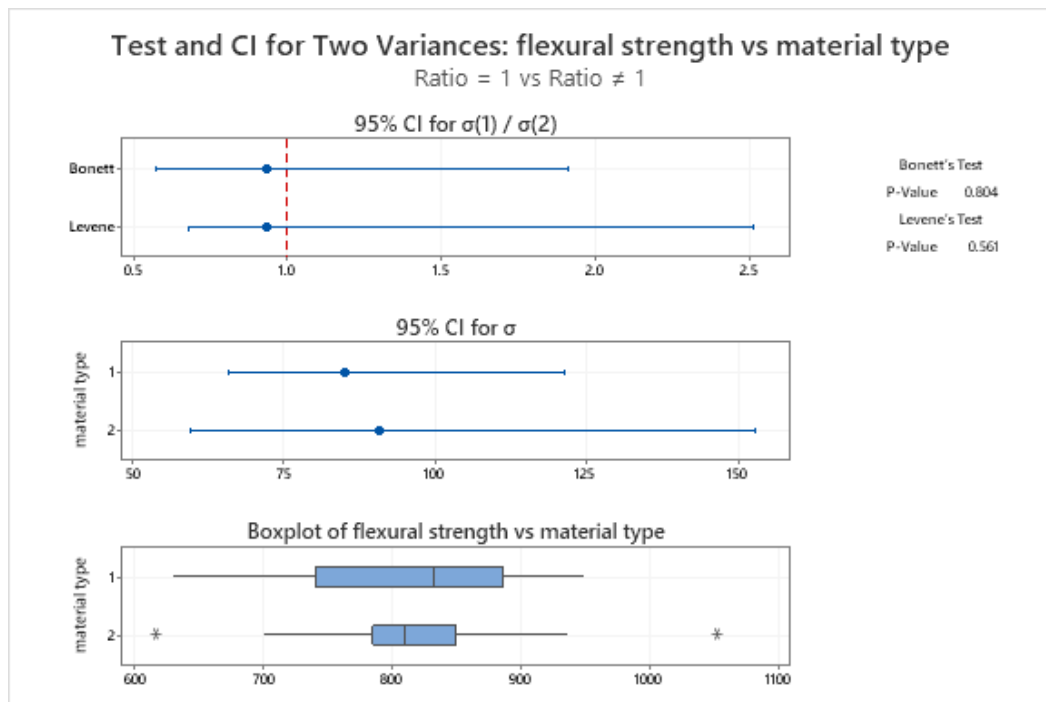


Figure 4.7: Levene test for equal variance

In this test, the null hypothesis that the two variances are the same cannot be rejected due to the p-value of 0.561 being greater than 0.1, as shown in Figure 4.7. This means that there is no evidence to say that the variances in the two material groups are unequal, and therefore that the equal variances assumption holds. Additional details from this test are found in Appendix C.

- **Random samples:** Due to material and chemistry differences in the tested specimens, this meant that it was advantageous to produce all of the rebars for one particular material type in one manufacturing process (i.e., one for TP materials, the other for TS materials). However, the samples selected and labelled for testing were done so randomly from the respective batch of produced composite materials, ensuring some randomness was present in the data.
- **Independent samples:** As mentioned in Table 3.2, each specimen was only subjected to one environmental exposure condition, and one composite specimen cannot have a TP and TS polymer in the resin matrix. Each sample was therefore independent from every other sample tested.

With these conditions checked, the analysis of variance via the general linear model was conducted for this 2x4 factorial design in Minitab. The null hypotheses here were that there was no difference between the mean flexural strength values from each material type, and that there was no difference between the means for each exposure type (i.e., all

effects were equal). The alternative hypotheses were that there was a difference between the means based on material type, and that not all of the means based on exposure type were equal (i.e., not all effects were equal). The main results from this test are shown in Table 4.5 below.

When observing the analysis of variance results from Minitab, we were most interested in the p-values presented in the ‘Analysis of Variance’ subsection, the data for which is shown in Table 4.5. More extensive results from the Minitab output of this test are found in Appendix C. As alluded to previously, with a significance level of $\alpha = 0.05$, a p-value greater than 0.1 means there is no evidence supporting the alternative hypothesis, whereas a p-value of 0.01 or lower means that there is evidence to support the alternative hypothesis. With this in mind, the following conclusions were made. In Table 4.5, a p-value of 0.962 was determined for the ‘Material Type’ factor. As such, this result means there was no evidence supporting the alternative hypothesis for material types declared before the test; that is, there was found to be no statistical difference in the means of the flexural strength values between the TS and TP materials tested. This gives some validity to the claim that the novel GFRP TP composite materials perform similarly to their existing TS counterparts.

Table 4.5: Overview of the p-value results from the analysis of variance for the general linear model

Source	P-value
Material Type	0.962
Exposure	0.002
Material Type*Exposure	0.553

For the ‘Exposure’ factor in Table 4.5, a p-value of 0.002 was found, which is statistically significant, meaning there was evidence to support the alternative hypothesis. That is, there was evidence to support the claim that not all of the means of flexural strength based on exposure type were equal, or that the effect of some of the exposure types was different. This was to be expected, as the environmental exposure procedures were intended to induce accelerated weathering characteristics on the materials, meaning that the exposures should be negatively affecting the material properties of the composites.

For the interaction between the material type and exposure factors (presented as Material Type*Exposure), a p-value of 0.553 was determined, as shown in Table 4.5. Similar to the case for the material type hypothesis, this result means that there was no evidence supporting the idea that the interaction between the ‘material type’ and ‘exposure’ has an effect on the measured flexural strength of the materials.

More fine-grained data from the analysis of variance is found in Table 4.6, taken from the ‘Coefficients’ subsection of the Minitab output found in Appendix C; for the sake of brevity, only the statistically significant results will be discussed. In this case, the only exposure types which were found to be significant were the hot/UV/water specimens and the caustic corrosive bath specimens. Therefore, there was evidence to suggest that the hot/UV/water and corrosion exposures had a greater effect on the mean of the flexural strength from the tested specimens than what typically occurred in the other exposure groups. This again makes some sense, as it would be expected these two exposure types

would cause more harm to the specimens than the cold environment exposure type. No interactions between individual material types or environmental exposures were found to be statistically significant.

Table 4.6: Additional details on the p-value results from the analysis of variance

Analysis of Variance	P-value
Material Type	
TS	0.962
TP	0.962
Exposure	
Control	0.706
Hot/UV/water	0.002
Cold	0.981
Corrosion	0.001
Material Type*Exposure	
TS*Control	0.596
TS*Hot/UV/water	0.165
TS*Cold	0.487
TS*Corrosion	0.855
TP*Control	0.596
TP*Hot/UV/water	0.165
TP*Cold	0.487
TP*Corrosion	0.855

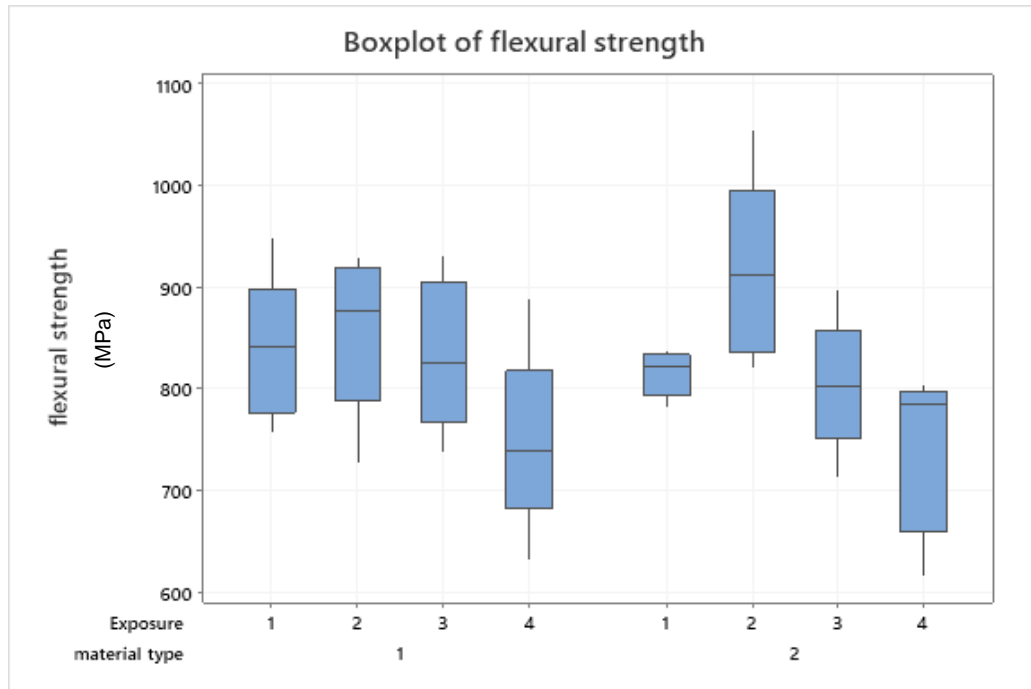


Figure 4.8: Boxplot of the flexural strength (MPa) of all tested TP and TS materials

The analyzed data is also show in the form of a boxplot in Figure 4.8 above. In this figure, material type 1 represents specimens made using TS polymer, whereas material type 2 represents specimens from the novel TP polymer. Exposure factor levels are as follows: 1 = control specimens, 2 = hot/UV/water exposure, 3 = cold environment, and 4 = corrosive caustic bath. As noted from the p-values determined from Minitab, exposure type 4 (corrosion) has a drastically different average flexural strength than the other exposure types, and in the case for TP composites (material type 2), the hot/UV/water exposure test resulted in a higher-than-average flexural strength. With the TP material exposed to hot/US/water testing, this difference in flexural strength was hypothesized to be attributed to residual stress in the manufactured specimens; that is, during the heating

phases of this particular exposure test, the added heat on the specimens acted as a stress relieving process, resulting in fewer residual stresses in the material after the exposure was performed. This theory can only be confirmed with additional testing of GFRP specimens, however, and may give insight to future improvements in mechanical properties of GFRP composites [51].

Overall, the statistical analysis of these flexural results shows that, as hypothesized, the novel TP GFRP composites have comparable mechanical properties in flexion to those of existing TS GFRP. Corrosive caustic bath exposure was shown to have the largest negative effect on the flexural strength of both composites, despite both materials having admirable corrosion resistance properties. Additional details from these statistical results are found in Appendix C.

4.3 Composite Life Cycle Analysis

The results from the LCA were again divided up into three sections for each of the LCA components (Energy Required, Environmental Impact, and Cost), followed by a final discussion for the LCA at the end of the chapter. The results in this section were based on the information provided in Chapter 2, as well as the procedures outlined both here and in Chapter 3.

4.3.1 Energy Required

Required energy values were converted to units of MJ/1m, representing the amount of energy necessary in megajoules to produce 1 metre of pultruded Ø9.5 mm round GFRP composite rebar, as this was the same size and diameter of the material produced during composite manufacturing stage of the research.

4.3.1.1 Raw Material Production

The production of raw materials was found to be the top contributor to the energy required to fabricate GFRP composites. Creating brand new materials for each individual composite component requires a lot of energy and resources, some of which can be avoided or reduced with recycling processes, later discussed in Appendix A. In this subsection, energy values for each component are explored.

In terms of resin production, since there are many different variations in composite resins used in industry within the two main polymer types (TP and TS), one specific resin of each of these types was explored. For TS, epoxy and vinyl-ester were used for analysis, as well as PMMA for the TP case. In order to convert these energy production values to MJ/1m of composite material, the literature data was multiplied by the mass of TS/TP resin per metre of composite material. This was estimated by determining the average mass of lab-produced TS and TP GFRP material per metre and subtracting the mass of glass per metre of material, the values for which are found in Table 4.7 below. The TS and TP average mass values were averaged from 5 specimens for each material type,

similar to those shown in Figure 3.5 previously, and the average mass of glass was determined by multiplying the manufacturer-defined density of each roving (4800TEX = 4.8 g glass/1m) by the number of rovings used (20 rovings).

Since no fillers were used in these composite materials, this method gives a reasonable estimation of the mass of the resin used. This resin mass per metre value multiplied by the energy per unit mass gives energy per metre, as shown in Table 4.8 below. This same process was also used for TP GFRP composites.

Table 4.7: Average mass values for GFRP materials

Average mass	Thermosetting (kg/1m GFRP)	Thermoplastic (kg/1m GFRP)	Glass fibres only (kg/1m GFRP)
Average mass of GFRP per metre	0.1302	0.1270	0.096
Average mass of resin only per metre	0.03416	0.03099	-

Table 4.8: Energy required for GFRP resin production

Energy	Thermosetting (MJ/1m)	Thermoplastic (MJ/1m)
Resin Production	2.596 - 4.680 [28]	3.595 - 6.424 [29]

The production of glass fibres is necessary to act as the reinforcement materials in GFRP composites. For the purposes of this comparison, it was assumed that both classes of composite (TS and TP) used the same amount of glass per unit length. As noted in Table 4.7 above, this was estimated at 0.096 kg/1m, or 96 g/1m.

This data range was converted to units of MJ/1m of composite material, similar to what was done above for TS and TP resin. The average mass of glass calculated for 1m of composite material was multiplied by the data range from Bachmann et al. to give results in MJ/1m required for glass production, which can be found in Table 4.9 below. Since both composite types in this analysis are using the same amount of glass, the required energy values for glass production apply to both cases.

Since no energy data was available for OP production, for the sake of comparison between the TS and TP composite materials investigated here, it was assumed that the energy impact on each of these materials from OPs is the same.

Table 4.9: Energy required for the production of glass fibres

Energy	Thermosetting (MJ/1m)	Thermoplastic (MJ/1m)
E-glass Production	0.9888 - 4.378 [28]	0.9888 - 4.378 [28]

4.3.1.2 Pultrusion Manufacturing

There are a number of different manufacturing processes that may be used for producing GFRP composites. In this experimental study, only a pultrusion manufacturing process was considered. Based on currently available data from literature and measured data from a lab setting, the following energy values for pultruding composite material were determined in Table 4.10 below.

During lab scale production, voltage and current ratings were collected with a clamp-meter, shown in Figure 4.9 below, the values for which were used to determine the wattage required. Since both types of composite material were pulled at different speeds, each type required a different amount of time to pultrude 1m of product. By summing the required wattage for each of the three heating zones and the pulleys of the pultrusion machine, this total required wattage was then multiplied by the required time to produce 1m of material, giving required energy values in terms of MJ/1m. Since the TP composites required a slower pulling speed in our lab process, this meant they require more time to produce 1m of material. This additional time resulted in more energy required when compared to TS composites. Effectively, time is money.

Table 4.10: Energy required for pultrusion manufacturing of GFRP composites

Energy	Thermosetting (MJ/1m)	Thermoplastic (MJ/1m)
Pultrusion (literature)	0.4036 [30] [31]	0.3937 [30] [31]
Pultrusion (lab)	0.1534	0.3303



Figure 4.9: Clamp-meter for measuring current and voltage from pultrusion machine

The calculated values were found to be slightly lower in than those found in literature, however, it is important to note that these values were taken from a custom-designed and -built pultrusion machine. In industry, a pultrusion machine would be ordered from a manufacturing company such as SVS Hydraulics Pvt. Ltd. and would operate at a much higher production scale (30 ton pulling capacity) compared to what is possible in a lab setting, which may therefore increase the manufacturing energy demands [40]. To keep this analysis true to all other metrics disclosed, the measured values from our lab scale production process were used as the governing energy data for comparison purposes.

4.3.1.3 Recycling

Since each type of material has their own respective recycling and repurposing techniques, the TS and TP composites were each analyzed differently to allow for a more accurate analysis on the recycling methods available. This allowed for better predictions into which recycling processes were found to be the most economical. The processes listed here follow the same options as shown in section 2.8.1.3.

With TS composites, the energy produced from the energy recovery process was determined by multiplying the calorific value for the vinyl-ester resin referenced in section 2.8.1.3 by the averaged mass of the resin contained in one metre of TS rebar, as described in Table 4.7. This energy produced per unit length value was determined to be 1.025 MJ/1m, which can be used towards other future processes or converted into electricity for use in conventional energy grids. Unlike other recycling processes that typically only draw energy, this method presents itself as an overall energy credit.

The energy demand discussed for mechanical grinding of TS composites per kg of material processed from section 2.8.1.3 was converted into a value of energy per unit length, for consistency with the rest of this LCA. This conversion, however, relied on the assumption that the TS composite material used in the referenced study had a comparable mass to that of the material of our analysis. The conversion to energy per metre length, as described in section 4.3.1.1, yielded values of 0.02213 - 0.2512 MJ/1m for the mechanical recycling of TS materials. The viability and uses of such recovered products

are further discussed in Appendix A. Mechanical recycling is currently the most economical and least energy-intensive recycling method for TS composite materials.

For this investigation of pyrolysis with TS materials, converting the energy demand for pyrolysis into energy per unit length of composite was beneficial to maintain consistency within the scope of this LCA. This converted the demand of 3 - 30 MJ/kg found in section 2.8.1.3 to 0.3905 - 3.905 MJ/1m, again following the process outlined in section 4.3.1.1.

With fluidized bed processes, the amount of electricity and energy required per unit of material were determined based on the provided cost and operation metrics found in section 2.8.1.3 coupled with the price of electricity and methane. Dividing the annual electrical costs used in the study (at a rate of \$0.04/kWh) into the kilowatt hour usage yielded 8,751,125 kilowatt hours per year of operation, which was then divided into the 6000 hours of operation in the model to determine the kilowatt rating per tonne of processed material [35]. This gave 1458.52 kilowatts per 1000 kg of scrap material processed per hour. Using the average mass density value of TS rebars in Table 4.7, the required electricity per metre of composite material was then converted to 0.1898 kWh/1m. Converting to base energy units, this yielded 0.6834 MJ/1m.

Equally, the amount of methane used in the combustion chamber of the fluidized bed process was calculated based on the overall cost estimate for annual processing divided by the cost of methane at \$0.12/kg used throughout the study [35]. The amount of

methane in terms of mass was then converted to the energy equivalent via its combustion yield/calorific value. This was then converted into the amount of energy required per kg of composite waste, which can be applied to the mass of the GFRP rebars for our consideration. The estimated methane gas requirement of \$103,704 was used to calculate a usage of 864,200 kg of methane gas per year. Converting this to an energy demand via the calorific value of 55.38 MJ/kg [52], an energy value of 47,860,000 MJ per year of production was found. Dividing this value into the 6000 hours of production time per year (based on 1 tonne of material processed per hour) and multiplied by the density/1m of TS material, as noted in Table 4.7, an energy requirement of 1.038 MJ/1m was found for the methane used. The total energy draw for a fluidized bed process was then summed as a combination of the two energy components, both electricity and methane, to a minimum of 1.722 MJ/1m.

The scrap material used in this fluidized bed experiment from Pickering would have a mean composition of 27% resin, 40% glass fibre, 30% mineral fillers and 3% polymer additives [35]. This composition is different from our lab-based TS DoE, which used a composition of ~25% resin, ~75% glass fibre (by volume). However, due to the polymer resin matrix being the biggest defining component to the processing rate of the fluidized bed, the 27% vs the ~25% TS resin matrix composition was similar enough to consider this a reasonable analysis on the energy demand per kg of material. The estimated energy required for each of these recycling processed are summarized in Table 4.11 below.

Table 4.11: Energy required for recycling TS GFRP composites

Recycling Processes for Thermosetting GFRPs	Energy Required (MJ/1m)
Energy Recovery	1.025 (Energy Released) [32]
Mechanical Grinding (Most Economical)	0.02212 - 0.2512 [33]
Pyrolysis	0.3905 - 3.905 [33]
Fluidized Bed	1.722 [35]

As mentioned above, the mechanical grinding recycling process was found to be the most economical for TS composites, as it has the lowest energy requirement of the procedures discussed. Therefore, in order to create a best-case scenario comparison for both materials, mechanical recycling was designated as the recycling method of choice in the total energy table at the end of this section.

When it came to thermoplastic recycling, it was found that thermoforming possibilities are limited for the $\emptyset 9.5$ mm rebars in this analysis; therefore, this particular reuse method was not considered in the energy analysis portion for recycling. These recycling processes and more are also discussed in Appendix A.

As noted in section 2.8.1.3 for mechanical grinding, it was estimated that the energy demand for grinding PMMA-based TP composites is 0.29 MJ/kg, which is converted to 0.03683 MJ/1m when taking into account the average density of TP composite material from Table 4.7 [29].

The energy demand for the pyrolysis of TP composites was estimated at 1 MJ/kg, found in section 2.8.1.3, was converted to 0.1270 MJ/1m based on the average density of TP composites from Table 4.7 [29].

For the distillation and evaporation types of dissolution for PMMA composites, the expected energy consumption was found to be 20.0 MJ/kg and 4.0 MJ/kg, respectively, as shown in section 2.8.1.3 [29]. When converted to a MJ/1m basis, these energy requirements became 2.540 MJ/1m and 0.5080 MJ/1m, respectively. These and the estimated energy values from the other recycling processes for TP composites are summarized in Table 4.12 below. As with TS composites, mechanical grinding was again found to be most economical option for recycling TP composites and was therefore used in the final energy analysis at the end of this section.

Table 4.12: Energy required for recycling TP GFRP composites

Recycling Processes for Thermoplastic GFRPs	Energy Required (MJ/1m)
Mechanical Grinding (Most Economical)	0.03683 [29]
Pyrolysis	0.1270 [29]
Dissolution/distillation/extrusion	2.540 [29]
Dissolution/evaporation/extrusion	0.5080 [29]

4.3.1.4 Total Energy Required

In order to create a direct comparison between the two composite materials on an energy basis, all values in the tables presented above in this section were condensed to produce a range of the total energy required over the lifetime of the material. For the sake of comparison, and since there was no data available on the energy required for OP production, it was assumed that these initiators affected the overall energy footprint to the same degree for each composite material.

For recycling purposes, the lowest energy expense was chosen for the overall energy comparison, providing the best-case scenario. Table 4.13 below gives a summary of all energy requirements for each material type, from production to end-of-life. All energy values were calculated for the production of 1 m of round, Ø9.5mm GFRP rebar, with units denoted in MJ/1m GFRP.

Table 4.13: Total energy required for the life cycle of GFRP composites

Energy	Thermosetting (MJ/1m)	Thermoplastic (MJ/1m)
Resin Production	2.596 - 4.680 [28]	3.595 - 6.424 [29]
E-glass Production	0.9888 - 4.378 [28]	0.9888 - 4.378 [28]
OP Production	Data not available	Data not available
Pultrusion	0.1534	0.3303
Recycling (Mechanical Grinding)	0.02212 - 0.2512 [33]	0.03683 [29]
Total Energy	3.761 - 9.463	4.951 - 11.17

4.3.2 Environmental Impact

For the purposes of this analysis, only CO₂ (and CO₂eq) values were considered for comparison. Other emissions such as NO_x, SO_x, and particulate matter (PM) are also important in environmental analyses, however, there was a lack of data on these metrics in the area of composite manufacturing.

Some of the environmental impact components of the manufacturing process in this analysis come from data in literature, however, there was less data available in some areas. For situations where no data exists, the equivalent of the amount of energy required for production from section 4.3.1 was used to determine the equivalent CO₂ output (CO₂eq) based on power production information in New Brunswick, Canada.

Based on carbon footprint data of energy production from the Government of Canada and NB Power, an average amount of CO₂ output per kWh of energy produced in New Brunswick was determined to be 0.2951 kg CO₂eq/kWh [53]. Units in megajoules (MJ) were converted to kWh, as 1 MJ = 0.2778 kWh, which when coupled with the CO₂eq/kWh value was used to determine the equivalent amount of CO₂ per 1m of GFRP, which were the units used for this section.

4.3.2.1 Raw Material Production

Just as the production of raw materials was found to be the largest contributor to the energy required for creating composite materials, it was also found to be the largest

contributor to GHG emissions. For this subsection, most materials had previously declared GHG outputs from literature, as noted in Chapter 2.

For TS resin production, data was again used for existing epoxies from Bachmann et al. Similar to the process to determine the energy required in section 4.3.1.1, the data range of 4.7 - 8.1 kg CO₂eq/kg resin from section 2.8.2.1 was multiplied by the equivalent mass of resin per metre of GFRP material, isolating the unit of kg CO₂eq/1m. The kg CO₂eq/1m value of PMMA production was determined similarly. A base CO₂eq/kg output of 5900000 mg/kg PMMA was found in section 2.8.2.1 [37]. This is equal to 5.9 kg CO₂eq/kg resin, which was again converted to kg CO₂eq/1m GFRP as done with the epoxy resin above. These final calculated values are shown in Table 4.14 below.

The GHG emission values calculated for glass fibre production on a per unit length basis are given in Table 4.15 below and were again determined by multiplying the literature data by the equivalent amount of glass per 1m, or 0.096 kg glass/1m GFRP. Since both TP and TS composites in this analysis use the same amount of glass, these calculated values again apply to both composite material types.

Since GHG emission data for OPs was not available, similar to section 4.3.1.1, it was therefore assumed that the GHG impact from OPs on each of these materials is the same.

Table 4.14: GHG emissions of resin production

Carbon Footprint	Thermosetting (kg of CO₂eq/1m GFRP)	Thermoplastic (kg of CO₂eq/1m GFRP)
Resin Production	0.1606 - 0.2767 [28]	0.1828 [37]

Table 4.15: GHG emissions of glass fibre production

Carbon Footprint	Thermosetting (kg of CO₂eq/1m GFRP)	Thermoplastic (kg of CO₂eq/1m GFRP)
E-glass Production	0.1536 - 0.2496 [28]	0.1536 - 0.2496 [28]

4.3.2.2 Pultrusion Manufacturing

Since the pultrusion process only requires electricity to heat the die and power the motors for the pulleys, there are no effective emissions due to pultrusion at the time of manufacturing. Rather, the equivalent emissions from this would be from the production of the energy used. By using the data collected in section 4.3.1.2 and the CO₂eq/kWh conversions at the beginning of this section, the equivalent amount of CO₂ output due to the energy used for pultrusion was determined. These values are shown in Table 4.16 below.

Table 4.16: Effective GHG output for pultrusion manufacturing

Carbon Footprint	Thermosetting (kg of CO₂eq/1m GFRP)	Thermoplastic (kg of CO₂eq/1m GFRP)
Pultrusion	0.01257	0.02707

4.3.2.3 Recycling

During the recycling phases of both composite material types, the processes involved all rely heavily on electrical energy to operate. For the processes below, it was only 'Energy Recovery' and 'Fluidized Bed' that were found to have CO₂ emissions beyond those from the electricity used.

As mentioned in section 2.8.1.3, the average CO₂ output from incinerating TS vinyl-ester resin was measured to be 1.87 kg CO₂/kg resin [38]. Based on the data provided in Table 4.7, the amount of TS resin per metre of GFRP material is 0.03416 kg resin/1m. Multiplying these two values gives an output of 0.06389 kg CO₂/1m GFRP for materials put through the energy recovery process.

For the fluidized bed process with TS composites, the equivalent carbon dioxide emissions were found for the electrically dependent energy data. This was determined according to the conversions at the beginning of this section and using the electrical energy value calculated in section 4.3.1.3, the CO₂ output due to electricity was found to be 0.05602 kg CO₂ eq/1m. The theoretical true CO₂ output of methane was then calculated for the incineration component to be 0.05144 kg CO₂/1m. This was calculated via 1.038 MJ/1m (also from section 4.3.1.3), which is the kg of methane usage over the year converted into mass per 1 metre, then due to the molar ratio of burning methane into carbon dioxide and converting the per metre combustion using the molar masses of both methane and carbon dioxide for the total kg CO₂ output. The sum of these two components was found to be 0.1075 kg CO₂/1m.

The GHG output of the pyrolysis and mechanical recycling processes for TS composites were determined by converting the MJ/1m energy values listed in Table 4.11 to the kWh/1m equivalent, based on the conversion listed at the beginning of this section. With these units, and again using the kg CO₂eq/kWh conversion for energy produced in New Brunswick, it was determined that the output of kg CO₂eq/1m for mechanical recycling is 0.001813 - 0.02059 kg CO₂eq/1m, and 0.03201 - 0.3201 kg CO₂eq/1m for pyrolysis. A summary of these values is found in Table 4.17 below.

Based on the recycling opportunities available for TP wind turbine blades, this information was extrapolated down to the TP GFRP rebar scale [29]. As mentioned above, the GHG output for pyrolysis and mechanical grinding for TP composites were determined by converting the MJ/1m energy values listed in Table 4.12 to kWh/1m equivalent, based on the conversion listed at the beginning of the section. With these units, and again using the kg CO₂eq/kWh conversion for energy produced in New Brunswick, it was determined that the output of kg CO₂eq/1m for mechanical recycling is 0.003019 kg CO₂eq/1m, and 0.01041 kg CO₂eq/1m for pyrolysis [29].

Table 4.17: Effective GHG output for TS GFRP recycling processes

Carbon Footprint	Thermosetting (kg of CO₂eq/1m GFRP)
Energy Recovery	0.06389
Mechanical Recycling (Most Economical)	0.001813 - 0.02059
Pyrolysis	0.03201 - 0.3201
Fluidized Bed	0.1075

Table 4.18: Effective GHG output for TP GFRP recycling processes

Carbon Footprint	Thermoplastic (kg of CO₂eq/1m GFRP)
Mechanical Grinding (Most Economical)	0.003019 [29]
Pyrolysis	0.01041 [29]
Dissolution/distillation/extrusion	0.04547 [29]

The carbon footprint of the dissolution process for TP composites was determined based on a more in-depth analysis from Cousins, again based on the recycling costs for TP turbine blades [29]. With an estimated energy requirement for dissolution and devolatilization at 17.9 MJ/kg of resin, this was converted into 0.5547 MJ/1m, based on Table 4.7 [29]. Megajoules were then converted to kilowatt hours, resulting in 0.1541 kWh/1m, which based on data from the Government of Canada outputs approximately 0.04547 kg CO₂eq/1m GFRP in a dissolution process [53]. A summary of these values is found in Table 4.18 above. Once again, mechanical grinding was found to be the least intensive recycling operation.

4.3.2.4 Total GHG Footprint

As discussed, the total estimated GHG footprint was tabulated by combining all of the above CO₂eq emissions, with mechanical recycling acting as the governing recycling method for both composite types. As mentioned, carbon footprints for OP production were not available, and so it is assumed that these outputs affect each material type equally. As show in Table 4.19 below, the GHG outputs are similar for both materials, with TP having a slightly lower high end, and TS having a broader range.

Table 4.19: Total estimated environmental footprint for GFRP materials

Carbon Footprint	Thermosetting (kg of CO₂eq/1m GFRP)	Thermoplastic (kg of CO₂eq/1m GFRP)
Resin Production	0.1606 - 0.2767 [28]	0.1828 [37]
E-glass Production	0.1536 - 0.2496 [28]	0.1536 - 0.2496 [28]
OP Production	Data not available	Data not available
Pultrusion	0.01257	0.02707
Recycling (Mechanical Grinding)	0.001813 - 0.02059	0.003019 [29]
Total	0.3286 - 0.5595	0.3665 - 0.4625

4.3.3 Cost

For the purposes of the cost analysis, a price estimation on a \$/1m basis was determined to be consistent with the rest of this LCA. Information presented here was based on pricing provided by industry partners, with estimates made where necessary. All units were converted to \$CAD/kg such that \$/1m units could easily be reworked based on the units previously used in this LCA.

4.3.3.1 Raw Materials

As discussed throughout, the three main raw materials of GFRP composites are the respective resin used, glass fibres, and OP initiators. Since the resin types are different for the two composite types considered, each has their own associated cost.

It was found that the TS resin had a higher unit cost than the TP resin, priced at \$7.47/kg vs. \$3.29/kg, respectively [40][29]. When calculating the cost of resin per unit length for each material, the average mass values for each resin type from Table 4.7 were multiplied by their respective costs listed here. This gave an estimated cost of \$0.2552/1m for TS resin, and \$0.1020/1m for TP resin, making TS resin ~2.5x more expensive than TP resin, in this case.

Since both composite materials used the same amount and type of e-glass fibres, the cost impact is the same for both. The Pulstrand 4100 (4800TEX) glass fibre rovings used from Owens Corning were estimated to cost \$2.14/kg [40]. As mentioned in Table 4.7, each composite material used ~0.096kg of glass per 1m of pultruded product, therefore giving a glass cost of \$0.205/1m for each material type.

Finally, for OPs, each initiator had a different quantity used during the pultrusion process for each material. In order to protect the intellectual property in the DoE used for lab-based manufacturing, the weight and cost breakdown of each initiator used is not included here. Rather, a total cost for OPs for each material on a per metre basis was calculated based on the cost structure in Table 2.1.

Calculating the cost of initiator per metre based on this cost structure resulted in \$0.01344/1m for TS products and \$0.04618/1m for TP products. While the initiators required for TP manufacturing end up costing more, these expenses are negligible

compared to the cost of the other components required. A summary of these and all other raw materials costs is provided in Table 4.20 below on a per metre basis.

4.3.3.2 Pultrusion Manufacturing

Determining the cost of electricity used for pultrusion manufacturing was simply calculated by using conversion factors previously discussed in this LCA. By using the energy requirements for data collected from our lab scale production process, the values given in MJ/1m were converted by using $1 \text{ MJ} = 0.277778 \text{ kWh}$, as declared in section 4.3.2. Units in terms of kWh/1m were then converted to \$/1m based on the cost of electricity in New Brunswick, Canada from NB Power given as \$0.1345/kWh [39]. As such, the calculated costs for pultrusion manufacturing were found to be \$0.005731/1m for TS composites and \$0.01234/1m for TP composites and are summarized in Table 4.21 below. At the per metre scale these costs are negligible, however, this further reinforces how economically viable pultrusion is as a manufacturing method.

Table 4.20: Cost of raw materials for GFRP composites

Cost	Thermosetting (\$/1m)	Thermoplastic (\$/1m)
Resin	0.2552 [40]	0.1020 [29]
Glass	0.205 [40]	0.205 [40]
OPs	0.01344 [40] [41] [42]	0.04618 [40] [41] [42]

Table 4.21: Energy usage costs for pultrusion manufacturing

Cost	Thermosetting (\$/1m)	Thermoplastic (\$/1m)
Pultrusion	0.005731	0.01234

4.3.3.3 Costs of Recycling

As with previous sections, pricing for recycling of each composite material type was found to be slightly different and was therefore determined separately.

The cost structure for recycling TS materials was estimated by converting energy requirements into energy costs, according to pricing data for the province of New Brunswick [39]. For energy recovery, since the overall energy from that process ends up being net positive, this in a sense would result in an economic gain as opposed to an expense. At 1.025 MJ/1m released, converting to kWh/1m and using the price of electricity at 0.1345 \$/kWh, this resulted in a best-case monetary gain of 0.03830 \$/1m [32]. This produced energy can be used to drive the “recycling” process as a whole, which may not be the best use of the material compared to the other processes.

With mechanical grinding of TS composites, an energy demand of 0.02213 - 0.2512 MJ/1m was estimated [33]. Following the same process as the previous paragraph, this resulted in a cost of 0.0008264 - 0.009385 \$/1m. Again, these costs are negligible at this scale, further showing that mechanical grinding is generally the most economical recycling option.

A TS pyrolysis recycling process was estimated to require 3 - 30 MJ/kg, or 0.3905 - 3.905 MJ/1m [33]. These energy requirements were found to cost approximately 0.01459 - 0.1459 \$/1m, which is considerably more expensive than the mechanical grinding option.

The fluidized bed process for TS materials from section 4.3.1 provides some details on the required costs of this recycling method. With an estimated electricity demand of 0.1898 kWh/1m, this would result in a cost of 0.02553 \$/1m based on NB Power pricing [35] [39]. For the required methane of 1.038 MJ/1m, using its calorific value, would result in 0.01874 kg methane/1m required [35]. Using the cost of methane at \$0.12/kg given previously, the cost of methane on a per metre basis was estimated at 0.002249 \$/1m [35]. Combining these two costs gave a total recycling cost for a fluidized bed process of 0.02778 \$/1m.

With TP recycling, some of the recycling processes here are shared with the TS composites above, notably mechanical grinding and pyrolysis. The energy intensity for mechanical grinding with TP composites was estimated at 0.03683 MJ/1m, which is 0.001376 \$/1m in electricity costs in New Brunswick [29] [39]. Pyrolysis on the other hand requires 0.1270 MJ/1m of processed material, costing 0.004745 \$/1m, nearly 3.5x more than mechanical grinding [29] [39]. In the recycling analysis for dissolution from Cousins, costs are broken down between costs for dissolution alone and the subsequent operating costs of the facility [29]. For dissolution, the energy demand was determined to be 0.5547 MJ/1m, as shown previously, which in terms of electricity is 0.1541 kWh/1m

[29]. With the cost of electricity in New Brunswick, this converts to 0.02072 \$/1m for the dissolution process [39]. When considering the costs of running the recycling facility, the total operational costs were estimated at \$11,767 per turbine blade [29]. With an estimated mass of 17,399 kg per turbine blade, this gives an average operating cost of 0.6763 \$/kg composite [29]. Since we know the average density of TP composites from Table 4.7, it was estimated the operational costs of recycling TP composites in a dissolution process is 0.08589 \$/1m. Overall, these combined costs give a total cost of 0.1066 \$/1m for dissolution recycling.

A summary of the recycling costs for all of the processes listed is found in Table 4.22 below. The most expensive recycling processes allow for the highest number of potential reuses of the recovered materials. While mechanical grinding was found to be cost-effective, its best use case is found as a concrete additive. On the other hand, a process like dissolution costs almost 100x that of grinding, however, this allows every component in the composite material to be recovered and reused with very little change in mechanical properties. Despite these relatively high recycling costs, the dissolution process is far cheaper to implement than producing new virgin materials every time; it is nearly 2x cheaper when compared to glass fibre production alone. For TP composites, this would be the most ideal process to use, considering the cost savings from not having to create new materials. Since this is a comparison of both TS and TP composites, and since mechanical grinding was used for previous comparisons, mechanical grinding was also used for the recycling method of choice for cost analysis.

Table 4.22: Recycling costs for TS and TP GFRP composites

Cost	Thermosetting (\$/1m)	Thermoplastic (\$/1m)
Energy Recovery (Money Gained)	0.03830 [32]	-
Mechanical Grinding (Most Economical)	0.0008264 - 0.009385 [33]	0.001376 [29]
Pyrolysis	0.01459 - 0.1459 [33]	0.004745 [29]
Fluidized Bed	0.02778 [35]	-
Dissolution (Most Opportunities)	-	0.1066 [29]

4.3.3.4 Total Cost

By reviewing the overall cost analysis in Table 4.23 below, it was determined that TP composites were generally cheaper to produce than TS composites of the same size. With TP composites offering initial costs at ~25% cheaper, comparable mechanical properties, and a recycling process that allows full material separation and reuse, it cannot be ignored that PMMA-based TP GFRP composites are an ideal replacement for current TS materials in industry.

Table 4.23: Cost data for GFRP raw materials and manufacturing

Cost	Thermosetting (\$/1m)	Thermoplastic (\$/1m)
Resin	0.2552 [40]	0.1020 [29]
Glass	0.205 [40]	0.205 [40]
OPs	0.01344 [40] [41] [42]	0.04618 [40] [41] [42]
Pultrusion	0.005731	0.01234
Recycling (Mechanical Grinding)	0.0008264 - 0.009385 [33]	0.001376 [29]
Total	0.4802 - 0.4888	0.3669

4.3.4 LCA Conclusion

The LCA showed that while the energy and environmental impact of TP composites were comparable to that of the TS composites, the TP materials were found to be up to 25% less expensive on a per unit length basis. Since TP polymer is also fully recyclable, this means that these composites have more repurposing opportunities than current TS materials.

These benefits of TP GFRPs, coupled with the fact that a similar pultrusion manufacturing process can be used for production, showed that these novel TP materials are comparable mechanically, recyclable, and a more economical alternative over existing TS composites to date.

Chapter 5 Conclusion and Future Recommendations

The hypothesis of this research was that the novel pultruded TP composite materials are competitive with existing TS materials in three key areas: mechanical properties, environmental resilience, and economics. Through the composite manufacturing process, the novel TP PMMA-based pultruded GFRP materials were found to be manufacturable in a lab setting, with preliminary results showing that the new TP materials had similar flexural strength properties to those of existing TS materials. It was also concluded that fillers such as kaolin and aluminum oxide do not increase flexural strength properties, but rather act as a detriment to the composite material.

With more extensive environmental and mechanical testing, specimens made of this novel TP GFRP material were subjected to a variety of environmental exposures, including heat/UV/water exposure, cold environment, and corrosion, after which a series of 3-point flexural bending tests were conducted. After evaluating the results from these tests according to the statistical design set forth, there was found to be no statistical difference in the means of the flexural strength values between the TS and TP materials tested, meaning that there was rather evidence that two materials performed comparatively. When considering the exposure type factor, however, it was found that there was evidence to support the claim that the effect of some of the exposure types was different. This was to be expected, as the environmental exposure procedures were intended to induce accelerated life characteristics on the materials, meaning that the exposures should be negatively affecting the material properties of the composites.

Finally, with the LCA, it was found that while the energy and environmental impacts of TP composites were comparable to those of the TS composites, the TP materials were found to be up to 25% less expensive on a per unit length basis. Since TP polymer is also fully recyclable, this means that these composites have more repurposing opportunities than the TS materials that currently exist.

This research showed evidence that with these benefits of TP GFRPs, coupled with the fact that a similar pultrusion manufacturing process can be used for production, that these novel TP materials are comparable mechanically, have a wider range of recycling use cases, and are a more economical alternative over existing TS composites to date. With this, the objectives of the research set forth were achieved, fundamental understanding of pultruded TP GFRP composites was developed, and evidence was presented supporting the hypothesis that these novel TP materials are competitive with existing pultruded TS GFRP materials.

The research presented in this thesis, however, is by no means a concluding one. There are now revealing aspects that require extensive data support, and more so in the LCF validation area. Readers are cautioned that the work only pertained to one manufacturing method (pultrusion) to collate and represent a vast field of composite materials manufacturing in the area of GFRP. Therefore, the following recommendations for future research must be carried out before the emanating benefits of the studied TP polymer matrix in pultruded GFRP composites (as an alternative to TS polymer matrix) can be fully (scientifically) appreciated and implemented as a benchmark industry solution:

- Determine the effects of incorporating a coupling agent into the polymer matrix of the composite material on the microstructural bonding properties of the GFRP.
- Test the inclusion of zinc stearate as a solid lubricant in the polymer matrix or try additional amounts of existing lubrication [54].
- Test different combinations of initiator to further optimize the chemistry of the experimental TP-based formula.
- Test the above while pultruding at different pulling speeds, and then subjecting samples from each pulling speed and chemistry combination to a flexural bending test, analyzing the results with statistical software to see if there is evidence of a difference in flexural strength between each group.
- Feed data to the proposed LCF to find the universality of the model both in terms of pultrusion and other composite manufacturing processes (i.e., resin transferred molding, injection molding, extrusion, etc.).
- With further improvements in the chemistry of these experimental materials, it is expected that the mechanical properties of these novel TP GFRP will only continue to improve.

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Appendix A: Recycling and Repurposing

In this section, the use of recycling and repurposed composite materials and their components is discussed. Each subsection focuses on one of the different recycling methods from section 4.3.1.3, some of which can be applied to both TS polymers and TP polymers. There is not a subsection designated to energy recovery, however, as there is no added repurposing benefit for the incineration of composite materials in this analysis, other than the energy output for use in the electricity grid or as a heating source in a process.

Mechanical Grinding

As shown in section 4.3.1.3, mechanical recycling of TS and TP composite materials at high processing rates is the most economic and energy efficient way in which to recycle these materials.

There are plenty of potential uses for mechanically recycled TS materials, however, they have not been feasible in entering traditional markets. This is due to the negative effect on the mechanical properties and the negative cost balance against most virgin products [32] [55].

Through conventional mechanical recycling, the fibres are shredded into small strands which severely impact their ability to contribute to the tensile strength of the material. Due to this impact on the length of the fibres, new applications are limited to those requiring lower mechanical properties. Some of the primary uses of mechanically

recycled TS composite materials are found to be used as filler material or reinforcements in other manufacturing processes [55]. During a comprehensive study on of the effectiveness and economic feasibility of recycling composites from Castro et al., the most promising repurposing methods for mechanically recycled TS materials were discussed [55].

The most extensive research work and economic success in this area is the addition of mechanically separated GFRP TS composite waste into cement [55]. The recycled material can be incorporated either as reinforcement, aggregate, or filler replacement [55]. One of the main ways of processing this is by mixing the recovered fibres with micro-silica while new resin is still in its liquid form [33]. This results in an increased adhesion between the fibres and concrete [33]. Some of the primary benefits of incorporating GFRP TS waste into cement is a decrease in permeability, improved durability, reduced drying shrinkage, and depending on mixing ratios, improved compressive, tensile, and/or flexural strengths [55]. The addition of waste material, however, has also shown significant losses in mechanical properties in high water-cement ratios required for desirable workability, as well as weak adhesion to the filler material [55]. One of the barriers to successfully using GFRP TS waste as a concrete additive is the negative cost association, especially compared to using low value fillers and additives already available [33].

The addition of crushed GFRP TS materials into particleboard was also studied, which was an attempt at reducing thickness while increasing strength. This posed many

challenges as the material did not show any increase in mechanical properties and did not meet the expected standards [56] [55].

The use of mechanically recycled TS composites in the form of a fine powder or dust used as an additive in wall paint. This was shown to increase UV stability and added protective capabilities. It has also been shown to have equal or better properties than normal additives [56]. Other uses for mechanically separated TS and TP GFRP composites include the use as filler material for artificial wood, an additive into high density polyethylene (HDPE) plastic lumber, rubber pavement blocks, and bulk or sheet moulding compounds (BMC/SMC) [55] [29].

Despite the wide array of potential repurposing, the most feasible and economically sound use of mechanically recycled TS composites is found in cement and concrete additives [55].

Pyrolysis

The pyrolysis recycling process does not have conventional yields when it comes to the recycling of TS composites. In the vast majority of recycling processes for TS GFRP materials, the only reusable part of the material is the fibres and fillers added to the resin matrix. In a pyrolysis process, however, there is also an extraction of hydrocarbons from within the resin matrix of TS and TP materials [29]. This enables the reuse of these hydrocarbons as they return to an oil-based state and allows them to be utilized in fuel and chemical feedstocks [34].

Throughout literature, it is possible to find sources for average yields from pyrolysis experiments. This is valuable information to understand the potential for the harvested hydrocarbons to be reused. As shown below in Table A.1 and Table A.2 from Torres et al. and Pickering, respectively, there are many factors that dictate the various hydrocarbon yields and efficiency of pyrolysis processes [34][32].

Table A.1: SMC pyrolysis yields (wt%) with respect to temperature (mean value \pm standard deviation of at least four pyrolysis runs) [34]

Temperature	300°C	400°C	500°C	600°C	700°C
Solid yield	82.6 \pm 1.73	75.2 \pm 0.39	74.9 \pm 0.40	73.9 \pm 0.72	72.6 \pm 0.36
Liquid yield	9.7 \pm 1.62	14.5 \pm 0.77	14.2 \pm 0.63	14.9 \pm 0.75	13.7 \pm 0.25
Gas yield	6.1 \pm 0.12	10.5 \pm 0.92	11.0 \pm 0.59	11.5 \pm 1.46	12.8 \pm 0.33

Table A.2: Pyrolysis products from various composites, expressed as % weight of composite [32]

Composite	Temperature (°C)	Solid yield (%)	Oil/wax yield (%)	Gas yield (%)
Polyester resin with calcium carbonate, alumina trihydrate fillers and glass fibre	500	45.8	45.7	8.5
Phenolic resin (24%) with calcium carbonate filler and glass fibre	500	90.2	8.8	1.0
Epoxy resin with carbon fibre	500	67.4	31.3	1.2
Polyester resin with (70-80%) with glass fibre	550	30.0	59.4	10.6
Polypropylene (60%) with glass fibre	550	44.8	46.8	8.4
Poly ethylene terephthalate (PET) (60%) with glass fibre	550	74.4	13.0	12.6
Vinyl ester resin (30%) with glass fibre	550	83.4	15.0	1.6

As shown in Table A.1, there is a temperature dependence that contributes to the various yield states during pyrolysis. From this table, it is possible to see the potential chemicals that can be reused commercially, such as high carbon ash, oils, and waxes, and even small amounts of natural gases such as methane, butane, propane, etc. [34]

Equally, Table A.2 shows that the chemical composition of the composite material has a large impact to the physical states of the yields [32]. This sheds light into the potential of several TS GFRP materials creating different hydrocarbon yields for various purposes. This essentially allows part of pyrolysis to act as an energy recovery process like in section 4.3.1.3. The combustion of PMMA from a pyrolysis process can be used to continue the process or be used to heat kilns by sacrificing part of the recovered monomer [29]. The recovered PMMA resin also has the ability to be reused in producing new products.

Along with the recovery of hydrocarbons in the resin matrix, pyrolysis also allows for the collection of the fibres and fillers from the end-of-life composite materials [29]. Due to the high and sustained heating process of pyrolysis, there is an impact on the fibres post-recycling, however; it is observed through literature that there is a 50% degradation of overall mechanical properties of the fibres [56]. Despite this degradation, there are successful cases where fibres are reintegrated into industrial products. This includes a case where pyrolysis-recycled fibres from TS composites were integrated at 25% into dough moulding compounds with little reduction in mechanical properties [56]. Notably, using recovered fibres post-pyrolysis also can be integrated into concrete.

Fluidized Bed

As discussed in section 4.3.1.3, the fluidized bed process for TS materials has a two-cycle system where the resin, fibres, and fillers are separated [35]. The resin is led off to be incinerated, whereas the fibres and fillers are collected for further repurposing, if the option is available [35]. There is no repurposing feasibility for the separated TS resin, and so it is incinerated with partial energy recovery from the process, if implemented. This naturally is the most sustainable option for using fluidized beds as less overall energy is lost throughout the process.

Throughout the fluidized bed process, due to the nature of the heated and velocitized silica, it is observed that there will be physical damage to the harvested fibres. Not only are the fibres typically shortened via shredding for improved efficiency in the fluidized bed itself, but the individual strands themselves tend to undergo some deformations throughout the process [35]. Observed in literature, a fluidized bed process brings about a 50% reduction in tensile strength while maintaining similar stiffness at 450 °C [35]. An increase in processing temperature is accompanied by an increased reduction in mechanical strength; this results in a 80% reduction in tensile strength of fibres at 550 °C, and a 90% reduction at 650 °C [35].

Speculations still exist to the main root cause of the degradation of the fibre's strength, but the most likely cause is the combination of high heat and an observation that the velocitized silica removes any treatments to the fibres (i.e., coatings or sizing), which

severely impacts the fibre's ability to bond with the resin matrix and its overall stress bearing capacity [32].

Despite the potential challenges from the lack of proper adhesion of the fibres, similar to the other recycling methods, the use of recycled fibres of various lengths from the fluidized bed process has the potential to create viable concrete composites.

Thermoforming

The thermoforming process for TP composites is one that TS composites are not capable of. By raising the temperature of the material above its glass transition temperature, TP composites can be re-formed into different shapes with the use of a heated mould and added pressure [29]. For the thin rebar rods analyzed in this analysis, thermoforming capabilities are limited; existing rebars have the ability to be bent into different shapes, however, reforming the material into pressed sheets may not be logical. Thermoforming has a wider range of uses with larger sizes of GFRP material, like wind turbine blades, which can be reprocessed into sheets and divided into building materials or skateboards [29]. This is particularly beneficial as the state of the fibres in the composite is maintained, no polymer matrix is lost, and it allows existing materials to gain a new life with minimal change.

Dissolution

As mentioned in section 4.3.1.3, there are different types of dissolution methods for isolating the recovered polymer. In a reprecipitation technique, an additional nonsolvent

(solvent that will not dissolve the polymer) can be added to the filtered slurry mixture, which will cause the recovered polymer to precipitate from the slurry into small fragments of pure polymer [36]. These isolated fragments of polymer can again be filtered out of the solvent/nonsolvent mixture and sent to another process for further repurposing [36].

In the event that expensive solvents like a mixture of chloroform and methanol are used for the dissolution process, it would also be ideal to separate these two solvents such that they can be reused in the future [29]. Through a distillation process, the chloroform/methanol mixture can be pressurized and heated in order to isolate both components [29].

With an evaporative process, the chloroform from the slurry mixture is allowed to evaporate from the polymer, where it is then recondensed and reused for future dissolution processes [29]. Acetone may also be used in place of chloroform as it too is an ideal solvent choice for isolating PMMA while also being safer and more cost effective [29]. In the event the recovered polymer is not completely free of the solvent used, a devolatilization extrusion process may be necessary; this would allow the polymer to become fully dry where it can then be reused further [29].

These recovered fragments of PMMA can be reused and extruded into new products such as children's toys, reprocessed into PMMA sheets, or upscaled and used to make new PMMA resins [10]. While energy intensive and requiring lots of solvent, these processes

allow every part of the composite material to be wholly reusable, making it one of the better choices for increasing the potential use factor of the materials.

Other

Large scale studies in the Netherlands on the recyclability and re-use of composite materials shed light onto some of the other interesting repurposing applications that exist for TS composite materials [56].

Within this study, it was found that if TS GFRP composite materials are large enough in size, there exists several possible applications for re-use [56]. Some of the more heavily discussed and researched possibilities include using large, end-of-life wind turbine blades of the TS variety for creating new products. These include constructing small bridges (after conducting adequate strength verification), constructing furniture frames, recreational playgrounds, and small structures, as well as applications of combining layers of composite materials to make hybrid composites [56]. Each of these applications have their own barriers and setbacks, including economics, testing requirements, design complexity, and usability.

Appendix B: Calculated Raw Data for Statistical Analysis

Table A.3: Raw flexural strength data used for statistical analysis

Material Type	Exposure	Replicate	Flexural Strength (MPa)
1	1	1	841.29479
1	1	2	847.943089
1	1	3	949.472117
1	1	4	758.191048
1	1	5	796.18133
1	2	1	908.632564
1	2	2	877.385557
1	2	3	928.957365
1	2	4	850.887336
1	2	5	726.849066
1	3	1	825.718774
1	3	2	794.946646
1	3	3	738.531078
1	3	4	931.04683
1	3	5	878.525266
1	4	1	739.385859
1	4	2	733.877268
1	4	3	889.352496
1	4	4	747.933672
1	4	5	631.588434
2	1	1	805.583925
2	1	2	837.495762
2	1	3	831.132389
2	1	4	781.555072
2	1	5	822.014722
2	2	1	853.926558
2	2	2	912.811495
2	2	3	820.400135
2	2	4	937.505178
2	2	5	1054.04037
2	3	1	897.90031
2	3	2	712.982613
2	3	3	802.069824
2	3	4	788.868201
2	3	5	817.170961
2	4	1	791.717472
2	4	2	616.582273
2	4	3	785.164148
2	4	4	701.77548
2	4	5	803.494459

The data presented in Table A.3 classifies each flexural strength value calculated for analysis in terms of material type, exposure type, and replicate number. Material type 1 in this case represents specimens made using TS polymer, whereas type 2 represents specimens from the novel TP polymer. Exposure factor levels are as follows: 1 = control specimens, 2 = hot/UV/water exposure, 3 = cold environment, and 4 = corrosive caustic bath. This table was imported directly into Minitab where statistical analysis was performed.

Appendix C: Statistical Results from Minitab

As described in Appendix B, material type 1 in this data represents specimens made using TS polymer, whereas type 2 represents specimens from the novel TP polymer. Exposure factor levels are as follows: 1 = control specimens, 2 = hot/UV/water exposure, 3 = cold environment, and 4 = corrosive caustic bath.

Minitab output for ‘equal variances’ as a check prior to conducting statistical analysis using the general linear model:

BASE DATA, N=5

Test and CI for Two Variances: flexural strength vs material type

Method

σ_1 : standard deviation of flexural strength when material type = 1

σ_2 : standard deviation of flexural strength when material type = 2

Ratio: σ_1/σ_2

The Bonett and Levene's methods are valid for any continuous distribution.

Descriptive Statistics

material

type	N	StDev	Variance	95% CI for σ
1	20	85.072	7237.278	(65.955, 121.652)
2	20	90.872	8257.667	(59.831, 153.011)

Ratio of Standard Deviations

Estimated Ratio	95% CI for Ratio using	95% CI for Ratio using
	Bonett	Levene
0.936179	(0.579, 1.913)	(0.682, 2.516)

Test

Null hypothesis $H_0: \sigma_1 / \sigma_2 = 1$

Alternative hypothesis $H_1: \sigma_1 / \sigma_2 \neq 1$

Significance level $\alpha = 0.05$

Method	Test Statistic	DF1	DF2	P-Value
Bonett	0.06	1		0.804
Levene	0.34	1	38	0.561

Minitab output for the 'general linear model' used as part of the statistical analysis of flexural strength on TS and TP specimens exposed to different environmental exposures:

General Linear Model: flexural strength versus material type, Exposure

Method

Factor coding (-1, 0, +1)

Factor Information

Factor	Type	Levels	Values
material type	Fixed	2	1, 2
Exposure	Fixed	4	1, 2, 3, 4

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
material type	1	13	12.7	0.00	0.962
Exposure	3	103201	34400.3	6.14	0.002
material type*Exposure	3	11926	3975.5	0.71	0.553
Error	32	179277	5602.4		
Total	39	294417			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
74.8492	39.11%	25.79%	4.86%

Coefficients

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	819.3	11.8	69.23	0.000	
material type					
1	0.6	11.8	0.05	0.962	1.00
2	-0.6	11.8	-0.05	0.962	*
Exposure					
1	7.8	20.5	0.38	0.706	1.50
2	67.9	20.5	3.31	0.002	1.50
3	-0.5	20.5	-0.02	0.981	1.50
4	-75.2	20.5	-3.67	0.001	*
material					
type*Exposure					
1 1	11.0	20.5	0.54	0.596	1.50
1 2	-29.2	20.5	-1.42	0.165	1.50
1 3	14.4	20.5	0.70	0.487	1.50
1 4	3.8	20.5	0.18	0.855	*
2 1	-11.0	20.5	-0.54	0.596	*
2 2	29.2	20.5	1.42	0.165	*
2 3	-14.4	20.5	-0.70	0.487	*
2 4	-3.8	20.5	-0.18	0.855	*

Regression Equation

$$\begin{aligned}
 \text{flexural strength} &= 819.3 + 0.6 \text{ material type}_1 - 0.6 \text{ material type}_2 \\
 &+ 7.8 \text{ Exposure}_1 \\
 &+ 67.9 \text{ Exposure}_2 - 0.5 \text{ Exposure}_3 - 75.2 \text{ Exposure}_4 \\
 &+ 11.0 \text{ material type} * \text{Exposure}_1 \text{ 1} \\
 &- 29.2 \text{ material type} * \text{Exposure}_1 \text{ 2} \\
 &+ 14.4 \text{ material type} * \text{Exposure}_1 \text{ 3} \\
 &+ 3.8 \text{ material type} * \text{Exposure}_1 \text{ 4} \\
 &- 11.0 \text{ material type} * \text{Exposure}_2 \text{ 1} \\
 &+ 29.2 \text{ material type} * \text{Exposure}_2 \text{ 2} \\
 &- 14.4 \text{ material type} * \text{Exposure}_2 \text{ 3} \\
 &- 3.8 \text{ material type} * \text{Exposure}_2 \text{ 4}
 \end{aligned}$$

Fits and Diagnostics for Unusual Observations

flexural					
Obs	strength	Fit	Resid	Std Resid	
18	889.4	748.4	140.9	2.11	R
30	1054.0	915.7	138.3	2.07	R

R Large residual

Curriculum Vitae

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- Mackin, C. D., Saha, G. C. (2019). Pultrusion manufacturing and flexural behavior analysis of thermoplastic polymer-based FRP composites for high-strength applications, *11th Canadian-International Conference on Composites (CANCOM 2019)*, Conference Proceeding, Vol. I, 8 pages.
- Mackin, C. D., Saulnier, B. T., Saha, G. C. (2021). A novel life cycle framework (LCF) development to study the comparative mechanical, environmental, and economic behaviour of pultruded thermoplastic vs. thermoset glass FRP composites, *The International Journal of Life Cycle Analysis*, In-progress, 57 pages.
- Mackin, C. D., Saulnier, B. T., Saha, G. C. (2021). Methodologies for recycling and repurposing of thermosetting and thermoplastic GFRP composites, *Encyclopedia of Materials: Plastics and Polymers*, In-progress, 25 pages.

Conference Presentations:

- Mackin, C. D., Saha, G. C. (2019). Pultrusion manufacturing and flexural behavior analysis of thermoplastic polymer-based FRP composites for high-strength applications. *11th Canadian-International Conference on Composites (CANCOM 2019)*.