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Recycling of fibreglass wind turbine blades into reinforced PLA composite with enhanced mechanical properties and toughness

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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présenté par **Amirhosein MOSLEHI ALALEH GOORABI**

en vue de l’obtention du diplôme de *Maîtrise ès sciences appliquées*

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DEDICATION

To my beloved wife

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RÉSUMÉ

Afin de pouvoir considérer l'éolien comme une alternative propre et durable aux énergies fossiles, des solutions de recyclage doivent être trouvées pour son nombre croissant de déchets composites. Ce travail vise à développer plus avant une solution de recyclage des composites renforcés de fibres de verre des pales d'éoliennes en incorporant les fibres récupérées dans de l'acide polylactique (PLA) pour en faire un composite renforcé aux propriétés améliorées par rapport au PLA pur. Les fibres peuvent être utilisées comme filament pour l'impression 3D. Pour ce faire, des parties de pales d'éoliennes à structure composite pure ont été meulées mécaniquement et la fraction riche en fibres du composite déchiqueté a été affinée par plusieurs opérations de tamisage pour obtenir des fibres de verre courtes avec des traces de résine. Ces fibres de verre recyclées sont utilisées à teneur fixe de 15 % poids et sont incorporées au PLA par extrusion bivis. Les propriétés mécaniques du composite obtenu ont été comparées au PLA pur. Les premières observations ont démontré non seulement des améliorations mineures de la résistance à la traction des échantillons, mais également une diminution de l'allongement à la rupture. Ce dernier paramètre est particulièrement important quand on considère que le désavantage principal du PLA est sa fragilité et sa faible ténacité. L'aspect le plus important pour avoir un composite renforcé de fibres acceptable est d'améliorer l'interaction entre la matrice et la fibre. Plus les interactions sont fortes, plus les propriétés mécaniques sont améliorées. Pour améliorer l'adhérence entre le PLA et les fibres de verre recyclées, un agent de couplage au silane a été utilisé pour les rendre compatibles. La compatibilisation a permis d'obtenir de meilleures propriétés mécaniques par rapport au PLA pur et au composite non compatibilisé, mais le problème de fragilité était toujours persistant. Pour résoudre ce problème, une stratégie de modification en bout de chaînes via l'incorporation d'un acide carboxylique, 1,2,3,4-butane tetracarboxylic acid (BTCA) dans le PLA a été employée. Cette modification a amélioré la ténacité du PLA de 15 % par rapport au PLA pur sans sacrifier la résistance. L'étape finale était une modification simultanée des fibres recyclées et du PLA via le silane et le BTCA, respectivement, par extrusion bi-vis. L'effet simultané de l'agent de couplage et de l’agent durcissantsur le comportement mécanique et thermique du composite a été étudié et comparé au PLA pur et au composite non traité. Enfin, pour évaluer la compétitivité du composite final, une comparaison a été faite avec un composite similaire disponible sur le marché composé de fibres de verre vierges et de PLA.

ABSTRACT

The wind power industry requires recycling solutions for its increasing composite waste, to be considered as a clean and sustainable alternative to fossil fuels. This work aims to further develop a recycling solution for glass fibre reinforced composites from wind turbine blades by incorporation of the recovered fibres into polylactic acid (PLA) to fabricate a reinforced composite with enhanced properties compared to the neat PLA for the purpose of 3D printing filament. To achieve this goal the composite part of the wind turbine blades was mechanically ground and the fibrous-rich fraction of the shredded composite was refined through several screening operations to achieve short glass fibres with traces of old resin. These recycled glass fibres are used to reinforce PLA at fixed content of 15% mass via twin-screw extrusion. The mechanical properties of the obtained composite were compared to the neat PLA. The preliminary observations demonstrated not only minor improvements in tensile strength of the samples but also a decrease in elongation at break. The latter comes of importance when one considers that PLA's main disadvantage is its brittleness and low toughness. The most important aspect of the success of a fibre reinforced composite is the interactions between the matrix and the fibre. The stronger the interactions, the more enhancement. To improve the adhesion between the PLA and the recycled glass fibres a silane coupling agent was employed to compatibilize them. The compatibilization resulted in better mechanical properties compared to neat PLA and non-compatibilized composite, however, the problem of brittleness was still persistent. To address this problem, a chain-end modification strategy via the incorporation of a carboxylic acid, 1,2,3,4-butane tetracarboxylic acid (BTCA), into PLA was employed. The final step was a simultaneous modification of recycled fibres and PLA via silane and BTCA, respectively, through twin-screw extrusion. The concurrent effect of both coupling agent and toughener on the mechanical and thermal behaviour of the composite was investigated and compared to neat PLA and non-treated composite. Finally, to evaluate the competitiveness of the final composite, a comparison was made with a similar composite available on the market comprised of virgin glass fibres and PLA.

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LIST OF SYMBOLS AND ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
APTES	(3-Aminopropyl) triethoxysilane
BTCA	1,2,3,4-Butanetetracarboxylic acid
CAN	Covalent adaptive network
DSC	differential scanning calorimetry
FFF	Fused filament fabrication
FTIR	Fourier-transform infrared spectroscopy
FRP	Fibre Reinforced Plastics
GF	Glass fibre
GFRP	Glass fibre reinforced polymer
IS	Impact strength
PCL	Polycaprolactone
PEEK	Poly ether ether ketone
PLA	Polylactic acid
R-GF	Recycled glass fibre
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
TPE	Thermoplastic elastomers
TPS	Thermoplastic starch
TPU	Thermoplastic polyurethane

CHAPTER 1 INTRODUCTION

1.1 Context

Green energies, specifically wind energy, are potential alternatives to conventional sources of energy such as fossil fuels due to their renewable and non-GHG emitting nature. The expectations are that wind energy could provide roughly 15% of the world's energy demand by the end of 2050 [1]. Canadian wind energy association (CanWEA) plans to cover 55 GW of the Canadian’s power need by the end of the year 2025 [2]. It is a fact that wind offers clean and renewable energy without any emission, however, this may not be correct considering its manufacturing stage. Harnessing the wind energy requires erecting tall towers consisting of a base, tower and turbine with cantilevered blades. These turbines transform wind energy into electrical power. Although most parts of these towers are made from recyclable materials, the turbine blades whose length can reach 100 meters [3], are mostly made of fibre reinforced composites that are considered non-recyclable materials. The end of service life for these turbine blades and their disposal makes them problematic for the environment. Fibre-reinforced materials have no established recycling method up to now. These composites, most of which are composed of glass fibre and thermoset polymers, make up more than 90% of the structure of a wind turbine blade [4]. This study investigates the composite part of the wind turbine blades and their possibility to be reused to establish a recycling method for the fibrous-rich fraction of the composites. The idea is to incorporate the recycled glass fibres into a homopolymer to achieve a composite with superior properties. This study aims to modify the interactions between the recycled fibres and PLA through silane coupling agents. The shortcoming of PLA also is addressed by employing a chain end modification strategy.

1.2 Objectives

Given that the rapid growth of wind turbine composite waste is a global challenge and landfilling endangers the environment and squander the resources, the main objective of this research is to find a solution to reuse components of wind turbine blade composites, specifically short glass fibres. This objective can be achieved by mechanically grinding the composite blades, which are mostly comprised of fibre reinforced thermosets, to obtain shredded composite and utilizing screening operations to refine the short fibres. The incorporation of the obtained fibres into a new homopolymer to fabricate a fibre reinforced composite enhances the mechanical properties of the homopolymer and makes it suitable for specific usages as well as giving those recycled fibres a new life and prevents them from landfilling. For the new composite to be competitive to the composites made of virgin materials, further development is needed to be done. Supplementary additives can be incorporated along with the recycled short fibres and the homopolymer to ensure a comparable product with enhanced properties.

1.3 Plan of dissertation

This thesis comprises 6 chapters. Chapter 2 will briefly review the current literature on wind turbine composite recycling and glass fibre reinforced composite fabrication. Chapter 3 is concerned with the applied methodology: techniques, materials, characterization, equipment, and facilities that made this study possible. Chapter 4 reports the obtained results of this research in the form of a scientific article. Chapters 5 and 6 present the general discussion and conclusions, respectively.

CHAPTER 2 LITERATURE REVIEW

2.1 Wind Energy

Wind energy is considered a promising green solution to the global warming problem caused by fossil fuels. Due to its advantages, there is a high demand for it globally and it has attracted many governmental funds and investments to itself and is expected to expand more in the forthcoming decades. 205 gigawatts (GW) is the amount of energy that is currently produced in Europe using wind power, which could grow by 90 GW five years from now. The wind industry in the EU will absorb €208 billion by the year 2023. This amount of green energy is responsible for 15% of the EU's energy consumption and in 2023 30% of energy consumption is going to be covered by wind power [5].

It has been many decades that wind power has been put to work in Canada, specifically in prairie lands. Most of the green energy production in Canada is from wind power. In the year 2019, the wind industry supplied 13 GW which covered 6% of the Canadians need [2]. The Canadian Wind Energy Association (CanWEA)'s plan is to expand wind power and hopes to supply Up to 55 GW by the year 2025, covering 20% of the Canadian electricity consumption [2]. More than $23 billion will be invested in wind power in Canada, which can create up to 60,000 person-years of employment [2]. At present, many operational wind farms in Canada can generate 100 megawatts (MW) and higher. The first plant with a capacity of at least 100 MW was Centennial Wind Power Facility in Saskatchewan. The largest operational farm in Canada is the 363.5 MW Seigneurie de Beaupré Wind Farms in Quebec [6, 7]

Among all the other advantages wind power has to offer, price competitiveness is the most appealing one. And with the innovations in technology, such as larger turbines and novel methods for optimizing the harvesting, the price drops even more which makes the production more affordable in the future. In contrary to conventional sources of energy, in which the fuel price determines the final cost of the produced energy, there is no fuel involved in the wind industry so the price can be kept stable in the long run. Wind power can also be a sustainable solution to the concerns about the impact of energy production on climate change. No air or water pollution is generated during power production and it also consumes less water than all the other means of power generation. Canada plans to emit 30% fewer greenhouse gases by the year 2030 compared to the year 2005, Which emphasizes the role of wind energy as a clean non-GHG emitting electricity generator. The estimations show that 17 megatons of GHG emissions per year can be avoided if the plans for the year 2025 are achieved [2]. To harvest wind energy, wind turbines are needed to transform the energy of the moving air into electricity. These turbines are usually erected in groups to form “wind farms” in places with suitable climates.

The average life span of a wind turbine is in the range of 20-25 years which means that thousands of wind turbines will be dismantled to be replaced by new turbines with more efficiency and newer technology. The wind industry, to fully achieve its goal of sustainability, needs to find sustainable end-of-life recycling solutions. Considering the lifespan of a turbine, most of the turbines erected in the early 2000s will be decommissioned in 2020-2030. More than 28% of the current turbines of the EU are older than 15 years [8]. The number of blades in the USA which needed to be replaced by the year 2021 will be 8000 and in the EU this number is 3800 per year [9]. A wind turbine is composed of several parts with different materials and designs. At present, many of these parts are recyclable and reusable but the wind turbine blades which are composed of thermoset polymers are not easy to recycle. Many different materials can be found in a blade such as thermoplastic coatings, fibre-reinforced polymers, glass fibre, carbon fibre, balsa wood etc. which makes the blades hard to recycle [10]. The wind industry, is one of the largest consumers of composite materials globally, with a demand of 2.5 million tons of it per year [11]. On average, a 5 MW wind turbine blade can have around 50 tons of polymer materials in it [12]. If the global trend stays the same, the amount of decommissioned blades that go to waste will surpass 45 million tons by the year 2050 [13]. With this trend, every megawatt in new wind plants will be responsible for 10 to 15 tons of composite waste [10]. These numbers emphasize the need for sustainable recycling methods to be developed to deal with the growing composite waste of this industry. Several methods are in use to deal with the end of life of these blades such as sending them to landfills, incineration and recycling [10].

2.1.1 Wind Turbine Blade Structure

A simple wind turbine is comprised of a rotor mantled on a tower, and three blades are attached to it. It can be 90 meters high and the length of the blades can be 45 to 90 meters [14]. A wind turbine blade is comprised of two parts attached by several links at the top and bottom.

Every turbine blade should withstand two loads, one from its weight and the other is wind force. The blade material should have low density and high stiffness in order to be successful in that situation [15]. Also, the industry demands larger size blades to reduce its operational costs. This size expansion results in weight load increase and also more structural stiffness is required. Firmness, fatigue resistance, corrosion resistance and appearance are the other factors that are important in blade design [16]. The above-mentioned specifications can be found in composites which makes them the best option for the turbine blades. To have composites, two or more components with different properties are needed to be combined. One component will be the matrix which supports the second component which usually is a fibre with much higher strength. By changing the proportion of each component in the composite, desired mechanical properties can be achieved. Blade compositions may vary between different suppliers, but these are some common compositions for the blades [17].

- Thermoset polymers such as epoxies, polyesters, polyurethane
- Glass, carbon, basalt, and aramid fibres as the reinforcement
- Balsa wood or foams as the core
- Thermoplastic coatings
- Metals such as copper and steel

The most common type of rotor blade is the Glass Fibre Reinforced Plastics (GFRP) [10].

2.1.1.1 Fibres

The importance of fibre in a composite usually is due to its contribution to the strength of the composite and this property depends on the strength of the fibre itself, the percentage of the fibre and also its affinity with the matrix. As the volume of the fibre increases in the matrix the mechanical properties of the composite improves but there is a threshold for the fibre content that if passed, there is the chance that the fibres in the absence of the resin interact with each other and mechanical properties such as fatigue strength start to decrease [18]. Glass fibre is the strand of extremely fine fibres made out of glass. For glass fibre production, silica-based materials are extruded into fibres with microscale diameters. At present several types of glass fibre are produced such as E-glass which its composition is mostly alumino borosilicate glass, A-glass which is alkali-lime glass that has no boron oxide in it, D-glass which has little Dielectric constant and R-glass which is aluminosilicate glass that has no magnesium oxide and S-glass which is aluminosilicate glass with high magnesium oxide [19]. From the mechanical properties' aspect, the glass fibres, generally, are inferior compared to the other alternatives such as carbon fibres and aramid fibres. But the advantage that the glass fibre has over the other options is its price and also it acts more ductile as the reinforcement in a composite. These advantages make the glass fibres the first choice for the reinforcement of the many plastics which results in the production of a composite with lower density than the metals but way stronger than them. These composites are named Glass Fibre Reinforced Plastics (GFRP). In the wind industry also most of the wind turbine blades are GFRPs with 45 to 70% of fibres and 30 to 55% of plastics. The advantages that make GFRPs the best option for the turbine blades are high strength to weight ratio, high fatigue strength and corrosion resistance and reasonable production cost [17].

Carbon fibres are an alternative to glass fibres as reinforcement in composites. Carbon fibres are tougher and have lower density compared to glass fibres and tougher turbine blades with smaller thickness and lighter weight can be produced using them. The disadvantages of these fibres are higher cost, less damage tolerance and less ductility [20].

Aramid and basalt fibres are other alternatives to glass fibre. Aramid fibres have better mechanical properties and are tougher but they are not compatible with resins and also tend to absorb moisture and UV degradation is another major problem [21].

Basalt fibres are mechanically stronger versions of glass fibres with less cost compared to carbon fibres. There have been some promising efforts to use basalt fibres along with carbon fibres to manufacture turbine blades [22, 23].

Some recent works investigated the possibility of the implementation of natural fibres such as flax, hemp, jute etc. as the reinforcement in blade composite. The driving force behind these works is the sustainability and lower cost of these fibres. But the dis-similarity of the fibres, high moisture, and low thermal tolerance are the natural fibre drawbacks [24]. In a study done by Holmes et al. [25], bamboo fibres were used to manufacture turbine blades. bamboo strand mats, which are way cheaper than glass and carbon fibres and also are sustainably recyclable, are implemented in the epoxy resin via the hot press. The obtained composite showed promising results with high strength and stiffness.

2.1.1.2 Matrices

Most of the practical wind turbine blades use thermoset polymers as the matrix but there are also a minority of blades in which thermoplastics have been used.

2.1.1.2.1 Thermosets

Back then the first option for the turbine blades was the polyester resins but now the epoxies have claimed their position due to their ability to be utilized in the production of longer and larger blades and most of the blade producers tend to use epoxy resins as the matrix [26].

2.1.1.2.2 Thermoplastics

The main reason behind the studies on thermoplastics is their recyclability. However, they have some drawbacks that make them less favourable in the case of composite production. Most of these polymers need high temperature in order to be processed which means they need more energy and consequently have more cost and also this high temperature can affect the quality of the fibres. Their higher viscosity also can be a problem for manufacturing large, thick parts. As a comparison, the viscosity of the thermoplastics area between 100 to 1000 Pa.s and this value in thermoset polymers is in the range of 0.1 to 10 Pa.s. thermoplastics can be melted as they have a melting temperature below their degradation temperature but thermosets since their molecules are cross-linked and formed a network cannot be reshaped once they are cured. In the case of fatigue resistance, thermoplastics cannot compete with thermosets [26]. Thermoplastics, generally, display larger elongation at break compared to thermosets and also their raw materials can be stored for a longer time without unwanted reaction [27].

2.1.2 Current Status of Blade Scraps

At present, end of service life turbine blades is dealt with in three main ways, landfilling, incineration, and recycling. Landfilling, which is the least preferred method due to its pollution, is the most common way to dispose of the blades in the US [28] but it is forbidden by law in some countries in the EU like Germany. Due to the large dimensions of the blades, lands on large scales are needed for this purpose. The blades are manufactured to be resistant to harsh climate and to withstand mechanical loads in long term, so their degradation in the landfill does not happen spontaneously and naturally.

Incineration, burns the flammable compounds in blades and reduces their volume and what remains after, are ashes that can be up to 60% of the materials. In this method, which is more common in Europe, energy can be recovered and be used in other industries. The drawbacks are the ashes that need to go to landfills and more importantly the toxic fumes and by-products that can be emitted from the resin combustion.

2.1.3 Recyclable Composites

Many researchers believe that the recycling problems of wind turbine blades should be solved at the production level. The wind industry is a fast-evolving industry with huge potentials and also it is very young which means most of the commissioned turbines are still at work and has not been yet reached their end of service life and in near future, the number of dismantled blades will blow up and the recycling section should be prepared for that. The above-mentioned problems and challenges on the path to sustainable recycling of the thermoset composite blades convinced researchers to work on recyclable materials with sufficient mechanical properties to replace thermoset composites. The focus of these studies is on thermoplastic polymers, bio-based and bio-degradable substances [10].

2.1.3.1 Thermoplastic Composites

Compared to thermosets, thermoplastics are re-mouldable by heat and their production time is shorter. However, their production needs high heat as well as specific cooling. Lystrup worked on the mechanical properties of polypropylene and polyethylene/fibre composites [29]. In [30] Tusavul et al. used Polyetheretherketone (PEEK) as the matrix (60%) and carbon fibre (40%) as reinforcement and obtained a thermoplastic composite via injection moulding and compared its mechanical properties with thermoset composite (epoxy/GF). Their results demonstrated that the thermoplastic composite is lighter 28% with higher stiffness. Anionic polyamide-6/glass fibre composite was developed by Joncas [31] and was compared to the epoxy-based composite and it showed the same properties with 3% less weight. In [32] Small parts made of polypropylene and glass fibre composite, manufactured via vacuum-assisted thermoforming, are attached to form blades. These blades were used in a small-scale wind farm and the obtained power was at acceptable levels. A new class of thermoplastic resins, Elium®, a two-part reactive acrylic-based resin, with room-temperature curability has been developed by Arkema. Murray et al. [33] used Elium to produce a 13 meters turbine blade and compared it to an epoxy-based blade. The results showed similar fatigue resistance, but the thermoset blades showed 5 to 7 times more structural damping. The recyclability and the possibility of welding the impaired parts of Elium composites make it a promising substitution for epoxy-based composites.

2.1.3.2 Recyclable Thermosets

The advantages of the thermoset resins, such as strength and low-temperature manufacturing make them the most used material for composites. The resin molecules react with each other through covalent bonds after being crosslinked and form one giant network of interconnected molecules and that is why they can not be reshaped with heat. Efforts have been made to make these reactions reversible so that the molecules can be detached from each other, reshaped, and again cured. In this way, the composites can benefit from the recyclability of the thermoplastics and the high performance of the thermosets. The reversion of the covalent bond can be done by an extrinsic factor such as heat, UV light, catalyst, or other chemical substances. Garcia et al. [34] developed a new class of thermosets with high young’s modulus, by condensation of paraformaldehyde with bisanilines. These thermosets can be degraded using low pH (<2) acid to bisaniline monomers. Recyclamine, introduced by Pastine et al. [35] as an epoxy hardener, enables thermoset recycling. The obtained bonds can be decomposed by heat and an acidic environment. By the addition of specific additives like acetals in tetrahydrofuran and hydrochloric acid, esters in aqueous sodium hydroxide, and aminals in concentrated sulfonic acid, to the epoxies, thermosets with decomposability can be produced [36]. Wu et al. used Cleavamine® patented by Adesso, to design a recyclable epoxy and used this resin as a matrix and produced a composite with glass fibre through vacuum infusion. The obtained composite was compared to the non-recyclable epoxy/GF composites and then recycled, and the recovered fibres also examined and compared. The results showed that the recyclable composite was comparable to the commercial ones. The recovered GFs' quality was comparable to virgin fibres. The resin residues were also reusable. However, the major drawback of their work is the component that is used to decomposes the epoxy is Hydrogen peroxide which impose a significant cost to the process and also is not that safe to work with [37].

Vitrimers and Diels-Adler polymers are new technologies based on reversible polymeric reactions that can lead to self-healing polymers and also recyclable resins [10]. Covalent adaptive network (CAN) is a concept developed by Bowman et al. [38] and is about the reversibility of the covalent bonds in cross-linked networks which enables the recyclability of the thermoset resins. The exchange reaction within the polymer network can be initiated via light [39] irradiation [40] or thermal processes [41]. The bonds can be cleaved and reshaped through disulphide exchange [42], siloxane equilibrium [43] Diels-Adler reactions [41]. Liebler et al. developed a novel class of materials and named them Vitrimers. Vitrimers are covalent-bonded networks of molecules that can change their topology by thermally activated bond-exchange reactions. Liebler and colleagues implemented transesterification in hydroxyl and ester groups in an anhydride-cured epoxy resin and developed a reformable thermoset. These silica-liked networks have been developed through transesterification of epoxy and fatty dicarboxylic or tricarboxylic acids and their viscosity resembles vitreous silica in case of behaving Arrhenius-like near the glass transition. Vitrimers can be welded to make complex objects by local heating. By heating these networks, the existing hydroxyl and ester groups go through transesterification and the network becomes ductile and can flow like a viscoelastic liquid, on the contrary, by lowering the temperature, the exchange reactions are frozen and the vitrimers act like normal thermosets [44]. Chen et al. [45], used epoxy vitrimers along with the graphene nanoplatelets to manufacture a composite via hot press. Their composite showed good mechanical properties and the epoxy vitrimer provided good heal ability and recyclability. Luzuriaga and colleagues [46], developed an epoxy vitrimer ,based on reversible exchange of aromatic disulfide, with diglycidyl ether of bisphenol A (DGEBA) as monomer, Diethyltoluenediamine (DETDA) as the reference hardener and 4-aminophenyl disulfide (AFD) as the dynamic hardener. They made glass fibre reinforced composite using this dynamic epoxy and evaluated its mechanical properties, recyclability and its repairability.

Although recyclable thermosets with reversible reactions are promising, more research and development is needed for them to be usable on industrial scales for purposes like wind turbine blades.

2.1.4 Wind Turbine Recycling

To comply with the global trends of sustainability and green economy, the wind industry is working on turbine recycling and trying to find a better end-of-service life upshot for them. Nevertheless, turbine recycling is complicated and challenging due to their complex structure as well as non-recyclability nature of the utilized resins.

Every wind turbine blade is a complex structure composed of different and heterogeneous parts such as shear webs, load-carrying beams, trailing edges, and shells. Each of the blade producers has its standards and produce their blades with their unique design and materials. The condition of the dismantled blades also, can vary drastically with each other due to their service life condition as well as their service life span. Some blades are damaged, and some are just dismantled to be replaced by the newer technology. This means that the quality of the obtained materials from different materials is not the same. Another challenge is the dissimilarity of the obtained amount of each specific material from different blades. consequently, finding an all-embracing recycling method that can be flexible toward the fluctuation in quality, quantity, material and design of the dismantled blades remained a challenge [26].

The other major obstacle on the path to blade recycling is the thermoset resins that are used along with the fibres are not recyclable. No melting point can be defined for the thermoset resins once they are cured; by heating, they can not be remoulded, they just burn. One possibility is to cut them and reuse them as components for the new composites. It is obvious that this option has limited applications and cannot be a solid solution on large scale. The other course of action which needs more processing and preparation is to convert the blade materials to a new source of raw material. Many studies focused on methods for separating the fibres from the resin and then reuse the fibres in new composites [47]. It is obvious that these separation methods need complex processes and significant energy since in most of these processes heat or chemical solvents are used to eliminate the resin part. In supercritical processes, a temperature of 280 °C is needed and in a fluidized bed up to 450 °C is needed [26, 48, 49]. This high temperature gets rid of the resin residue but on the other hand, it can affect the recovered glass fibres' properties. The recovered fibres become brittle and are no longer comparable to virgin fibres in case of mechanical properties and also cost. Since the virgin fibres are not that expensive, the recovered fibres that energy and money spent for them can not compete with the virgin fibres in industrial scales. Another way to give the blade scraps a new life is to crush them and utilize them as cheap fillers. For example, this method is in use in the EU, and crushed blade scraps are used in the cement industry [50]. From all the information above it can be deduced that several integrated methods along with each other are needed to be combined to overcome the recycling problem of the wind turbine blades and a straightforward and feasible solution that can cover all the variations does not exist up until now.

Recycling methods in the case of polymers and composites can be categorized into four groups, primary recycling which is reusing the materials for the same purpose, secondary recycling which is reusing the materials for a purpose other than the primary use, in tertiary recycling chemical methods are used to recover the polymeric components of the composite and in quaternary recycling, incineration is used for heat energy recovery [10, 51].

In primary recycling, before performing any process on decommissioned blades, it is investigated that whether the blade or some part of it is reusable regarding the safety issues. In Netherland, 20% of the blades are recovered and refurbished and find their way back to the market [52].

Secondary recycling is about mechanical processes to make blades reusable without any chemical alteration. The composites being crushed, milled and sieved to achieve a fibrous-rich portion and resin-rich portion. Due to the high mechanical properties of GFRPs even after mechanically altered they retain most of their properties and are still strong materials. These crushed scraps can reinforce new materials. The company LafargeHolcim uses Crushed blade scraps in cement manufacturing [53, 54]. They also use the resin residue as fuel for their cement production plant.

Tertiary recycling tries to separate the fibres from the resin utilizing thermal or chemical processes. A thermal process, that is in use, is the pyrolysis in which at a high temperature (450 to 700°C), without Oxygen being present, the resin is decomposed and turns into gas and oil and the fibrous part remains free of resin. The Refiner company recovers the fibres from the blades using this method, but their fibres are 50% less strong. Another thermal process is the fluidized bed, in which the composite is heated up to 550°C with hot air and the remained fibres can be recovered [55]. In a work done by Akesson et al. [49] microwave heating used for decomposing the composite and the recovered fibres showed a 25% decrease in their strength.

Solvolysis uses chemical substances like acids, ammonia or glycol to degrade the resin portion of the composite and recover the fibres [17]. The recovered fibres are implemented in wall paints, concrete or particleboards or core material sandwiched between panels [17]. The major problem with most of these methods is that they are not feasible economically due to the expensive processes compared to the cheaper virgin materials.

2.1.4.1 Mechanical Recycling of Wind Turbine Blades

Mechanical recycling is one of the most straightforward methods to deal with decomposed blades. the industrial utilization of this method is in progress [56]. By grinding the composite, a mixture of single fibres, chunks of resin and fibre mats embedded in resin are obtained. The quality of the crushed material depends on the obtained long fibre amount since the most valuable portions are the ones with high GF content and long fibres. The major drawback of this method is the breakage of the fibres regarding the fact that the continuous fibres are more useful. The mechanical grinding can also diminish the mechanical properties of the fibres, but this decrease is less significant compared to the other methods of fibre recovery such as pyrolysis.

Th recovered materials can reinforce new materials such as cement and asphalt that are used in the construction industry [57]. Schmidl et al.[50] mechanically ground the blade composites and incorporated them in cement production.

Beauson and colleagues [58], studied the reuse of shredded composite materials as reinforcement for new composites, and observed a reduction in the mechanical properties compared to virgin reinforcement, by increasing the shredded composite percentage. It has been suggested that in order to have a successful reinforcement, using the recovered fibres in new composites, it is necessary to adjust and optimize the process factors. In another work by Beauson and colleagues [59], the shredded composites obtained from a 26 meters long blade, incorporated into polyester resin. The decomposed blade first has been ground using a miller and the obtained materials went through sifters. Composites with different concentrations of shredded materials from 10 to 30 wt% were manufactured via vacuum resin infusion. The stiffness of the final composites increased significantly compared to the pristine polyester resin. However, the ultimate tensile strength and the elongation at break of the composites showed a decrease compared to the neat polyester. the Scanning electron micrograph (SEM) imaging of the samples demonstrated the spacing and cracks at the interface of the matrix and fibres and also fibre pull-out could be observed in composite surface and both of these phenomena are signs of weak interfacial adhesion. They suggested chemical treatment of the shredded composites to improve the adhesion between the recovered fibres and matrix. As it is mentioned before, the size and length of the recovered fibres play an important role in their ability to successfully reinforce new composites. Most of the studies on the reincorporation of the shredded composites suggest that using the recyclates can deteriorate the final mechanical properties of the new composites and this degradation can be due to the breakage of the fibres after milling (granulation process) [60] or the poor bonding between the recovered fibres and the new resin [61]. The use of shredded composites as cheap fillers makes them a low-value product. Palmer et al. [62] suggested that with careful separation, classification and reformulation a more reliable and profitable solution can be developed. They used an air-classifier to separate the useful glass fibres with mechanical properties comparable to virgin fibres and produced new composites with acceptable properties. Mamanpush et al. [63] worked on recycling the wind turbine blades as the raw material for the new composites. They hammermilled the scrap blades and incorporated them into methyl-diisocyanate (Rubinate 1840) (pMDI) to produce a new composite in the form of panels. They suggested that these panels can be developed and used in form of floor tiles and plastic road barriers. They also used recycled wind turbine blades to produce reinforced thermoplastic composite using High-Density Polyethylene (HDPE). They also investigated the effect of coupling agents (Silane and Maleic anhydride) on the composite properties. The addition of modifiers significantly increased the module of rupture and module of elasticity compared to non-modified composites [64].

Figure 2-1 shows a summary of the current methods used for recycling thermoset blades.

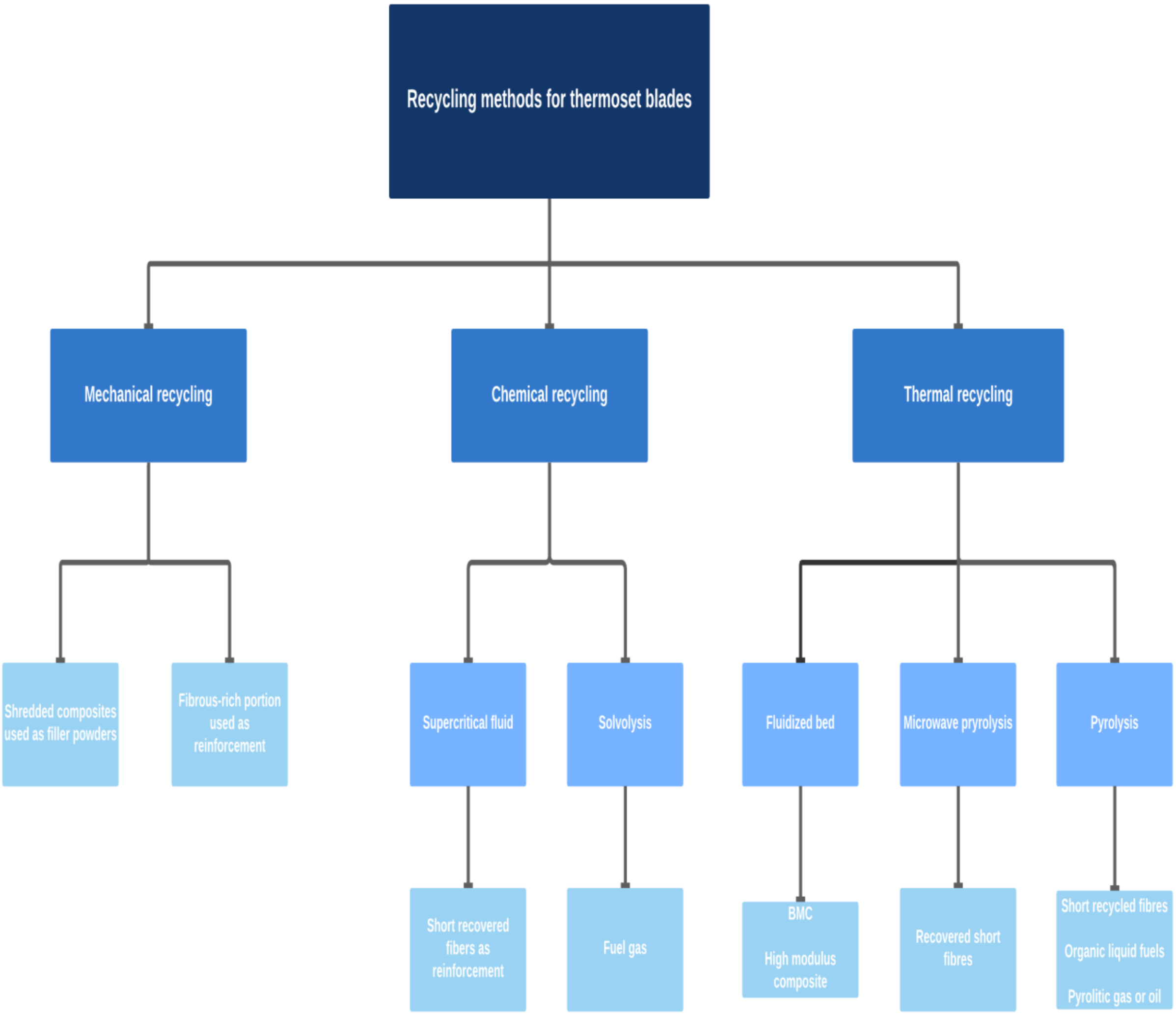


Figure 2.1 A summary of recycling methods for thermoset blades

2.2 Additive Manufacturing

The joint ISO/ASTM terminology standard has defined additive manufacturing (AM) as the "process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies [65]." AM has been commonly referred to as 3D printing. Basically, a sequence of computer-controlled processes fabricates actual 3D objects employing layer-by-layer methods using materials such as metallic, plastic, ceramic, composites.

Conventional manufacturing processes such as machining, forming, and casting are remarkably unlike any AM process. They are so many advantages associated with AM technologies. Unlike other manufacturing processes, essential parts for requested personalization and customization can be easily made. It significantly reduced the production cost as well as manufacturing time of individualized parts even when these parts are fabricated in small quantities. It eliminates the necessity of specific tooling existence in part creation. Moreover, AM excessively minimizes material waste. Some additive manufacturing technologies can even facilitate the production of objects with complex geometries and heterogenous compositions. Furthermore, AM is an environmentally friendly process in which no toxic chemical exists [66].

Many AM technologies have been developed since their debut in the mid-1980s. Most of them have been evolved through the years. Some of the best-known processes include Stereolithography (SLA), Selective Laser Sintering (SLS), Fused Filament Fabrication (FFF) process, Fused Layer Modelling (FLM), Laminated Object Manufacturing (LMO), Selective Laser Melting (SLM), Direct Metal Deposition (DMD), Laser Metal Deposition (LMD), and others [67-69].

The major drawbacks of additive manufacturing the fibre reinforced composites are weak interaction and bonding between the matrix and fibre, the presence of voids in printed parts which can act as weak points and the challenges associated with continuous fibre printing. Also, the addition of fibres can lead to blockage of the printer nozzles, wear, and an increase in manufacturing time.

In order to achieve the desired mechanical properties, some crucial parameters such as fibre sizing and its exact placement must be considered. Longer fibres in continuous form result in higher mechanical properties.

There are recent works that used composites as the raw material for AM processes to manufacture stiff and high strength products [70-73]. The most common material for FFF processes is thermoplastics which makes produced parts with inferior strength and stiffness [74-76]. Incorporating reinforcement such as fibres and nanoparticles in the thermoplastics as the feedstock for the FFF is getting popular and makes the path to production of high-performance products using these processes. Most of these studies focus on the incorporation of short fibres. Carneiro et al. [77] produced polypropylene filled with glass fibres and used them in FFF processes and the mechanical tests demonstrated 30% and 40% improvement in modulus and strength. In [78] the production possibility of Polylactic acid nano-hydroxyapatite composites using 3D printing has been studied. Up to 15% of filler has been integrated into the PLA without any solvent or chemicals usage and the obtained filament has been printed via a cheap 3D printer and the printed bone substitute showed promising results compared to the pure PLA. In another work [79] Thermoplastic starch (TPS) was used to enhance the mechanical properties of the Acrylonitrile butadiene styrene (ABS). To modify the interactions between the matrix and the filler, glycerol was used to plasticize the composite. The obtained filament showed improvement in thermal and mechanical properties. Another work on ABS was the addition of iron powder to it. This addition resulted in a strength decrease but on the other hand, it improved the thermal conductivity and heat capacity which guarantees printed parts with consistency in dimensions.

Besides the fillers, fibres also have been enlisted for reinforcing the thermosets in FFF processes. Shofner and colleagues [80] used Vapor-grown carbon fibres (VGCFs) as the reinforcement in an ABS copolymer and used the composite for FFF processes. The 10% VGCFs were integrated into the ABS via Banbury. The dispersion was observed with SEM imaging. The mechanical tests demonstrated that the tensile strength and modulus of the VGCF-filled ABS improved 39 and 60 % respectively compared to the pure ABS. The results from dynamic mechanical analysis demonstrated a 68 % improvement in stiffness. In another work, [81] short glass fibres were added to ABS to overcome the low strength of the ABS. Although the short-glass-fibre-filled ABS showed improved strength and was suitable for FFF processes, the presence of fibres decreased the flexibility of the final composites. To tackle this problem compatibilizer and plasticizer have been added to the system. The final filament showed promising results. Pristine carbon fibre was used in [82] as reinforcement for ABS to produce FFF feedstock. The mechanical tests on their specimen demonstrated that the addition of carbon fibre increased the tensile modulus and strength but contrarily it diminished the ductility and toughness of the composite. The highest value for strength was obtained at 5% carbon fibre while the highest value for Young’s modulus was observed at 7.5% of carbon fibre. Natural fibres also have been used as reinforcement in FFF processes. In [83] poly propylene (PP) filled with harakeke, hemp fibre or recycled gypsum contents to produce filaments for fused deposition modelling. The best mechanical results were obtained from the filament with 30 % harakeke fibre which showed 74 % and 214 % improvement in strength and modulus compared to pure PP. However, these improvements were not consistent and diminished after printing. Most of these works were using virgin materials as the reinforcement and there are not many works on reusing the recovered materials as the fused deposition modelling feedstock in the literature. Huang et al. [84] used supercritical n-butanol to recover carbon fibres from reinforced composites. The recovered fibres were added to poly ether ether ketone (PEEK) to produce 3D printing filaments. The presence of carbon fibres significantly improved the electrical conductivity of the printed parts which makes them suitable for sensing purposes. The reinforced composite also showed improvement in flexural strength and flexural modulus compared to pure PEEK. Morsidi and colleagues [85] worked on the addition of recovered fibres from composites to ABS for the purpose of additive manufacturing. The improvement of 43% in tensile strength was reported compared to pure ABS. The possibility of incorporating the shredded composites from wind turbine blades into materials for additive manufacturing technologies, like Fused Filament Fabrication (FFF), is studied by Rahimizadeh and colleagues [86]. The shredded composites went through sieving and then co-extruded with polylactic acid (PLA) to produce glass-filled 3D printing filaments. Although a significant increase was observed in the stiffness of the final products, the tensile strength and the elongation at break decreased compared to pure PLA. Comparing the obtained composite to the PLA/virgin glass fibre showed improvement in modulus and tensile strength.

In the present work, the possibility of the compatibilizing of PLA and the recovered fibres from mechanical recycling of the wind turbine blades are assessed.

2.3 Polylactide

Engineering polymers have outperformed other materials in daily life due to their advantages such as being lightweight and strong and easily processable. The major drawback of these polymers is that they are petroleum-based materials, and their production requires petrochemical raw materials which contributes to the GHG emissions and also their end of use produces a huge amount of non-degradable waste annually that endangers the environment and the marine life. These problems encouraged the researchers to work on bio-based and bio-degradable polymers. Considering the number of petroleum-based polymers produced and the plastic waste annually, replacing these polymers with bio-sourced polymers is crucial to sustainable development. Polylactic acid (PLA), a thermoplastic polymer with high strength and modulus, is bio-sourced and biodegradable. PLA is an aliphatic polyester composed of a-hydroxy acids including polyglycolic acid or polymandelic acid. It can be used as packaging and also has many bio-compatible medical usages. PLA can be easily processed using the common equipment to form films, parts and fibres [87]. The degradation of the PLA happens naturally through hydrolysis. The ester bonds which exist in the PLA chains are broken by water [88]. The degradation rate depends on the size and shape as well as the temperature of the hydrolysis. PLA is a promising alternative to petroleum-based polymers. Nevertheless, PLA has its drawbacks such as being brittle with low elongation at break and relatively poor impact strength. These drawbacks limited its application. The strength and stiffness of PLA are comparable to common polymers like polystyrene and polyethylene terephthalate, but its low toughness made it less favourable in applications where flexibility and ductility are of importance [89]. Therefore, the PLA to be used for these deformations' required applications, need to be toughened and its mechanical properties enhanced.

2.3.1 Toughening the PLA

Various methods can be applied to a polymer in order to improve its mechanical properties. The homopolymer characterizations like molecular weight and stereochemistry can be changed. The degree of crystallinity and its formation and orientation can be tailored to achieve different properties. Moreover, the addition of other components such as homopolymers or fillers and fibres can be used to alter the properties. Finally, copolymerization can also be used to develop new materials with enhanced properties[89]. Many studies worked on improving the PLA properties via stereo-complex crystallization [90-92]. The problem with this method was its expensive production which limited its application. Among other methods for enhancing the PLA properties, blending with elastic polymers shows the best results. Nonetheless, achieving a proper blend with enhanced properties through simple blending is not easy due to the poor compatibility and immiscibility and weak interfacial interactions. Thermoplastic elastomers (TPE) are excellent materials for blending with PLA. TPEs have hard fractions and rubber fractions in their structure. Examples of TPEs to be blended with PLA are polyurethane thermoplastic elastomer, a polyolefin thermoplastic elastomer, polyamide thermoplastic elastomer, bio-based and bio-degradable elastomers [93]. Huang et al. prepared PLA/TPU blend through direct physical blending. By incorporating 30% TPU into the PLA matrix the elongation at break of the blend marked 602%. However, the tensile strength of the blend drastically diminished [94]. Zhang et al. prepared PLA and a bio-based copolymer of lactic acid, butanediol, sebacic acid, and itaconic acid (PLBSI) blend. The impact strength of the PLA/PLBSI (60/40) blend improved up to 35.7 kJ m−2 and the elongation at break of the blend improved to 324% but the tensile strength decreased [95].

2.3.1.1 Plasticizers

Plasticizers are materials that can be added to glassy polymers to improve processability and also increase ductility and flexibility [96]. The plasticizer should be compatible with the polymer to be able to reduce its glass transition temperature. For the PLA, a lactide monomer is a good option for plasticizing. Jacobsen et al. [97] added 17% of lactide to PLA and observed the elongation at break increased to 288%. But due to the low molecular weight of the lactide, it migrates to the surface of the blend over time and the PLA gets brittle after a while. Another common plasticizer for the PLA is the Citrate esters. The elongation at break of the plasticized PLA using 30% triethyl citrate improved to 600% but the tensile strength decreased 85% [98].

2.3.1.2 Blending with other polymers

Blending PLA with another homopolymer to get favourable properties is a common method in the plastic industry. Usually, the two homopolymers are not compatible and a compatibilizer (usually a block copolymer) is required to increase the compatibility and improve the properties. Poly caprolactone (PCL) is one of the widely used degradable polymers along with the PLA to prepare a blend with desirable properties. PCL has a low glass transition temperature with rubbery behaviour and its elongation at break is around 600%. Washburn et al. observed the addition of the PCL does not change the elongation at break of the system until it reaches 60 wt% of the blend [99]. Maglio et al. [100] observed significant improvement in elongation at break with PLA/PCL (70/30) blend after the addition of the PLLA-PCL-PLLA triblock copolymer were used as a compatibilizer. It is common for the organic additives that the improvement of the elongation at break in the blend comes with the price of strength decrease.

2.3.1.3 Addition of fibres and fillers

The fibres and fillers also can be used to improve the mechanical properties of PLA. While most of the composites with common polymers use synthetic fibres such as carbon and glass fibres, there has been a trend for researching the incorporation of the natural fibres into PLA to produce fully bio-degradable composites with enhanced mechanical properties. The problem with the natural fibres is their weaker strength and their high water content and also these fibres are highly polar and absorb water in the composite. The common natural fibres which are used as the reinforcement for the PLA are lignin[101], Jute fibre [101], tannin [102], cellulose [103-105], coir [106] and others.

Delgado et al. added 30% jute fibre to PLA and observed improvement in mechanical properties of the composite [101]. Incorporation of the nanocellulose to PLA along with the epoxidized soybean oil significantly improved the ductility of the composite [103]. Abaca fibre influence as the reinforcement for the PLA was compared to GF and cellulose and it was observed that the abaca fibre/PLA composite showed weak mechanical properties [107]. It is concluded that the incorporation of the natural fibres without compatibilizer could not enhance the properties of PLA.

Synthetic fibre such as carbon and glass fibres can also be used as fillers to improve the mechanical properties of PLA. Synthetic fibres are way stronger than natural fibres and make better reinforcers. Among these synthetic fibres, glass fibre is more favourable due to its reasonable price and strength. However, the Incorporation of GF into polymers can result in increasing brittleness and reduced ductility especially if the interactions between the fibres and matrix at the interface are weak [108, 109].

2.4 Silane coupling agents

The adhesion and bonding at the interface of the polymeric matrix and the fibre determine the final properties of the polymeric composites. Achieving even a weak interaction between the components at the interface of the matrix and fibre goes a long way from the mechanical properties point of view. In the production of the composites containing fibres as the reinforcement, the sizing of the fibre is the most important component and decides the success or failure of the composite.

Size, is the thin coating, commonly an organic material, which is applied on the surface of the fibres [110]. The size's, usually an organofunctional silane named coupling agent, responsibility is to ensure that the fibre and matrix develop some kind of bonding, and also ensures the dispersion of the fibres, as well as wetting of the fibres by the matrix, happens in the duration of production time. Silane coupling agents are the most common sizing for glass fibres. Their ability to bond organic and inorganic materials is of importance. Its usual structure is like $R-(CH_2)_n-Si-X_3$ where X is a hydrolysable group and R is the organofunctional group [110]. After the hydrolysis, the siloxane linkage can happen due to the condensation of the newly formed silanol groups and the silanol groups on the surface of the siliceous particles. These bond formations can improve the wetting and adhesion capability of the fillers and the formation of a covalent bond between the organic and inorganic substances.

Organosilanes usually have one organic functional group and three hydrolysable functional groups. There are four steps for modifying a surface with silane. First, the three unstable groups go through hydrolysis and then condensation to oligomers happens. The surface, laden with OH groups, bonds through hydrogen bonding with the oligomers. For the final step, which is drying, the water loss and covalent bonding happen. Each organosilane is bond to the surface through one of its silicons. Two other silanols can be free or condensed. The R substituent is free to react covalently or in other forms with the other substances [111].

Coupling agents such as silane are used widely in polymer composites. Based on the polymer characteristics the silane could react with the polymer molecules or be copolymerized with the monomer before polymerization. The former usually happens in thermoplastics and the latter is achieved in thermosets.

The adhesion of the filler via silane coupling agents to the thermoplastics is different from the thermoset's adhesion. The difference is in the interaction of silane with monomers in thermosets and with the finished polymers in thermoplastics. Condensation polymers such as polyesters and polycarbonates do not provide many opportunities for covalent bond formation. The adhesion mechanism in these polymers is high energy groups and hydrogen bonding at the interface or the end-group reactions [111].

Silanes are also known to be able to heal the flaws on the surface of the fibres. These flaws can form during mechanical abrasion (fibre to fibre abrasion and fibre to equipment collision). These flaws can severely damage the mechanical properties of the fibres. The siloxane network on the surface of the fibres can protect the fibre surface against damages. Silane can also improve the hydrophobicity of fibre surfaces [110].

Noda et al. [112] prepared a polyamide short glass fibre composite and studied the interface of the fibre and matrix. The sets of fibres were used in the production of the composites, one was unsized and the other sized with (3-Aminopropyl) triethoxysilane (APTES). They reported polyamide was attached strongly on the surface of the silane-treated fibres. Also, the Tg of the Polyamide layer on the silane-treated fibre was higher than the Tg of the polyamide layer on the surface of the unsized fibre which suggests that the motion of the polyamide molecules was limited due to their strong adhesion to the GF surface. The conclusion was that the silane treatment enhanced the adhesion between the GF and the matrix through covalent bonding. Bergeret et al. [113] studied the interface in glass fibre/poly(butylene terephthalate) composite. The glass fibres were sized using aminosilane sizing and two different epoxy film formers. By categorizing the interface into two groups, fibre-sizing area and matrix-sizing area they reported that the mechanical properties enhancement was the result of coupling agent and a multifunctional epoxy film former which could react both with a coupling agent and the matrix. Mäder et al. [114] investigated the adhesion and interphase of the cyclic butylene terephthalate/glass fibre composites. Glass fibres with various sizing formulations of silane and epoxy film formers were used to produce the composite. SFPO testing, AFM, and SP testing were conducted on the composites to measure the interfacial bond strength of the different composites and the final verdict was that the best adhesion of the fibre and matrix achieved with the APTES and epoxy sizing.

While most of the investigations suggest that the adhesion enhancement of the silane sizing is due to the chemical reactions and bonding of the sizing at the interface of the matrix and fibre, some studies suggest that the shrinkage stresses can be the reason behind the stress transfer at the fibre/matrix interface [115-117]. The production of the thermoplastic polymers happens at high temperatures and then the product is cooled down. During and after the cooling process, due to the marked difference between the higher thermal expansion coefficient of the polymers and the lower thermal expansion coefficient of the glass fibres, compressive radial stress is developed at the interface (σ_r) [115]. By presuming that the coefficient of static friction (β) is not zero at the interface, the aforementioned compressive stresses can contribute to the interface shear strength via a frictional component $\tau = \beta.\sigma_r$. In thermoplastic polymers with small chemical bonding contributions at the interface, most of the interface shear strength comes from these types of frictional stresses. This mechanism points out the importance of the fibre wetting by the matrix on the static friction value and consequently the interface shear strength value. In [118] it is suggested that in the case of thermoplastic and glass fibre sized with silane, the silanes statically tend to react with each other instead of reacting with the matrix. The interfacial shear strength of the thermoplastic composites attributed to physical phenomenon mostly the residual compressive stresses developed at the interface of these composites.

The bonding and adhesion in microscale at the interface of the matrix and fibre play a significant role in the mechanical properties of the final composites. Many studies have been conducted to compatibilize the matrix and fibre and fillers to achieve a better interaction at the interface and consequently enhancement in mechanical properties of the composite. In a work by Monticelli et al. silsesquioxanes used as a compatibilizer for the PLA/PCL blend and the final blend showed significant improvement in ductility [119]. The effect of the silane coupling agent on the PLA/kenaf fibre composite was studied by Lee et al. [120]. It has been observed that a small amount of silane agent could increase the moduli and heat deflection temperature of the composite. Georgiopoulos et al. [121] treated the flax fibres with amino-silane and prepared the PLA/unidirectional flax fibres composite. The 2% silane treatment improved the adhesion of the fibre and matrix which reflected in improved mechanical properties of the composite. Wangsoub et al. studied the mechanical properties of the PLA/pineapple leaf fibre (PALF) composite. PALF was treated with 4% sodium hydroxide solution and then the silane solution. The silane treatment increased the strength of the composite.

Jing et al. [122] investigated the effect of two surface modifications of glass fibre on the properties of PLA/GF composite. They treated fibres with silane coupling agents and graphene oxide. The PLA/GF composite without any treatment showed weak adhesion at the interface and worst mechanical properties compared to the other composites. The silane-treated GF in the PLA improved the mechanical properties and also prevented the decrease in the toughness of the composite. Incorporation of the graphene oxide treated GF to PLA acted as a nucleating agent for

PLA and caused crystal formation on the surface of the fibre and also increased the modulus of the composite. Wang et al. [123] prepared fibre-reinforced PLA composite with silane-treated GF and studied its mechanical properties, thermal characteristics and foaming ability. GFs were treated using coupling agent Hexadecyltrimethoxysilane. The PLA/S-GF was prepared using the extruder and the samples were injection moulded. The SEM image of the fractured surface of the composite with 20% S-GF showed good dispersion and distribution. The addition of S-GF increased both rigidity and strength of the composite however the elongation at break of the composite decreased with the GF load increase. Akindoyo et al [124] worked on the simultaneous impact modification and chain extension of PLA/GF composite and investigated the mechanical and thermal properties of the obtained composite. The toughness of PLA was modified using a commercial impact modifier and a Joncryl based chain extender. With the incorporation of 10% glass fibre, impact modifier and chain extender to PLA through extrusion, they reported 63% and 66% improvement in impact strength and modulus of the composite compared to pure PLA. However, there is not enough reports on the literature concerning the chemical modification of the recycled fibres composites to enhance the mechanical thermal performance.

As it is mentioned before the current situation of decomposing and landfilling of the wind turbine blades which are mostly composed of fibre reinforced thermoset polymers are a threat to the environment and there is no appropriate approach for recycling them. The most common solution for the turbine blades is landfilling due to its cheap operation cost but in the long run, it is not a sustainable solution due to the waste of resources and also environmental pollution. The focus of this work is to find a solution for reusing the shredded composite, specifically the glass fibres, derived from wind turbine blades. For this purpose, the mechanically recycled glass fibres (R-GF) are incorporated into PLA to produce a glass-reinforced composite with superior properties compared to its components. This composite could be used as the raw material for the 3D printing filaments. To further improve this solution, efforts are made to modify the interactions between the R-GF and PLA to enhance the adhesion between the fibre and matrix. This modification was done through sizing of the R-GF in order to heal their flaws and also make them favourable for PLA to react with. The inherent brittleness of PLA is well known to polymer researchers and industry. This brittleness could also be enhanced by the addition of the fillers to PLA due to the way higher stiffness of the filler. Various methods and materials have been investigated to overcome this problem and make the PLA and its composites more ductile. Plasticizers, compounding and chain extending are some common methods. The problem with most of these methods is that their ductility enhancement comes with the price of deterioration of other mechanical properties. Our focus in this study was to enhance the overall mechanical properties of the composite for it could compete with the commercial like products produced with virgin materials. Another aspect was the final cost of the production of this composite. There has been an effort to find solutions and materials with reasonable prices and high improvement efficiency with small loading of the material. Most of the plasticizers and homopolymers are needed to be heavily loaded to the composite to express significant improvement. The toughener that is used in this study works through chain end engineering and modification and improves the toughness with minimal loading into the system [125].

This work aims to incorporate the short glass fibers from mechanically recycled wind turbine blades, into a biodegradable and bio-based thermoplastic, namely PLA, to prepare a reinforced composite. Furthermore, the possibility of compatibilization and toughening of the final composite using coupling agents and modifiers is investigated. The objective of this study is to find a solution for the reuse of the shredded composites derived from decommissioned wind turbine blades and preventing them from landfilling and make them an economical alternative to the virgin materials for production of value-added products and also an enhancement in the mechanical properties of a glass fibre reinforced thermoplastic using these scrap materials.

CHAPTER 3 EXPERIMENTAL METHODOLOGY

3.1 Materials

The matrix used in this work is polylactic acid (PLA) 4043D, with 94% l-lactide and 6% d-lactide content (NatureWorks IngeoTM) which is a semi-crystalline multipurpose extrusion grade that can be used to produce 3D printing monofilaments. The molecular weight of this PLA is 181 kDa, with melt flow index rate of 6 g/10 min at 210 °C and 2.16 kg load. The density of the polymer is 1.24 g/cm^3 with a melting temperature of 145-160 °C. The scrap glass fibres with an average length of 0.1 to 0.4 mm were derived from the mechanical recycling of turbine blades composed of glass fibre and epoxy. To improve the adhesion between the recycled fibres (R-GF) and PLA, the R-GFs were treated with organic silane coupling agent Hexadecyltrimethoxysilane CAS 16415-12-16 (Sigma-Aldrich). The 1,2,3,4-butane tetracarboxylic acid (BTCA, 99%), was purchased from Sigma-Aldrich which is a carboxylic acid to modify the chain ends of the PLA.

It should be noted that R-GF, SR-GF, BTCA will be used to address recycled glass fibre, silane treated recycled glass fibre and 1,2,3,4-butane tetracarboxylic acid, respectively, in this work.

3.2 Methods

3.2.1 Preparation of recycled glass fibres

Mechanical recycling is used in this study to shred the turbine blades. Mechanical recycling compared to the other methods of composite recycling such as chemical and thermal recycling is faster with low cost, low energy consumption and no toxic solvent is involved in it. Since the most fibre-reinforced 3D printing filaments use short fibres in order to be compatible with the 3D printing equipment nozzle size, the size of the recovered glass fibres was reduced by milling and grinding. First the part of the blades which solely was composed of glass fibre composite cut into square pieces. A hammer mill (ECO-WOLF, INC.) ground the squares into a shredded composite. After grinding a mixture of glass fibres and resin powder was achieved. The glass fibre length was between 0.1 to 3 mm. Rahimizadeh et al. [126] in a work on the same recycled glass fibres, conducting a fibre pull-out test on a single fibre, determined a critical length range of 0.57 mm to 1.14 mm for the recycled glass fibres to achieve the best interaction in fibre/matrix interface .

Figure 3.1 wind turbine blades after grinding

Figure 3.1 shows the ground wind turbine blades. In order to separate the epoxy powder and fibres with length out of the desired length, a sieving operation was conducted to ensure refined fibres. The screening is done using a sieve with a 0.06 mm mesh size.

1. Wind turbine blades
2. Blades cut into 20*20 cm pieces
3. Grinding the pieces
4. Sieving Operation

Figure 3.2 Mechanical recycling of the wind turbine blades [86]

To treat the R-GFs with a silane coupling agent, an aqueous alcohol solution was prepared under constant conditions to deposit the silane on the surface of the fibres. The solution consisted of 95 wt% of the total solvent methanol and 5 wt% of deionized water. The pH of the solution adjusted to 4.5-5.5 using acetic acid. The solution homogenized using a stirrer and magnet. The concentration of silane coupling agent in the stirring solution was 0.6 wt% of the total solvent. After 1 hour of hydrolysis and silanol formation, R-GFs were dipped into the solution for 30 minutes and after decanting the solution, fibres dried in an oven at 70 °C.

3.2.2 Preparation of fibre reinforced composites

The hygroscopic nature of PLA makes it prone to absorbing water. Moisture can hydrolyze PLA and speeds its degradation and also absorbed moisture in PLA can cause bubble formation during the melt processing of this thermoplastic. Moisture also can be absorbed by the glass fibres and form clusters which leads to non-uniform dispersion of the fillers in the melt. To avoid these problems both the SR-GFs and PLA (in pellet form) were dried in a vacuum oven at 70 °C prior to processing. After drying, the PLA pellets and SR-GF were compounded using a twin-screw extruder (Leistritz ZSE18HP-40D) to produce PLA/SR-GF composite. The PLA was fed from the main hopper and the SR-GFs were fed through the side feeder. The extrudate strand was cooled in a water bath and after cooling a pelletizer chopped the strand into granules. The obtained granules went through drying overnight to remove any excess moisture and then were fed into a Carver laboratory hot press (MODEL 3912) to prepare the test specimen. The plates' temperature was set at 195 °C and both the compounding and moulding were done under nitrogen purge. Table 3.1 shows the technical information of the extrusion. The content of fibre was fixed at 15% to be comparable with the commercial filament. For comparison purposes PLA/R-GF was also prepared under the same condition. Figure 3.3 and Figure 3.4 show a Twin-screw extruder as well as its heating zones and the screws.

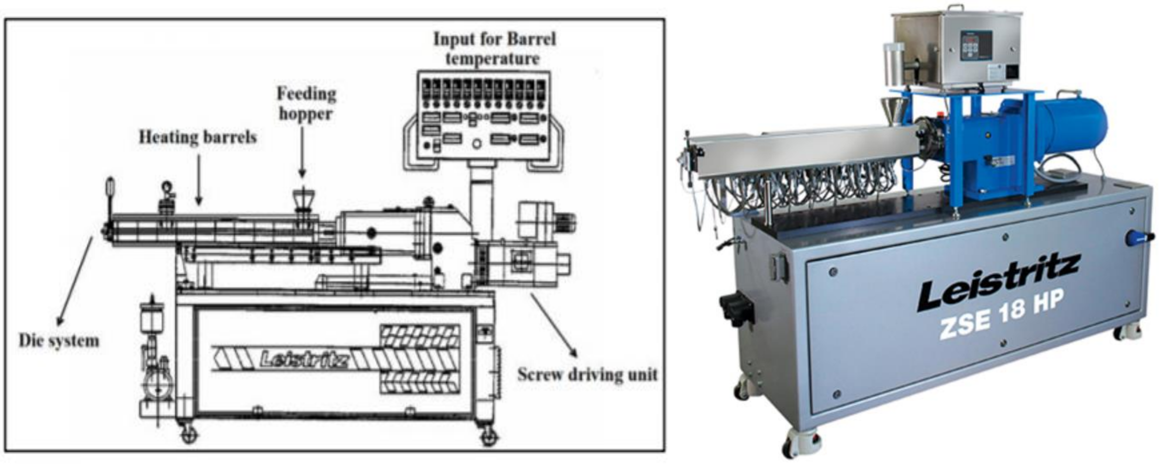
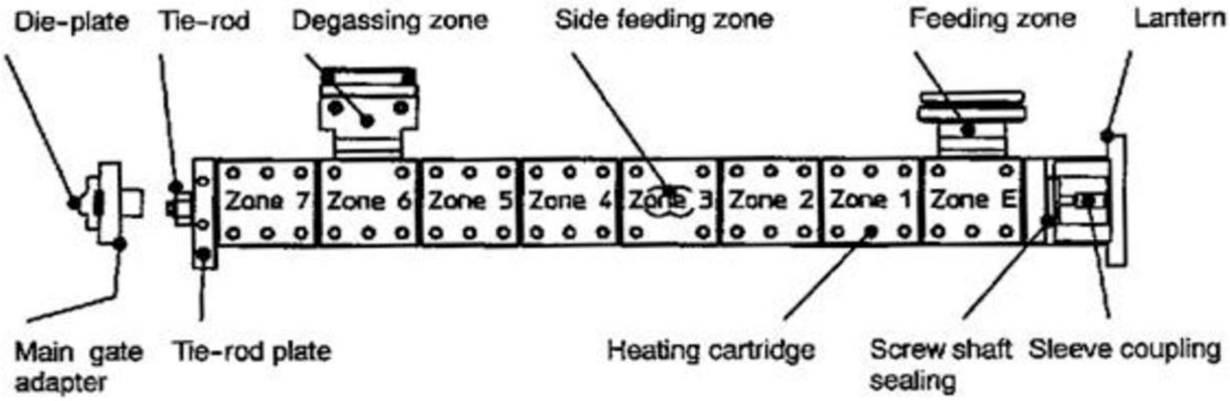
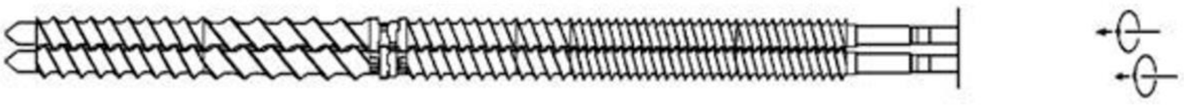


Figure 3.3 Schematic of a Twin-screw extruder [115]



HEATING BARRELS



CO-ROTATING SCREWS

Figure 3.4 Schematic of an extruder's barrel, screws and heating zones [115]

Table 3.1 Twin-screw extrusion technical data

PLA/TSR-GF extrusion		PLA/SR-GF extrusion	
Screw speed	150 rpm	Screw speed	120 rpm
profile	Temperature (°C)	profile	Temperature (°C)
Zone 1	200	Zone 1	190
Zone 2	200	Zone 2	190
Zone 3	195	Zone 3	185
Zone 4	195	Zone 4	185
Zone 5	195	Zone 5	180
Zone 6	190	Zone 6	180
Zone 7	185	Zone 7	170
Zone 8	180	Zone 8	170

3.2.3 Impact modified composite preparation

For the final composite, which was composed of predetermined content (wt%) of PLA, SR-GF and BTCA, components were compounded through extrusion. The obtained composite was analyzed and compared to neat PLA and also the commercial 3D printing filament. All the materials involved were dried overnight in a vacuum oven at 70 °C to remove any traces of moisture. Soon after drying, the compounding was conducted via a twin-screw extruder (Leistritz ZSE18HP-40D). For the extrusion PLA was fed directly to the hopper by the main feeder. The

SR-GF and BTCA were dry mixed before extrusion and fed through the hopper by a side feeder. the content of BTCA was set at 0.5 wt% of the PLA and the amount of GF was set at 15 wt% of the total composite. The extruded strand was then cooled in a water bath and chopped using a pelletizer. The pellets again went through overnight drying to remove the excess moisture and then placed in a Carver laboratory hot press (MODEL 3912) to prepare the test specimen. The plates' temperature was set at 195 °C and both the compounding and moulding were done under nitrogen purge. Table 3.1 shows the technical data of the extrusion. The melting temperature of the BTCA is in the range of 195 – 237 (°C). BTCA needs to react with PLA in the molten state to enhance the properties of PLA properly [125]. For this purpose, for the preparation of the toughened PLA composite, the temperature profile of the extrusion was shifted to a higher temperature to ensure BTCA melting and its consequent reaction with PLA. Each BTCA molecule can react through its COOH to OH groups of PLA and create a crosslinked network of chains by connecting to up to four of PLA molecules. By reducing the chain-ends, BTCA can toughen the PLA.

In order to compare the obtained composite with the commercial 3D printing filament, a spool winder was used to make filament with a diameter of 1.75 mm diameter out of the extruded strand.

3.3 Characterization

3.3.1 Mechanical properties

Dog-bone-shaped samples type V based on ASTM D638 was prepared via compression moulding at 195 °C. To measure the tensile properties an Instron tensile machine (3365) was employed and tensile strength, modulus, and elongation at break of the samples evaluated according to ASTM D638. 5 kN Crosshead with Pneumatic grip the speed of 5 mm/min was used. To reduce the risk of error at least five samples were tested for each composite and the average results were reported.

Izod impact test was employed to determine the impact strength of the composites using a Ray-Ran Universal Pendulum Impact Tester according to ASTM D256. The dimension of specimens for impact testing was $63.5 \times 12.7 \times 3.0\ \text{mm}^3$. at least eight specimens were tested for each sample.

3.3.2 Scanning electron micrograph

After the tensile test, the fractured surface of the composite samples was investigated by scanning electron microscopy (SEM) at room temperature. Before the test, the samples were dried to avoid electrical discharge and coated with platinum vapour. Hitachi TM3030 microscope was employed to observe the morphology. SEM observation also was done on the ground recycled fibres to investigate the surface of the fibres.

3.3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was also conducted to investigate the thermal stability of the different composites. Samples for TGA analysis were placed in a platinum sample pan and the test was conducted in a nitrogen atmosphere with a 40 ml/min gas flow rate. TGA instrument (Q500 V6.7) heated the samples in the range of 25 to 800 °C with a heating rate of 10°C/min. Also, TGA was used to measure the amount of matrix residue on the surface of the recycled fibres. After grinding and screening samples were loaded into the TGA machine and was heated from 25 to 800 °C and 10 °C/min in presence of nitrogen and additional oxidative step ensured no ash content on the surface of the fibres.

3.3.4 Differential scanning calorimetry

Differential scanning calorimetry (DSC) test was carried out via a TA instrument calorimeter (DSC), Q1000, TA Instruments, New Castle, DE, in the presence of nitrogen. Samples were heated from 25 °C to 250 °C with a heating rate of 10 °C /min. The obtained data from the second heating cycle was used to determine glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c).

CHAPTER 4 ARTICLE 1: POLYLACTIC ACID/ RECYCLED WIND TURBINE GLASS FIBRE COMPOSITES WITH ENHANCED MECHANICAL PROPERTIES AND TOUGHNESS

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Abstract

The amount of composite waste from decommissioned wind turbine blades grows rapidly and recycling solutions should be generated to overcome this environmental challenge. This research aims to further develop a recycling method to recover components of dismantled turbine blades by reusing them as reinforcement for new composites. Recovered short glass fibres from shredded blade composites are incorporated into polylactic acid (PLA) to fabricate a composite (15 wt% fibre) that could be used for 3D filament fabrication. To improve the mechanical properties of the composite, a coupling agent was employed to refine the interactions between PLA and recycled glass fibres at the interface of the two components and enhance the adhesion. Due to the inherent brittleness of PLA, which is aggravated with the addition of recycled glass fibres, a toughening agent involving chain-end modification was incorporated into the composite to improve the toughness of the system. The concurrent outcome of the coupling agent and the toughener on the morphology, mechanical properties and thermal behaviour of the composite was evaluated. The incorporation of 1,2,3,4-butane tetracarboxylic acid and silane-treating of the recycled fibres improved the strength by 30% and elongation at break and impact strength of the composite 3 and 2 times, respectively.

Keywords: Wind turbine blades, Polylactic acid, Toughening, silane

4.1 Introduction

Wind energy is a fast-growing industry with the aim to replace fossil fuels as a green and renewable source of energy. In the year 2019, the wind industry supplied 13 GW which can cover 6% of the Canadians needs [1]. The Canadian Wind Energy Association (CanWea)'s plan is to expand wind power and hopes to supply up to 55 GW by the year 2025, covering 20% of the Canadian electricity consumption [1]. The wind industry is one of the largest consumers of composite materials globally, with a demand of 2.5 million tons per year [2]. On average, a 5 MW wind turbine blade can have around 50 tons of polymer materials in it [3]. If the global trend stays the same, the number of decommissioned blades that go to waste will surpass 45 million tons by the year 2050 [4]. Although wind industry provides power with far less CO_2 emission compared to fossil fuels, they produce a large amount of non-recyclable waste. This problem emphasizes the importance of discovering recycling solutions. A simple wind turbine is comprised of a rotor mantled on a tower, and three blades are attached to it. It can be 90 meters high and the length of the blades can be 45 to 90 meters [5]. The most common type of rotor blade is the Glass Fibre Reinforced Plastics (GFRP) [6]. Landfilling, which is the least preferred method due to its environmental cost, is the most common way to dispose of the blades in the US [7]. Many studies focused on methods for separating the fibres from the resin and then reuse the fibres in new composites [8-11]. Mechanical recycling is one of the most straightforward methods to deal with decomposed blades. The industrial utilization of this method is in progress [11]. By grinding the composite, a mixture of single fibres, chunks of resin and fibre mats embedded in resin are obtained. The recovered materials can reinforce new materials such as cement and asphalt that are used in the construction industry. Beauson and colleagues [9] studied the reuse of shredded composite materials as reinforcement for new polymer-based composites and observed a reduction in the mechanical properties compared to virgin reinforcement, by increasing the shredded composite percentage. It has been suggested that in order to have a successful reinforcement, using the recovered fibres in new composites, it is necessary to adjust and optimize the process factors. In another work by Beauson and colleagues [10], the shredded composites obtained from a 26 meters long blade were incorporated into polyester resin. The decomposed blade first has been ground using a miller and the obtained materials went through sifters. Composites with different concentrations of shredded materials from 10 to 30 wt% were manufactured via vacuum resin infusion. The stiffness of the final composites increased significantly compared to the pristine polyester resin. However, the ultimate tensile strength and the elongation at break of the composites showed a decrease compared to the neat polyester. Scanning electron micrograph (SEM) imaging of the composite samples demonstrated the spacing and cracks at the interface of the matrix and fibres, and also fibre pull-out could be observed in composite surface and both of these phenomena are signs of weak interfacial adhesion. They suggested chemical treatment of the shredded composites to improve the adhesion between the recovered fibres and matrix. Most of the studies on the reincorporation of the shredded composites suggest that using the recyclates can deteriorate the final mechanical properties of the new composites and this degradation can be due to the breakage of the fibres after milling (granulation process) [8] or the poor bonding between the recovered fibres and the new resin [12]. The use of shredded composites as cheap fillers makes them a low-value product. Palmer et al. [13] suggested that with careful separation, classification and reformulation a more reliable and profitable solution can be developed. They used an air-classifier to separate the useful glass fibres with mechanical properties comparable to virgin fibres and produced new composites with acceptable properties. Mamanpush et al. [14] worked on recycling the wind turbine blades as the raw material for new composites. They hammer milled the scrap blades and incorporated them into methyl-diisocyanate (Rubinate 1840) (pMDI) to produce a new composite in the form of panels. They suggested that these panels can be developed and used in form of floor tiles and plastic road barriers. They also used recycled wind turbine blades to produce reinforced thermoplastic composite using High-Density Polyethylene (HDPE). They also investigated the effect of coupling agents (Silane and Maleic anhydride) on the composite properties. The addition of modifiers significantly increased the flexural strength and young’s modulus compared to non-modified composites [15].

There are recent research that used composites as the raw material for additive manufacturing processes to manufacture stiff and high strength products [16-19]. Shofner and colleagues [20] used Vapor-grown carbon fibres (VGCFs) as the reinforcement in an ABS copolymer and used the composite for Fused Filament Fabrication (FFF) processes. The 10% VGCFs were integrated into the ABS via a melt mixer. The dispersion was observed with SEM imaging.

The mechanical tests demonstrated that the tensile strength and modulus of the VGCF-filled ABS improved 39 and 60 % respectively compared to pure ABS. The results from dynamic mechanical analysis demonstrated 68% improvement in stiffness. In another work [21], short glass fibres were added to ABS to overcome low strength. Although the short-glass-fibre-filled ABS showed improved strength and was suitable for FFF processes, the presence of fibres decreased the flexibility of the final composites. To tackle this problem compatibilizer and plasticizer have been added to the system. The final filament showed promising results. Pristine carbon fibre was used in Mengal et al.'s work [22] as reinforcement for ABS to produce FFF feedstock. The mechanical tests on their specimen demonstrated that the addition of carbon fibre increased the tensile modulus and strength but on the other hand it diminished the ductility and toughness of the composite. The highest value for strength was obtained at 5% carbon fibre while the highest value for Young's modulus was observed at 7.5% of carbon fibre. Natural fibres also have been used as reinforcement in FFF processes. Marquis et al. in [23], filled polypropylene (PP) with harakeke, hemp fibre or recycled gypsum contents to produce filaments for fused deposition modelling. The best mechanical results were obtained from the filament with 30% harakeke fibre which showed 74% and 214% improvement in strength and modulus compared to neat PP. However, these improvements were not consistent and diminished after printing. Most of these works were using virgin materials as the reinforcement and not many works on reusing the recovered materials as the fused deposition modelling feedstock in the literature. Huang et al. [24] used supercritical n-butanol to recover carbon fibres from reinforced composites. The recovered fibres were added to poly ether ether ketone (PEEK) to produce 3D printing filaments. The presence of carbon fibres resulted in electrical conductivity of the printed parts which makes them suitable for sensing purposes. The reinforced composite also showed improvement in flexural strength and flexural modulus compared to pure PEEK. Morsidi and colleagues [25] worked on the addition of recovered fibres from composites to ABS for the purpose of additive manufacturing. An improvement of 43% in tensile strength was reported compared to pure ABS. The possibility of incorporating the shredded composites from wind turbine blades into materials for additive manufacturing technologies, like FFF, was studied by Rahimizadeh and colleagues. [26] The shredded composites went through sieving and then co-extruded with polylactic acid (PLA) to produce glass-filled 3D printing filaments. Although a significant increase was observed in the stiffness of the final products, the tensile strength and the elongation at break decreased compared to pure PLA. Comparing the obtained composite to the PLA/virgin glass fibre showed improvement in modulus and tensile strength.

The strength and stiffness of biobased PLA are comparable to common synthetic polymers like polystyrene, but its low toughness makes it less favourable in applications where flexibility and ductility are of importance [27]. Many studies worked on the mechanical properties' enhancement of PLA [27-34]. Li et al [35] developed a chain-end engineering strategy to toughen PLA. A carboxylic acid was melt-mixed with PLA and its mechanical properties investigated and compared to pure PLA. The addition of 0.5 wt% of the carboxylic acid resulted in significant improvement in toughness of PLA. They reported that unlike plasticizers, their strategy did not diminish the strength and modulus of PLA.

Many studies have been conducted to compatibilize the matrix and fibres or fillers to achieve a better interaction at the interface and consequently enhancement in mechanical properties of the composite [36-39]. Jing et al. [40] investigated the effect of two surface modifications of glass fibre on the properties of PLA/GF composite. They treated fibres with silane coupling agents and graphene oxide. The PLA/GF composite without any treatment showed weak adhesion at the interface and worst mechanical properties compared to the other composites with silane or graphene oxide treatment. The silane-treated GF in PLA improved the mechanical properties and also prevented the decrease in the toughness of the composite. Incorporation of graphene oxide treated GF to PLA acted as a nucleating agent for PLA and caused crystal formation on the surface of the fibre (Transcrystallization) and also increased the modulus of the composite. Wang et al. [41] prepared fibre-reinforced PLA composite with silane-treated GF and studied its mechanical properties, thermal characteristics and foaming ability. GFs were treated using coupling agent Hexadecyltrimethoxysilane. The PLA/s-GF was prepared using a co-rotating twin-screw extruder and the samples were injection moulded. The SEM image of the fractured surface of the composite with 20% S-GF showed good dispersion and distribution. The addition of s-GF increased both rigidity and strength of the composite however the elongation at break of the composite decreased with the GF load increase. Akindoyo et al [42] worked on the simultaneous impact modification and chain extension of

PLA/GF composite and investigated the mechanical and thermal properties of the obtained composite. The toughness of PLA was modified using a commercial impact modifier and a Joncryl^{TM} based chain extender. With incorporation of 10% glass fibre, impact modifier and chain extender to PLA through extrusion, they reported 63% and 66% improvement in impact strength and modulus of the composite compared to pure PLA. However, there is not enough reports on the literature concerning the chemical modification of the recycled fibres composites to enhance their mechanical and thermal performance.

This work aims to incorporate the components of mechanically recycled short glass fibres obtained from wind turbine blades, into a biodegradable and bio-based thermoplastic, namely PLA, to prepare a reinforced composite. The objective of this study is to find a solution for the reuse of the shredded composites derived from retired wind turbine blades and preventing them from landfilling and make them a cheap alternative to virgin materials for production of value-added products. Furthermore, the possibility of compatibilization and toughening of the final composite using coupling agents and modifiers are investigated and their concurrent effect on the mechanical and thermal behaviour of the composite evaluated. The final composite could be used as filaments for 3D printing. Although, in this study a filament was prepared using the obtained composite, but the printing and characterization of the printed objects could be investigated in the future works.

4.2 Materials and Methods

4.2.1 Materials

The matrix used in this work is polylactic acid (PLA). Grade 4043D Natureworks Ingeo^{TM} is a multipurpose extrusion grade that can be used to produce 3D printing monofilaments. The molecular weight of this PLA is 181 kDa, with melt flow index rate of 6 g/10 min at 210 °C and 2.16 kg load. The density of the polymer is 1.24 g/cm^3 with a melting temperature in the range of 145-160 °C. The scrap glass fibres have an length in the range of 0.1 to 1 mm derived from mechanically recycled turbine blades composed of glass fibre and epoxy. To improve adhesion between the recycled fibres (R-GF) and PLA, the R-GFs were treated with organic silane coupling agent Hexadecyltrimethoxysilane CAS 16415-12-16 (Sigma-Aldrich). 1,2,3,4-butane tetracarboxylic acid (BTCA, 99%), was purchased from Sigma-Aldrich which is a carboxylic acid to modify the chain ends of the PLA. A commercial 3D printing filament made of short glass fiber and PLA with the diameter of 1.75 mm was purchased from 3D-Fuel© to be compared with the obtained composite.

It should be noted that nomenclature R-GF, SR-GF, BTCA will be used to address recycled glass fibre, silane treated recycled glass fibre and 1,2,3,4-butane tetracarboxylic acid, respectively, in this work.

4.2.2 Methods

4.2.2.1 Preparation of the recycled glass fibres

Mechanical recycling is used in this study to shred turbine blades. Mechanical recycling compared to other methods of composite recycling such as chemical and thermal recycling is faster with low cost, low energy consumption and no toxic solvent. Since most fibre-reinforced 3D printing filaments use short fibres in order to be compatible with the 3D printing equipment nozzle size, the size of the recovered glass fibres was reduced by milling and grinding. First the part of the blades which solely was composed of glass fibre composite was cut into square pieces. Hammermill (ECO-WOLF, INC.) ground the squares into a shredded composite. After grinding, a mixture of glass fibres and resin powder was achieved. The glass fibre length was between 0.1 to 3 mm. Rahimizadeh et al. [43] in a work on the same recycled glass fibres, conducted a fibre pull-out test on a single fibre, determined a critical length range of 0.57 mm to 1.14 mm for the recycled glass fibres to achieve the best interaction in fibre/matrix interface. In order to separate fibers within the desired length range from the epoxy powder and fibres with undesirable length, a sieving operation was conducted to obtain refined fibres. The screening is done using a sieve with a 0.06 mm mesh size. For better results, the sieving operation was repeated twice. To determine the average length of the recovered fibres, they were scattered randomly under a microscope and a minimum of 200 fibres length was measured.

To treat the R-GFs with a silane coupling agent, an aqueous alcohol solution was prepared under certain conditions to deposit the silane on the surface of the fibres. The solution consisted of 95 wt% of the total solvent methanol and 5 wt% of deionized water. The pH of the solution was adjusted to 4.5-5.5 using acetic acid. The concentration of the silane coupling agent in the stirring solution was 0.6 wt% of the total solvent. After 1 hour of hydrolysis and silanol formation, the R-GFs were dipped into the solution for 30 min and dried in an acid oven at 70 °C. The process of silane treating specifically dipping recycled fibre glasses into the aqueous alcohol solution and the decanting helped to remove more epoxy powder from the recyclate. The treatment also helped to reduce the amount of glass fibre fuzz balls that resulted from mechanical grinding.

4.2.2.2 Composite preparation

Table 4.1 shows different composites compositions. The hygroscopic nature of PLA makes it prone to absorbing water. Moisture can hydrolyze PLA and speeds its degradation and also absorbed moisture in PLA can cause bubble formation during the melt processing of this thermoplastic. Moisture also can be absorbed by the glass fibres and form clusters which leads to non-uniform dispersion of the fillers in the melt. To avoid these problems both the SR-GFs and PLA (in pellet form) were dried in a vacuum oven at 70 °C, over night, prior to processing. After drying, the PLA pellets and SR-GF were compounded using a twin-screw extruder (Leistritz ZSE18HP-40D) (D = 18 mm, L/D = 40) to produce PLA/SR-GF composite. The temperature profile from hopper to the die is presented in Table 3.1. The PLA was fed from the main hopper and the SR-GFs were fed through the side feeder. The extrudate strand was cooled in a water bath and after cooling a pelletizer chopped the strand into granules. The obtained granules again went through drying overnight to remove any excess moisture and then were fed into a Carver laboratory hot press (MODEL 3912) to prepare the test specimen. The plates' temperature was set at 195 °C and both the compounding and moulding were done under nitrogen purge. The samples were heated first without pressure for 4 minutes and then 1, 2 and 3 tons of pressure force were applied to the samples for 2 minutes each. The samples then were cooled to the room temperature. The content of glass fibre was fixed at 15%. For comparison purposes PLA/R-GF was also prepared under the same condition.

Table 4.1 Composition of the different samples and their code names

Sample code	PLA (%)	GF (%)	BTCA (%)	Silane treated
PLA	100	0	0	×
PLA/R-GF	85	15	0	×
PLA/SR-GF	85	15	0	✓
PLA/TSR-GF	84.575	15	0.425	✓

For the toughened composite, which was composed of predetermined content (wt%) of PLA, SR-GF and BTCA, components were compounded through extrusion. The obtained composite was analyzed and compared to neat PLA as well as a commercial 3D printing filament, which is a glass-filled PLA filament produced by 3D-fuel company. All the materials involved were dried overnight in a vacuum oven at 70 °C to remove any traces of moisture. Soon after drying, the compounding was conducted via a twin-screw extruder (Leistritz ZSE18HP-40D). For the extrusion, PLA was fed directly to the hopper by the main feeder. The SR-GF and BTCA were dry mixed before extrusion and fed through the hopper by a side feeder. the content of BTCA was set at 0.5 wt% of PLA and the amount of GF was set at 15 wt% of the total composite. The extruded strand was then cooled in a water bath and chopped using a pelletizer. The pellets again went through overnight drying to remove the excess moisture and then placed in a Carver laboratory hot press (MODEL 3912) to prepare the test specimen. The plates' temperature was set at 195 °C and both the compounding and moulding were done under nitrogen purge. Table 4.2 shows the technical data of the extrusion. The melting temperature of the BTCA is in the range of 195 – 197 (°C). BTCA needs to react with PLA in the molten state to enhance the properties of PLA properly [35]. For this purpose, for the preparation of the toughened PLA composite, the temperature profile of the extrusion was shifted to a higher temperature, presented in Table 4.2, to ensure BTCA melting and its consequent reaction with PLA.

In order to compare the obtained composite with a commercial 3D printing filament, a spool winder was used to make filament with a diameter of 1.75 mm diameter out of the extruded strand.

Table 4.2 Twin-screw extrusion technical data

PLA/TSR-GF extrusion		PLA/SR-GF extrusion	
Screw speed	150 rpm	Screw speed	120 rpm
profile	Temperature (°C)	profile	Temperature (°C)
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Zone 3	195	Zone 3	185
Zone 4	195	Zone 4	185
Zone 5	195	Zone 5	180
Zone 6	195	Zone 6	180
Zone 7	185	Zone 7	170
Zone 8	180	Zone 8	170

4.2.3 Characterization

Dog-bone-shaped samples type V based on ASTM D638 were prepared via compression moulding at 195 °C. To measure the tensile properties, an Instron tensile machine (3365) was employed and tensile strength, modulus, and elongation at break of the samples were evaluated according to ASTM D638 with a speed of 5 mm/min. To get a representative set of data at least five samples were tested for each composite and the average results were reported.

After the tensile test, the fractured surface of the composite samples was investigated by scanning electron microscopy (SEM) at room temperature. Before the test, the samples were dried to avoid electrical discharge and coated with platinum vapor. Hitachi TM3030 microscope was employed to observe the morphology. SEM observation was done on the ground recycled fibres to investigate the surface of the fibres.

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability of the different composites. Samples for TGA analysis were placed in a platinum sample pan and the test was conducted in a nitrogen atmosphere with a 40 ml/min gas flow rate. TGA instrument (Q500 V6.7) heated the samples in the range of 25 to 800 °C with a heating rate of 10 °C/min. Also, TGA was used to measure the amount of matrix residue on the surface of the recycled fibres. After grinding and screening, samples were loaded into the TGA machine and were heated from 25 to 800 °C at 10 °C/min in presence of nitrogen, and an additional oxidative step ensured no ash content remained on the surface of the fibres. Izod impact test was employed to determine the impact strength of the composites using a Ray-Ran Universal Pendulum Impact Tester according to ASTM D256. The dimension of specimens for impact testing was $63.5 \times 12.7 \times 3.0\ \text{mm}^3$. At least eight specimens were tested for each sample.

Differential scanning calorimetry (DSC) was carried out using a TA instrument calorimeter (DSC), Q1000, TA Instruments, New Castle, DE, in the presence of nitrogen. Samples were heated from 25 °C to 250 °C with a heating rate of 10 °C/min. The obtained data were used to determine glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c). The degree of crystallinity of each sample was also calculated.

4.3 Results and Discussion

The mechanical and thermal behaviour of the recycled fibre reinforced PLA with enhanced toughness was investigated in this section. Before that, the characterization of the recovered fibres was performed through SEM imaging and thermogravimetric analysis.

4.3.1 Recovered fibres

According to the method reported in section 4.2.2.1, the glass fibres were recovered from the shredded composite. After the screening operation, a rough 70% of the shredded composites came out and was used in the following experiments. Figure 4.1 demonstrates the distribution of the fibre lengths. Comparing the shredded composite and the refined fibres visually by their appearance, the latter became more uniform, after long fibres in the form of a network with big pieces of resin on the surface, were separated. However, the epoxy powder is still present in the composition of the recyclate. Rahimizadeh et al. [26] measured the diameter of the recycled fibres and reported a range of 16 – 20 μm.

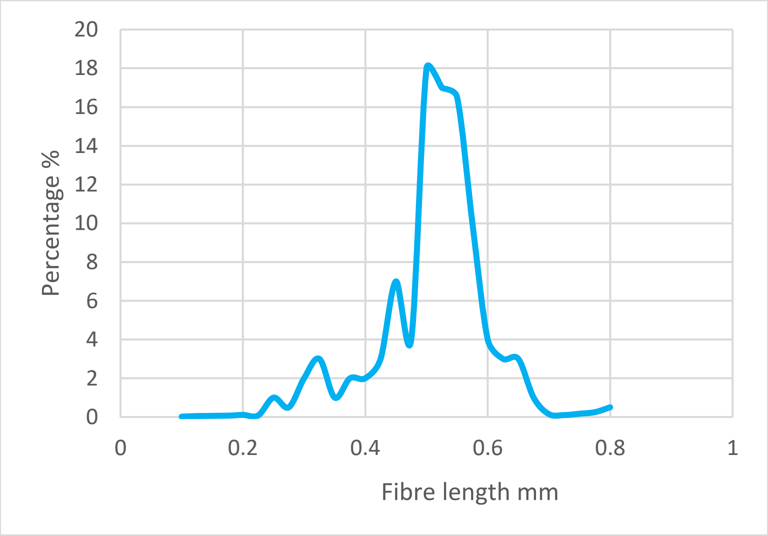

Figure 4.1 Length distribution of the recycled fibres after sieving

SEM analysis of the recovered fibres is demonstrated in Figure 4.2. It can be seen that some fractions of the mechanically ground fibres' surfaces are still covered by the original resin. Given that the wind turbine blade is composed of epoxy/GF composite, those particles are traces of epoxy resin.

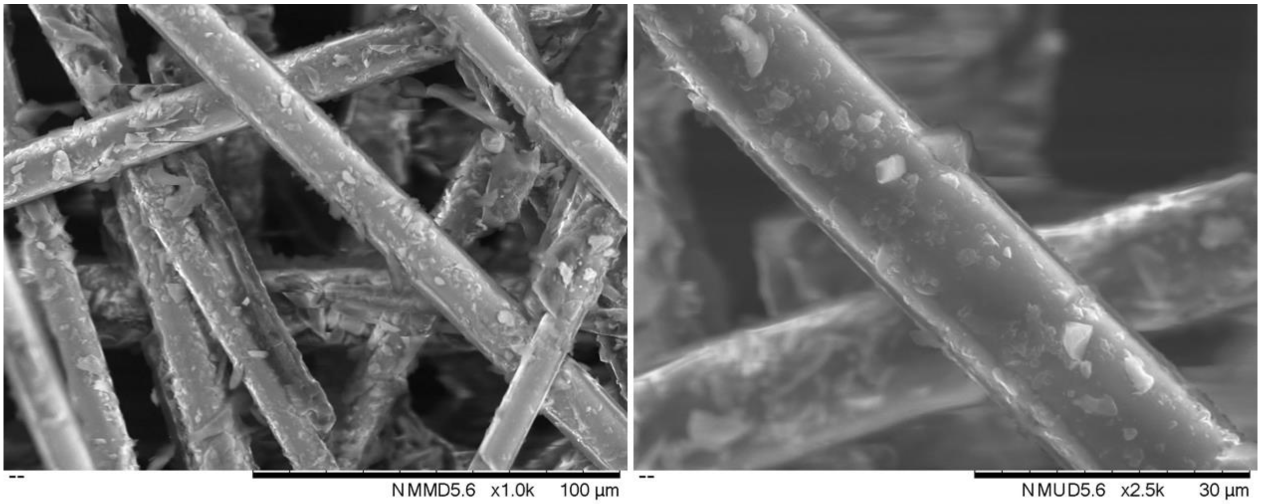

Figure 4.2 SEM micrograph of the recycled fibres which demonstrate the presence of the original resin on the surface of the fibres

The intuitive conviction was that these resin traces could act as stress concentration points and result in poor mechanical properties of the composite. However, the presence of these resin particles on the surface of the fibres could be advantageous to the interfacial adhesion of PLA and recovered glass fibres through mechanical anchoring and chemical bonding possibility [26, 43, 44]. Other than that, the common methods for removing the resin traces off the fibres such as pyrolysis and chemical treatments require a large amount of energy or toxic chemicals. Moreover, the damage of these methods to the recovered fibres drastically decreases their mechanical properties. To evaluate the resin content of the recovered fibres, a TGA analysis was conducted. Figure 4.3 illustrates the weight loss of the fibres after the screening operation. As seen, 28% of the recyclate is composed of resin residue either as particles on the surface of the fibres or resin powder.

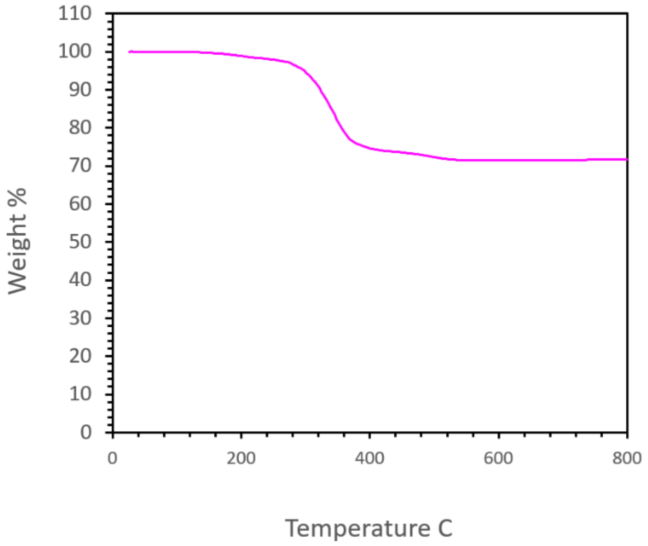

Figure 4.3 The thermogravimetry thermograms of the recovered fibres

4.3.2 Morphology

The surface of the samples after the tensile test was investigated via SEM imaging. Figure 4.4 presents the morphology of the fractured surface of the samples. As seen in Figure 4.4 (a), the fracture surface of neat PLA, which was prepared in the same conditions as the composites, shows no roughness and is smooth which is attributed to the fracture surface of brittle materials. Figure 4.4 (b) represents the fracture surface of PLA and the non-treated R-GFs composite. It can be seen that the R-GFs were distributed properly. However, fibre pull-out and spacing between fibres and matrix is obvious throughout the composite. The adhesion between the fibres and matrix is poor and at the interface of the PLA and fibres, void is seen. After treating the fibres in both PLA/SR-GF and PLA/TSR-GF composites (Figure 4.4 (b) and 4.4 (a)), the number of fibre pull-outs is reduced and the enhancement at the interface resulted in good bonding between the matrix and fibres. At higher magnification, it can be seen that the void at the interface is gone and the matrix attached to the fibres. With this improvements, Mechanical loads are better transferred from the matrix to fibres. Fibres, instead of pulling out of the matrix, broke from the surface of the matrix and consume a higher amount of exerted energy, from the mechanical loads, which results in better mechanical properties and a higher impact strength.

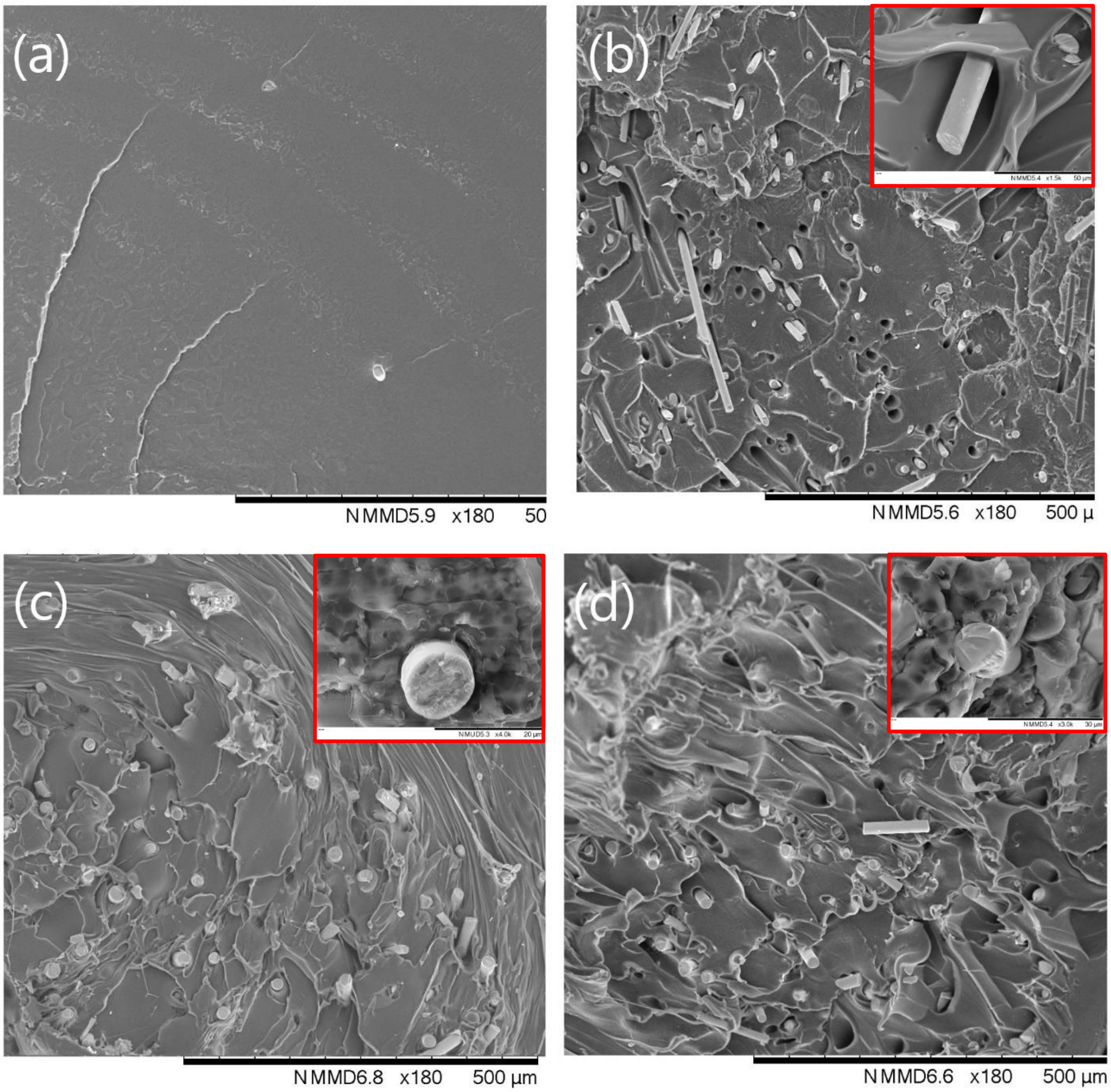

Figure 4.4 SEM micrograph of the fractured surfaces of neat PLA (a), GF reinforced PLA (b), modified glass fibre reinforced PLA (c), and modified glass fibre reinforced toughened PLA (d)

With the evolution of the composites from Figure 4.4 (a) to (d), the smooth fracture surface of the PLA becomes rougher with the addition of each component, which could be attributed to the improved stress transfer and higher toughness, such that in Figure 4.4 (c) and (d) the fracture surface is more rugged than in Figure 4.4 (b) due to better adhesion of the fibres to the matrix. In Figure 4.4 (d), the fibril formation in chain-end modified PLA, due to its increased molecular weight, and rough surface of the matrix indicates that the PLA and consequently, the composite, became tougher. Incorporation of the toughener and treating the fibres, enhanced the interactions at the interface and improved the adhesion between PLA and fibres. The stresses are better handled by the composite, such that the fibres instead of pulling out, broke at the surface of the matrix which results in better mechanical properties. These improvements will be discussed in the following section.

4.3.3 Mechanical properties

Figure 4.5 represents the mechanical properties of different composites. Comparing the PLA/R-GF composite and neat PLA, a 10 % increase in modulus is observed and for the tensile strength, no meaningful improvement was seen. However, the elongation at break of the samples was decreased approximately 40% compared to neat PLA. This can be attributed to the addition of stiffer glass fibres to the system. Comparing PLA/SR-GF to neat PLA, it can be seen that both tensile strength and tensile modulus increased 36 % and 45 % respectively which shows the

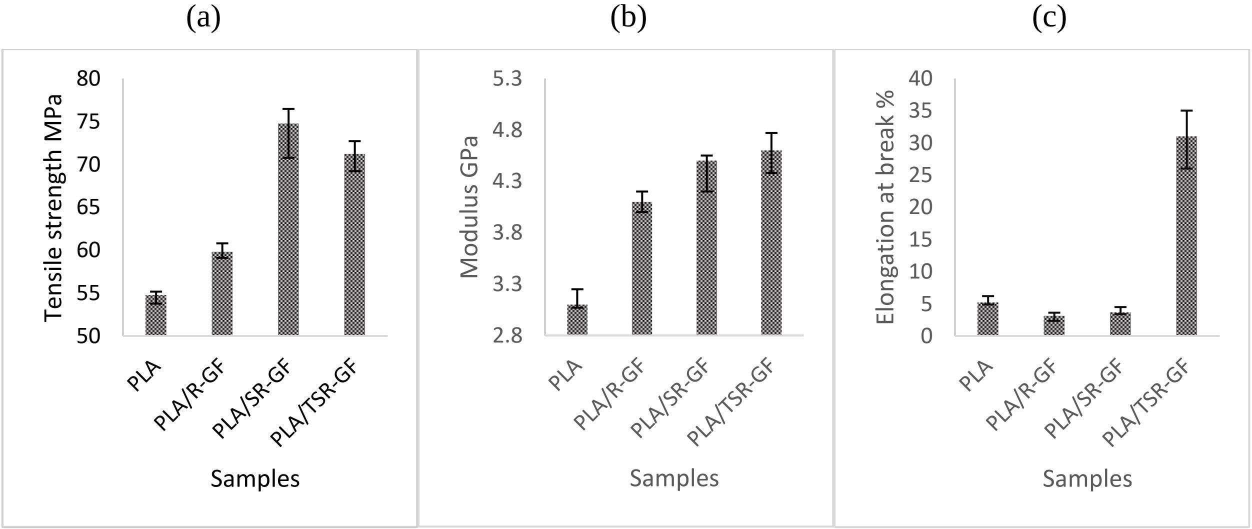

Figure 4.5 Tensile strength (a), tensile modulus (b) and elongation at break (c) of neat PLA, GF reinforced PLA, modified glass fibre reinforced PLA and modified glass fibre reinforced toughened PLA

modified glass fibre potential for enhancing the strength and rigidity of PLA [41]. Comparing the PLA/SR-GF that contains fibres modified with organic silane, with PLA/R-GF, the tensile strength and modulus were improved by 20% and 10%, respectively. Although the addition of modified fibres reduced the elongation at break of PLA, the amount of reduction decreased compared to non-modified fibre composite which can be related to the improved compatibility between SR-GFs and PLA due to silane modification. This reduction in elongation at break of the composite is due to the higher rigidity of glass fibres which show less flexibility than the polymeric matrix and limit the deformation of the polymer.

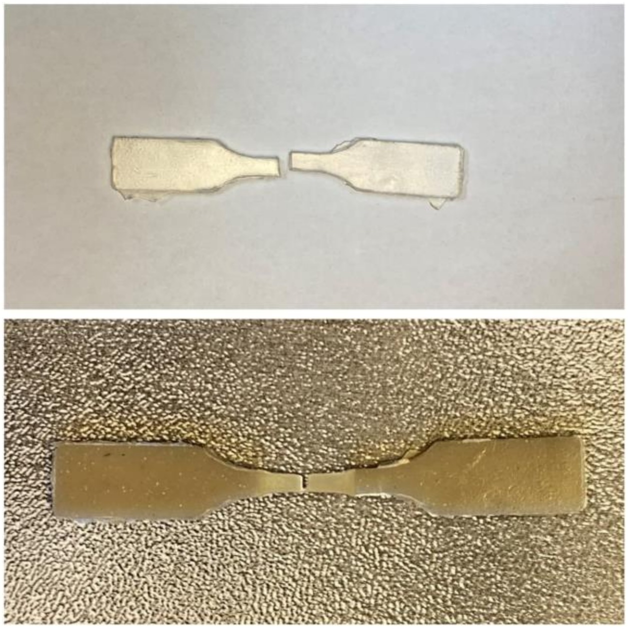

Figure 4.6 Tensile samples after the test, Up: pure PLA, Down: PLA/TSR-GF

The addition of BTCA as the toughener to the composite in PLA/TSR-GF resulted in a significant improvement in the ductility of PLA. BTCA is a multifunctional carboxylic acid that can bond with multiple PLA chains by reacting its COOH groups to OH groups in PLA [35]. After the addition of BTCA to the composite, the samples become stretchable and less brittle. They broke in the tensile machine after necking which is something that would not happen in the case of neat PLA (Figure 4.6). The tensile strength and modulus of the composite remained roughly the same after the addition of the BTCA. This is the advantage of this method over plasticizer usage since most of the plasticizers increase the toughness of PLA but sacrifice its strength [45]. It is crucial to understand the mechanism of BTCA/PLA reaction to understand better how the BTCA toughens PLA. Each BTCA molecule can bond with four PLA chains and in this way reduce the number of chain ends. In polymers, chain ends are weak points that can fail the polymer under mechanical stresses [35].

The impact strength (IS) of PLA and other composites are presented in Figure 4.7. The small increase of IS after incorporation of the R-GFs to PLA could be attributed to the distribution of the fibres inside the PLA which could limit the propagation of the cracks inside the matrix. The other thing is that although in PLA/R-GF composite the main failure mechanism is fibre pull-out due to the weak interactions between the matrix and fibres, these fibre pull-outs consume a large sum of energy which inhibits crack formation and propagation and consequently enhances the impact strength of the composite. Comparing the silane-modified composite with non-modified, it is obvious that with improving the interface and the adhesion between the matrix and fibres, the amount of energy that a fibre pull-out consumes increases, which enhances the impact strength. Furthermore, with the addition of BTCA to the composite, an entangled network of PLA chains forms with reduce chain end effect and makes PLA tougher. Branched network evolution in the polymer matrices limits the crack formation and propagation [42, 46]. Longer branched chains with fewer chain ends and higher molecular weight are phenomena that contribute to inhibiting crack formation [47] as well as impact strength. So synergistic effect of the silane-modified recycled glass fibres improved the interface with PLA and BTCA which toughened PLA through chain end reduction is the reason behind significant improvement in impact strength of the PLA/TSR-GF composite.

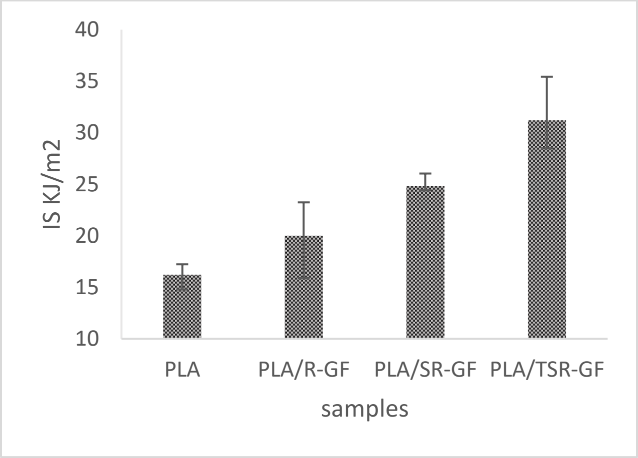

Figure 4.7 Impact strength of neat PLA, GF reinforced PLA, modified glass fibre reinforced PLA and modified glass fibre reinforced toughened PLA

For comparison purposes, a commercially available 3D printing filament was purchased from the market and its mechanical properties evaluated. The filament was made by 3D-Fuel© and composed of PLA and short glass fibres with a diameter of 1.75 mm and is illustrated in Figure 4.8 (b).

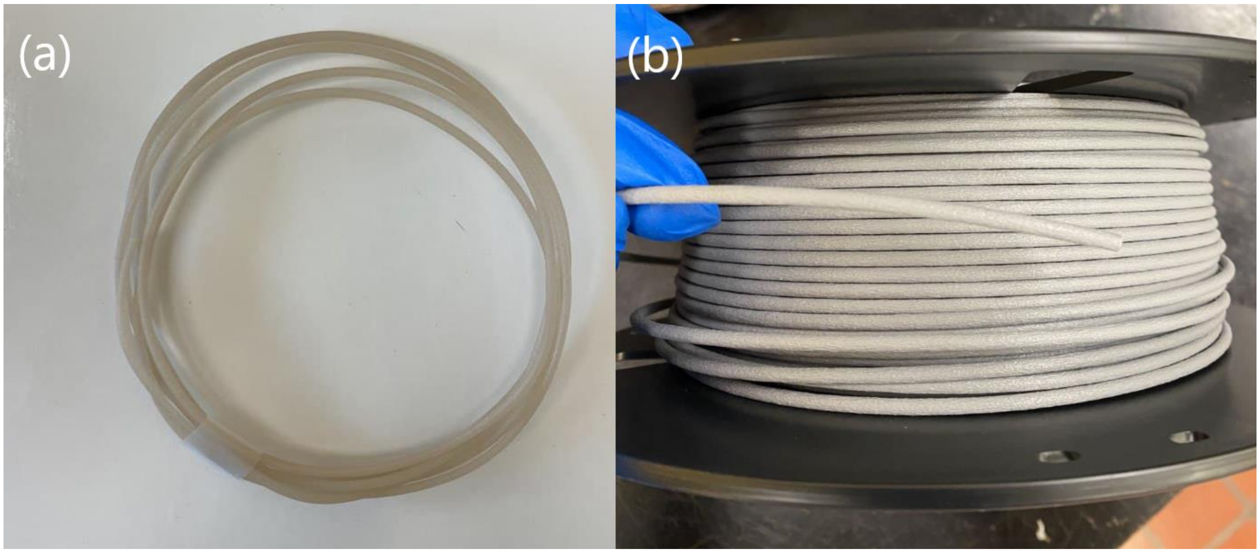

Figure 4.8 PLA/TSR-GF (a) filament from this work, 3D-Fuel filament (b)

A test setup with grips designed for filament tensile testing was used to investigate strength and elongation at break of the filaments. The obtained mechanical properties are presented in Figure 4.9. The 3D-Fuel filament is slightly stronger (which is within experimental error) than the PLA/TSR-GF filament however in case of Elongation at break, PLA/TSR-GF filament showed much better performance.

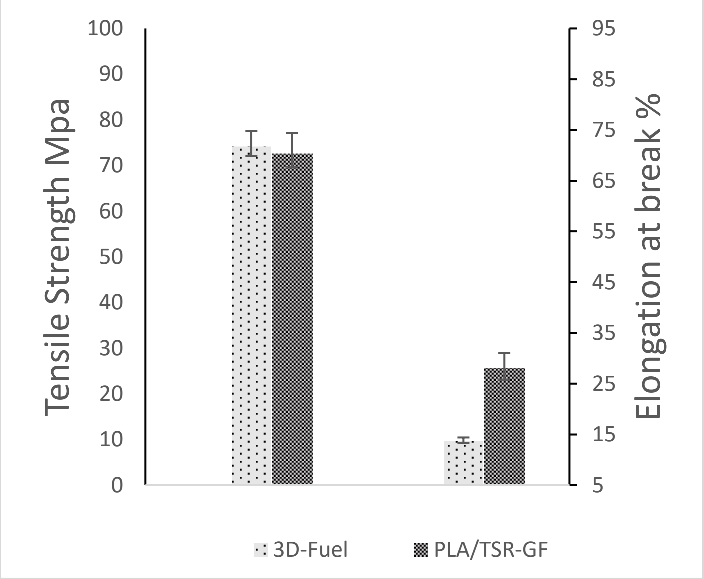

Figure 4.9 Tensile strength and elongation at break of 3D-Fuel filament and PLA/TSR-GF filament

4.3.4 Thermogravimetric analysis

TGA analysis was utilized to investigate the thermal stability of the neat PLA and the composites and the results are presented in Figure 4.10. For neat PLA, the degradation initiates at 301 °C and the degradation of all the other samples happens approximately in the same range with no significant shift. However, the addition of R-GF and SR-GF resulted in a minor shift to higher degradation temperatures. This suggests that GF incorporation slightly improved the thermal stability. The effect of R-GFs on the thermal stability sounds acceptable compared to PLA composites reinforced with bio-based fibres [48, 49] in which the incorporation of fibres aggravate thermal degradation. The addition of BTCA reduced the amount of chain ends through reaction with multiple PLA chains and resulted in slightly increased thermal degradation temperature. Any decrease in the number of active chain-ends per mass limits chain end scission and transesterification, which are among PLA degradation processes and leads to better thermal stability [50]. The thermal properties of PLA and other composites are presented in Table 4.3.

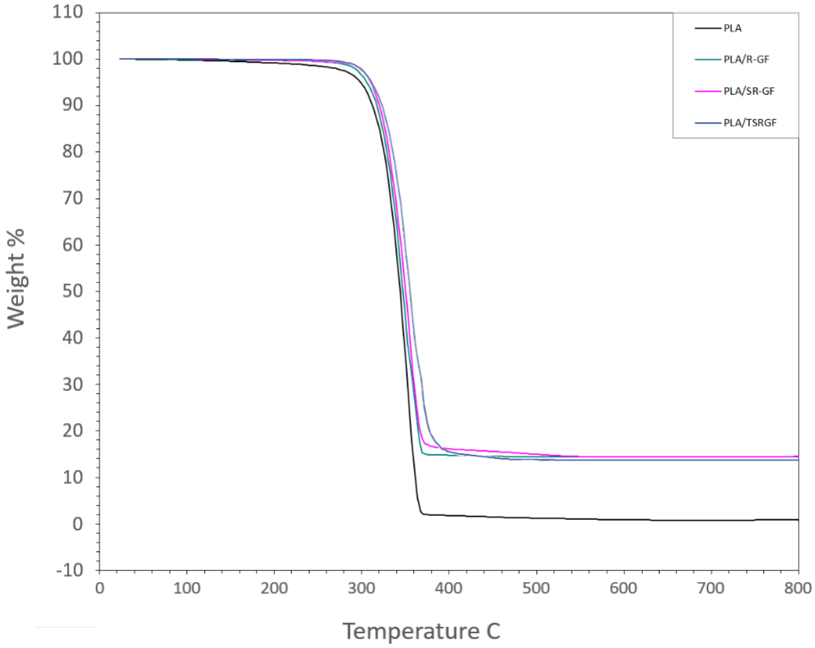

Figure 4.10 Thermogravic analysis of neat PLA, GF reinforced PLA, modified glass fibre reinforced PLA and modified glass fibre reinforced toughened PLA

4.3.5 DSC analysis

The second heating of the neat PLA and the composites from DSC curves are illustrated in Figure 4.11 and the parameters are listed in Table 4.3. To study the crystallinity of PLA and different composites, the degree of crystallinity (χ %) of the samples was calculated using Equation 1:

$$\chi\,(\%) = \frac{\Delta Hm - \Delta Hc}{\Delta Hf \times W} \qquad (1)$$

where ΔHm is the enthalpy of fusion, ΔHc is the enthalpy of cold crystallization, ΔHf is the enthalpy of fusion of 100% crystalline PLA which is 93 J/g [51] and W is the weight fraction of PLA in the composite.

Table 4.3 Thermal properties of PLA and its composites

Sample	**T_{onset} °C**	**Tg °C**	**Tc °C**	**Tm °C**	**χ (%)**
PLA	309	57.2	121.2	149.6	5.4
PLA/R-GF	314	57.9	121.1	150.1	6.8
PLA/SR-GF	317	60.3	123.4	151.0	7.0
PLA/TSR-GF	320	58.8	119.8	154.4	4.7

In the graph, three zones are witnessed. The first endothermic peak demonstrates the glass transition temperature, T_g. The following exothermic peak demonstrates crystallization temperature, T_c while the third region (endothermic) attributed to melting temperature, T_m. It can be seen that the incorporation of the glass fibres did not change T_g of composite compared to neat PLA.

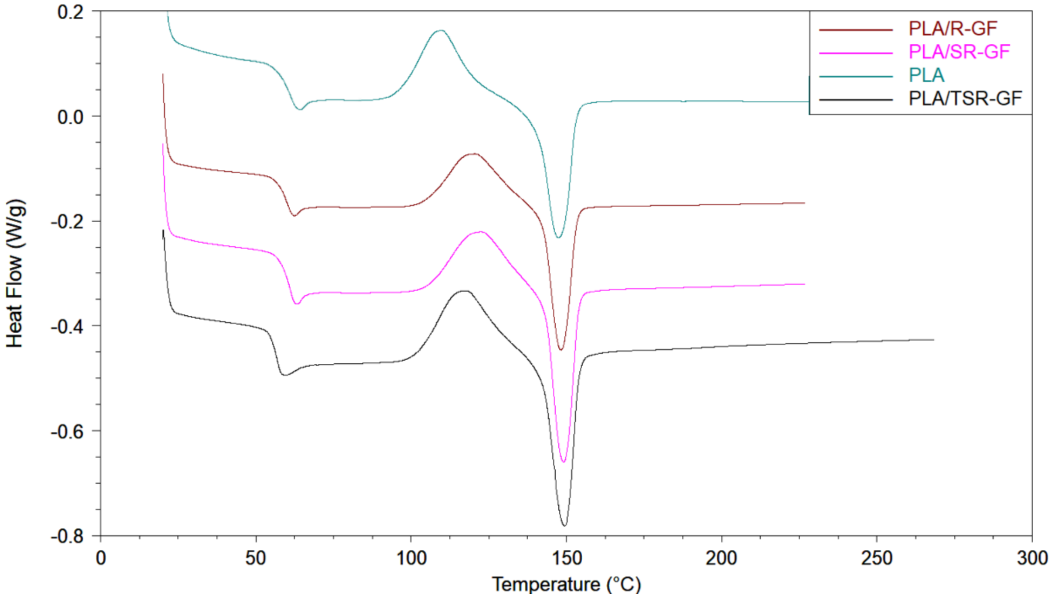

Figure 4.11 DSC curve of PLA and different composites

The incorporation of silane-treated fibres and BTCA slightly increased Tg compared to PLA. This increase could be attributed to the better interaction between the fibre and matrix which results in limitation in chain movements. This restriction in the movement was observable in Figure 4.4 (c) and (d) in the form of fibres attaching to the matrix. The incorporation of R-GFs to PLA did not provide sufficient nucleation sites for PLA due to their large size which could be the reason behind that the T_m of PLA/R-GF did not increase and the T_c peak shifted to the right due to nucleation that hold back of the fibres. After incorporation of BTCA, the crystallinity and T_m decreased. This decrease shows the toughening effect of BTCA which agrees with previous works [35, 52] which show that mechanical behaviour of PLA depends on its crystallinity. Crystallization can make PLA more brittle at room temperature. The reaction of the BTCA with PLA molecules seems to restrict crystal formation.

4.4 Conclusion

In this work glass fibres were recovered from mechanical shredding of a composite part of wind turbine blades and were refined into fibres with desirable lengths. Recycled fibres, with traces of old resin on the surface, were incorporated into polylactic acid to fabricate a reinforced composite in the form of 3D printing filaments. In order to further modify the interaction of the matrix and fibres, the fibres were treated by a silane coupling agent to improve the interface. A carboxylic acid was also used to address the inherent brittleness of PLA, which was intensified with the presence of fibres, through chain-end modification. Composites with 15 wt% of non-treated fibres and silane-modified fibres with 0.5 wt% of BTCA were produced via twin-screw extrusion and the effect of silane coupling agent and the toughener on the mechanical, morphological, and thermal behaviour of the composite was investigated. Based on the morphological analysis, the interaction between recycled fibres and PLA improved and lead to better adhesion between fibre and matrix. This improvement's effect on the mechanical properties was quantified with tensile and impact tests. The incorporation of BTCA and silane-treated fibres improved the strength by 30% and elongation at break and IS of the composite 3 times and 2 times respectively. This study showed the potential of these waste materials from wind turbine blades and their outcome could be a promising recycling solution for waste composite management.

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CHAPTER 5 GENERAL DISCUSSION

Wind power is known to be a renewable source of energy with zero CO_2 emission, but it might not be true considering the huge amount of non-recyclable waste this industry produces annually with decommissioning of wind turbine blades. Most of these turbine blades, which are composed of fibre reinforced polymers, go to landfills due to their low operation cost, but landfilling is the least favourable method to treat wastes due to its damages to the environment and squandering resources. Rahimizadeh et al. [86] developed a method to recover glass fibres from wind turbine blade composites via mechanical recycling and reincorporated these fibres into a thermoplastic polymer (PLA) to fabricate raw material for additive manufacturing. Although the fibre recovery was successful the desired improvement in mechanical properties of the produced composite compared to pure PLA was not achieved. This study continued their work by focusing on the compatibilizing the recovered fibres and PLA. The recovered fibres were treated using an organic silane in order to heal the flaws on the surface of the recovered fibres as well as making them favourable to be attached to PLA at the interface. Efforts have been made to overcome the inherent low ductility of PLA which was aggravated by the addition of glass fibre. For this purpose, a carboxylic acid was chosen to toughen PLA through a chain-end modification strategy. The treated fibres and the toughener were incorporated into PLA through melt mixing and the improvements in mechanical properties of the composite compared to pure PLA were quantified via different equipment and tests. The parts of the blades with the pure composite structure were cut and ground using a hammer mill. The shredded composite was a mixture of resin powder and short glass fibres which still had resin residue on their surface. The short fibres had various lengths from 0.1 mm to several mm. The first step was to make the fibres uniform as well as removing the resin powders as much as possible. So, several sifting operations were preformed in order to eliminate the unwanted particles and each sieving operation was time-consuming and to obtain a desired amount of uniform recovered fibres a huge amount of time and material is needed. Other contaminations like metal fillings as well as balsa wood were observed in the refined fibres which could act as stress concentration centers in the composite and cause failure. The modification of the recovered fibres was done using an organic silane. For the application of silane on the fibres, a cosolvent of 95 wt% methanol and 5 wt% deionized water was used to dissolve the desired amount of silane and the fibres were dipped into the mixture. The usage of this much methanol could raise the final cost of production. Also, the aim of this work from the beginning was to find an alternative to thermal and chemical recycling methods to avoid the significant usage of energy and chemicals. This use of chemicals is in contrast with the primary goal of this study and in order to scale up this method, the silane should be applied in a more efficient manner. The hygroscopic nature of PLA is well known. PLA tends to absorb moisture when left at room temperature and this moisture can speed up its degradation rate. The other problem with absorbed moisture in PLA is that it can emerge as microbubbles during extrusion and other melt operations. Before every mixing and moulding, drying should be done not only with the PLA but also all the involved components which are recovered glass fibres and toughener in this case. The melt processing should be done as soon as the components are taken out of the vacuum oven. Since in a city like Montreal in which this study was done, the relative humidity could be as high as 70% during the day [127]. Melt processes such as extrusion, moulding and mixing also should be done under nitrogen purge with excessive care to avoid any moisture bubble formation in the melt since these bubbles could act as a weak point and fail the composite. The final goal of this project was to produce 3D printing filaments using PLA and recycled fibres, however the possibility of printing 3D objects with a commercial printer, using the obtained composite, and the resulting mechanical properties was not investigated

In this work, only the parts of blades composed of pure composite were used and the other parts which are hybrids of metal, wood and composite, are still a challenge and can not be recycled using this method. The other limitation is the various composites that are used for production of blades. In this work, mechanically recycled blades are composed of epoxy and fibre glass. There are blades which composed of different polymers and different fibres that may not be recyclable using this method. One point that worth mentioning is that the disproportionate number of recycled materials that could be derived from a single blade and the amount that could be reused using this method. Considering the size of each blade as well as the fibre fraction of its composite, reusing the shredded composite as the reinforcement for the 3D printing filaments, may not be the solution that can address this challenge solely. Either the novel usages should be found for the obtained composite, or other complementary methods should be developed for recycling the shredded composites.

The purpose of this study was to find a solution for recycling thermoset composite materials since up until now there is no well-established method for recycling such materials. Although this study developed a method for the fibrous fraction of the composites, the resin fraction still remains non-recyclable and either go to a landfill or is used as fuel. The main effort should be on developing new materials with acceptable mechanical properties as well as being recyclable.

CHAPTER 6 CONCLUSION AND RECOMMENDATIONS

Glass fibres were recovered from mechanical shredding of the composite part of wind turbine blades and were refined into desirable lengths. Recycled fibres, with traces of old resin on the surface, were incorporated into polylactic acid to fabricate a reinforced composite for 3D printing purposes. In order to further modify the interaction of the matrix and fibres, a silane coupling agent was used to improve the interface. A carboxylic acid was also used to address the inherent brittleness of PLA, which was intensified with the presence of fibres, through chain-end modification. Composites with 15 wt% of non-treated fibres and silane-modified fibres with 0.5 wt% of BTCA were produced via twin-screw extrusion and the effect of silane coupling agent and the toughener on the mechanical, morphological, and thermal behaviour of the composite was investigated. Based on the morphological analysis, the interaction between recycled fibres and PLA improved and lead to better adhesion between fibre and matrix. This improvement's effect on the mechanical properties was quantified with tensile and impact tests. The incorporation of BTCA and silane-treated fibres improved the strength by 30% and elongation at break and IS of the composite 3 times and 2 times respectively. This study showed the potential of these waste materials from wind turbine blades and its outcome could be a promising recycling solution for waste composite management.

For future works, it would be interesting to investigate the rheological behaviour of the obtained composite and evaluate its melt viscosity. The obtained data from rheology such as loss modulus and storage modulus combining with the data from size exclusion chromatography (SEC) could be used to investigate the effect of the BTCA on the molecular weight of the PLA which is an indication of the reaction between the two. Although a filament with the similar diameter to a commercial 3D printing filament was prepared but the possibility of printing of an object using the obtained filament was not investigated. It would be interesting to print 3D objects and characterize its mechanical properties. The properties of a composite fabricated with the higher fiber content could also be investigated. This method was applied to shredded composites from turbine blades made of epoxy as matrix and glass fibres as reinforcement. There are other compositions which are in use to produce turbine blades such as polyester/GF, epoxy/carbon fibre, etc. The validation of this method for the recycling of these composites needs to be verified. A feasibility study on the costs and operations is needed to be done on this method to verify whether the final product could compete with the similar commercial products available on the market, made of virgin materials, or no.

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