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Development of Short Bamboo Fiber Reinforced Recyclable Epoxy Composites

TUDelft

Development of Short Bamboo Fiber Reinforced Recyclable Epoxy Composites

By

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Preface

This report showcases the outcome of my research conducted at the Faculty of Aerospace Engineering at TU Delft. The past two years have been quite challenging, especially the final year dedicated to the thesis. The thesis not only provided me with a valuable opportunity to gain hands-on experience in the laboratory but also enabled me to connect with numerous individuals and exchange diverse ideas. What initially seemed like a challenging endeavour became more manageable with the assistance of those around me.

First and foremost, I would like to express my appreciation to my supervisors, Dr. Kunal Masania and Dr. Baris Kumru, for their unwavering support and guidance throughout the entire duration of the thesis project. I am grateful for their valuable advice, even during unconventional hours. I always looked forward to our meetings and the feedback they provided. Secondly, I would also like to thank Mr. Johan Kocks and Mr. Marc Bokeloh from Bambooder Biobased Fibers B.V. for providing me with this wonderful opportunity. Along with the fiber materials, I received valuable guidance and support from them which helped me in accomplishing this project successfully. I am also thankful to the DASML and DEMO staff, including Victor, Alexander, Dave, Johan, Roy, and others, for their consistent support and enthusiasm.

Lastly, I would like to extend my heartfelt gratitude to my parents for their encouragement and belief in me. I also owe a special thanks to Shachi Phatak for her continuous support and motivation during moments when I felt discouraged.

Thus, with God’s blessings, my journey as a master's student at TU Delft has come to a conclusion. Looking forward to new beginnings!

Abstract

In the recent years, the global concern over depleting fossil fuels and the increasing decomposition of composite waste has led to a growing interest in alternative recyclable and environmentally friendly materials. Polymer composites, despite their desirable properties, are often non-recyclable and contribute to environmental problems when dumped into landfills. These materials take a long time to decompose and can release harmful chemicals and greenhouse gases during the process.

To address these issues, research is focusing on recyclable materials and eco-friendly solutions such as bio composites. Bio composites, made from natural fibers and resins, offer recyclability, lightness, cost-effectiveness, and a smaller ecological footprint. Bamboo fiber is one natural alternative, it grows quickly, is abundant, and has similar mechanical properties to glass fibers. Bamboo cultivation is being explored in different countries, offering a sustainable solution to reduce the carbon footprint. Majority of the global production of bamboo (~70%) takes place in India and China whilst leading to reduction of carbon footprint by almost 2.5-3 Gt (Gigaton) individually in each of those two countries. Hence, tropical countries in Europe like Portugal, Spain have also initiated bamboo cultivation for prospective use in industries.

Recycling composites, both synthetic and natural fiber reinforced, is another option to reduce the impact of waste decomposition. While thermoplastic matrices have been effectively recycled, thermosets still pose a challenge in recovering fibers, especially short fibers. Lately, a technique of recycling thermosets has been developed where the epoxy hardener consisting of acid-cleavable groups allow for the recycling of the epoxy when exposed to acidic environment.

This thesis aimed to manufacture and test a prototype short bamboo fiber reinforced epoxy composite, while employing the acid-cleavable hardener and recycle it using the specific acid basic recycling process to recover both fibers and resin. This would result in tackling the problem of poor recyclability of thermosets whilst also adopting sustainable bio-fibers as reinforcements.

Overall, this would set the ball rolling towards development of fully sustainable and recyclable suitable composites suitable for use in the industries. At the same time, it will also reduce the environmental impact to a great extent, leading to a more sustainable aviation industry in the future.

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1. Introduction

The global concern over depleting fossil fuels as well as the gradual increase in composite waste decomposition have heightened the interest in the usage of alternative recyclable and environmentally friendly materials. Polymer composites are commonly used in various industrial and consumer applications due to their desirable properties such as strength, durability, and lightweight. However, these materials are often non-recyclable and end up being dumped into waste and landfills, leading to several environmental problems.

Dumping polymer composites into landfills is disadvantageous as they take a very long time to decompose. In some cases, these materials can take hundreds of years to break down [1], which means that they will occupy landfill space for a very long time. As a result, landfills may become full more quickly, and there may not be enough space to accommodate other types of waste. Also, when polymer composites break down, they can release harmful chemicals like volatile organic compounds (formaldehyde, benzene, toluene), polyaromatic hydrocarbons and greenhouse gases. These chemicals are carcinogens, causing respiratory, neurological, gastrointestinal issues to the human health as well as causing air pollution, water contamination, soil degradation. Additionally, as these materials decompose, they can release methane, a potent greenhouse gas that contributes to climate change.

According to a report by the United Nations Environment Programme (UNEP), plastic waste is one of the fastest-growing environmental challenges facing the world today. It is estimated that more than 8 million tons of composite waste enter the world's oceans each year, and this number is expected to increase if measures are not taken to address the issue. Regarding the composites, it is estimated that 70% of fiber-reinforced composite waste goes to landfills while only about 9% is recycled. Thus, decomposition of composites due to non-recyclability is a huge problem currently. In the image given below, statistical data of direct decomposition of polymer composites has been given. It could be understood similar to the above stated fact that, in 2015, almost 35000 tons of waste was generated globally out of which 26000 tons was landfilled and just 3000 tons was recycled , highlighting the required improvement in efforts to recycle composites.

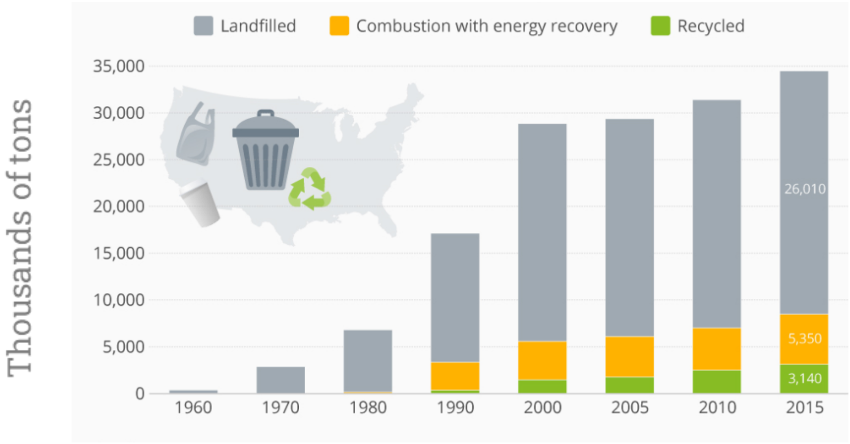


Figure 1: Polymer composite decomposition statistics [1]

The decomposition of such waste into landfills and oceans has led to increased research into recyclable materials. Employing recyclable composites will lead to lower waste being generated which will not only lower the environmental impact, but also lead to resource conservation and cost-effectiveness due to reuse of the materials. To further boost sustainability, eco-friendly solutions such as bio composites have started to develop. Bio-degradability, low density make bio composites an area of interest for researchers. Bio composites consist of using either natural fibres, resins or both together and may serve as alternatives to petroleum-based non-renewable plastics. Bio composites have a smaller ecological footprint, making them safer for humans and other habitats. Moreover, some of the bio composite based fibres and resins are recyclable and reusable.

Figure 2: Circular economy for sustainability [3]

A lot of studies are being conducted on natural fibres acting as a viable alternative to replace the existing synthetic fibres. Bamboo fiber is one of them, acting as an attractive alternative to synthetic polymer reinforcements in a new era of environmentally friendly composites. Given below is an optical image of short bamboo fibers showing the overall physical appearance of the fibers.

Figure 3: Short bamboo fibres [4]

Bamboo is a plant that is effective in preventing global warming. With this, bamboo has several advantages over other natural fibers: it grows quickly, some species can grow up to 21 cm per day, is present in abundant quantities, and is useful for reforestation of degraded land [5]. There are an estimated 15 million hectares of "giant bamboo" available for fiber extraction. With over 1600 known species and distributed worldwide, it is a highly diverse plant [5]. Bamboo has always been native to all continents except Antarctica and Europe. Although bamboo's natural distribution is mainly found in tropical and subtropical climate regions, some bamboo varieties are native to temperate climates and therefore adapted to growth in European regions. One of the companies, BambooLogic Europe based in the Netherlands have already started bamboo cultivation in Portugal and plan to start cultivation in Spain and Italy, while Bambooder Biobased Fibers B.V. also based out of Netherlands have started production of fibers.

Significant research has been conducted regarding the mechanical properties of the bamboo fibers and it has been reported that overall, bamboo and glass fibres possess similar specific characteristics. Bamboo is a natural composite material itself in which bamboo fibers with high cellulose content are held together by lignin. In this, cellulose provides the maximum strength and stiffness properties while lignin acts as the matrix providing qualities like load transfer, flexibility, protection against pests, aging etc. Also, similar to glass fibres, bamboo fibers have good resistance to chemicals and provide good UV resistance. They are thus suitable for a wide range of applications including construction, manufacturing, and textiles. Hence, it can be said that as rapidly growing natural renewable material, bamboo offers an excellent sustainable solution for reducing the carbon footprint.

Along with using natural fibres, recycling composites to reuse them is an evident option to reduce the impact caused by the composite waste decomposition. However, in the case of recyclable composites, both synthetic and natural fiber reinforced, recycling to reuse both fibres and resin has been more or less achieved effectively using thermoplastic matrices until now. This is due to the fact that thermoplastics are meltable and hence recycling methods like remolding, pyrolysis have been utilized efficiently for recycling of thermoplastics. Thermosets have better creep resistance than thermoplastics making them a better alternative for aerospace applications. Also not only do they surpass thermoplastics in possessing higher mechanical properties, but they also possess better impact, abrasion, chemical and UV resistance than thermoplastics. The traditional methods used for recycling thermosets are mechanical recycling and pyrolysis. However, mechanical recycling doesn't allow for successful recovery of fibers, causing a lot of damage, while pyrolysis is a highly energy intensive process and also causes a lot of emissions. Also, due to the high temperature conditions, pyrolysis is suitable only for synthetic fiber reinforced composites. Thus, formulating an alternative recycling process for thermosets which can allow for recovery of both the resin and fibres for reuse would prove to be an ideal solution. At the same time, using natural fibres as reinforcements in combination with such a recyclable epoxy resin using a novel method would lead to a truly recyclable composite.

In this thesis, the aim is to manufacture, recycle and test short bamboo fiber reinforced epoxy composites using a novel platform chemistry. This chemistry employs novel amine-based curing agent which can covert thermoset epoxies to thermoplastics by breakage of bonds near the crosslinking sites upon subjecting it to specific conditions. Overall, this project will lead to an effective combination of employing both bio-based fibers and recyclable thermosets at the same time and contribute a step towards development of truly sustainable and recyclable composites.

2. State of the Art

2.1 Natural fibers as composite reinforcement

Various environmental issues like climate change, shortage of energy resources, increasing danger of contaminated landfills, mining residues saturated with toxic substances are some of the disadvantages of using non-degradable synthetic fibers. An effective and practical approach to mitigate the negative impacts of polymer compounds is the introduction of natural fibers as reinforcing materials. Natural fibers have already been applied in various technological applications over the previous years in various forms of complex structures such as ships, tools of war, from catapults to simple structures like bows and also in ordinary applications such as flags and sails. Natural fibers are considered very important for modern industrial applications due to their low cost, low density, low wear properties in addition to very high energy saving potential. Thus, their market is growing at an exponential rate. This can be attributed to the high recycling potential of natural fibers which is in line with the objectives of the governments, regions and the world law. Recycling of materials used in industrial applications/products is a very important topic at the moment. The global goal is to recycle 100% of composite waste, but in reality, not all waste can be recycled.

Although natural fibers have lower tensile strength than synthetic fibers, they have many advantages over synthetic fibers. They are usually rigid, do not break during processing, and have specific strength and stiffness comparable to E-glass fibers. They have low densities and competing elastic moduli or elasticity. Few of them feature high density, tensile strength, stiffness, and elongation. A comparison of the properties of natural and synthetic fibers was resumed by Asim et al. [6]. Natural fibers had lower density, cost and energy consumption than synthetic/glass fibers. Natural fibers, of course, were renewable and also some of them were carbon-neutral, whereas glass fibers were the opposite. Both natural and glass fibers are widely used. Glass fibers wear out on machines and are a health hazard if inhaled, whereas most of the natural fibers lack these properties. From a disposal perspective, natural fibers are degradable whereas glass fibers are non-biodegradable. Attractive properties of natural fibers include low density resulting in light weight, substantial cost, biodegradability, abundant availability, minimal health hazards during processing, fairly good specific strength and modulus, excellent thermal insulation and acoustic properties, high physical properties, and ready availability. To enhance and improve sustainability, the physical, mechanical, chemical, morphological and anatomical properties of natural fibers should be considered in rationally optimized applications.

2.2 Bamboo Fibers

Bamboo is the oldest building material known to humans and one of the fastest growing grasses in the world which is also easily accessible globally [7]. About 64% of the bamboo forests come from the southeast Asia. 33% of the total bamboo population is grown in South America, the rest in Africa and Oceania [8]. Bamboo culms or stems are the most recovered parts of the plant recovered from bamboo and are used in a wide range of products, from household to industrial. Examples of bamboo products are food containers, Crafts, toys, furniture, flooring, boats, musical instruments, weapons, airships, windmills, strings and cables among many others. Advances in science and technology and limited supply of wood, development of a wide range of technologies has led to development and processing of bamboo to make it more durable and easier to use as building blocks in various materials.

The main components of bamboo are culms, nodes, internodes, leaves and roots as shown in the figure below.

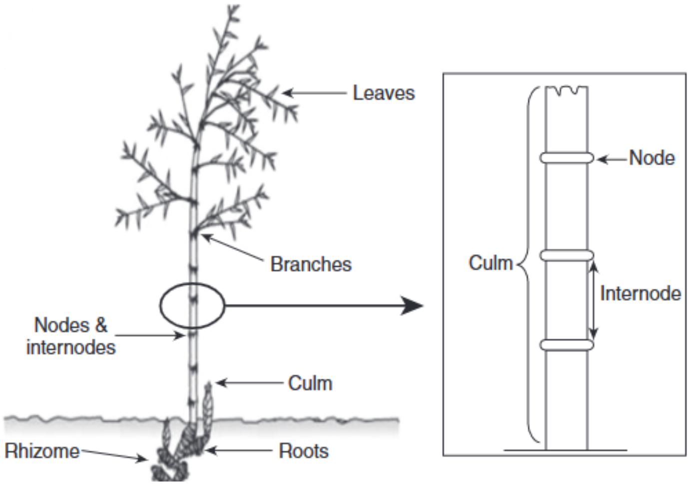


Figure 4: Bamboo structural components schematic [9]

The culm is a hollow stem, probably cylindrical, but the nodes are situated between the culms throughout the length of the bamboo and act as a disc shaped structure between each culm segment. The function of the nodes is very important as the bending of the bamboo due to buckling is avoided because of the nodes. Generally, all of the bamboo the fibers are extracted from the culm of the bamboo plant as they possess the highest mechanical and other functional properties.

Overall, bamboo fiber can be categorised as natural bamboo fiber, bamboo pulp fiber, and bamboo charcoal fiber [10]. Natural bamboo fibers are fibers obtained directly from bamboo by physical or microbial refining. The crystalline structure characteristics of the original bamboo fiber remain unchanged during the extraction process, making the fiber natural [10]. Bamboo pulp fiber is made from bamboo pulp, which is suitable for making fibers, from which fibers are obtained. Bamboo charcoal fiber is made by surface-treating bamboo charcoal powder at the nano level, adding slurry to viscose, and stretching it into a linear shape. This process is mainly used in the textile industry.

2.2.1 Composition

Bamboo fiber is a natural bio-composite material, and the main chemical ingredients of bamboo fibers are cellulose, hemicellulose and lignin. This is well represented by the figure shown below.

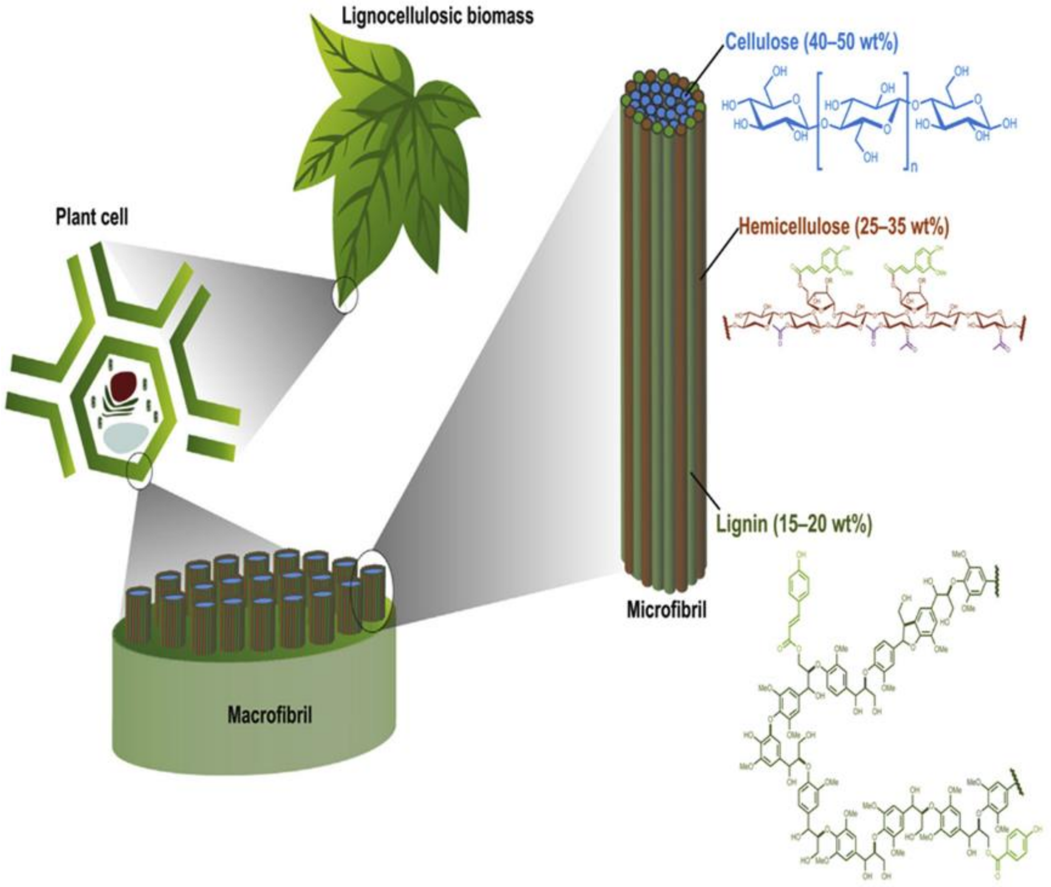


Figure 5: Bamboo/natural fiber microstructural composition [11]

Cellulose (40-60 wt%)

Cellulose is the basic substance that mainly consists of three components namely, carbon, hydrogen, and oxygen, forming the cell walls of bamboo fibers [11]. It is a hydrophilic glucan polymer that is more thermally stable than hemicellulose and is composed of linear chains of glucose units linked by β(1→4) bonds with a high degree of polymerization. Cellulose plant fibers typically swell on contact with water, resulting in high hygroscopic capacity and low dimensional stability. The adhesion between fiber and matrix using natural fibers as reinforcement can be affected by both the hydrophobic and hydrophilic properties of the fiber and its interaction with the matrix [11]. The properties and degradability of natural fibers are influenced by the different cell wall polymers of lignocellulosic materials. In addition, cellulose affects the strength of natural fibers and lignin improves degradation and carbonization by UV light. Cellulose normally remains in the cell walls of plants in the form of microfibrils. Generally, the percentage of cellulose content in bamboo stem ranges around 40-60%. Cellulose is the main factor affecting the tensile strength along the grain of bamboo fibers, and the cellulose content is closely related to the bamboo age. Notably, the cellulose content of the same bamboo material decreases as the bamboo ages.

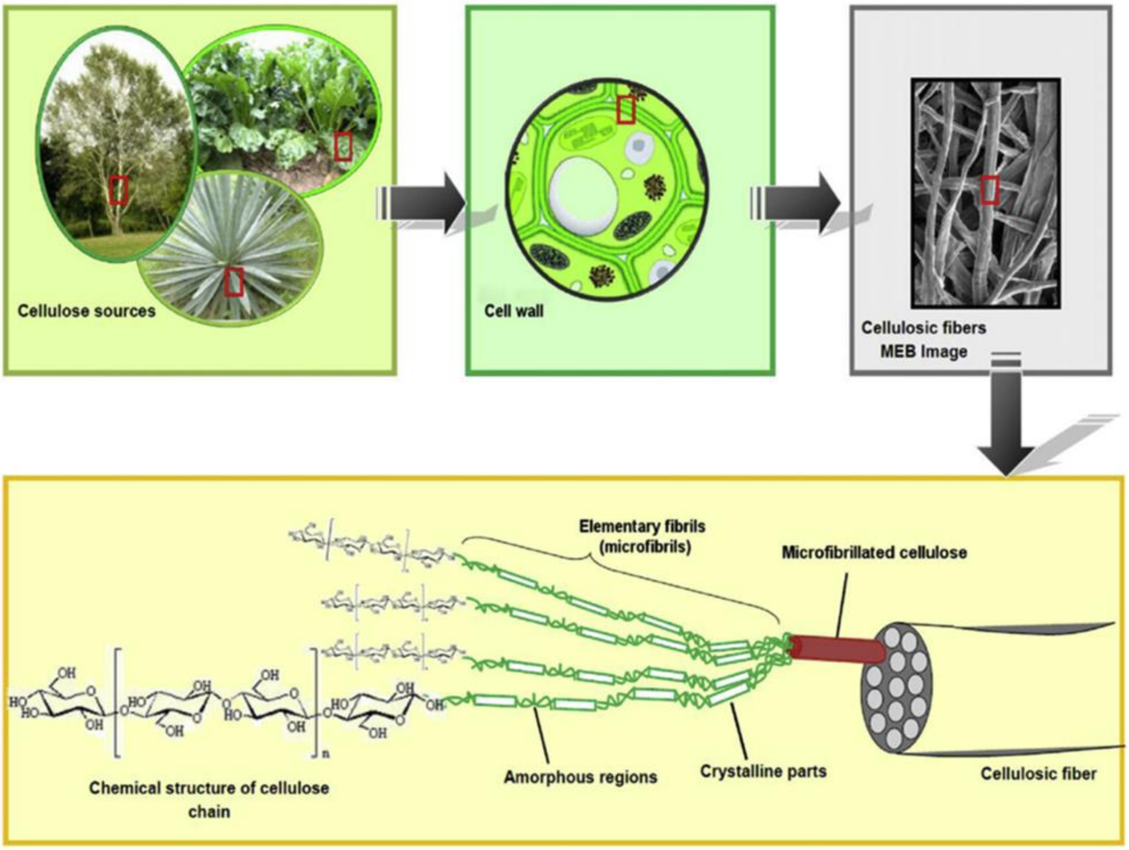


Figure 6: Cellulose chemical structure and microstructural analysis[11]

Hemicellulose (25-35 wt%)

Hemicellulose is an amorphous substance with a low degree of polymerization rate existing between fibers. Hemicellulose is a complex polysaccharide with xylan as the backbone, while 4-O-methyl-D-glucuronic acid, L-arabinose and D-xylose are the constituents present as the branches. Sun et al. [13] analyzed the polysaccharide content of bamboo extracted by two different methods and found that most of the polysaccharide content was glucose after distilled water extraction, and the xylose content was higher after alkaline extraction. In bamboo, hemicellulose plays a key role in giving the plant its unique strength and durability. It also regulates the growth and development of bamboo cells, allowing the plant to maintain its structure and shape for a long period of time.

Lignin (15-20 wt%)

Lignin is a class of polymers with complex structures and many types. The basic units of lignin mainly include guaiacyl, syringyl, and p-hydroxyphenyl monomers out of which guaiacyl is predominantly prese in bamboo [14]. The connection between the structural units of lignin is achieved by ether bonds and carbon-carbon single bonds. Lignin is not evenly distributed in the secondary walls of bamboo fibers. In general, wide layers have low lignin concentrations and narrow layers have high lignin concentrations. The presence of lignin also gives the bamboo material some stability. The lignin content also varies with the age of the bamboo. Along with the three main ingredients, lignins also generally contain different types of sugars, fats, proteins and small amounts of ash [14]. These chemical compositions not only have an impact on the bamboo properties, but also the uses of bamboo fibers. The lignin in bamboo result in it providing resistance to attack by pests and rot, making it a popular building material for housing, furniture and other products. Additionally, the lignin found in bamboo can be converted into biofuel or used to make paper and other materials. One of the chemical structures of lignin is shown below for reference.

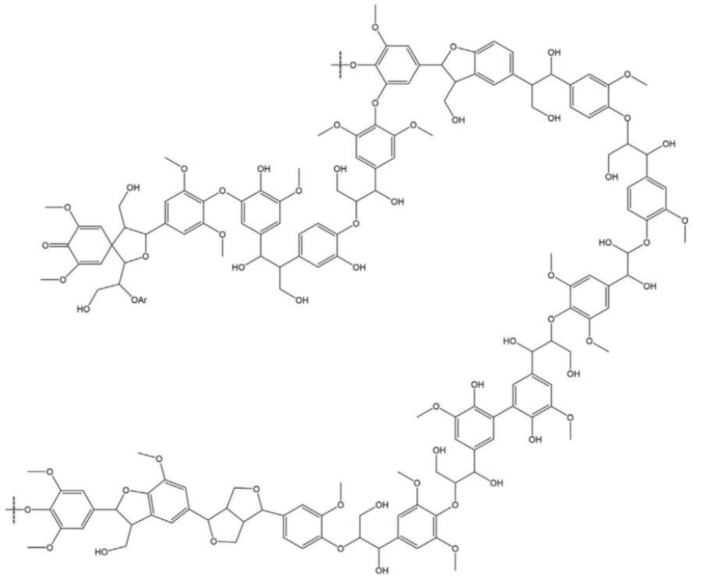


Figure 7: Lignin chemical structure [14]

In the case of the structure, bamboo cells broadly consist of fiber cells(~45%), parenchymal cells(~30%), ducts(~10%), epidermal cells(~7%), sieve ducts(5%), accessory cells(~2%), and other cells(~1%) with specific volume fractions as given. According to studies conducted previously, bamboo fiber cells do not have an inner wall, and the middle layer of the secondary wall is multi-layered. The orientation of microfibers varies not only between layers of bamboo fiber cell walls, but also between different bamboo species. The orientation of the microfibers in the narrow layer is approximately horizontal helical alignment, and the orientation of the microfibers in the wide layer is approximately axial helical alignment. Bamboo is anisotropic because the fiber orientations of the narrow and wide layers are different. Different distribution of vascular bundles will have different longitudinal permeability of bamboo fiber, which will affect the penetration of chemical reagents and have a certain impact on the composition analysis and bamboo fiber production.

2.2.2 Properties

Extensive research has been reported on bamboo fiber properties, highlighting its short production cycle once matured (which takes 2-4 years) and environmental benefits in comparison with the synthetic fibers. The presence of large voids in between bamboo fibers caters in absorbing various odors, dust and other harmful substances, purifying the air and controlling humidity. Bamboo fibers have a strong antibacterial effect, and contain sodium copper chlorophyll, which provides an anti-ultraviolet effect as well. However, bamboo fiber also has some drawbacks, such as high-water absorption, corrosiveness, and low durability. Still, bamboo has one of the best performance among natural fibers upon subjected to moisture absorption.

Influence on mechanical properties

Many factors affect the mechanical properties of bamboo fibers, including the chemical composition and structure of bamboo fibers, moisture content, age of bamboo, and location in the plant (top, bottom, inside, outside).

Tian [15] reported that removal of hemicellulose decreased the tensile modulus of bamboo, whereas removal of lignin did not significantly change it. The tensile strength of bamboo fibers also decreased with the removal of chemical constituents, while the ductility decreased slightly with the removal of lignin but increased with the removal of hemicellulose. The bamboo fiber cell structure is complex, where the secondary wall middle section of the cell has a multi-layered structure. Therefore, the lignification of the thin and thick layers of the multi-layer structure is different, and the microfibril orientation is different, resulting in relatively large differences in mechanical properties between adjacent wall layers. The multi-layered cell wall structure results in better fracture resistance and causes cell wall layers to slide under tension. The angle of microfibrils is also an important factor affecting the mechanical properties of fibers. Generally, the tensile strength and tensile modulus of fibers increase with decreasing microfibril angle. Therefore, the small angle of microfibrils is an important factor contributing to the excellent mechanical properties of bamboo fibers.

There are large gaps between the bamboo fiber molecules, making it highly absorbent. Wang et al. [16] used macroscopic and cell wall scales to study the effects of water content on the mechanical properties of bamboo and found that below the fiber saturation point, the tensile strength of the bamboo fibers decreased with increase in moisture content. The figures given below represent the degradation as discussed.

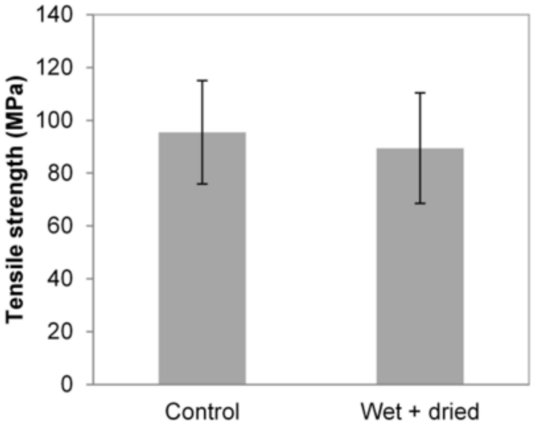


Figure 8: Tensile strength reduction of bamboo-polyester composites [16]

Several studies have been conducted which indicate that natural fibers such as bamboo fibers improve the toughness of brittle thermoset polymers like polyesters and epoxies. Bamboo fiber has been used to form new materials such as polyester-based bamboo fiber reinforced composites, epoxy-based bamboo fiber reinforced composites, phenolic resin-based bamboo fiber reinforced composites, and polypropylene-based bamboo fiber reinforced composites [4]. It can be blended with various polymers like polyvinyl chloride-based bamboo fiber reinforced composites, and polystyrene-based bamboo fiber reinforced composites [5].

2.2.3 Manufacturing of short bamboo fiber composites

There have been several research studies conducted on understanding effective manufacturing techniques for short natural fiber composites. The table given below describes a brief review of some of the studies conducted which determined suitable manufacturing methods, especially for short bamboo and other short natural fiber composites.

Table 1: Review of suitable manufacturing techniques for short bamboo fiber reinforced composites

Sr no.	Short Fiber	Matrix	Manufacturing Method	Ref no.
1.	Bamboo	epoxy	Compression molding	[26]
2.	Manicaria	PLA	Hot press forming	[27]
3.	Sugar palm	PP	Injection moulding	[28]
4.	Bamboo	Cornstarch	Hot press forming	[29]
5.	Bamboo	polyester	Hand layup-hot press forming	[30]
6.	Bamboo	PP/MAPP	Hot press forming	[28]
7.	Cellulose	PLA	Injection moulding	[31]
8.	Bamboo	epoxy	Vacuum infusion	[30]
9.	Bamboo	epoxy	Compression moulding	[30]

It was understood from the above studies, that the most suitable and widely method used by the researchers is compression molding/hot press forming. Compression molding, being highly flexible, comparatively fast and easy to perform, is the most preferred one according to the research studies. Moreover, good dimensional accuracy is also achieved using the CM, making it an obvious choice suitable for the industry as well. An additional advantage of the compression molding process is that is suitable for both thermosets as well as thermoplastics as seen in the above references and hence can we use in wide variety of applications.

Furthermore, research was also conducted in order to understand the optimum fiber-matrix volume fraction for manufacturing short bamboo fiber composites using compression molding/hot press forming technique. One such study [34] investigated the mechanical properties of bamboo fiber-reinforced composites fabricated by hot pressing. It was found out from the results that the tensile and flexural strengths of the composites increased with increasing fiber content, and the optimum fiber content was found to be 30%.

In a study by Chattopadhyay et al. [35], short bamboo fiber reinforced polypropylene composites were manufactured and the optimum fiber volume concentration was investigated. The fibers were also pre-treated and compared with raw fibers to evaluate the effect of pre-treatment on fiber properties The results showed that fiber treatment significantly improved the mechanical properties of the composites, and the optimum fiber content was found to be 40%.

Overall, it was reported that the optimum fiber content varied somewhat depending upon the type of resin employed, but was ranging in between 30-

40% for majority of the studies. Also, fiber pretreatment can also lead to improved properties and lead to better bonding between the fibers and the matrix, thus leading to a better-quality composite.

Overall, it can be clearly understood that the reported research results clearly show that bamboo fibers offer excellent mechanical properties. In addition, they have been shown to improve the performance of epoxy-based composites. Compression molding is one of the most widely used methods suitable for manufacturing short bamboo fiber composites, with the optimum fiber volume fraction to achieve a good quality composite being in the range of 30-40%. Additional research is needed on the general characterization of bamboo fibers and extraction methods to facilitate their use in a variety of technical and everyday product applications.

2.3 Resin

2.3.1 Thermosets and Thermoplastics

Thermosets and thermoplastics are two of the most commonly used polymers in the manufacturing and construction industry. Both types of resins have similar physical and chemical properties, but behave differently when subjected to heat and pressure. In case of the chemical structure, thermosets and thermoplastics differ greatly, affecting their physical and chemical properties.

Thermosets are cross-linked polymers formed by a chemical reaction known as curing. During curing, polymer chains are held together by covalent bonds, forming a three-dimensional network of polymer chains that, once formed, cannot be melted or reformed traditionally. Examples of thermosetting resins include epoxy resins, polyester resins, and phenolic resins. Thermoplastics, on the other hand, are linear or branched polymers that can be melted and reformed many times without chemical change. These polymers have weaker intermolecular attraction forces than thermosets, so they flow and deform when heated. Examples of thermoplastic resins include polyethylene, polypropylene, polycarbonate and the like. Thermosets and thermoplastics are also processed differently. Thermosets are typically cured using heat, pressure, or a combination of both. This process can be done at room temperature or elevated temperature, depending on the specific resin and hardener used. Once cured, thermosets cannot be reshaped or melted without breaking the covalent bonds that hold the polymer chains together. Thermoplastics, in contrast, can be processed in a variety of ways, including injection molding, extrusion, blow molding, and thermoforming. These processes heat the resin to its melting point and shape it into the desired shape using a mold or dies. The resin is then allowed to cool and solidify, retaining its new shape.

2.3.2 Why thermosets over thermoplastics?

Thermosets have a significant advantage over thermoplastics in terms of creep resistance. Creep is the deformation that occurs over time under a constant load, and the crosslinked molecular structure of thermosets provides them with better resistance to this phenomenon. During the manufacturing process, thermosets undergo curing and crosslinking, which chemically bonds the polymer chains into a rigid structure. This restricts chain movement and reduces the material's tendency to deform under load. In contrast, thermoplastics have linear or branched structures that allow them to be melted and reformed multiple times but make them prone to creep.

In addition to their superior creep resistance, thermosets offer other advantages. They can withstand high temperatures without melting or losing shape, making them suitable for high-temperature environments like aerospace applications. Thermosets are also resistant to various chemicals, acids, and bases, making them well-suited for use in harsh chemical environments. Once cured, traditional thermosets become hard and strong, exhibiting high mechanical properties, impact resistance, and abrasion resistance. Overall, the crosslinked structure of thermosets provides them with better dimensional stability and resistance to long-term deformation, making them advantageous for specific applications. The plots given below represent the comparison of stress strain properties of carbon fiber reinforced thermosets and thermoplastics which clearly report thermosets performing better than thermoplastics.

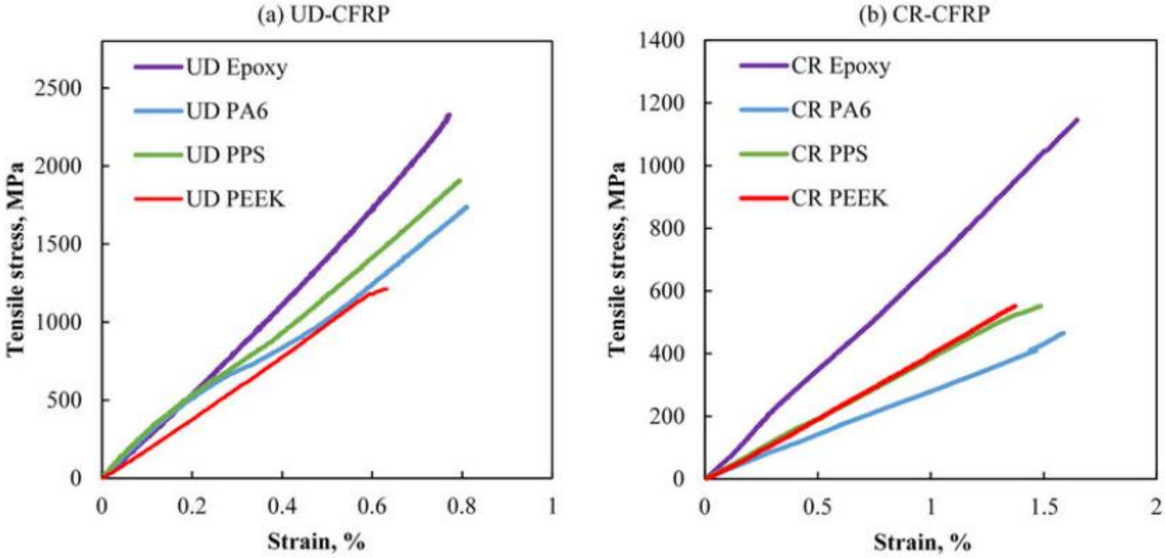


Figure 9: Thermoplastic vs Thermosets tensile stress strain plot [18]

Also, a comparison between the tensile and flexural properties of bamboo fiber reinforced thermosets and thermoplastic composites can be seen below. It can be understood that the epoxy-based composites provide the best performance in comparison to the other two.

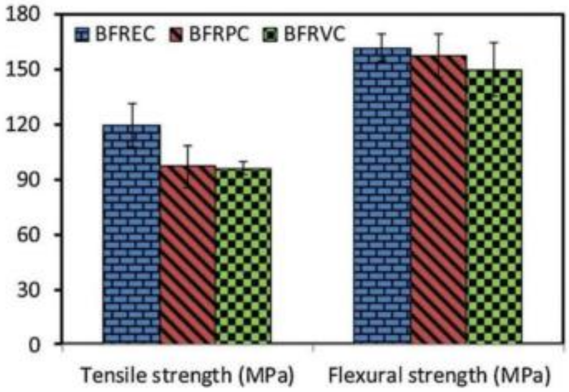


Figure 10: Mechanical behavior-thermoplastics vs thermosets [18]

In addition, thermosets are often used in life-critical applications. Thermosets maintain their shape and size over a wide range of temperature and humidity, making them ideal for use in applications where dimensional stability is critical such as electronic components and structural composites. Along with this, many thermosets have excellent electrical insulating properties, making them useful in applications where electrical conductivity is undesirable or even dangerous.

Even with all the advantages described above, thermoplastics are still preferred over thermosets due to one of the major disadvantages of thermosets. It is recyclability, meaning that thermoplastics can be melted and reshaped many times while making the resin and fiber recovery possible to a certain extent after recycling. Thus, designing a solution for recycling of industry suitable thermosets to achieve the resin and the fiber recovery, especially while using natural fibres as a reinforcement would result in creating a recyclable, sustainable and a better-quality composite being suitable for the industry standards. This would also make it suitable for applications that require flexibility and adaptability, such as: B. Packaging, consumer goods, auto and aircraft parts.

2.3.3 Epoxy resins

Epoxy resin was discovered by Prileschaev in 1909. They are defined as low molecular weight prepolymers with multiple epoxide groups of the following form.

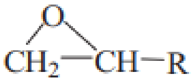


Figure 11: Epoxide ring [22]

Epoxy resins are one of types of thermosetting polymers that are widely used in various industries such as aerospace, electronics and telecommunication, automotive and construction. Epoxy resins are the most used thermoset resins due to them possessing excellent mechanical properties, chemical resistance, and adhesion properties. Epoxy resins are formed by the reaction of epoxy functional groups with curing agents such as amines and anhydrides shown below.

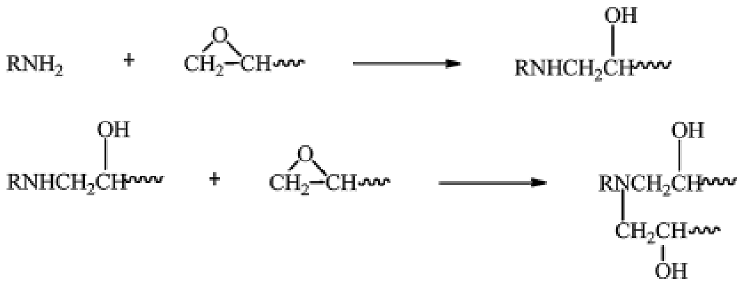


Figure 12: Epoxy curing reaction with amines [22]

The resulting polymer has a three-dimensional crosslinked network structure that gives it unique properties. Epoxy resins have high strength, stiffness, toughness, and excellent chemical and environmental resistance. It also has high adhesiveness and can be attached to various substrates such as metals, plastics, and ceramics. The mechanical properties of epoxy resin can be adjusted by adjusting curing conditions such as temperature and time.

Epoxy resins are generally processed using various techniques such as casting, molding techniques, and pultrusion. Processing conditions vary depending on the specific application and desired properties of the final product. For example, high temperature curing is used for applications requiring high heat resistance, and low temperature curing is used for applications requiring dimensional stability. A curing cycle representing the degree of cure with respect to time is shown here.

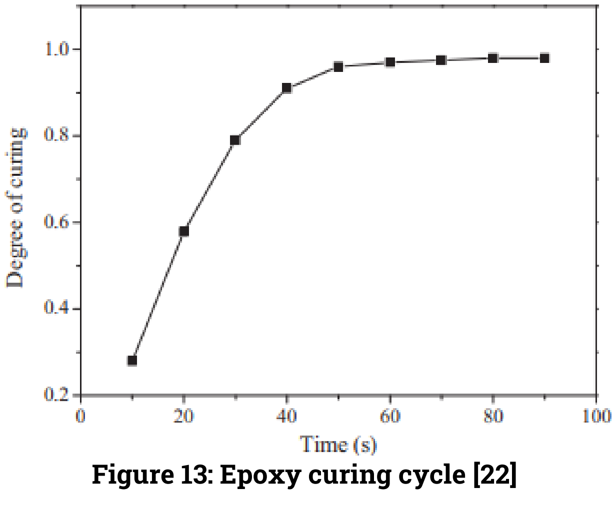


Figure 13: Epoxy curing cycle [22]

Epoxy resins are versatile materials used in coatings, adhesives, composites, and electrical insulation. Adding fillers like glass and carbon fiber enhances their mechanical properties. They are extensively employed in the aerospace industry to reduce weight and improve fuel efficiency in aircraft structures. Epoxy coatings protect concrete structures from corrosion, while epoxy adhesives join metals, plastics, and ceramics in automotive and electronic applications. Recent advancements focus on improving thermal and mechanical properties through additives like carbon nanotubes and graphene oxides. Bio-based epoxy resins derived from renewable resources offer a sustainable alternative to petroleum-based counterparts. Epoxy resins have broad applications across industries, and further research is being conducted to explore new possibilities in biomedicine and energy storage.

2.4 Recycling

2.4.1 Challenges in recycling of thermoset composites

In recent years, there has been a growing interest in the recycling of thermoset composites due to the demand for sustainable materials. Thermoset composites, which have superior properties compared to thermoplastics, are challenging to recycle because they cannot be melted or reshaped. The current methods for recycling thermoset composites include mechanical recycling, where the materials are broken down into small particles and used as fillers, and pyrolysis, which breaks down the crosslinked polymers through high temperatures. Solvolysis and hydrolysis are also being explored as chemical recycling methods. However, further research is needed to optimize the efficiency and cost-effectiveness of these approaches.

As for the two most used methods, mechanical recycling and pyrolysis are promising methods for recycling thermoset composites, but both have several drawbacks which can be seen below.

Disadvantages of mechanical recycling:

1) Degradation of mechanical properties: During the mechanical recycling process, thermoset composites are comminuted into small particles, which can lead to degradation of mechanical properties such as strength, stiffness and toughness. This can limit the uses of recycled materials.

2) Fiber Damage: Refining processes can also damage reinforcing fibers, leading to reduced mechanical properties and potential degradation of recycled materials. Also, the recovered fibers have chunks of matrix present on them which makes them unsuitable for direct reuse.

3) Energy-intensive: Mechanical recycling requires large amounts of energy to break down thermoset composites. This can lead to increased CO2 emissions and greater environmental impact.

4) Limited uses: Recycled materials produced by mechanical recycling are typically used as filling materials in other products, which limits their potential uses.

Disadvantages of Pyrolysis:

1) High energy demand: Pyrolysis is an energy-intensive process that requires high temperatures and large amounts of energy. This can lead to increased CO2 emissions and greater environmental impact.

2) Limited scalability: Currently, pyrolysis processes are limited in terms of scalability, making it difficult to scale up to industrial applications.

3) Quality Control: The quality of recycled materials produced by pyrolysis varies depending on the specific conditions used, and consistent quality and performance can be difficult to achieve.

4) By-product management: Pyrolysis processes can produce by-products such as gas and oil that must be properly managed and disposed of to avoid adverse environmental impacts.

5) Unsuitable for natural fibers: Due to the high temperature conditions used in the pyrolysis process, it is impossible for natural fibers to survive and causes burning, resulting into complete damage of the fibers.

In summary, mechanical recycling and pyrolysis offer potential solutions for recycling thermoset composites, but both have several drawbacks. Chemical recycling is another way of recycling, but it is still in the development phase and has not been employed largely at an industrial scale. Thus, conducting research to develop new methods that are efficient, cost-effective and environmentally friendly is still the need of the hour.

2.4.2 Recyclamine®

Recently, a new formulation of epoxy resin hardeners called Recyclamine® has been developed to provide recyclable thermosets that can be converted into ready-to-use thermoplastics. A decisive factor in recyclability was the production of hardeners modified with acid-cleavable groups. The work of the acid cleavable hardener can be seen below.

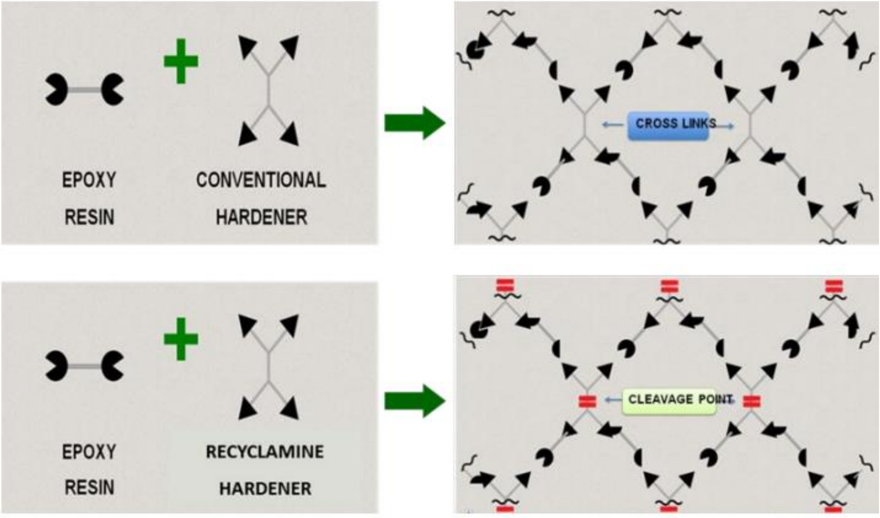
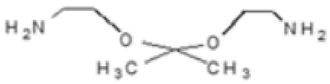


Figure 14: Recyclamine® induced cleavage [25]

A common design for recyclable epoxy curing agent molecules is derived from a polyamine structure, with amino end groups attached to each other through a central cleavable group. The conditions necessary to induce rapid epoxide crosslink cleavage are the combination of temperature (70-100 °C) and pH (acidic) required to induce conversion to thermoplastic polymers. According to various studies conducted, practical thermoplastics can be produced from equimolar mixtures of bisphenols and epichlorohydrin under suitable conditions. A wide range of amorphous, malleable polymers, often called poly (hydroxy ether)s or phenoxy resins, have been reported with glass transitions (T_g) ranging from 80°C to 175°C, depending on the bisphenol chosen for polymerization [24].

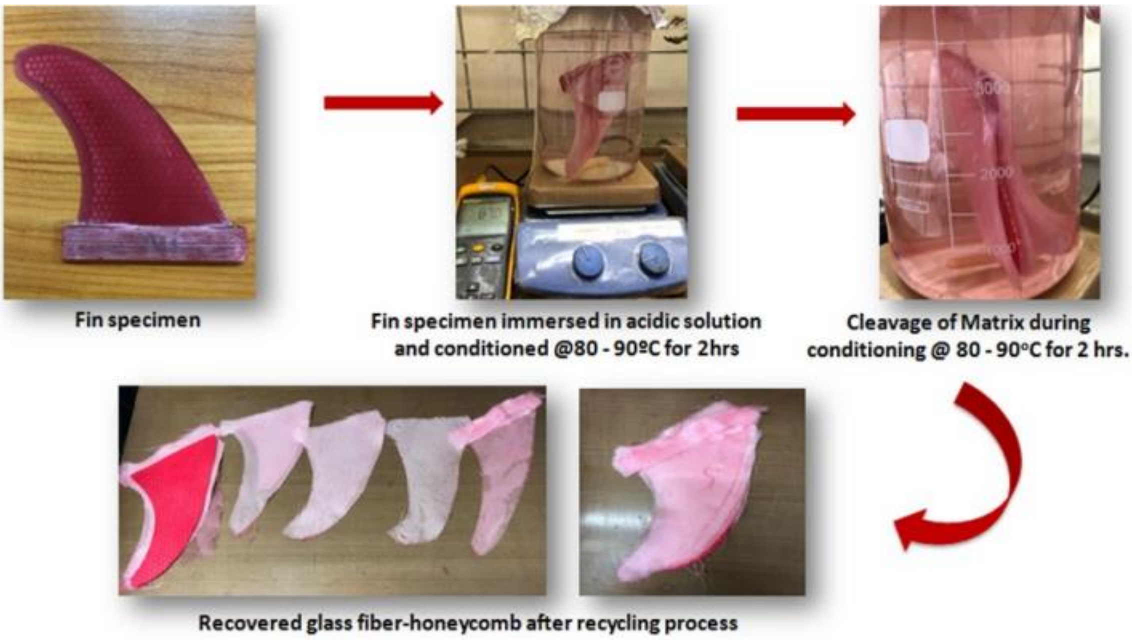
An example of a chemical backbone of one such recyclable hardener Recyclamine®- 101 is shown below.



R101

Figure 15: Recyclamine®-101 chemical backbone [25]

In one of the studies published by Aditya Birla chemicals [25], glass fiber composites employing Recyclamine® were used and both the resin and the fibres were successfully recovered for reuse. The specimen and the corresponding recycling process for the same is explained in the figures below.



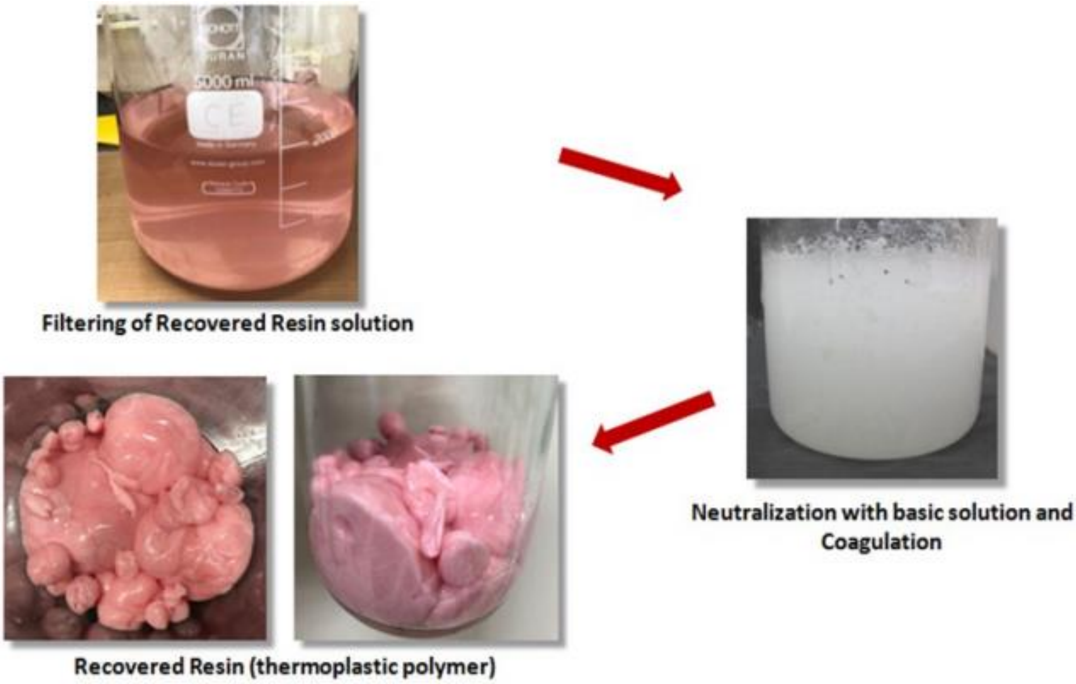
Fin specimen

Fin specimen immersed in acidic solution and conditioned @80 - 90ºC for 2hrs

Cleavage of Matrix during conditioning @ 80 - 90ºC for 2 hrs.

Recovered glass fiber-honeycomb after recycling process

Figure 16: Recycling process using Recyclamine®-fiber recovery [25]



Filtering of Recovered Resin solution

Neutralization with basic solution and Coagulation

Recovered Resin (thermoplastic polymer)

Figure 17: Recycling process using Recyclamine®-resin recovery [25]

In another study by Aditya Birla Chemicals Ltd [25], carbon fiber (CF)/epoxy composites were fabricated by high pressure resin transfer molding (HP-RTM) and chemically treated to recover clean CF and thermoplastic epoxy polymer as recycled products. However, in both the above studies, the mechanical properties of the recycled materials were not investigated to effectively determine the suitable application for the same.

La rosa et al. [36] also investigated the mechanical and thermal properties of recycled carbon fiber reinforced epoxy composites produced using this Recyclamine® technology. As a result, it was found that the recycled fibers had similar mechanical properties to the original material, causing about 7% degradation in tensile properties, while they also retained the thermal stability of the material. Overall, Recyclamine® was able to effectively achieve the recycling process while making possible the recovery of both the recycled resin and the fibres.

Furthermore, in a study published in the Journal of Cleaner Production in 2018 [24] evaluated the environmental performance of Recyclamine® technology compared to other recycling methods such as mechanical recycling and pyrolysis. This study found that Recyclamine® technology has the lowest environmental impact in terms of energy consumption and carbon emissions based on the use of acetic acid for recycling, and is a cost-effective and scalable solution for recycling thermoset composites. Upon using the recyclamine based recycling process, it was estimated that the energy demand reduces by almost 70% and the global warming impact reduces by approximately 600 Kg CO2 eq when considered that the recycled fibers could be directly reused.

Overall, from all the studies conducted till date about Recyclamine® indicate that, in addition to efficacy and sustainability, the Recyclamine® technology offers many advantages for recycling thermoset composites. This is a relatively low temperature, low pressure process that helps reduce energy consumption and production costs. The process can also be run using different solvents (even though the studies conducted till date used acetic acid), allowing flexibility in the recycling process. Overall, the Recyclamine® technology is promising for recycling thermoset composites. However, more research needs to be conducted to evaluating the properties of the recycled components and the compatibility of Recyclamine® with various fibers to understand the possible degradation before reuse. Researchers and industry leaders are actively looking for ways to optimize processes and develop new applications for this technology.

3. Conclusion

It can be understood from the review that natural fibre composites have become popular for numerous reasons. Recyclability, reduced carbon footprint, reduced weight and density, cost-effectiveness are few of the major reasons for the popularity of the natural fibre composites. Among these natural fibres, bamboo fibres are one of the fibres with the highest and fastest global production rate, possessing good mechanical and functional properties and thus can be viewed as a earliest suitable replacement for the synthetic fibre composites.

At the same time, the problem of the global waste plastic decomposition is becoming severe, and it is obvious that incorporating recyclable composites is the need of the hour. Until now, recycling thermosets has not been a very efficient process and the recovery of fibres and resin to an extent where both can be reused has remained largely difficult.

Lately with the introduction of the new Recyclamine® technology, some studies have reported efficient recycling of synthetic fibre reinforced thermoset composites for reuse of both the resin and the fibres. However, just one study has been performed using natural fibres fully as a reinforcement where the compatibility of flax fibres with Recyclamine® and the corresponding recycling process has been understood. There has been no study till date concerning the use of bamboo fibres with this Recyclamine® technology.

There are various challenges involved in production of natural fibre composites like achieving good compatibility of natural fibres with synthetic resin, achieving good dimensional stability etc. Also, the recycling process for Recyclamine® involves processing in highly acidic environment and it's effect on the bamboo fibres must also be understood to avail the possibility of reuse of the fibres. The properties of the recycled resin must also be studied in more depth to understand the degradation characteristics.

This research is aimed at manufacturing short bamboo fibre reinforced epoxy composites employing Recyclamine® as the hardener and study of the properties of the raw and the recycled material while understanding the suitable future application for this composite. This will lead to a development of a novel composite comprising of natural fibers and a fully chemically recyclable thermoset, a combination of technologies yet to investigated.

Overall, this thesis will lead to another step on the pathway of producing fully sustainable and recyclable composites for the aviation industry.

3. Research Definition

The research definition includes the research objectives and the subsequent formulation of research questions for fulfilling the research objectives. Below are a set of research objectives and the corresponding research questions are formulated to achieve the required objective of this master thesis.

3.1 Research Objectives

The main research objective of the proposed study is:

To manufacture short bamboo reinforced epoxy composites employing Recyclamine® as the curing agent, followed by recycling of the composite to evaluate the recycled resin and fibers for reuse in prospective applications.

Achieving this main objective would result in providing insight into the viability of recycling bamboo fiber reinforced epoxy composites and act as an alternative to the traditionally recyclable thermoplastic composites. This aim can be achieved through the completion of sub-objectives such as:

1) Gaining knowledge behind the working chemistry of Recyclamine® to use it effectively with the desired epoxy resin.
3) Determination of a suitable composite manufacturing method and the composite production parameters to manufacture a good quality composite.
4) Application of the Recyclamine®-specific acid-based recycling process to achieve the required recycled composite constituents.
5) Understand the effect of acidic environment during recycling on the fiber and matrix properties.
6) Perform suitable characterization tests using ASTM/ISO standards to evaluate the performance of the recycled and non-recycled components.

3.2 Research Questions

To achieve the proposed goals, a research question and corresponding various sub-questions have been formulated. Answering these questions will result in providing important useful information to fulfill the required research objectives. The proposed research question is as follows:

What are recycling characteristics of a fully recyclable short bamboo fiber reinforced epoxy composite employing Recyclamine® as a curing agent?

The corresponding various sub-questions will be as follows:

1) What are the mechanical properties of bamboo/epoxy composite manufactured using Recyclamine® based recyclable epoxy?

2) How successful is the recycling of the natural fiber epoxy composite such that recovery of both fibers and the resin is achieved for reuse?

3) What is the extent of degradation caused to the bamboo fibers due to the acidic recycling process to be reusable?

4) What are the characteristics and physical properties of recycled resin achieved by recycling the composite?

4. Experimental Methodology

4.1 Materials

Bamboo Fibers

Short fibre mats with a density of 150 kg per metre cube were supplied by Bambooder Biobased Fibers B.V. The bamboo were Toe and Kurung species of Indonesian origin. Bamboo fibers break down at temperatures between 170°C - 200°C, which varies based on the environment and duration of exposure to high temperatures. Consequently, the polymers used for making composites with natural fiber reinforcement, and especially bamboo fibers were supposed to possess processing temperatures below the threshold where fiber degradation occurs, in order to ensure the optimum quality of fibers in the composite.

Recyclable thermoset epoxy

The resin system chosen for study was supplied by R-concept, a company based out of Spain. The recyclable resin system known as Polar bear® consisted of the epoxy and recyclable hardener. The resin contained a bio-based component of about 19%, making it a partially bio-based resin as well.

Figure 18: Bamboo Fiber mats, Polar bear epoxy

4.2 Composite-Manufacturing

This chapter describes the production method employed to manufacture the required short bamboo fiber composites. It was evident from the review presented above that hot press forming/compression moulding and injection moulding were the two most suitable choices for manufacturing of these short natural fiber composites. Thus, in consideration with the availability of equipment at the Delft Aerospace Structures and Materials Laboratory as well as the very low pot-life of the epoxy, wet-layup followed by hot press forming was selected to manufacture the required composites.

4.2.1 Bamboo fibers preparation

The short bamboo fibers were received from Bambooder B.V. in the form of two mats, each 1m^2. These mats needed to be cut into the desired size of 150mm x 90mm to perfectly fit inside the selected mould. For this, initially the fabric was dried in an oven at 40°C for 1 hour to remove any possible moisture content and also ensure proper resin flow through the fibers. Once the mats were dried, they were then transferred to the Gerber cutting machine to achieve the required samples which can be seen in *figure 19*.

For production of each composite plate, two such cut samples were used, each of them weighing approximately 3g.

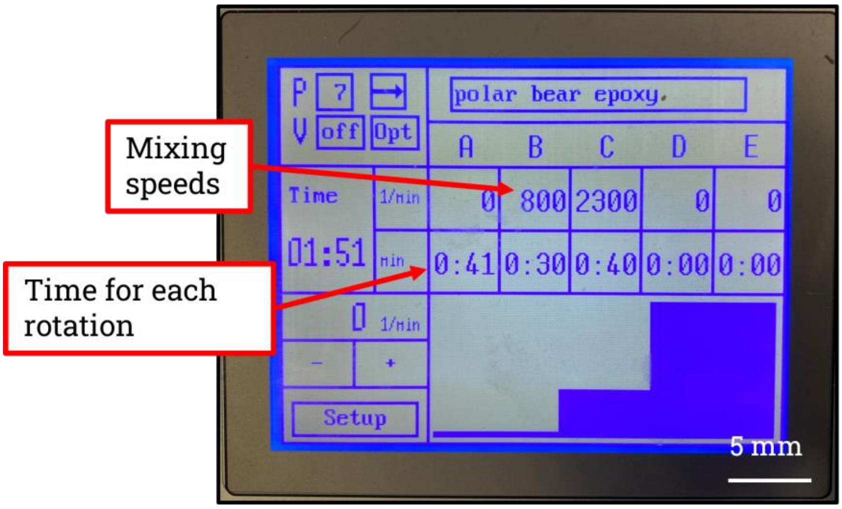
Figure 19: Gerber Cutting Machine cutting bamboo fiber mat

4.2.2 Epoxy-preparation

For the epoxy preparation, the required resin-hardener mix ratio was 100:30. Thus, firstly about 20g resin was collected in one of the plastic containers and was weighed using the weighing scale. For weighing, it was ensured that the weighing scale was zeroed after including the weight of the empty plastic container. After the resin, the hardener was added to the container very slowly in order to achieve the desired resin-hardener ratio accurately.

Once the resin and hardener were added to the container, it was also very important to have a uniform and a degassed mixture. Thus, the container was transferred to the speed mixer as shown in the *figure 20* and a program for vacuum degassing and mixing was set which can be understood from *figure 21.* Once the resin-hardener mixture was degassed and a uniform viscous solution was achieved, the layup process was started which is described in the next section.

Figure 20: Speed Mixer



polar bear epoxy.

Time		A	B	C	D	E
	1/min	0	800	2300	0	0
01:51	min	0:41	0:30	0:40	0:00	0:00
0	1/min					

Figure 21: Degassing Program

4.2.3 Lay-up

For the manufacturing of the composite, the wet-layup method was used. Once the resin was mixed and degassed, the fibers, the resin-hardener mixture, the 3M resin spreader, a brush and the mold with all its components were gathered together on the worktable. All of these components can be seen in the *figure 22* shown below.

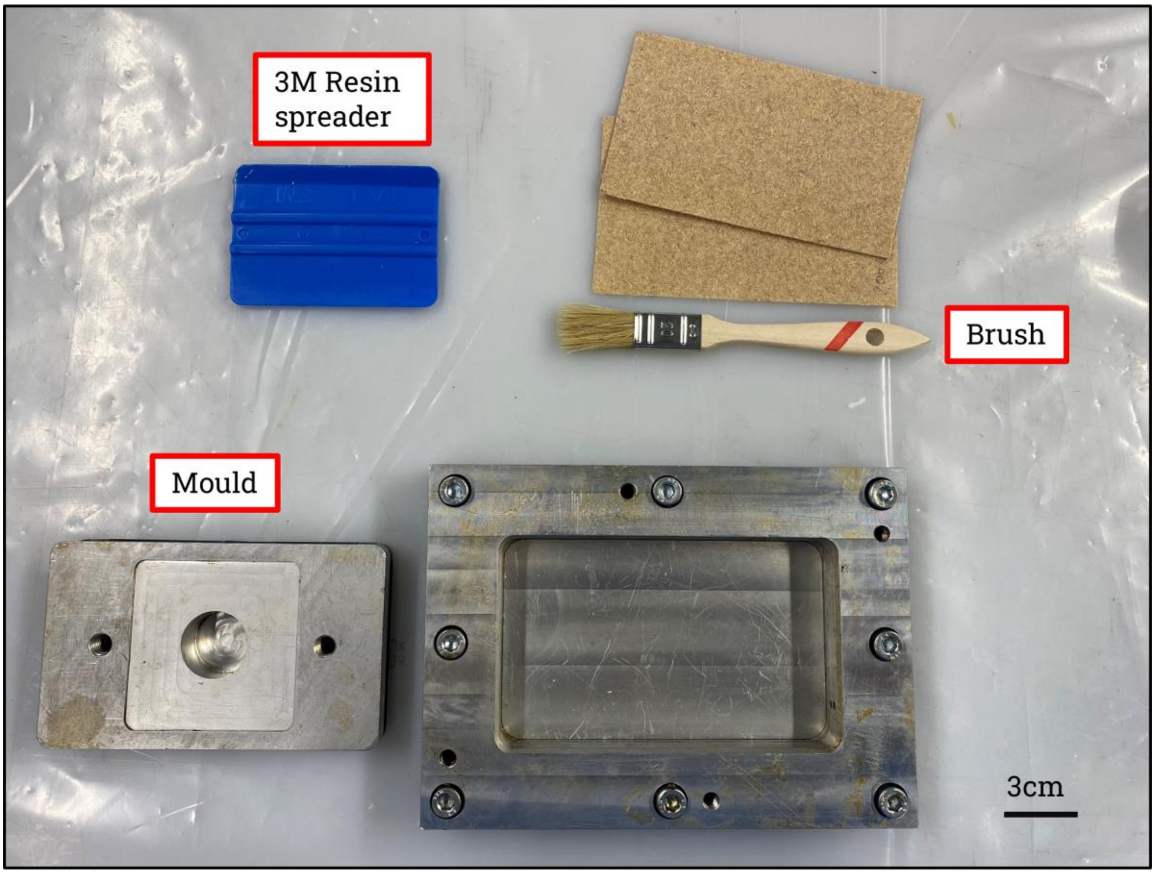


Figure 22: Setup: Mould, Brush, 3M resin spreader

The process started by placing the first layer of the short bamboo fiber mat on the bottom surface of the steel mold. The resin was poured onto the fabric, while keeping in mind the required fiber volume fraction of ~30%.
The resin was evenly spread using the 3M resin spreader tool. Once the side on which resin was applied was adequately absorbed by the fiber mats leaving no dry spot as represented by darkening of the mat shown in the *figure 23*, the mat was flipped to the other side and again the resin was poured and applied using the resin spreader.

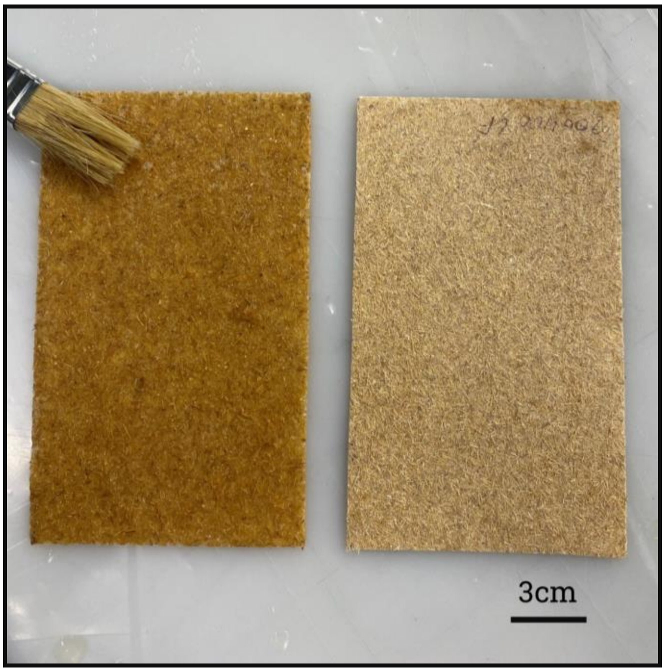


Figure 23: Resin impregnation of fibers

Once the resin application on the first layer was finished completely, the next layer of fabric was then placed on top of the previous layer, and the exact same resin spreading process was repeated for the second layer. In all, this was done for a total of two fabric layers, creating a composite with an approximate nominal thickness of 1mm.

All fabric layers were placed over a film to ensure easy removal after curing. The mold was then closed with an upper die and placed in the press for 25-minute curing cycle with an applied pressure of 10 bar and a constant temperature of 85 °C during the curing cycle.

Once, the press reached the ambient temperature conditions, the mould was removed from the press and unscrewed to demould the composite. However, upon demoulding it was understood that almost all the resin was squeezed out, which indicated that the applied pressure was too high for the resin.

The cycle was again repeated, where this time, a pressure of 2 bar was used. A similar procedure of resin-hardener mixing and degassing followed by wet layup was performed. While the pressure conditions were changed, the temperature setting for the press was kept the same as the resin appeared to be fully cured for the previous cycle. Thus, the same 25 min curing cycle was performed and the mould was allowed to cool upon completion of the cycle.

A representative of the temperature and the pressure cycles can be seen in the *figure 24* and *figure 25* respectively. The temperature cycle shown is the actual cycle used for the process, while the pressure cycle is a close to accurate representation of the pressure cycle where a pressure rate of 5bar/sec was used. A representation for the pressure cycle is shown as the press used for the purpose provided inaccurate data points in relation to the actual climbing pressure.

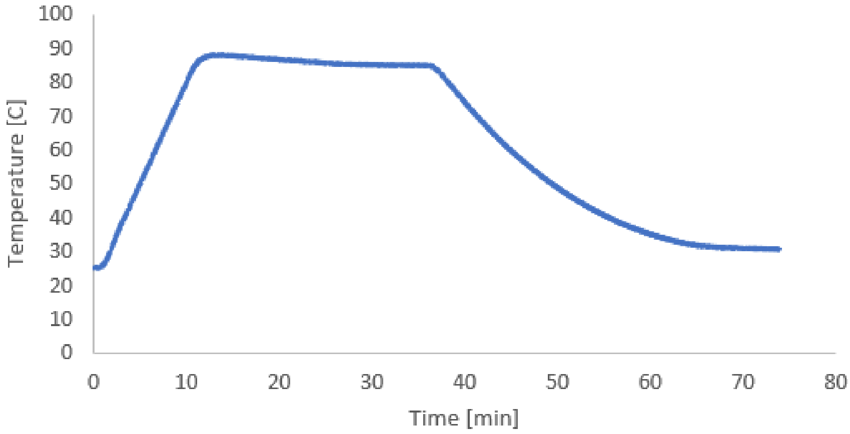


Figure 24: Curing temperature cycle

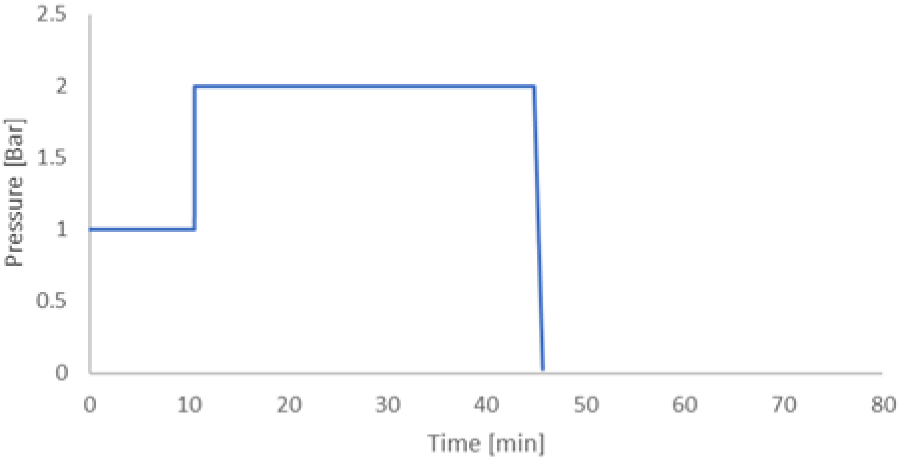


Figure 25: Curing pressure cycle

Once the mould was cooled sufficiently, the composite was demoulded. This time, the composite was consolidated perfectly and also appeared to be completely cured. To validate the curing cycle as well as to evaluate the properties of the composite, it was then subjected to various tests as described later. For the specimens, the samples were chosen from the middle section of the composite, avoiding the edges where the resin-fiber ratio could prove to be non-uniform. Also, visual reference was used to understand to avoid sections having any possible surface irregularities.

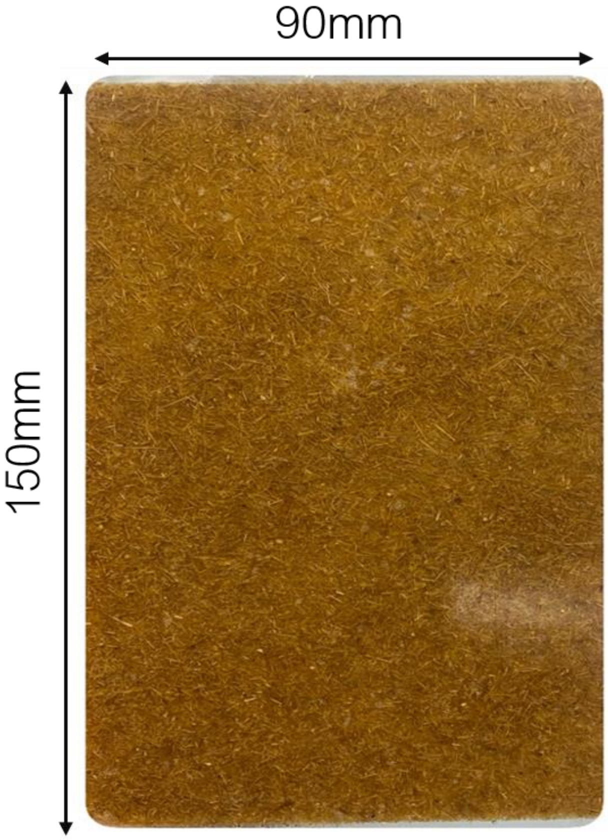


Figure 26: Manufactured Composite

4.2.4 Sample preparation for testing

Once the composite plates were prepared, the next step involved cutting them into smaller sample sizes for different tests, adhering to the established standards. *The figure 27* illustrates the utilization of a diamond cutter for this purpose.

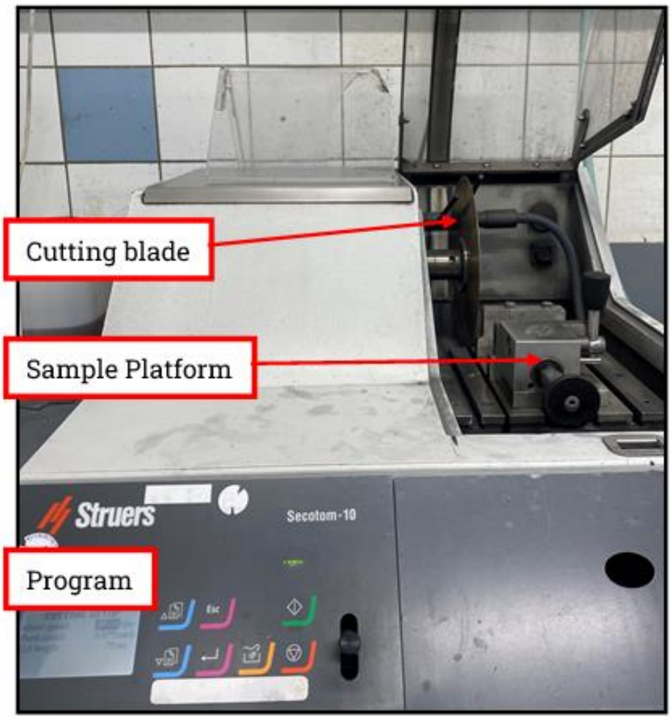


Figure 27: Diamond Cutter

The composite plates were then sliced into various dimensions, as specified in *table 2*, corresponding to the standard requirements for the different tests.

Table 2: Sample preparation for testing

Test	Standard	Dimensions
DSC	ISO 11357	8mg sample
Tensile Test	ASTM D 3039	125 mm*12.5mm
Flexural Test	ISO 14125	60mm*15mm
Water Absorption Test	ASTM D570	50mm*30mm

Subsequently, the cut samples were placed inside a 40°C oven for another round of drying to eliminate moisture absorption. It is necessary to eliminate any additional moisture introduced during the cutting process, as the diamond cutter employs water as a coolant. For most of the cutting processes, the water flow was not utilized to avoid even a little moisture to be absorbed, but after a couple of rounds of cutting, the diamond blade started to heat up vigorously and the water flow needed to be turned on. Finally, the cut samples were collected and subjected to their respective tests.

4.3 Composite-Testing

This chapter describes the different types of tests and techniques used for evaluating the manufactured bamboo/epoxy composite. All of the tests were conducted adhering to specific standards and the results of the same can be seen described below.

4.3.1 DSC measurement

To determine phase transition temperature such as glass transition, melting and crystallization, DSC-Differential Scanning Calorimetry is performed. Thus, to understand the resin curing state in the manufactured bamboo/epoxy composite, a composite specimen weighing between 5 and 25 milligrams underwent a differential scanning calorimetry bracket (DSC) measurement following ISO 11357 standard.

To prepare the samples, a TA standard pan, and lid (P/N: 901670.901, 901671.901) were used as shown below.

Figure 28: DSC sample pan & lid

Both the lid and the pan were first weighed individually and then, approximately 8 milligrams sample was placed in the pan. A small hole was made in the lid to release any gases during heating. The pan and lid were sealed together using a manual press, as depicted below, to secure the sample. Additionally, a reference pan without any material was prepared to compare heat flow with the sample pan.

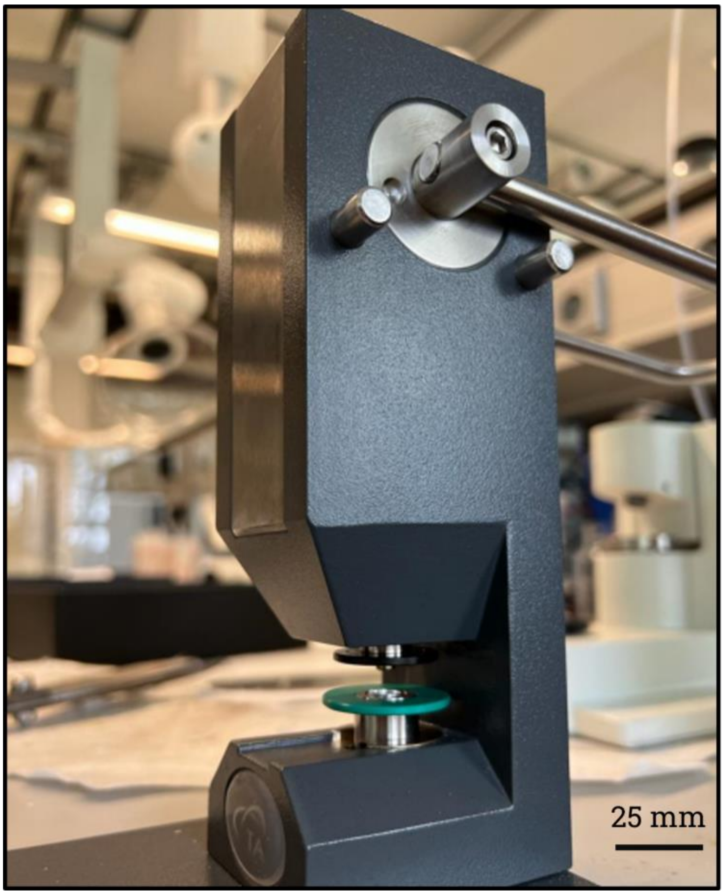


Figure 29: DSC- sealing of pan & lid

The reference and sample pans were then placed in the DSC machine tray, and the heat-cool-heat program was initiated. This program erased any previous thermal history of the material, and the data for the study was collected during the second heating cycle. The samples were subjected to a heat-cool-heat-cool-heat cycle ranging from 0°C to 150°C with a heating rate of 5°C per minute using the TA Instruments DSC 250. To ensure high repeatability the samples weight was maintained constant across multiple trials.

The test reported the individual glass transition temperatures for the multiple heating cycles that were conducted. The resulting graphs provided insights into these different T_g's which were then analysed to understand the stage of curing of the composite.

4.3.2 Tensile Test

For understanding the tensile strength and modulus of the bamboo/epoxy composite, tensile tests were also conducted. The Zwick 10kN universal testing machine, present in DASML, was used to test the tensile properties of manufactured composite materials. A load cell of 10kN, the maximum capacity which the Zwick could handle, was used for the tests. Initially, the load cell and the mechanical clamp fixture were fixed onto the machine for conducting the required tests. The mechanical clamps were chosen as they have a rougher clamping surface, which provides better clamping grip on the composite.

Figure 30: : Test setup- Tensile testing of composite

As discussed in the above *table 2* specimens measuring 125mm in length, 12.5 mm in width, and approximately 1.1mm in thickness were prepared for the experiment following the ASTM D 3039 standard.

Figure 31: Samples- Tensile testing of composite

The tests were conducted at a displacement-controlled rate of 5 mm/min. Data was reported in the form of an excel sheet, where the increments in forces, grip to grip separation and testing time were measured during testing of each individual specimen.

4.3.3 Flexural Test

Along with tensile strength and modulus, the flexural strength and modulus of the bamboo/epoxy composite were also investigated. The composite's flexural properties were evaluated using ISO 14125 three-point bending tests. For the 3-p bending tests, the distance between the supports was set at 40 mm to ensure a span-to-thickness ratio exceeding 16, while the radius of the supports was 2 mm which can also be seen in the *figure 32.*

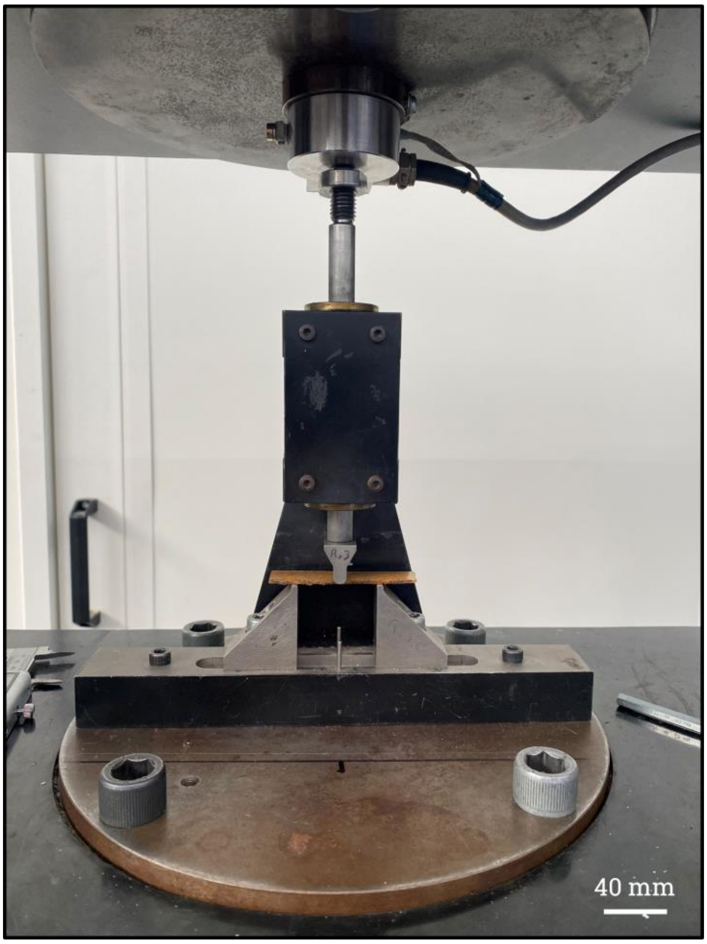


Figure 32: Test setup- Flexural testing of composite

The samples with length of 60mm, width of 15mm and an approximate thickness of 1.1mm were prepared in accordance with the decided standard.

Figure 33: Samples: Flexural testing of composite

The tests were performed on the same machine used for tensile testing, the Zwick 10KN universal testing machine. However, for these tests, since the expected forces were not very high, the Zwick was equipped with a 1 kN load cell instead of the 10kN one. Also, a displacement-controlled rate of 4 mm/min was applied during the tests. Here also, the data was collected in the form of an excel sheet, where the increments in forces, grip to grip separation and testing time were measured during testing of each individual specimen.

4.3.4 Water absorption Test

Along with the mechanical properties of the bamboo/epoxy composite, the water absorption property was evaluated according to the ASTM D570 standard. This test method involved immersing the specimen in water for an extended period to determine the increase in weight as a percentage. It was important to assess this property as polymers and fibres have a tendency to absorb water, leading to changes in the material's properties such as electrical insulation resistance and mechanical strength, which are closely related to moisture levels.

For conducting this test, certain criteria needed to be considered, including immersion time, water temperature, sample thickness, and material type. In this particular experiment for the bamboo/epoxy composite, since a standard was followed, all the variables were adjusted adhering to the same. Thus, a sample measuring 50mmx30mm was cut and it’s weight and appearance were reported. Then, it was placed in glass beaker filled with distilled water and was kept immersed for 24 hours as shown.

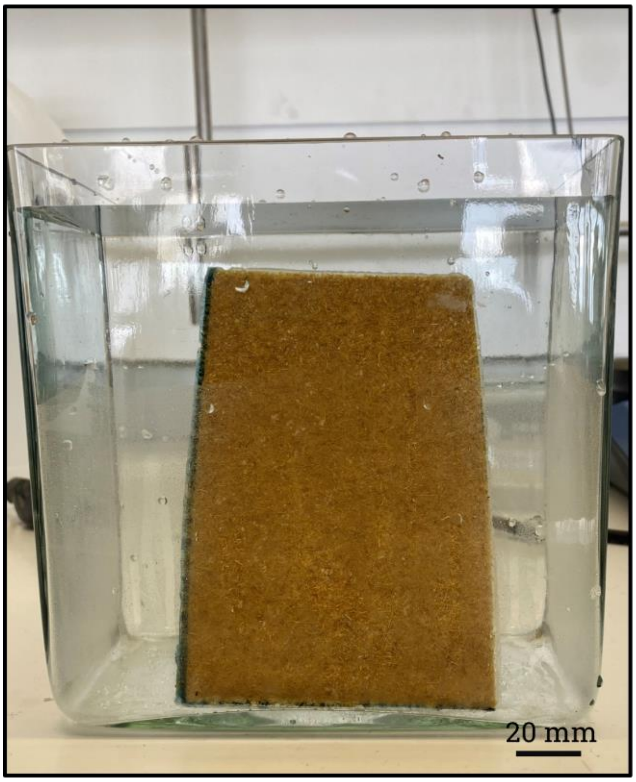


Figure 34: Water absorption testing of composite

After 24 hours, the samples were then removed from the glass beaker and the change in appearance was analyzed. Also, the weight change in percentage was calculated for which the analysis can be seen in results chapter.

4.3 Composite – Recycling

As the characterization of the bamboo/epoxy composite was completed, the recycling process of the composite was then performed. As described in the state-of-art, recycling process utilizes a solution-based method with low energy consumption to recycle Recyclamine® composites.

Based on literature, 50% glacial acetic acid was chosen to induce the required acidic conditions.

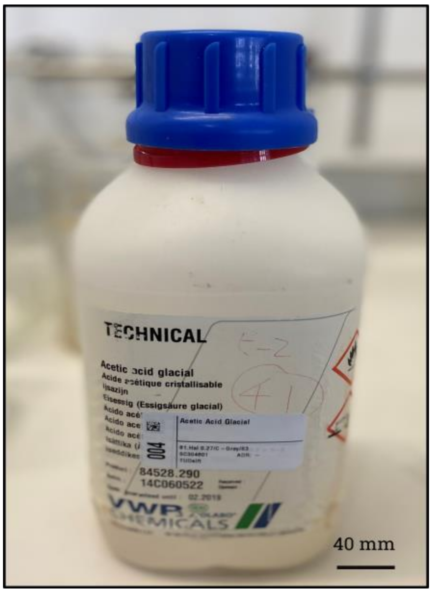


Figure 35: Glacial acetic acid

Distilled water was poured into a glass beaker followed by adding Glacial acetic acid to achieve a concentration of 50%. This beaker was then immersed in an oil bath and the whole set-up was transferred onto a magnetic stirrer. Magnetic stirrer was used both for heating up the required acetic acid solution as well as to constantly stir the acidic solution. Thus, initially, the heating was turned ON and the solution was heated up to 95°C at a rate of 10°C/min. A thermo-sensor was kept dipped inside the acidic solution to constantly monitor the actual temperature of the solution. As the temperature gradually increased, the magnetic tool used for stirring was added to the solution. This helped the solution to achieve a uniform temperature. Once the acidic solution reached the required temperature, the cured epoxy composites were immersed for approximately a total of 75 minutes.

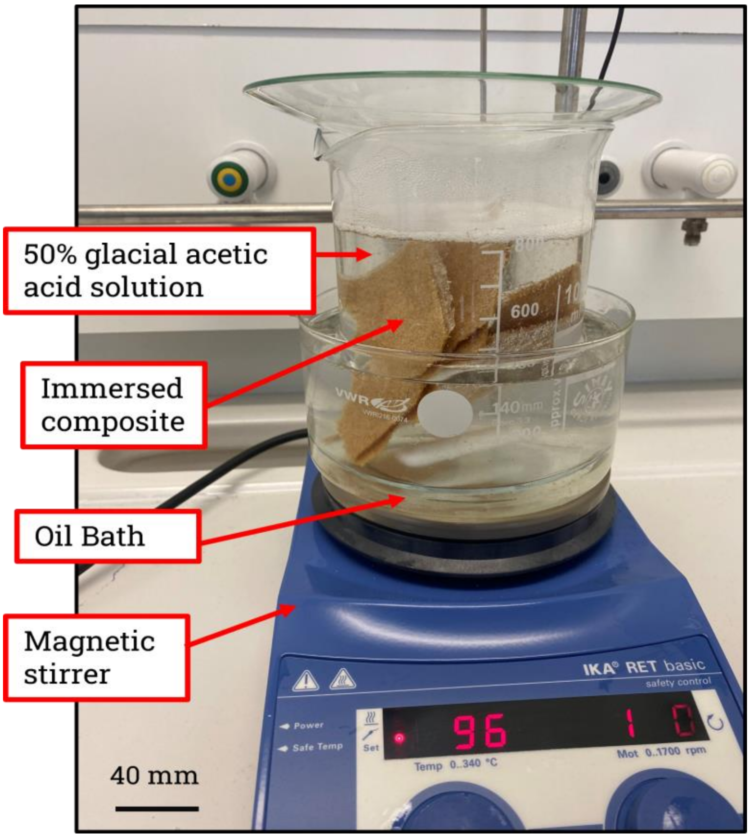


Figure 36: Setup- Recycling of composite

As time progressed, the thermoset matrix dissolved completely in around 65 minutes, allowing the bamboo fibers to be separated, which started to accumulate at the bottom of the beaker. Once all the epoxy was completely dissolved into the acidic solution, the fibers were separated from the solution using filter papers. After collecting all the short fibers, they were rinsed with distilled water and then they were transferred for drying inside an oven at 50°C for 24 hours.

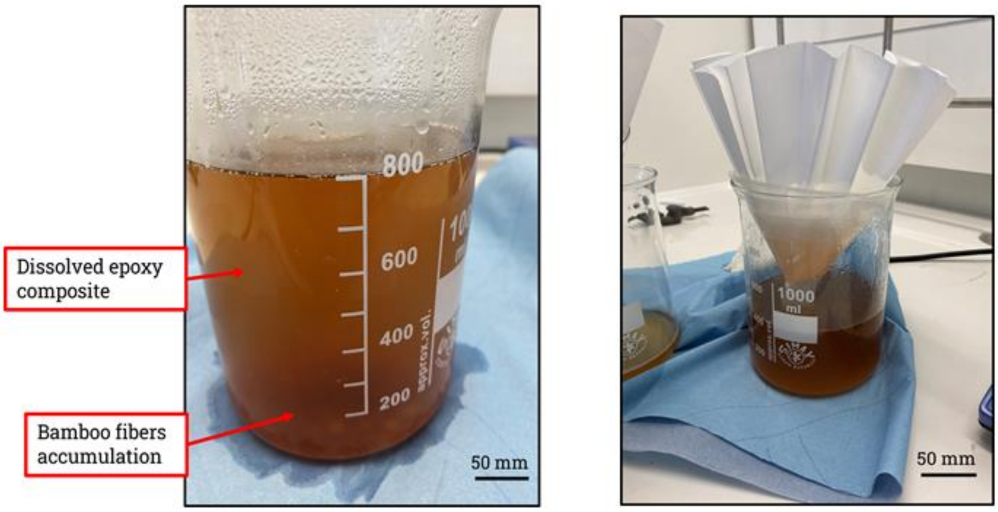


Figure 37: Dissolution of epoxy composite; Filtering to recover recycled fibers

Meanwhile, to recover the recycled resin, it was necessary to neutralize the epoxy acid solution to achieve coagulation. Thus, a sodium hydroxide solution (NaOH) was prepared and was added steadily to the epoxy-acid solution until a pH of around 7 was obtained. The pH was checked at regular intervals by dipping a pH paper inside the solution and analyzing the resulting color. As the pH of the solution came closer to 7, the insoluble recycled resin precipitated out gradually of the solution. This resin was then filtered, rinsed, and transferred to the oven for drying.

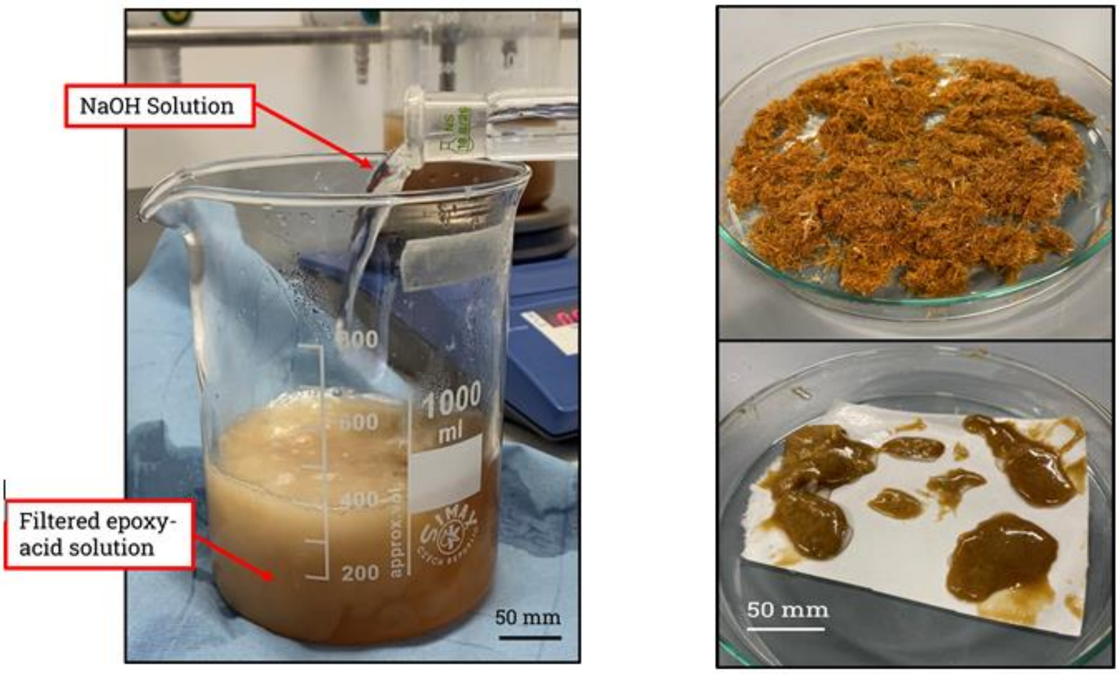


Figure 38: Neutralization of epoxy-acid solution; recycled fibers and resin

Once the resin was fully dried, it was taken out from the oven and a sticky semi-solid recycled resin was obtained.

At this stage, the recycling solution which was remaining was essentially a saltwater solution and did create any additional waste. Thus, it was directly disposed of into the sink. The recycled fibers and recycled resin were then evaluated using various techniques which are described in the next chapter.

4.4 Recycled Components-Evaluation

As described in the previous chapter, both the recycled fibers and the recycled resin were recovered successfully from the recycling process. Once they were rinsed and dried sufficiently, their degradation as well as physical properties were analyzed to understand the suitability of such a recycling process to the bamboo/epoxy composite. For this analysis, various methods were used which are described below.

4.4.1 Microscopy- Raw & Recycled fibers

The first step undertaken was performing microscopy of the raw short fibers as well as the recycled fibers so as to evaluate any potential degradation visually. Thus, both the raw and the recycled fibers were subjected to laser microscopy to achieve good quality images. A Keyence laser microscope was used for the purpose as shown in the *figure 39.*

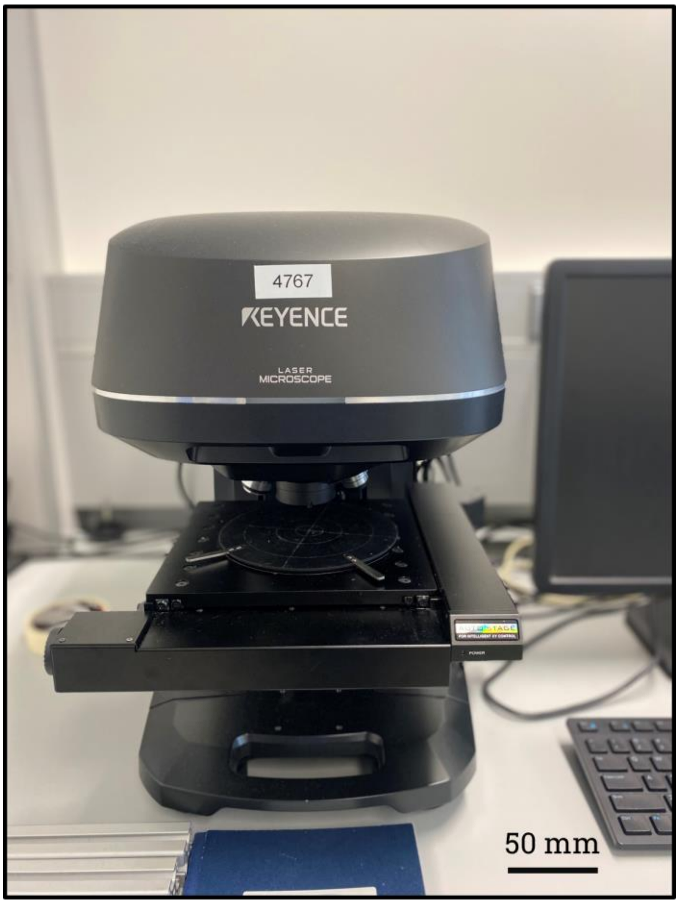


Figure 39: Keyence Laser Microscope

The microscope was already set up in a suitable location with minimal vibration and stable environmental conditions with all the necessary objectives, filters, and detectors installed.

Firstly, the raw short fibers sample was placed on a microscope slide or a specialized sample holder and positioned accurately on the microscope stage, ensuring it is in the focal plane. Using the microscope's focus control, the sample was brought into focus and the scanning parameters, such as scan speed and resolution, were adjusted to achieve a high-resolution image. Once a high-quality image was seen on the screen, image acquisition was started while defining the region of interest (ROI) to be scanned. Thus, the image was acquired by scanning the laser beam across the sample while capturing the emitted or reflected light using the detectors. Finally, image processing software was used to enhance, filter, or reconstruct the images as needed. Average fiber length, diameter of multiple fibers as well as the topographic structure of bamboo fiber surfaces was captured.

The same exact process was followed the second time using recycled fibers. These images were then compared to analyze the change in the diameter, length and structure of the fibers and determine any possible degradation of the fibers.

4.4.2 FTIR- Raw & Recycled fibers

Fourier Transform Infrared Spectroscopy (FTIR) is a technique used in analytical chemistry to identify and analyze chemical substances based on their infrared absorption properties. Infrared (IR) spectroscopy involves the interaction of infrared radiation with a sample, and FTIR is a method that enhances the sensitivity and accuracy of IR spectroscopy.

Figure 40: Perkin Elmer FTIR instrument

In FTIR, a broad spectrum of infrared light is passed through a sample, and the resulting absorption pattern is recorded. The sample absorbs specific frequencies of infrared light, which correspond to the vibrational modes of its constituent molecules. These absorption frequencies are characteristic of different functional groups and can be used to identify the presence of particular compounds or to analyze the composition of a sample. Thus, to analyze the change in composition of bamboo composition before and after recycling, FTIR of the raw and the recovered fibers was performed.

Initially, FTIR instrument was turned ON and allowed to warm up for a specified time. It was ensured that the instrument was calibrated beforehand. The process of measurement started by measuring the background signal. This measurement accounted for any interference from the instrument or the environment. Once the background was measured, the raw fibers sample was placed on the circular shaped diamond platform, ensuring it was properly aligned with the beam path. Then, a preview of the scan was performed to ensure that measurement was being performed correctly followed by actual scan of the fibers. A graph of absorption/transmittance vs wavenumbers was reported to various peaks being seen at specific wavenumbers.

After measurements of raw fibers, a similar procedure was executed for reporting FTIR scans of recovered fibers after recycling. A similar graph of absorption/transmittance peaks being seen at various wavelengths was achieved.

Upon analysis of both the fibers, the graphs were compared to each other. The significance of each peak was analyzed by referring to the reference FTIR chart which led to understand the possible change in composition of the recovered fibers by comparison of the peaks in both the graphs. Thus, the analysis for the same was performed for which the results can be seen in the next chapter.

4.4.3 DSC- Recycled Resin

As understood previously, DSC can be used to determine phase transition temperature such as glass transition, melting and crystallization. Thus, for thermal characterization of the resin recovered after recycling of the composite, DSC was performed.

Similar to the process of DSC of composite performed previously using ISO 11357, sample pan and lid were weighed individually and then sealed with about 6mg of the recycled resin. This setup was then subjected to a heat-cool cycle in reference to a reference pan. A heating cycle ranging from 0°C–130°C with a heating rate of 5°C/min was used for the process. To ensure high repeatability the samples weight was maintained constant across multiple trials.

The test reported the phase transition regions of the recycled resin. The results for the same can be understood in the results chapter of this report.

4.4.4 FTIR- Epoxy & Recycled resin

Along with DSC, it was also necessary to evaluate the composition change of the recycled resin from the composite compared to the original epoxy to understand and confirm the working chemistry behind the recycling process.

Thus, initially, FTIR of pure epoxy was performed. Similar to the process followed during the FTIR of fibers, the machine was warmed up, ensured it was calibrated and the process of measurement was started. Initially the background signal was measured to account for any interference from the instrument or the environment. Once the background was measured, the epoxy sample was placed on the circular shaped diamond platform, ensuring it was properly aligned with the beam path. Then, a preview of the scan was performed to ensure that measurement was being performed correctly followed by actual scan of the fibers. A graph of absorption/transmittance vs wavenumbers was reported to various peaks being seen at specific wavenumbers.

After measurements of the epoxy, a similar procedure was executed for reporting FTIR scans of resin recycled from the composite. A similar graph of absorption/transmittance peaks being seen at various wavelengths was achieved.

Upon analysis of both the epoxy and the resin recycled from the composite, the graphs were compared to each other. The significance of each peak was analyzed by referring to the reference FTIR chart which led to understanding the possible change in composition and therefore confirm the underlying chemistry behind it.

Along with the above measurements, it was also necessary to validate if any contents from bamboo have been dissolved into the recycled epoxy resin of the composite. Thus, a pure cured epoxy sample (without the fibers) was manufactured and recycled to achieve a pure recycled resin. FTIR of the same was also performed to compare and analyze if there was any possible difference in composition of resin recovered from the composite to the pure recycled resin. This led to understanding the whole recycling process and its effect on the bamboo fibers to a greater extent.

4.4.5 DMA - Recycled resin

Dynamic mechanical analysis (DMA) was employed to understand the quality of the recovered resin from recycling. DMA is a process which examines how materials respond to dynamic or cyclic pressures, considering temperature, frequency, and time. The storage modulus (G') represents the elastic behavior or stiffness of the sample, while the loss modulus (G") characterizes the dissipation of energy or damping under cyclic loading. The damping coefficient (tanδ) is a ratio of G" to G'. By plotting G', G", and tanδ against temperature, valuable insights into molecular structure, material behavior, product attributes, and processing can be obtained.

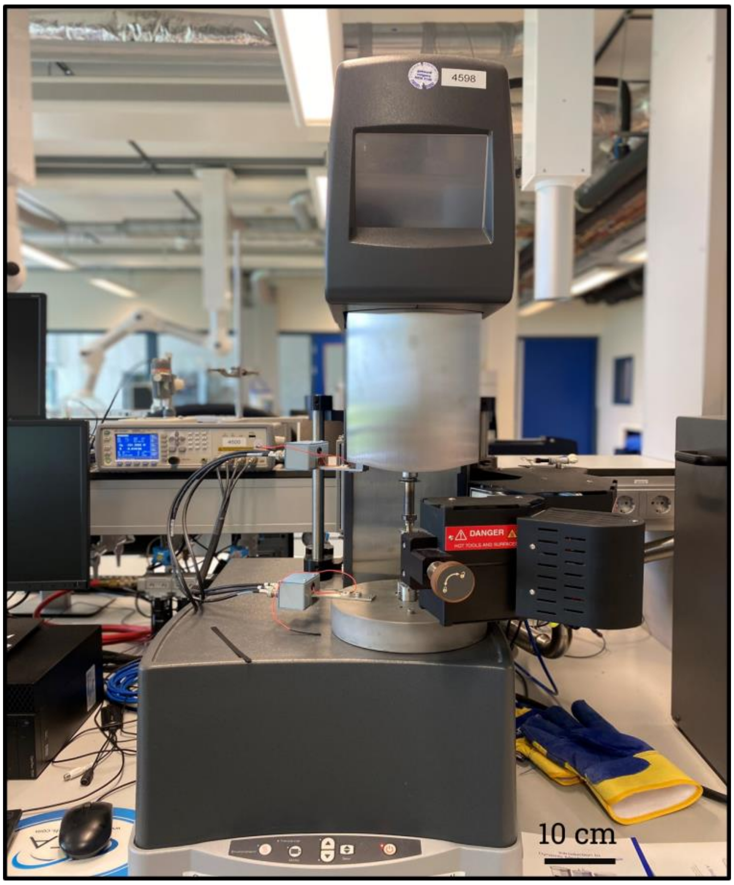


Figure 41: RSA-G2 Solids Analyzer DMA instrument

The experiment was conducted using the RSA-G2 Solids Analyzer by TA instruments as shown in the *figure 41*. A Standard Oscillatory Temperature Sweep (SOTC) was conducted at a frequency of 1Hz, starting from 0°C and increasing to 120°C at a rate of 2°C per minute. The sample was placed inside the equipment and the program for heating was started. A graph of storage modulus and tan δ vs temperature was generated to understand the property degradation.

4.4.6 Tensile testing- Recycled resin

To understand the tensile strength and modulus of the recovered resin, tensile testing was also performed. However, the resin was a bit sticky and was in a semi-solid state at ambient temperature. Thus, a very low tensile strength and modulus was already assumed.

Therefore, a 1kN load cell was used on the 10kN Zwick universal testing machine. Mechanical clamps were used similar to the one used for the testing of the composite. Dog-bone shaped specimens with a gauge length of 10 mm and a width of 6mm were used for the tests as per the standard ASTM D638. Also following the standard, a displacement-controlled rate of 5mm/min. Data was reported in the form of an excel sheet, where the increments in forces, grip to grip separation and testing time were measured during testing of each individual specimen.

Figure 42: Sample: Tensile testing of recovered resin

5. Results

The following chapter discusses the manufacturing and recycling results of the composite. The first part is based on the results related to the composite while the second part is based on the recycling results of the composite.

5.1 Composite

5.1.1 DSC

The first test performed on the manufactured composite was to understand if the epoxy in the composite was cured to a stable state before estimating its mechanical properties. As described before, DSC, with a heat-cool-heat-cool-heat cycle was performed ranging from 0°C to 150°C with a heating rate of 5°C/min.

As DSC is used to understand the glass transition and melting regions of a material, glass transition temperatures for three separate heating cycles were analyzed. Based on the variation of the glass transition of first cycle with the next two, the curing state of the composite could be determined. It was expected that all the three heating cycles would show the approximately the same glass transition temperature. This was derived from the fact that if it was inadequately cured before the test started, the glass transition temperature in the first heating cycle would have been lower than the one in the next two cycles as the epoxy would have then cured to a higher extent due to that first heating cycle resulting into higher T_g's in the next two cycles.

The sloping region representing the glass transition region in the generated DSC curves is focused upon below.

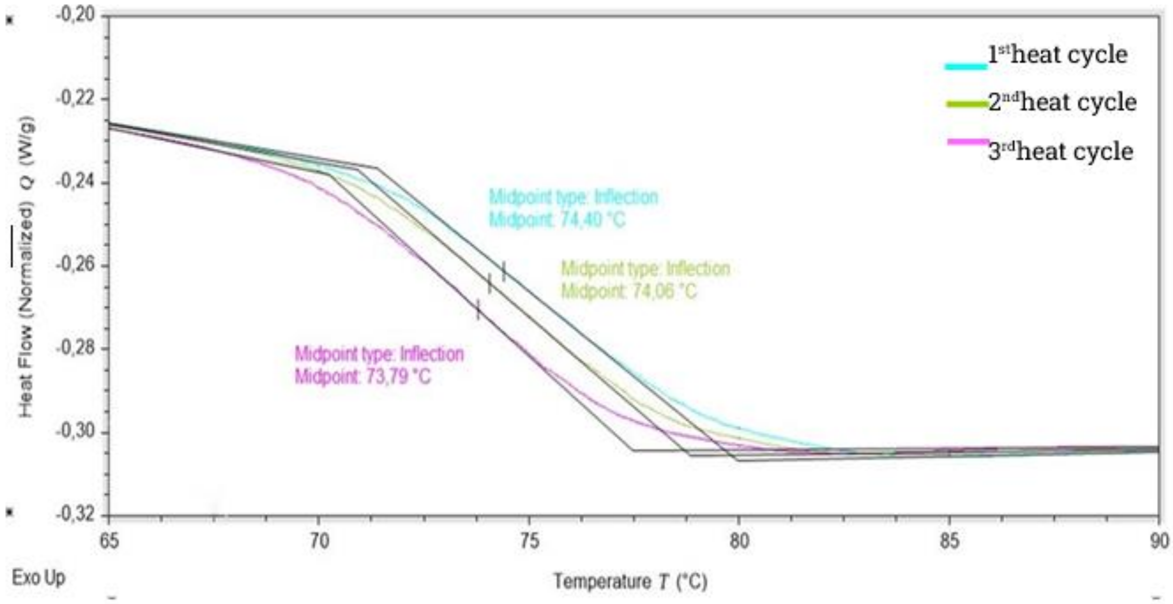


Figure 43: DSC of composite

Table 3: DSC of composite- Tg for three heating cycles

HEATING CYCLE	GLASS TRANSITION TEMPERATURE
1	74.40°C
2	74.06°C
3	73.79°C

From the above table, it can be clearly understood that the glass transition temperature of all the three cycles was almost equal, ranging around 74°C. The little variation seen was only due to the small variation in determining the mid-point of the glass transition slope.

This proved that the epoxy in the manufactured composite was cured to a stable state as no increase in the T_g s' of the second and the third heating cycle was reported with respect to the first heating cycle. Of course, it couldn't be said that 100% cross-linking was achieved as achieving the same is a very energy-intensive process extending up to multiple days. However, a stable cure degree was confirmed indicated by the constant T_g's across multiple heating cycles as described above.

5.1.2 Tensile Testing

Following the DSC of the composite, tensile testing was performed in accordance to the ASTM D3039 standard. The composite was cut into dimensions of 125mm*12.5mm and tests were performed on a Zwick Universal Tensile testing machine. The stress strain curves for the samples were obtained as shown in the figure below.

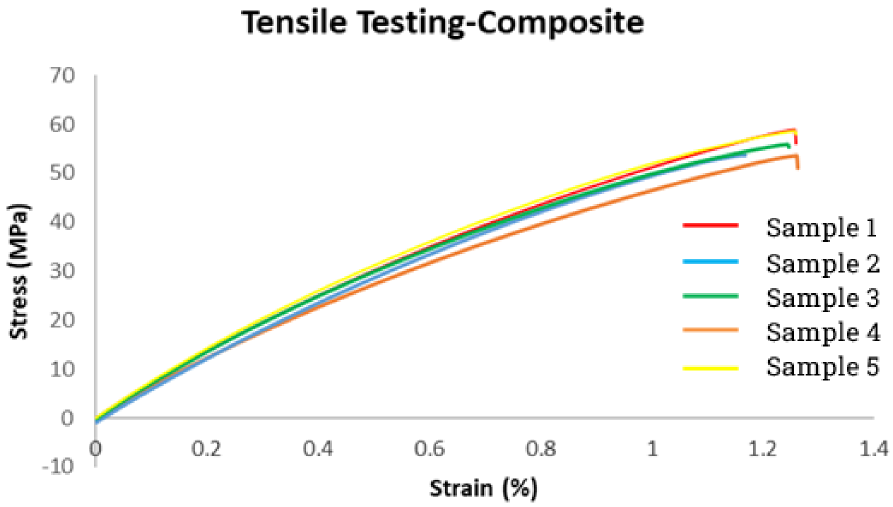


Figure 44: Stress strain curves- Tensile testing of composite samples

For the calculation of the stresses, strains used in the given graph as well as the corresponding young's modulus, the following three equations were used.

$\sigma = \frac{F}{A}$ (stress)

$\epsilon = \frac{\delta L}{L}$ (strain)

$E = \frac{\sigma}{\epsilon}$ (Young's Modulus, E)ε

Where L= gauge length, σ= stress, F= Force, A= Area of cross-section (width*thickness), ε = strain

For each of the samples, individual thickness was measured whereas the width was constant as the samples were cut using an automatic cutting machine with a specified cutting width. The gauge length was measured to be 85mm in consideration to the grip to grip separation. Thus, the strength and the modulus values for individual samples were calculated.

Table 4: Results- Tensile Testing of composite samples

Sample	Fmax (N)	dL at Fmax (mm)	Fbreak (N)	dL at break (mm)	Thickness (mm)	Width (mm)	σMax (MPa)	E (GPa)
1	793.46	1.08	760.71	1.13	1.15	12.50	55.19	4.34
2	734.69	1.01	703.27	1.04	1.09	12.50	53.92	4.53
3	757.53	1.06	750.50	1.10	1.11	12.50	54.59	4.37
4	701.10	1.08	687.08	1.13	1.11	12.50	50.52	4.07
5	808.37	1.07	784.37	1.14	1.14	12.50	55.27	4.39

Average Tensile Strength: 53.89±1.39 MPa **Average Tensile Modulus: 4.34±0.19 GPa**

Overall, it could be understood that performance of all the samples was more or less the same, indicating homogeneity in the manufacturing process at a macroscopic scale. Also, the average strength and the stiffness values were very close to what was expected due to the use of short fibers. To quantify it, the use of short fibers led to an increase of about 25% to the strength and 60% to stiffness of the composite.

Following the tensile testing, the flexural testing of the composite was performed.

5.1.3 Flexural Testing

The flexural testing of composite was performed in accordance to the ISO 14125 standard for which the test description is mentioned in the methodology section. The composite was cut into dimensions of 60mm*15mm and tests were performed on a Zwick Universal Tensile testing machine. The stress strain curves for the samples were obtained as shown in the figure below.

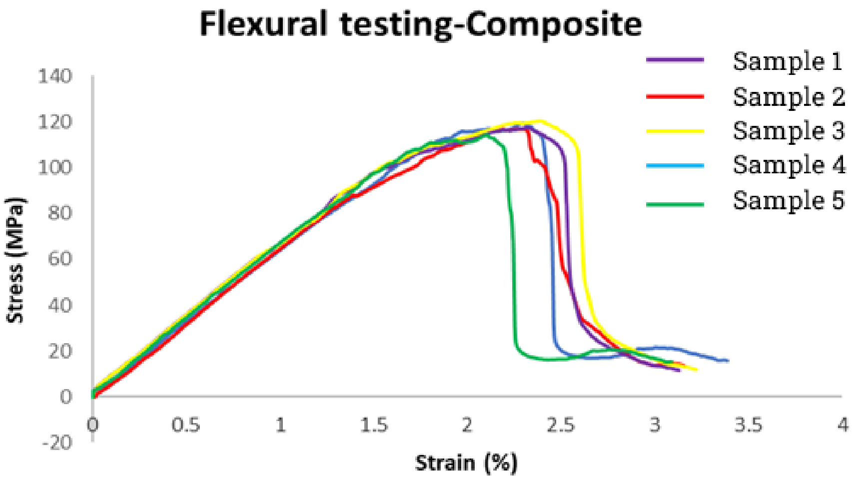


Figure 45: Stress strain curves- Flexural testing of composite samples

For the calculation of the stresses, strains used in the given graph as well as the corresponding modulus, the following equations were used.

$$\sigma = \frac{Fl}{bh^2}$$

$$E_f = \frac{l^3 m}{4bh^3}$$

where l= gauge length, σ= stress, F= Force, b=width, h= thickness, m=slope of load-deformation curve

For each of the samples, individual thickness was measured whereas the width was constant. The gauge length, i.e., the distance between the supports of the 3-p bending setup which was 40mm. Thus, the strength and the modulus values for individual samples were calculated and collected as shown in the table below.

Table 5: Results- Flexural Testing of composite samples

Sample	Fmax (N)	dL at Fmax (mm)	Fbreak (N)	dL at break (mm)	Thickness (mm)	Width (mm)	Flexural strength (MPa)	Flexural stiffness (GPa)
1	59.31	5.58	5.92	8.18	1.16	15.00	117.53	6.11
2	57.57	5.41	5.95	8.20	1.14	15.00	118.12	6.24
3	56.39	5.74	5.83	8.26	1.12	15.00	119.87	6.27
4	59.29	5.53	5.92	8.55	1.16	15.00	117.49	6.33
5	54.92	4.39	5.70	8.06	1.13	15.00	114.69	6.29

Average Flexural Strength: 117.54±2.32 MP   Average Flexural Modulus: 6.24±0.09 GPa

Thus, the average tensile and flexural strength and modulus of the composite samples were calculated.

Based on the results, it could be said that the achieved strength and the stiffness values were comparable to the traditional bamboo epoxy composites. The studies conducted on short bamboo/epoxy composites with the fiber fraction of 30% till date reported values no higher than 60 MPa and 120 MPa for tensile and flexural strengths respectively for fiber lengths varying between 2mm to 9mm. This indicated that the use of Recyclamine® did not cause any specific degradation to the strength properties of the composite. Also, it was evident that this composite was not suitable for use in structural applications of an aircraft, but more applicable towards the interior applications like tray tables, zone dividers among others. Further study needs to be conducted on the same to assess all the properties required for the material to be used in the interior of an aircraft.

5.1.4 Water Absorption Test

As discussed previously, the water absorption test of the composite was performed in order to understand the moisture absorption properties of the composite. Using the ASTM D570 standard, a 50mm*30mm composite was immersed inside a water bath for 24 hours, removed and assessed. The visual comparison for the same is showcased in the *figure 46*.

Figure 46: Composite samples- before water absorption test; after water absorption test

After taking a close look of the specimens before and after immersion, it was understood that there is almost no visual difference in the appearance of the composite as well as the distilled water solution. No specific heterogeneity at the macroscopic level was induced in the short fiber mats due to the water absorption phenomenon. A very minute difference may be seen in the two samples shown in the figure 46, only due to the ambient lighting conditions as well as camera characteristics. This led to understanding that there was no significant disbursement of any resin from the composite in the water beaker, indicating that the resin was not affected by water once cured.

Along with this, as the composite sample was taken out after 24 hours, almost no significant dimensional variation was reported in it. Though the length increased by about 0.8mm, it was almost negligible with respect to overall dimensions of the sample. In consideration to the weight change, the sample weighed 19.4 g before the test while the weight after the test was found to be 20.1 g. Thus, a weight increase of just about 3.6% was reported, which was very less, keeping in mind the absorption tendency of bamboo fibers.

This indicated that the manufactured bamboo/epoxy composite had a high resistance to water and moisture absorption. It also pointed out that the interface between the bamboo fibers and the cured epoxy was excellent as no bamboo must have been directly exposed to water and undergo absorption significantly.

5.2 Recycled Fibers

5.2.1 Recovery analysis

After the recycling of the composite, the recovered fibers were initially rinsed with distilled water, dried and transferred for measurement of weight. This was done in order to understand the extent of loss of fibers due to the recycling process. For the raw fiber mats, only the weight of the raw fibers was considered and the weight of binding material used to form the mat was not considered. The analysis of the weight recovery is seen below.

Table 6: Recycling analysis of fibers

Fibers	Weight
Raw	5.8 g
Recycled	5.6g

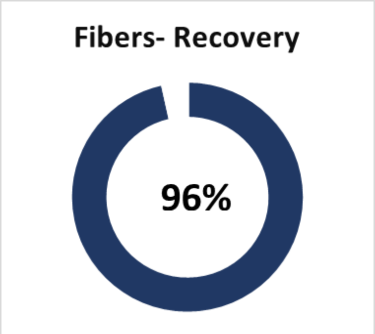


Figure 47: Fiber recovery percentage after recycling

Overall, 96.55% of the fibers were recovered after recycling. This was more than expected and indicated that the recycling process was extremely successful, especially in consideration with the use of short fibers. The loss of the remaining fibers was attributed to the recovery process performed after the dissolution as well as due to filtering process. It was expected that about 2% loss occurred during fiber recovery in each of the dissolution and filtering process. loss During both times, it was easily possible that not all of the fibers were not collected leading to the loss. Also, some composition loss may also been possible, thus also being part of the overall 4%.This was investigated later.

Following the recovery analysis, microscopy and FTIR of the fibers were performed to analyze the physical degradation and composition variation in the fibers.

5.2.2 Microscopy comparison analysis

After the recovery of the fibers, the first step performed was a microscopy analysis in comparison to the original fibers. Shown below is a comparison of the raw and the recycled fibers. In the microscopy performed, a singular fibers were studied to analyze the surface texture and the overall physical features of fibers.

Regarding the comparison of the fibers, it could be seen that the fibers before and after recycling were typically long and slender, with lengths ranging from 3.04 millimeters to 5.98 millimeters. Overall, the length distributions with percentages of distributions before and after recycling are shown in the *figure 48*.

It could be seen that the mean length was almost constant ranging around 4.23 mm before recycling to 4.19 mm after recycling without no significant change due to recycling. The width of the fibers was also constant and did not vary much before and after recycling. Before recycling the average width was around 0.14 mm while after recycling it was found out to be approximately 0.15 mm. Also, the width was generally uniform along the length in both the cases.

In the measurement of the dimensions, it should be understood that the mean thickness and length of both the fibers were calculated after measurement of a set of fibers and it was almost impossible to find and measure the exact same set of fibers after recycling. Thus, the very slight increase in the mean dimensions of the raw fibers should be neglected as it didn’t specifically mean an increase in the mean length due to recycling, but was just a function of the set of the fibers which was considered during measurement.

Overall, no distinct and substantial variation in the mean dimensions could be seen in fibers before and after recycling at the macroscopic level.

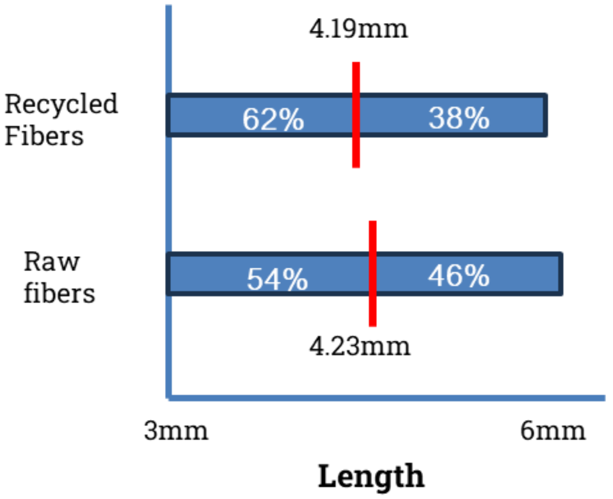


Figure 48: Fiber length distribution for individual subsets- Before recycling; After recycling

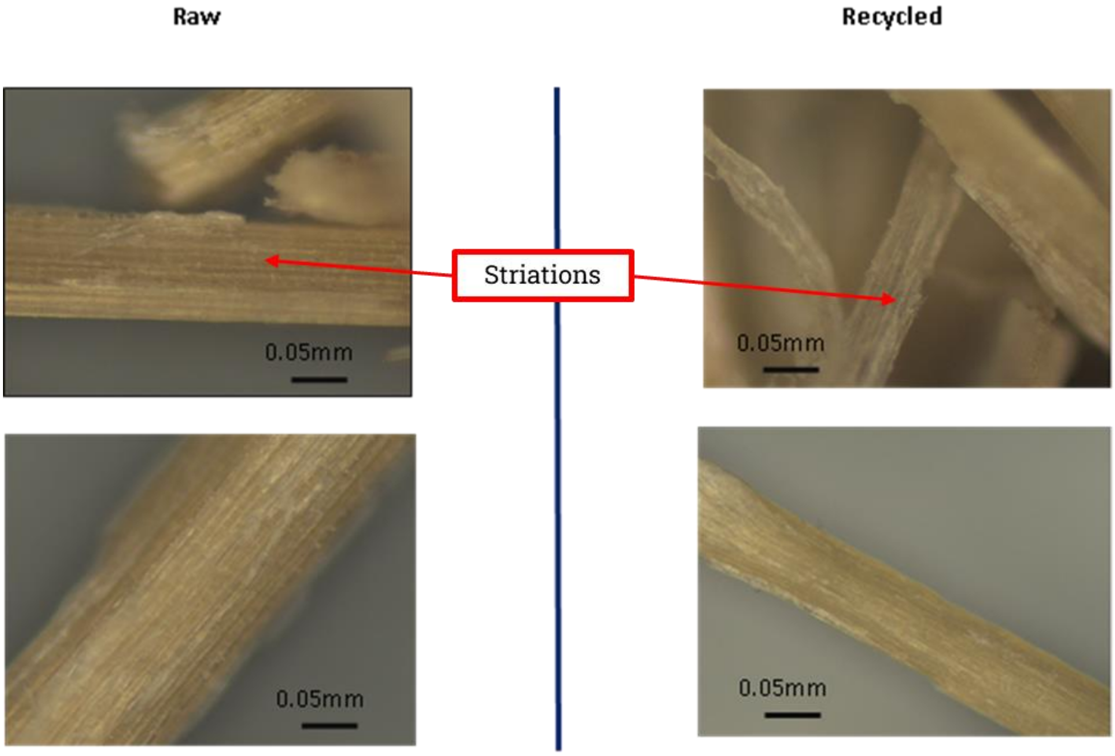


Figure 49: Microscopy comparison analysis of singular fibers before and after recycling

Even at a microscopic level, both the fibers did not exhibit any considerable variations. Regarding the surface texture, both the type of fibers showed a pattern of parallel slender striations or ridges which are a characteristic of the fibrous structure of the bamboo attributed to the cellulose strands. Overall, the surface of the fibers appeared similar before and after recycling.

Along with the surface characteristics, the appearance of the fibers also did not change significantly. Both the fibers possessed a light beige/light yellow kind of a colour with a little variation between themselves as also seen in the images.

Thus, both macroscopically and microscopically, no significant change was seen in the fibers due to the acidic recycling process. The composition analysis was performed then to analyze any possible variation.

5.2.3 FTIR comparison analysis

Along with microscopy, a composition comparison analysis between the raw and the recycled fibers was performed using Fourier Transform Infrared Spectroscopy (FTIR). The figure below shows the comparison between the two where the red and the black curve represent the FTIR spectra of raw and recycled fibers respectively. The important peaks in the fingerprint region are also indicated with their respective wavenumbers for the analysis. The table 50 provides detailed information about bond types corresponding to the individual elements for individual numbers followed by which the analysis and the important findings are highlighted.

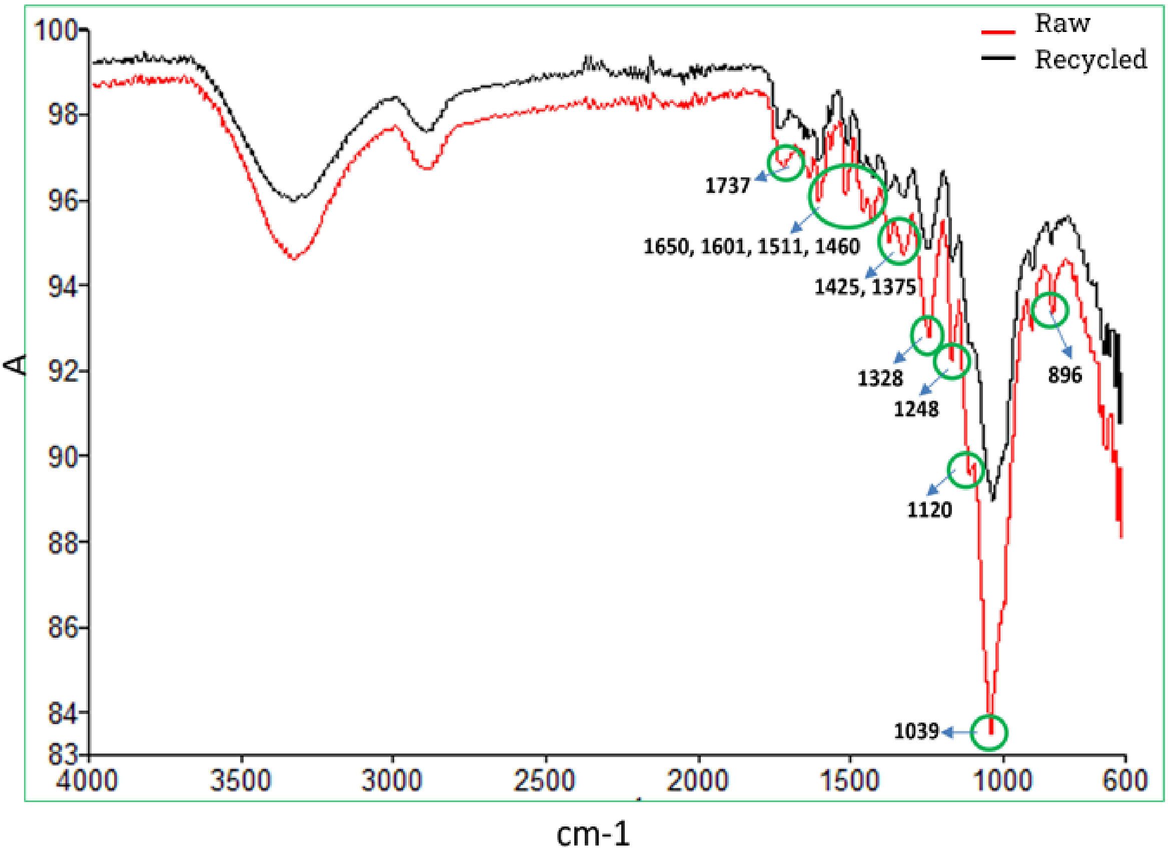


Figure 50: FTIR Comparison- Raw and Recycled Fibers

Table 7: FTIR of fibers- bond analysis

Wavenumber	***Bond type***	***Description***
1737	-COOH (C=O)	free carbonyl groups, Stretching of acetyl or carboxylic acid **(hemicelluloses)**
1650	C = O	quinines and quinine methides, adsorbed water
1601	C=C	Aromatic ring **(lignin)**
1511	C=C	Aromatic ring **(lignin),** stronger guaiacyl element than syringyl
1460	C-H	Asymmetric bending in CH3 **(lignin)**
1425	CH2	Aromatic skeletal vibrations **(lignin)** and C H deformation in plane **(cellulose)**
1375	C-H	C H deformation in cellulose and **hemicellulose**
1328	O-H	phenol group **(cellulose)**
1248	C-O	Guaiacyl ring breathing with CO-stretching **(lignin and hemicelluloses),** esters
1120	C-H	Guaiacyl and syringyl **(lignin)**
1039	C-O, C-H	Primary alcohol, guaiacyl**(lignin)**
896	C-H	C H deformation in **cellulose**

Overall, from the table it was understood that the peaks values 1601 cm^{-1} ,1511 cm^{-1},1460 cm^{-1}, 1425 cm^{-1},1120 cm^{-1}, 1039 cm^{-1} represented the bonds specific to lignin, the values 1425 cm^{-1}, 1328 cm^{-1}, 896 cm^{-1} indicated cellulose presence while 1737 cm^{-1} , 1375 cm^{-1} , 1248 cm^{-1} represented hemicellulose.- Main finding

A closer look was then taken between the fingerprint regions in the two spectra as shown below, to understand any possible difference in peak positions, absence/appearance of peaks to understand any possible change in composition.

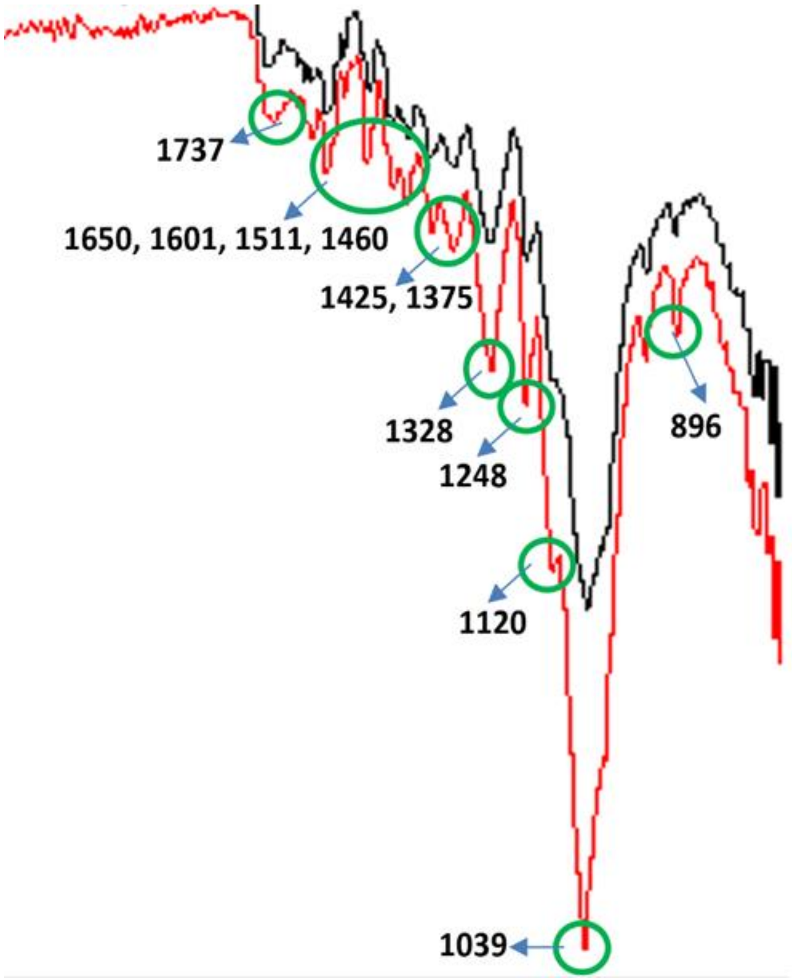


Figure 51: FTIR- comparison analysis of raw and recycled fibers-II

Upon comparison, it was understood that there was not a difference of even a singular peak between them. Both the spectra had exact similar peaks at the same exact wavenumbers. Also, there was not any new presence of peaks in the spectra of the recycled fibers. In FTIR, the magnitude of the absorbance generally depends on the extent of contact of the sensor with the sample. Hence, the minute difference in the magnitude of the two spectra did not mean anything significant. Thus, it could be confirmed that there was not any significant change in the composition of the bamboo fibers due to the specific recycling-based process which was employed. – Main finding

These results in combination with the recovery percentage and the microscopy analysis led to the understanding this recycling process was extremely well-suited for bamboo fibers and the recovered fibers could be reused for a suitable application.

5.3 Recycled Resin

5.3.1 Recovery analysis

After the recycling of the composite, the recovered resin was initially rinsed with distilled water, dried, and transferred for measurement of weight. This was done in order to understand the extent of conversion and recovery of the recycled resin with respect to the original epoxy resin. The table given below gives a comparison between the weight of the pure epoxy resin vs recycled epoxy resin recovered from the composite.

Table 8: Recycling analysis of resin

Resin	Weight
Epoxy	12.2 g
Recycled Epoxy	9.8 g

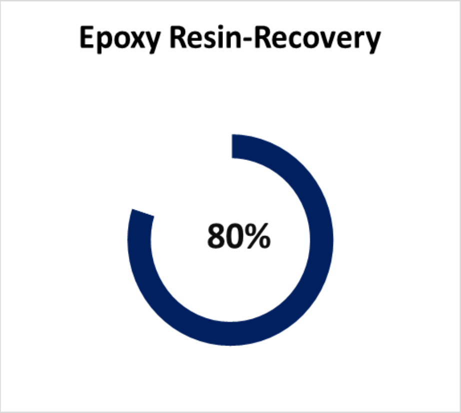


Figure 52: Resin recovery percentage after recycling

Overall, the recovery of the resin was 80.33% after the recycling process. The extent of the loss was estimated and attributed to following three reasons:

1) Acidic process (10%): Loss of epoxy during the cleavage as some specific bonds present in the original cured epoxy are lost during the formation of the recycled resin due to the chemical reaction. Since a part of the original resin itself was lost here, the majority loss was estimated to be attributed to this process. This part was remained dissolved in the acidic solution and was later expected to turn into acetone, leaving a salt water solution behind after neutralization.
2) Neutralization process (4%): Loss of recycled epoxy during neutralization process as all of the dissolved epoxy may not coagulate after the addition of NaOH.

3) Recovery process (6%): Loss of recycled epoxy during collection as very minute quantities were present on the beaker and spatula used for recovering the recycled epoxy resin.

Thus, after the weight analysis of the recycled resin, DSC was performed to understand the characteristics of the resin.

5.3.2 DSC

For characterization of the recycled resin, DSC was performed at first. As described previously, DSC analysis analyzes the glass transition and the melting temperatures of the composite.

For the analysis of the resin, a heat-cool cycle ranging from 0°C–130°C with a heating rate of 5°C/min was used for which the resulting graph can be seen below. The first downward trend at around 40°C represented the glass transition temperature due to the transition to a rubbery state. This was expected as the resin was already in a semi-solid state at room temperature. The exact T_g was calculated as a midpoint between the onset and the end of the downward transition which equalled to 42.06°C.

The melting temperature was represented by a comparatively narrow endothermic peak at around 120°C. The exact vale was calculated as the end point of the peak which equalled to 119.46°C. The heating cycles were repeated for two more times and similar transition regions were seen at around 40°C and 120°C, confirming the values reported in the first heating cycle.

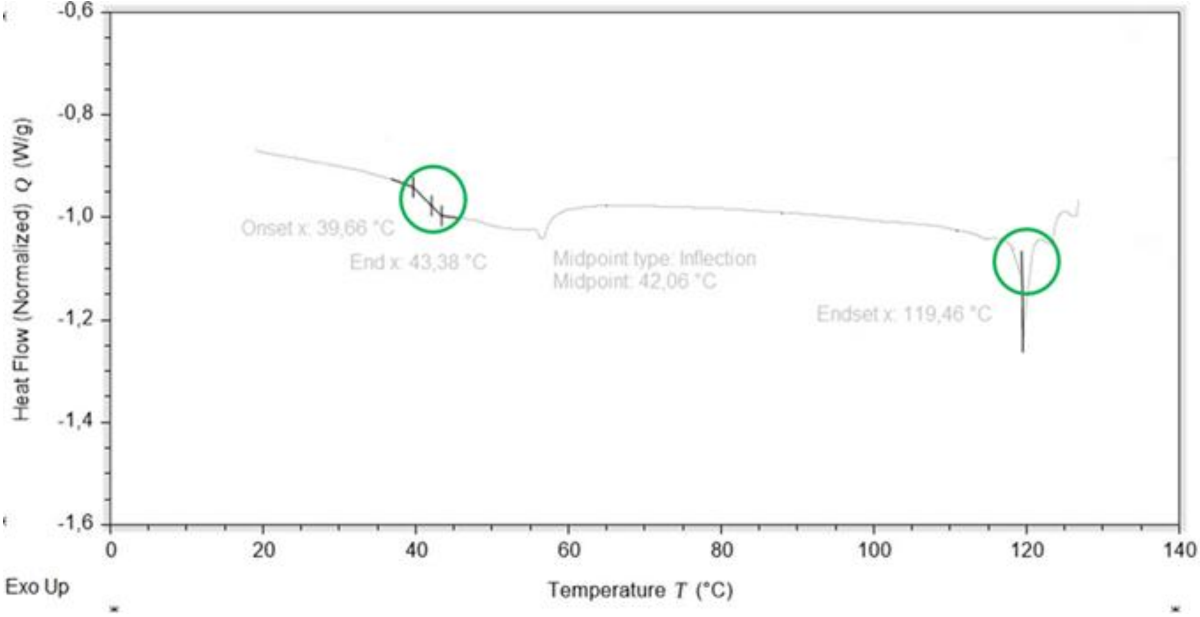


Figure 53: DSC analysis of recycled resin

The DSC resulted in understanding of the two most important characteristics of the resin. The first was the glass transition and the melting temperatures of the recycled epoxy. This would help to understand a suitable application for the resin as a function of the operating temperature range. The second was that the resin was identified as a semi-crystalline thermoplastic resin. This was owing to the presence of a fixed melting point of a resin, which is characteristic of the crystalline behavior only seen in thermoplastics. Thermosets are generally known to be amorphous and hence this characteristic led to the understanding of the resin to be thermoplastic in nature.

5.3.3 FTIR comparison analysis

For the recyclable resin system, it was necessary to understand whether the required cleavage reaction had taken place. This would be identified by the bond breakage happening in the epoxy due to the introduction of an acid. Thus, along with the FTIR spectra of resin recovered from the composite, FTIR analysis of a pure epoxy was also performed for comparison purpose. *Figure 54* represents the FTIR spectra of the recycled resin from the composite where the peaks in the spectra have been analyzed in the *table 9* whereas the FTIR spectra of pure epoxy are showcased in the *figure 55.*

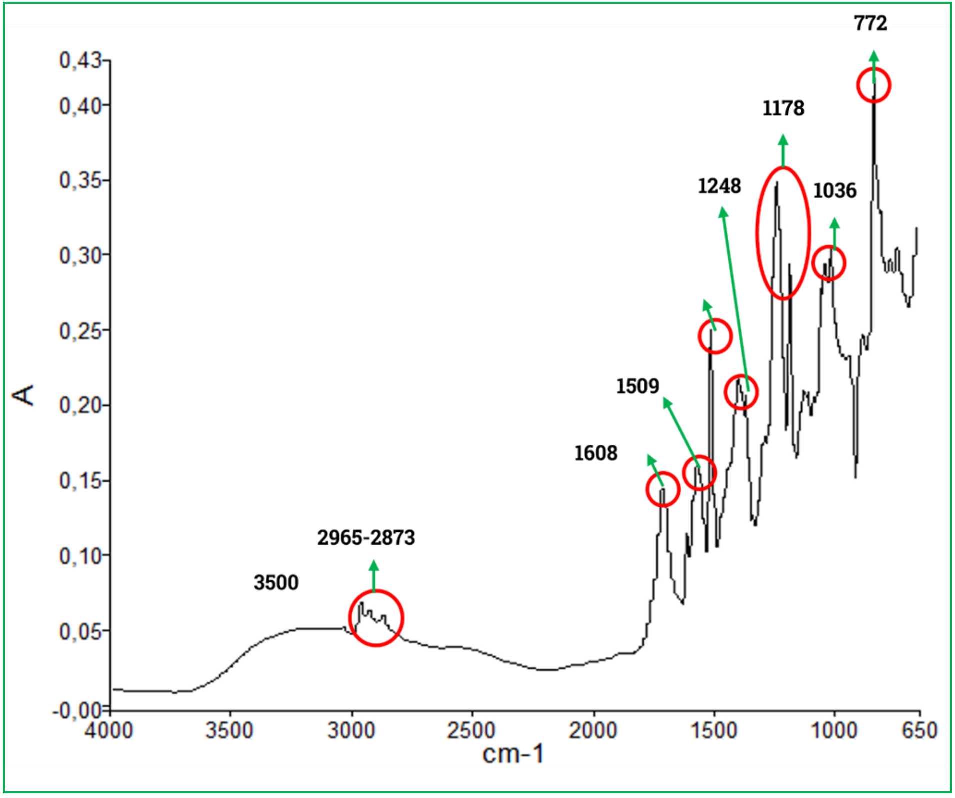


Figure 54: FTIR spectra of recycled resin

Table 9: FTIR of recycled resin- bond analysis

Wavenumber	***Bond Type***
3500	O-H stretching
2965-2873	Stretching of C-H of CH2 and CH aromatic and aliphatic
1608	Stretching C=C of aromatic rings
1509	Stretching of C-C of aromatic rings
1248	C-N stretching
1178	C-O stretching of ester links
1036	Stretching C-O-C of ether links
772	Rocking CH2

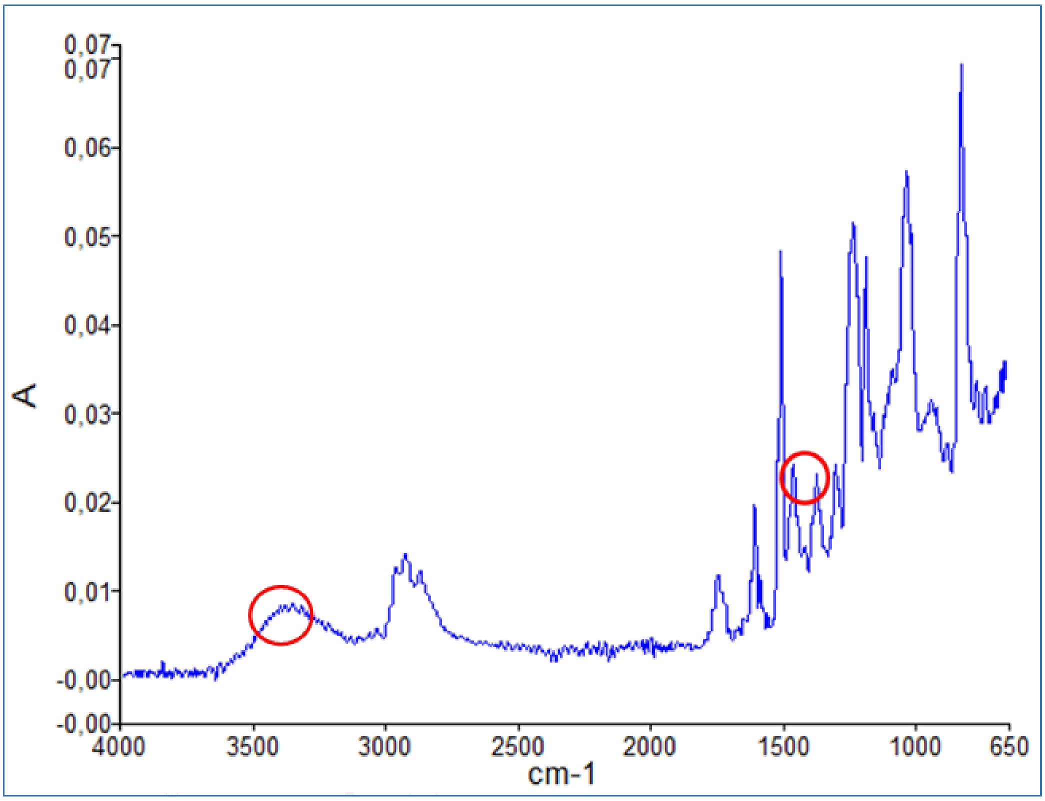


Figure 55:FTIR spectra of pure epoxy

Overall, looking at both the FTIR spectra it was understood that the peak differences were not very substantial as expected. However, in the FTIR spectra of pure epoxy, there was a clear presence of three additional peaks at two distinct wavenumbers in the shown by red circled region in the above peak. When compared to a reference FTIR spectra, the three peaks indicated the presence of following bonds as shown in the *table 10.*

Table 10: FTIR of pure epoxy- bond analysis

Wavenumber	*Bond type*
1262	C-O stretching of ether links
1296	C-O stretching
3500	O-H stretching

The presence of these three peaks was definitely what was expected. To understand this, the hardener chemical backbone is shown followed by the representation of the backbone after cleavage as shown in the *figure 56.*

When the epoxy was introduced to the acid water solution, there was a breakage of acetal bond, resulting into loss of multiple C-O bonds. These were the exact additional peaks in the pure epoxy seen at the peak values 1262 cm^{-1} and 1296 cm^{-1}, which were not present in the recycled resin. The only common peak seen in the recycled resin and the pure epoxy at around 1200 cm^{-1} was the C-N stretching peak which was seen at an exact peak value of 1248 cm^{-1}. This was due to the fact that C-N bond does not undergo any breakage during the reaction. This was a satisfactory explanation for the absence of the two C-O peaks in the recycled resin compared to the pure epoxy.

Along with this, additional hydroxy groups were formed at the end of the recycled resin chain due to the bond cleavage. Thus, the number of OH groups drastically increased in the recycled resin compared to the pure epoxy. This explained the last difference, a wider peak at 3500 cm^{-1} in the recycled resin, compared to the pure epoxy.

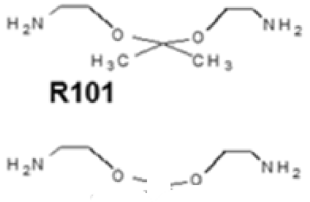


Figure 56: Bond cleavage reaction in recyclable resin system

Thus, FTIR of the recycled resin and the pure epoxy provided a sufficient explanation of the chemical reaction taking place in the used novel recycling process.

In addition to understanding the chemical reaction taking place in the background, it was also essential to see whether the resin recycled from the composite did not contain any components of the bamboo fibers dissolved in it. For this was necessary to acquire a pure recycled resin and compare it to the resin recycled from the composite.

Thus, initially a small sample of pure epoxy without the fibers was fully cured. This was then recycled using the similar process employed for the recycling of the composite. Upon recycling a pure white sample of recycled resin was acquired which was transferred for drying. Once the sample was ready, it was transferred for the required comparison analysis using FTIR.

The *figure 57* represents the comparison of FTIR spectra of a pure recycled resin to the resin recycled from the composite. Upon detailed comparison of the spectra, it was reported that both the spectra had the similar absorption peaks at the exact same wavenumbers. There was not a presence or an absence of even a single peak in the FTIR spectra of the resin recycled from the composite compared to the pure recycled resin. However, the recycled resin from composite was brown in colour compared to the normal thermoplastic resin which was white in colour as described above. This directed to the fact that some lignin and hemicellulose dissolution may have occured in the resin recycled from the composite, bit it was not as significant compared to the overall composition, leading the overall same FTIR spectra for both the resins.

Thus, after these tests it could be affirmed that the recycling process proved to be extremely conducive for achieving a reusable resin and fibers from a bamboo fiber reinforced composite without significantly affecting any of the individual recycled components.

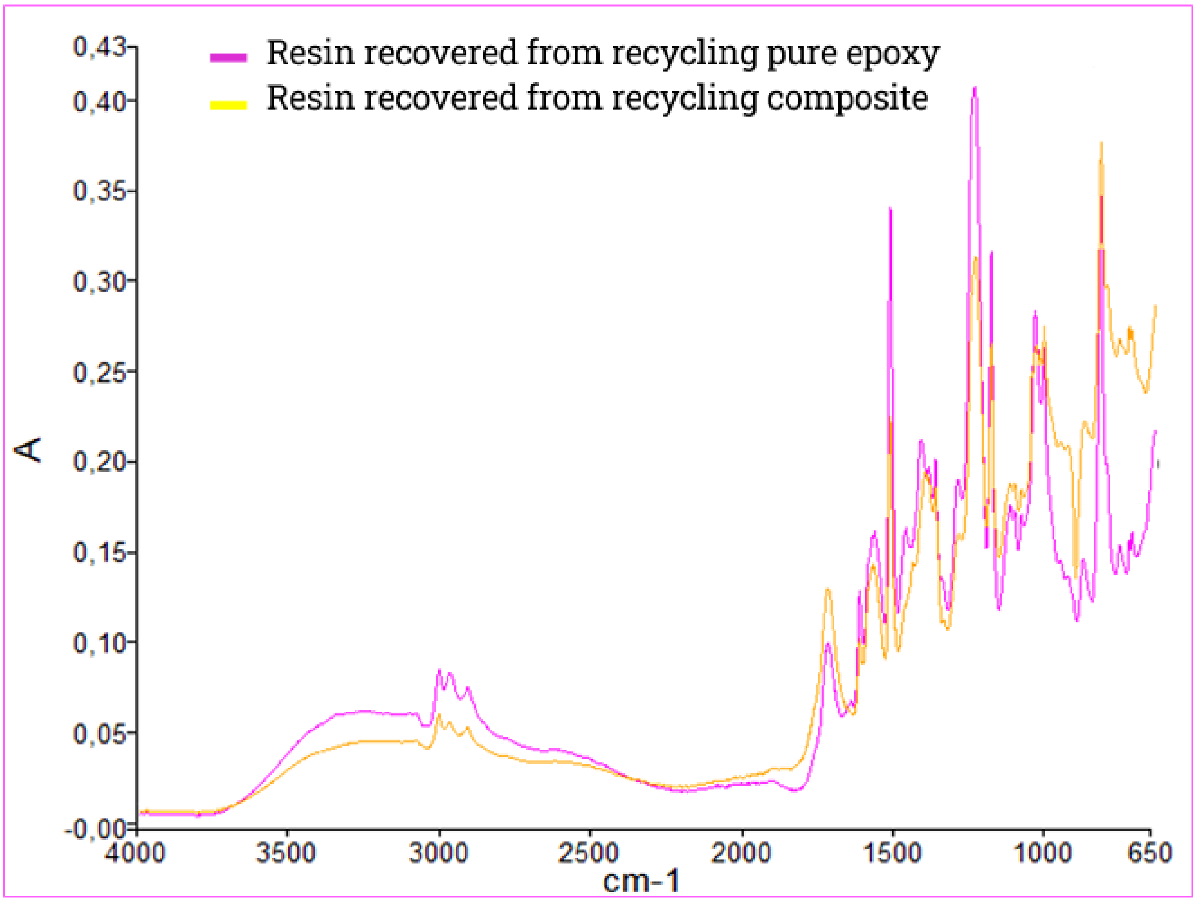


Figure 57: FTIR comparison analysis of composite recycled resin and pure recycled resin

5.3.4 DMA

Dynamic Mechanical Analysis (DMA) of the recycled epoxy was also performed in order to understand the storage modulus which in turn helped to understand the suitable application for the same.

The temperature-dependent behavior of the material was measured using a tan δ versus temperature curve, with a frequency of 2 Hz. The test was conducted from 0°C to 120°C. The obtained results, shown in the *figure 58*, clearly indicated the presence of a single transition region. This region represented the softening of the recycled epoxy thermoplastic. The glass transition temperature (T_g) was also seen as a peak for the tan δ occurring around 40°C. This was almost similar to the what was reported during DSC of recycled epoxy- thermoplastic resin where a T_g of around 42°C was seen.

Along with validation of $T_{g,}$ the storage modulus values were also analyzed with DMA. The storage modulus ranged between 10 and 20 MPa for temperatures lower than 30°C. However, for temperatures higher than 30°C, the modulus was drastically lower. This was attributed to the resin crossing it's glass transition temperature and transitioning into a rubbery state, resulting in very low properties. Thus, overall, it was understood that the recycled resin was suitable for use only around the ambient temperature conditions.

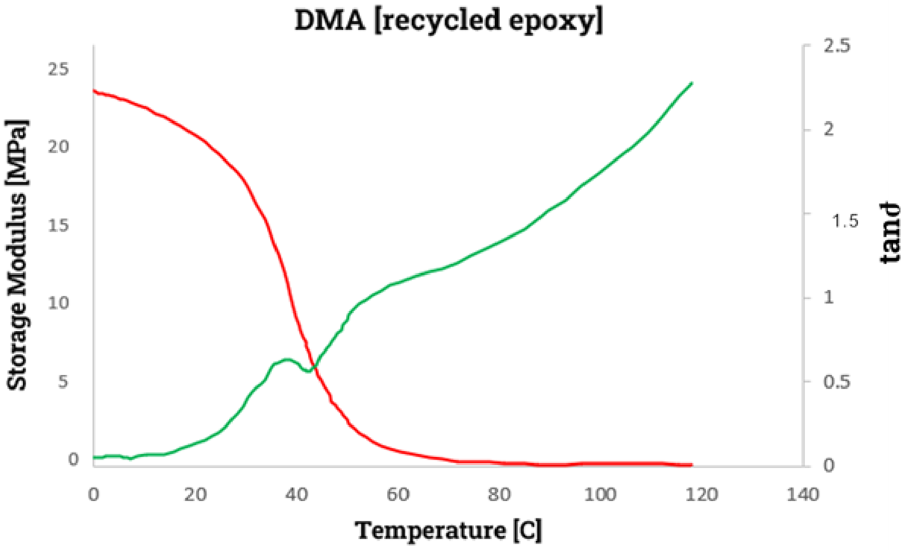


Figure 58: DMA analysis of recycled epoxy

These values were taken into consideration and tensile testing of the resin was performed after which the suitable prospective application for the recycled epoxy- thermoplastic which can be found below.

5.3.5 Tensile Testing

Along with DMA of the recovered resin, tensile testing was performed in accordance to the ASTM D638 standard. The composite was cut into gauge dimensions of 10mm*6mm of dog-bone shaped specimens and tests were performed on a Zwick Universal Tensile testing machine. The stress strain curves for the samples were obtained as shown in the figure below.

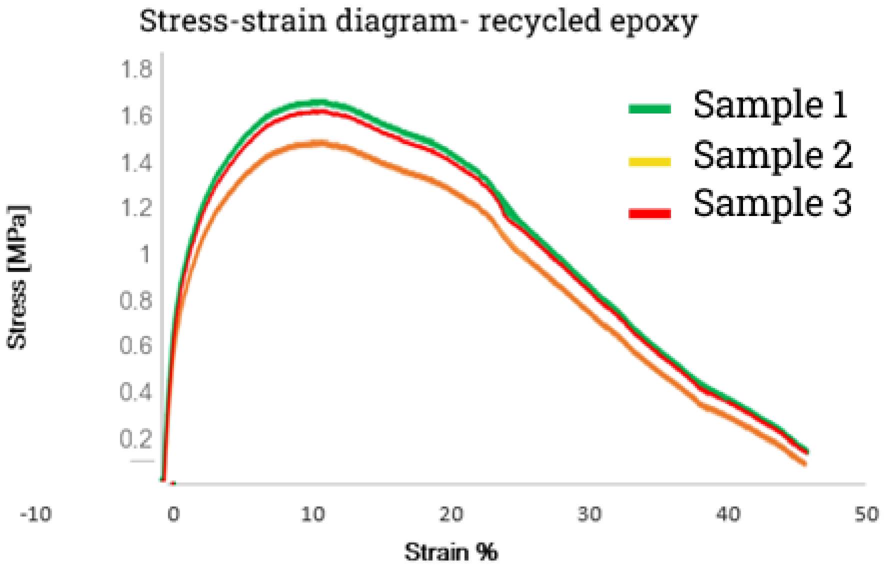


Figure 59:Stress Strain curves- Tensile testing of recycled resin samples(from composite)

Sample	Fmax (N)	dL at Fmax (mm)	Fbreak (N)	dL at break (mm)	Thickness (mm)	Width (mm)	σMax (MPa)	E (MPa)
1	8.16	1.56	1.08	4.62	0.82	6.00	1.66	10.64
2	6.92	1.82	0.83	4.68	0.79	6.00	1.46	8.02
3	7.77	1.69	1.05	4.61	0.80	6.00	1.62	9.58

Table 11: Results- Tensile testing of recycled resin samples

Average Tensile Strength: 1.58±0.24MPa Average Tensile Modulus: 9.41±1.23MPa

Overall, it could be understood that performance of all the samples was more or less the same, indicating uniformity in the samples. Also, the average strength and the stiffness values were very close to what was expected. The recycled resin samples were sticky-semisolid in nature and hence high strength and stiffness were not possible to achieve.

This, in combination with the storage modulus achieved from DMA, a suitable application for the resin was analyzed. Considering the low strength and stiffness values of the resin, the best possible way to reuse the resin was in low load bearing applications like decorative parts, housings etc. It could also be potentially used as an adhesive and also could be analyzed for other factors before using it for 3-D printing for manufacturing of small prototypes. Overall, the recycled resin was not suitable for use in structural elements but definitely reusable in other applications as described above.

6. Conclusion

Recyclamine® technology is one of the promising developments in the field of recycling of thermosets, making it possible to achieve a reusable thermoplastic upon recycling. However, there has been no study regarding natural fibers, especially bamboo fibers to have been manufactured and recycled using the Recyclamine® technology.

Keeping sustainability in consideration, the plan was to manufacture short bamboo fiber reinforced epoxy composites employing a Recyclamine®-based curing agent and recycle it to evaluate the recovered components.

Based on literature and availability, compression moulding technique was selected for the manufacturing of composites. Hand-layup technique was used for application of resin onto the fibers, and a heated press was used for the application of required temperature and pressure conditions. The curing cycle recommended by the manufacturer was employed while applying some pressure as well to generate void-free composites. The composites showcased an average tensile strength and modulus of 53.89 MPa and 4.34 GPa respectively while an average flexural strength and modulus of 117.54 MPa and 6.24 GPa respectively.

Upon manufacturing and testing of the composites, recycling was performed by immersing them into a 50% glacial acetic acid solution. The dissolved resin was recovered using neutralization while the fibers were recovered by filtering. Microscopy and FTIR of the raw and the recycled fibers was performed, followed a comparison analysis to understand possible physical degradation as well as composition change in the fibers due to recycling.

Microscopy revealed that there was no change in the structure as well as the average dimensions of the fibers. FTIR also indicated that no significant composition change occurred in the fibers due to the acidic conditions during the recycling process. Overall, it was understood from the tests that the recycling process was successful in achieving non-degraded bamboo fibers suitable for reuse.

The recovered resin was characterized initially using FTIR to verify the understanding of the working chemistry behind Recyclamine®. Thus, FTIR spectra of epoxy and recycled epoxy were compared and analyzed. There were distinct variations in the bonds identical to the expected changes which led to fully understanding of the chemistry of the process.

The recycled resin was also characterized to determine the possibility of reuse and prospective application as well. Thus, at first DSC was performed to understand the glass transition and the melting temperatures, which were found to be around 42°C and 120°C respectively. It was also understood the recycled epoxy was a semi-crystalline thermoplastic as it also possessed a melting temperature, characteristic to crystalline behavior of a thermoplastic. DMA was performed which indicated a storage modulus of 20MPa around ambient temperature conditions while tensile testing indicated a tensile strength of 1.58 MPa and modulus of 9.41MPa respectively. With these properties, it was predicted that low load bearing applications like decorative parts, housings as well as use as an adhesive could prove to be suitable prospective applications for the recycled epoxy-thermoplastic.

This study demonstrated that bamboo fiber reinforced epoxy composites can be successfully manufactured and recycled whilst achieving successful recovery of fibers and the resin using the Recyclamine® technology.

The results of this research indicated that bamboo fibers were a suitable and compatible choice in regards to application with the Recyclamine® technology. Neither the fibers nor the recyclable resin did have any adverse effect on each other due to the whole recycling process employed. At the same time, the recycled resin was also mechanically characterized and even though it did not have significant mechanical properties, it was suitable for low-load bearing applications as proposed. Lastly, the overall performance of the manufactured composite was also evaluated and it was understood that the performance was comparable to the traditional non-recyclable bamboo/epoxy composites.

Overall, this research aims to set the ball rolling in developing fully recyclable and sustainable bio-inspired composites for use in the aviation industry. The results of this research will contribute to advancing the use of bamboo fiber reinforced composites, showcasing its circularity, and minimized environmental impact. At the same time, it will also contribute in developing recyclable thermosets in the future with higher performance, making it suitable for reuse of the recycled resin in even in high load applications for e.g., structural applications.

Thus, these findings hold great importance in advancing the field of high-performance materials employing materials from sustainable sources.

7. Scope for Future work

The following chapter discusses some of the future ideas that can be implemented to advance the research conducted in this thesis.

7.1 Fillers & Delignification

The addition of filler material to the current composite could be interesting to investigate the effect of the acidic recycling process on the filler material while at the same time achieving higher strength and modulus. Fillers can enhance mechanical properties, such as tensile and flexural strength, by improving fiber-matrix adhesion and reinforcing the composite. Additionally, fillers can provide functional properties like flame retardancy, thermal conductivity, and electrical conductivity and it could be interesting to use fillers in future.

In the context of delignification, it could be done using an alkaline solution like NaOH, which will improve the fiber's compatibility with polymer matrices, enabling better interfacial adhesion and enhancing the overall performance of bamboo fiber reinforced composites. Moreover, delignification can influence the mechanical properties of bamboo fibers. Thus, by removing lignin, the fibers could become more flexible and could exhibit improved tensile strength, elongation, and toughness. This would make them suitable for applications that require high strength and flexibility, such as in the manufacturing of structural composites or reinforcement in polymer-based materials. Additionally, the removal of lignin creates a more reactive surface that can be easily modified with various chemical treatments or coatings. Thus, specific functionalities like flame retardancy, antimicrobial properties, or UV resistance could also be induced in the fibers.

Overall, fillers and delignification of bamboo fibers could play a vital role in expanding the potential applications of this renewable and sustainable material, enabling its utilization in a wide range of industries, including automotive, construction, textiles, packaging, and more.

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