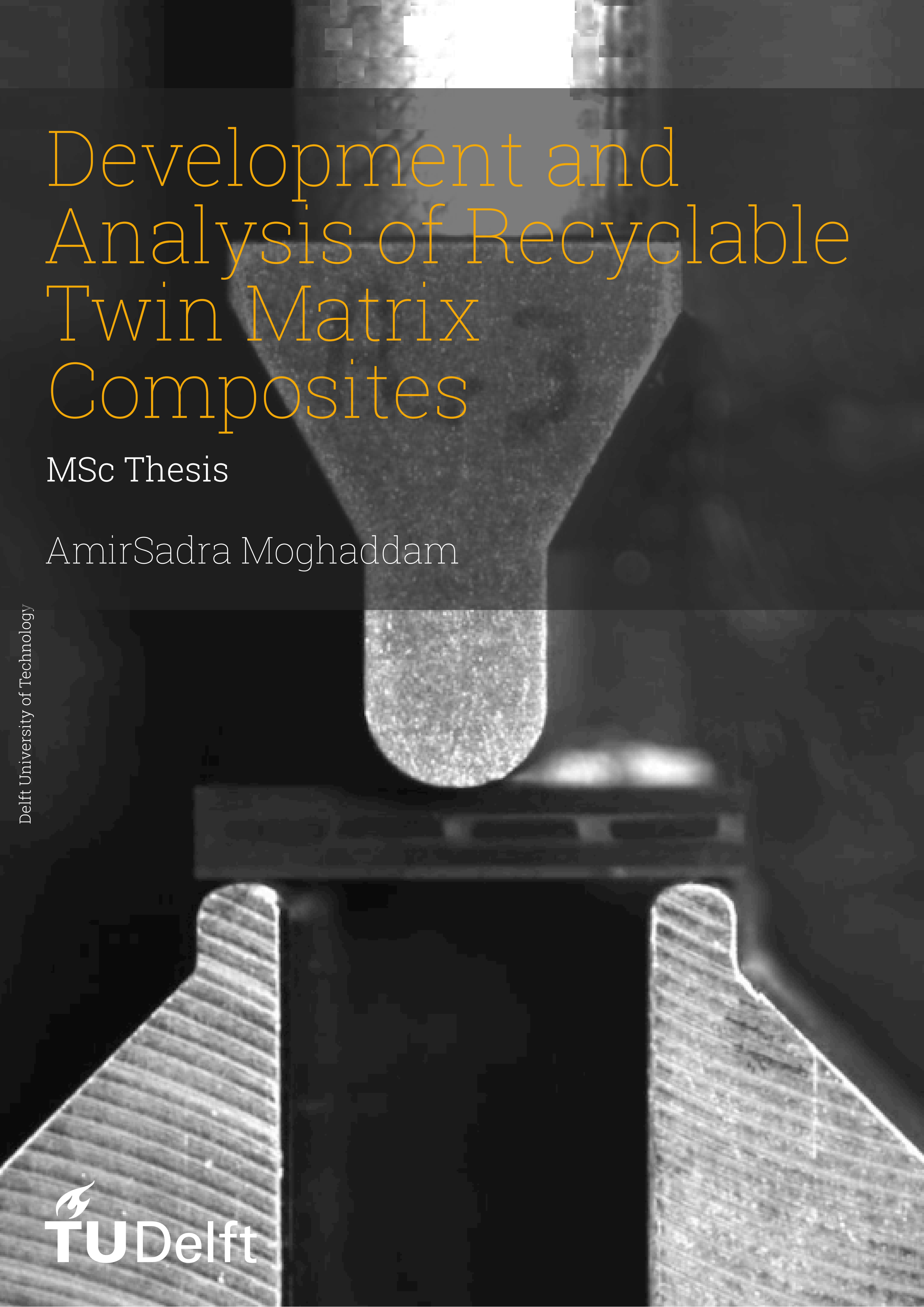

Development and Analysis of Recyclable Twin Matrix Composites

MSc Thesis

AmirSadra Moghaddam

Delft University of Technology

Development and Analysis of Recyclable Twin Matrix Composites

MSc Thesis

by

AmirSadra Moghaddam

Student Name	Student Number
AmirSadra Moghaddam	4536932

Project Duration:	September 14, 2023 - June 14, 2024	
Thesis Committee:	Dr. Otto Bergsma	Main Supervisor
	Dr. Baris Kumru	Daily Supervisor
	Prof. Clemens Dransfeld	Chair Person
	Nathan Eskue	External Member
Faculty:	Faculty of Aerospace Engineering, Delft	

Cover: Interlaminar Shear Stress Testing of a Twin Matrix Composite

An electronic version of this thesis is available at `https://repository.tudelft.nl/`

TU Delft

Acknowledgements

Many people have helped me during this thesis study and I would like to thank them for their support and assistance to me during the past several months.

First of all, I would like to thank my supervisors Dr. Otto Bergsma and Dr. Baris Kumru for their guidance and support. I am very grateful that they believed in my vision and were so enthusiastic about the outcome of my thesis project. Having two supervisors who are passionate about my thesis has been definitely a great boost for my motivation and passion to carry out this study. They were both always available for me and did their best to assist me during any stage of my thesis project.

Secondly I would like to thank Prof. Clemens Dransfeld and Nathan Eskue for reviewing my thesis report and agreeing to be on my committee.

I also thank the DASML staff of the Aerospace Engineering faculty. I would like to thank Victor and Johan who have helped me greatly regarding the manufacturing of composite samples. I also like to thank Dave for his assistance regarding the mechanical testing of my samples. I also would like to thank Pietro for his help during 3D printing stage, Caitlin for her help with the chemical procedures in the chemical lab and Roy for his support in the physical lab.

Furthermore, I would like to express my gratitude to the staff of Van Dijk Pultrusions company who have provided me the reinforcements of my composites. Additionally, I would like to thank the staff of R*Concept company who have provided me with matrix components for my thesis. The staff of both companies have also assisted me as much as possible and answered all of my questions regarding the products.

I am also grateful for my friends and fellow master students who have been by my side throughout these times. I would like to thank Kevin, Sasan, Xiaopeng, Fransisco, Morteza, Ioannis and anyone else who has helped me.

I am very grateful to my parents who made all this possible for me and have wished the best for me. Without their support, I would not have been here. I also thank my brother who has always motivated me to keep trying and moving forward. Lastly, I would like to thank my loving girlfriend Dieke who has supported me every day and kept her faith in me.

Executive Summary

The need for applying circular economy into today's industries grows every day. One of the most common ways to achieve this is to use recyclable materials. On the other hand, composites have proved to be worthy components for any application that requires high mechanical properties and low weights. In this thesis study, a composite has been created and analyzed that its reinforcements can be recycled and reused. How this works is that during the recycling procedure, these reinforcements will be separated from the matrix and then reused with a new set of matrix to create a new composite.

The proposed composites in this thesis study have a Twin Matrix Composites (TMC) composition. This means that they are made of fibers and two distinct types of matrices. The most important general reason for studying or using TMCs is that these composites offer more functionalities than conventional composites. These added functionalities are the reason for using the second additional matrix. The added functionality for all previous TMCs so far was to have a higher ultimate transverse tensile strain than conventional single matrix composites. However, this thesis study is after another added functionality and that is recycling.

The TMC of this study is made of composite rods engulfed by the other outer matrix (hereafter this outer matrix will be referred to as the secondary matrix). These composite rods are pultruded carbon fibers with a Bisphenol A Epoxy matrix. The secondary matrix is made from a bio-based epoxy and an amine-based hardener known as recyclamine. The manufacturing method to create these TMCs is hand lay up. Once the TMC has been made from this components, it can be recycled by dropping it in an acetic acid solution. The result is full decomposition of the secondary matrix and the recovery of the composite rods. Once extracted, these rods can be used again to create a new TMC with a new dosage of secondary matrix.

What is yet unknown and hence the purpose of this thesis study is to understand to what extent the performance and properties of TMCs will be affected by recycling and how does extreme numbers of recycling will affect these features? Two different approaches will be taken to understand recycling's influence on the composite. One will be to use Scanning Electron Microscopy and Water Contact Angle analysis to understand how recycling affects the surface features of the composite rods and the other will be to perform Interlaminar Shear Strength (ILSS) testing to understand how recycling affects the interface strength between the rods and the secondary matrix.

The results have indicated that recycling leads to the creation of very small surface dents and individual surface fiber discontinuation on the surface of the composite rods. Doing more recycling procedures has been shown to only increase the probability of seeing these features and not have an influence on their severity. Regarding the effect of recycling of TMC's interlaminar performance, it has been observed that TMCs that have been recycled have slightly less interlaminar shear strength (only 0.8 % less) than the TMCs that have been never recycled. Another interesting result is that recycling a TMC multiple times also seems to have very little effect on its ILSS performance and its performance is very similar to the TMCs that have been recycled once or never.

Thus what the results of this study have indicated is that recycling has insignificant effects on the performance of TMCs and a TMC that has been recycled multiple times will display very similar performance to a fresh one. This counts as a great advantage for a composite considering the need for circular economies and sets a solid motivation to continue more research on this matter.

Contents

Nomenclature

Abbreviations

Abbreviation	Definition
ILSS	Interlaminar Shear Strength
SEM	Scanning Electron Microscopy
TMC	Twin Matrix Composites

Symbols

Symbol	Definition	Unit
E	Young modulus	[GPa]
E_b	Effective bending stiffness	[GPa]
F_{max}	Maximum shear force	[N]
I	Moment of inertia	[mm^4]
l	Sample length	[mm]
l_{span}	Span length	[mm]
t	Sample thickness	[mm]
T_g	Glass transition temperature	[^{o}C]
V_r	Rod volume	[-]
w	Sample width	[mm]
δ_{Max}	Displacement at ultimate load	[mm]
τ_{max}	Ultimate interlaminar shear stress	[MPa]
$\tau_{max_{Vr}}$	Ultimate interlaminar shear stress per rod	[MPa]

1 Introduction

Over the past few decades composites have shown to be worthy materials to be applied in structural components thanks to their high mechanical properties and at the same time, lower densities. Their role in industries has been seen to expand and yet, there lies plenty of opportunities for these materials. There are still many unknown features of composites and the benefits they can bring are worth investigating. On the other hand, given the increasing importance of circular economy approaches, lower material consumption and waste-management, recycling can be an important feature that composites could incorporate and make them even more appealing to today's industry. For instance, the European Composite Industry Association[1] (EuCIA) has proposed a concept known as the "European Composites Recycling Concept (ECRC)" [30]. According to this concept, a green label will be given to composites that are recycled according to the ECRC standards.

When the recycling of composites is discussed, thermoplastic-resin composites mainly come to mind. That is because thermoplastic polymers are known to be reshapable and offer the possibility to be reused [25]. Thermosets polymers, the other polymer family that is is widely used in composites, lack this feature and hand over the recyclability advantage to thermoplastic polymers. This thesis study investigate the possibility of recycling composites with thermoset resins and to what extent it affects its properties.

This however would not be the first time the recyclability of composites with thermoset resin is investigated. In fact several research studies have been devoted to manufacturing composites with thermoset resin that are also recyclable. The majority of these studies have obtained their recyclable thermoset resin via recyclamine technology, a method that basically means creating the thermoset matrix from the mixture of bio-based epoxies and recyclamine hardeners. What makes this thesis study unique is that the reinforcement of this study is a composite on its own whereas the reinforcement of other studies are fibers. In other words, the composite of this study has two types of matrices; one will be the recyclable matrix that will engulf the reinforcing composites and the other one would be the matrix within the reinforcing composite. Because of this unique architecture, this composite is classified as **Twin Matrix Composite** (TMC).

The topic of twin matrix composites has been investigated only a couple of times. What those studies have in common with this thesis study is they all acknowledge that TMCs are created to increase the functionality of the composite. In the case of this thesis, the added functionality is that the composite can be recycled and reused. This function will be provided by the outer matrix - hereafter refereed to as secondary matrix. The job of the other matrix - hereafter referred as primary matrix, will be to show high mechanical properties same as any other matrix for a conventional high performance composite.

A TMC that is recyclable has been never made before. This means that the composite of this study will be a novel material and furthermore its manufacturing procedure may also be novel. As one could expect, to access its recyclability and performance after recycling, the TMC samples shall also be recy-

[1] an composite-focused agency that most composite companies are directly or indirectly a member of.

cled. This means that in addition to its manufacturing, its recycling will be novel too. Once the samples have been prepared, they can be tested, analyzed and evaluated.

This thesis study begins with carrying out a literature study to collect information about TMCs as well as composites that have used the recyclamine technology. The results of this literature study are presented in chapter 2. This chapter divides further into a section that presents the collected information about composites that are officially classified as TMC as well as composites that have similar features to a TMC. The next section of this chapter is dedicated to recyclamine technology and shows literature studies applying this method.

In chapter 3, the research prospective will be discussed. There, the research questions which are the result of literature study are stated. Following that, the research methodology will be explained which aims to provide answers for the research questions. Lastly, a set of hypothesises are described which present the students expected answers to research questions and any other possible outcome in this research study.

Chapter 4 introduces the main components that will create the TMC together; these would be the reinforcements and the secondary matrix. In chapter 5 the manufacturing procedure of the TMC will be discussed. The TMCs of this study will be made via the hand lay up method, however because of unique properties of this composite (such as the shape of its reinforcement), this type of hand lay process will be state of art. This chapter begins with presenting the state of art mould which had be made specifically for this study's TMCs. Then it is time to describe the manufacturing procedures of TMC. Note that there will be different manufacturing procedures explained as there will be different versions of TMC needed to answer the research questions of this study. For example, some TMC are made just be to tested while some other TMC are made to be first recycled and then tested and some other are recycled multiple times and then tested.

In chapter 6, the testing schemes of TMCs will be described. This chapter starts with describing testing methods that help to assess how recycling affects the surface features of the recycled reinforcements. This includes introducing the Scanning Electron Microscopy (SEM) and Water Contact Angle method that aid to study the desired surface features. The next section introduces Interlaminar Shear Strength (ILSS) testing which aims to obtain values about how strong the interlaminar strength between the reinforcements and the secondary matrix is. Another goal of performing these tests is to understand whether recycling will have an effect on ILSS performance of TMCs. Additionally this section includes several post processing steps that will help to obtain the required parameters (such as interlaminar strength) and make sure that the only independent variable affecting the result will be the amount of recycling cycles.

Chapter 7 is dedicated to present and discuss the results of the tests mentioned in chapter 6. This chapter begins with displaying and discussing SEM and then Water Contact Angle analysis results and then moves on to show the results of ILSS testing and analysis.

Chapter 8 is dedicated to evaluating the resultant TMC samples and give suggestions for further studies that will be based on this thesis study. The last chapter is chapter 9 which is the conclusion of this thesis study.

It is hoped that this thesis study will expand the knowledge there is on TMCs as well as composites that have incorporated recyclable thermoset resins. More importantly, it is hoped that this study will lay a foundation for recyclable twin matrix composites and pave the way for more research and investigations on this composite and ultimately make this composite applicable in industries.

2
Literature Study

This thesis study began with carrying out a literature study. The purpose of this literature study was to gather sufficient amount of information to be able to set up a methodology and research plan for this thesis study.
The created TMC in this thesis study is unique in three ways: one is that it has two matrices, the other is that it uses the recyclamine technology (as the secondary matrix) and the last one is that it has brick and mortar (BAM) structure. Section 2.1 focuses on the information that has been gathered about the TMCs and section 2.2 focuses on the literature on the recyclamine technology. The Literature research phase did also include looking at research results about composites with BAM architecture. However while the composite made in this study has incorporated the BAM structure, the research itself does not include investigating the effects of this structure and how it influences the composite behaviour. Still, the information found on the BAM architecture during the literature study phase are worthy of interest and have been therefore shown in appendix A.

2.1. Twin Matrix Composites

This section represents all studies which are done on composites that have a TMC composition. It starts with subsection 2.1.1 which includes the works of authors who have recognized their composite as a TMC. Next, in subsection 2.1.2, a summary of several researches done on comparable composites to a TMC have been presented.

2.1.1. Studies Done Specifically On Twin Matrix Composites

The first study done specifically on TMCs was by Vasil'ev and Salov in which they had glass fiber filaments surrounded with a rigid epoxy as the first matrix and then cured together [44]. Then via the method of filament winding, the resultant pultrusions were impregnated with the secondary matrix which was more elastic. The samples that they have made in their studies are in the format of pressure vessels.
Their reason for choosing a secondary matrix with more elasticity was to have a higher transverse flexibility; more specifically to have a higher transverse tensile failure strain. It is not feasible to embed the glass fibers solely with the flexible secondary (and therefore not using the stiff matrix) because the flexible matrix would not be as efficient as the stiff matrix when it comes to transferring stress to and among the fibers. Another reason why a stiff matrix is required is to provide a high longitudinal strength for the composite. Therefore, having both the stiff and flexible matrices seemed like a good idea if one wishes to have a composite that has both stiffness and high transverse flexibility.

Having a higher allowable transverse strain threshold is a significant advantage as one of the weaknesses of conventional composites is their low allowable strain. For example in case of composites with carbon based matrices, the tensile failure strain in the longitudinal and transverse direction to the fibers is 1.5% (at most) and 0.5 % respectively [44] [28]. This anisotropic feature of composites is problematic in case of composite with plies oriented in different orientations because the whole composite is expected to have the same strain however different plies will have different allowed strains for a given load. This mismatch between allowed ply strain yields into matrix cracks [8] which further leads to lower mechanical properties of the composites as well as speeding its deterioration rate. Offering a more flexible resin covering the reinforcements is another advantage that motivated Vasil'ev and Salov to introduce TMCs [44] [2].

The flexibility of this matrix came from the addition of elastomer (Rubber SKN) [44]. The authors made different secondary matrices each with different amounts of rubber (the exact ratios of this rubber to epoxy is not specified). The most flexible secondary resin they had created had an ultimate elongation of 120 %, tensile strength of 17 MPa and modulus of 140 MPa [45]. The pressure vessel made with resultant TMC has the mechanical properties shown in table 2.1 and has the microscopic view shown in figure 2.1.

Property	Unit	TMC	Single matrix composite
Total Volume fraction	-	0.51	0.67
Density	kg/m^3	1830	2070
Longitudinal modulus	GPa	40	52
Longitudinal strength	MPa	1420	1470
Ultimate longitudinal strain	%	3.7	2.9
Transverse modulus	GPa	2	18.2
Transverse tensile Strength	MPa	11.2	46.7
Ultimate Transverse Strain	%	3	0.31

Table 2.1: Longitudinal and transverse tensile properties of a TMC and a single matrix composite. Both composites are made from glass fibers. The first matrix of the TMC is epoxy and the secondary matrix is a blend of epoxy and rubber. The matrix of the single-matrix composite is epoxy (same epoxy as the first matrix of TMC) [45].

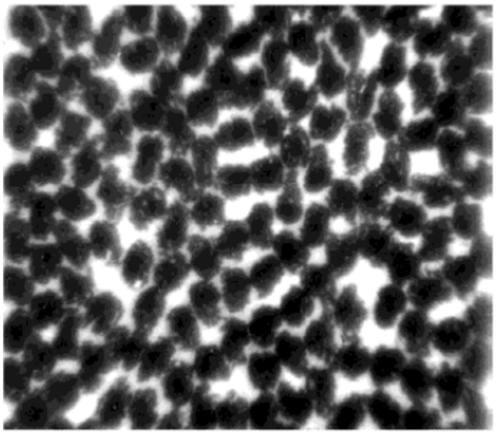

Figure 2.1: Microscopic view of a TMC made from pultrusions of glass fiber/epoxy embedded in a mixture of epoxy and rubber. The manufacturing method is filament winding [45].

As it can be seen in above table, TMCs have lower tensile strength and modulus values than single matrix composites both in longitudinal and transverse directions. It is worth mentioning that this difference is very significant in the transverse direction. It can be seen that the TMC has a lower density which will increase its specific properties. Regarding the strain values, it can be seen that in the longitudinal direction the TMC has a higher strain. It is in the transverse direction that TMC's nature shows its uniqueness. It can be seen that the allowed transverse strain of the TMC is almost ten times bigger than that of the single matrix composite. This is mainly due to fact that ultimate strain of the secondary matrix is (120 %) 30 times the ultimate strain of matrix in single matrix composite (4 %) [45]. The last area of comparison is regarding the total fiber volume. As expected, the TMC has a lower total fiber volume than the single matrix composite. What is impresive is that Vasiliev managed to obtain a TMC with a total fiber volume of 51 %. This is the highest fiber volume observed for a TMC compared to to any other TMC from other studies as well as this thesis study.

Vasiliev also manufactured a pressure vesele from a TMC a with less flexible secondary matrix [44]. This matrix (also flexibilized with rubber) has an ultimate tensile stain of 58 %, tensile strength of 62 MPa and modulus of 240 MPa. Note that comparing to the secondary matrix of the previous TMC, its ultimate tensile strain is halved but tensile strength and modulus is significantly more. His results showed high pultrusion volume fractions (the exact value is not specific) and sufficient impregnation of the pultrusions within the flexible matrix. However voids and inconsistent cross sections were seen across the resultant TMC.

In another study aimed to investigate the possibility of creating TMCs with 3D printing, Azarov and Antanov represented a TMC made from pultrusions of Carbon Fibers/Epoxy embedded in Polyamide [2]. These poltrusions are sent through an extruder of the 3D printer which is loaded with molten polyamide. An observation made by the authors is that these pultrusions are damaged significantly less than individual carbon filaments during 3D printing manufacturing steps. That means that they maintain their initial strength until at least the operational stage. Also, it was observed that the wetting of the pultrusions (by the secondary thermoplastic matrix) was at a sufficient level. Figure 2.2 represents cross sections of the pultrusion fibers and the TMC that Vasil'ev produced in his study. They concluded that these TMCs have the potential to be used in 3D printing, a technique for which neither thermoset and thermoplastic composites are suitable for.

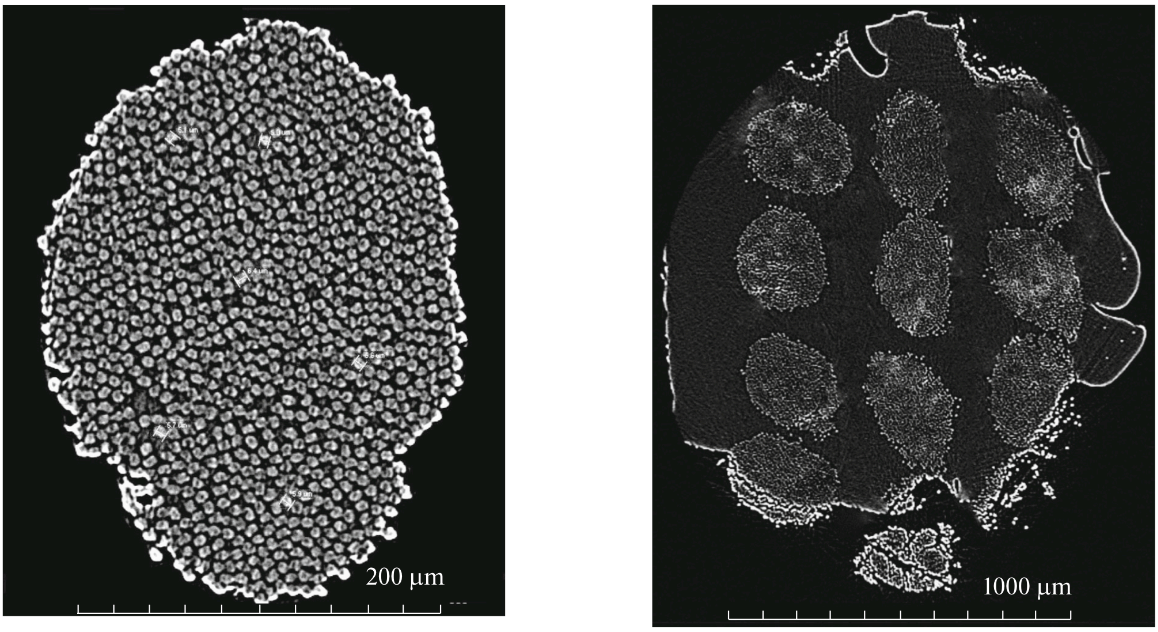

Fig. a. Microstructure of a pultrusion fiber   Fig. b. Microstructure of a TMC

Figure 2.2: Cross sections of TMC with the first matrix of epoxy and secondary matrix of polyamide. This TMC has been manufactured via 3D printing. Figure a represents a fiber pultrusion with an epoxy matrix and figure b represents a TMC made with such pultrusions covered with a polyamide secondary resin[2]

These authors performed tensile loading tests on the samples on their TMC and compared it with samples that are made from either epoxy or polyamide as the matrix. Results are shown in table 2.2. It is not specified which test standard they have followed or in what shape they had created their samples, so care must be taken while comparing the results with other literature. That being said, their results indicate that TMCs have remarkably lower tensile properties (strength and modulus) than the single matrix composite which makes sense considering the lower total fiber volume of TMC. After all, it is the carbon fibers that provide the tensile strength of a composite.

Property	Unit	Type of Matrix		
		Epoxy	Polyamide	Epoxy and Polyamide (TMC)
Total fiber volume	%	62	50	35
Density	kg/m^3	1580	1450	1230
Longitudinal elastic modulus	GPa	130	110	65
Longitudianl tensile Strength	MPa	1950	1600	750

Table 2.2: Results of tensile loading tests preformed on single and twin matrix composites. All samples have carbon fiber as reinforcement. The matrices vary from epoxy, polyamide and epoxy/polyamide [2].

By dividing the tensile strength with the elastic modulus for each composite type in table 2.2, its ultimate tensile strain value can be found. Doing so yields an ultimate strain of 1.50 % for the epoxy-based composite, 1.45 % for the polyamide-based composite and 1.15 % for the TMC. Therefore according to their results, TMCs have a lower ultimate tensile strain value than the single matrix composite. This is opposite to the result of their previous study (shown in table 2.1) which indicated the TMCs have a higher ultimate tensile strain (3.7 %) than single matrix (epoxy) composite (2.9 %). That being said, in terms of other parameters, table 2.2 displays similar trends as table 2.1.

A more recent study specifically for TMCs was done by Callens in which he studied the longitudinal compression response of TMCs. His approach was to have TMC samples in the shape of thin-walled rings to avoid global specimen buckling. An advantage of such specimen design was that opposite rectangular specimens, there was no need for clamping, thus there would be no damages due to clamping. The diameter of (micro)pultrusions that were applied for his study were 280, 500 and 700 μm. The micropultrusions used in that study were made from carbon fibers pregnated with Bismaleimide (BMI) matrix in case micropultrusions with 280 μm diameters or epoxy matrix in case of bundles with 500 and 700 μm diameters [1] These micropultrusions had circular cross sections. The second matrix was a flexible epoxy based on DGEBA with a bisphenol A-based monofunctional and aliphatic epoxy as the flexibilizing resin.
The selected method to create these TMCs for this study was filament winding. His bobbins in this case were the pre-made micropultruisons. These bobbins were fed to the winding machine which dipped them into the flexible resin. It is worth mentioning here that according to him, an advantage of TMCs as opposed to single-matrix composites when it comes to manufacturing with filament winding is that manufacturing with TMCs takes around half the time of filament winding of single-matrix composites. That is because there are some steps that are not needed in filament winding of TMCs but are required for single-matrix composites. For instance, it is not required to apply tension on the micropultruions or there is no need to impregnate the fiber filaments inside the micropultrusions. In filament winding of TMCs, all that is required is for the secondary matrix to cover the micropultusions (Callens did it by depositing this resin in the mandrel slots during the winding process). This also removes the need for the step of pulling the micropultrusions through the resin bath. The next steps are curing, cooling and dismantling which are similar to that of conventional single-matrix (epoxy) composites.

His results showed that at least 40% of the secondary matrix needs to be made from the flexibilizing resin in order for the stiffness of the secondary matrix to be reduced and furthermore, the amount of this flexibilizing agent should not exceed 70%, otherwise the secondary matrix will be too flexible. It was also observed that having 0% of the flexibilizer leads to tensile failure strain of 2.5% and having 68% of flexibilizer leads to tensile failure of 35.4%. Another consequence of adding the flexibilizer is the change in the T_g: Adding the flexibilizer causes a reeducation in T_g from 82 $^\circ$C at 0% flexibilizer to 37°C (that is if T_g is determined from reading loss modulus data; if one prefers to read loss factor data, then T_g 57°C) at 35.4% flexibilizer.
Regarding the fiber volume content, the fiber volume within the micropultrusion is reported to be 70–75%. Considering now that the packing density of the micropultrusions with the TMC was 60-65%, that means that the fiber volume within the whole TMC was 42-49%. Callens reported that a lower amount of voids were seen in the cross section of the TMCs in comparison to the single matrix composites that were made via the filament winding method. Another advantage of having micropultrusion is that because their bending stiffness is higher than that of fiber filaments, the alignment of micropultrusions

[1] Note that the pultruded rods in his study were remarkably smaller than 1.7 mm diameter rods Vasiliev and Salov in the study.

is easier [7].
One of the flaws that was detected from Callens work were the resin pockets that were observed in the cross sections of the TMCs. Figure 2.3 shows such a pocket in case of TMC with micropultrusion diameter of 500 μm. Please notice that these resin pockets count as defects and Callens observed more resin pockets in TMCs than single matrix composites. Another flaw in his TMC is the small amount of space between the pultruded rods. An example is shown in figure 2.3 by a red arrow, indicating that two rods are touching each other. Such closely packed rod regions count also as defects as interface failures can occur there leading to reduction in composite's performance such as having lower transverse failure strains [29]. It is important to aim to have the least amount of resin pockets as they decrease the transverse stiffness and failure strain of the composite [29]. It was these resin rich regions that inspired pursuing a TMC with brick and mortar architecture instead of using circular rods. In that case, it would be easier to prevent such regions.

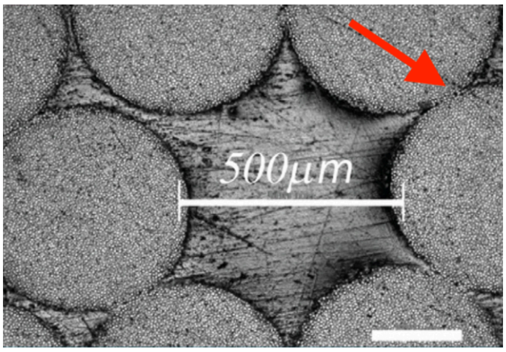

Figure 2.3: Cross-sectional micrography of TMC with a resin pocket with the length of 500 μm. The micropultrusion diameter here is also 500 μm [8].

As said earlier, Callens tried TMCs with different micropultrusion diameters. The conclusion is that the diameter of micropultrusions affects the failing mode. He observed that in case of small diameters (280 μm), the failing mode is the kinking of the micropultrusions. In case of larger diameters (700 μm), the failing mode is the splitting and crushing of the micropultrusions. In case of TMCs with a micropultrusion diameter of 500 μm, these was a mix of failure modes from smaller and bigger diameters: both splitted and inclided fracture surfaces were observed. Furthermore, most consistent results were obtained for the small pultrusions due to their lower sensitivity to defects [7].
That all being said, the compression strength of TMCs are shown in figure 2.4. As can be seen in these graphs, the compression strength is not affected by the diameter of the pultruded rods. This figure shows also that in case of thinner micropultrusions, the stiffness of the TMCs increases with increasing the stiffness of the secondary matrix (noted as E_m in this figure). The main reason for this trend is that the higher the stiffness of the secondary matrix, the higher its strength will be against compression and also the fact that stiffer matrices hinder the deflections of micropultrusions more. In case of TMCs made from thicker rods, it can be seen that the compression strength of the TMC samples is not affected by the stiffness of the secondary matrix. According to callens, the reason is the different failure modes that have occurred for these samples. Another conclusion that can be made from this figure is that the result uncertainties in case of thicker micropultrusions are more than the uncertainties of the TMC samples made from thinner rods. That is because the misalignment of mircopultrusions was found to be rarer in case of TMCs made from thin micropultrusions [7].

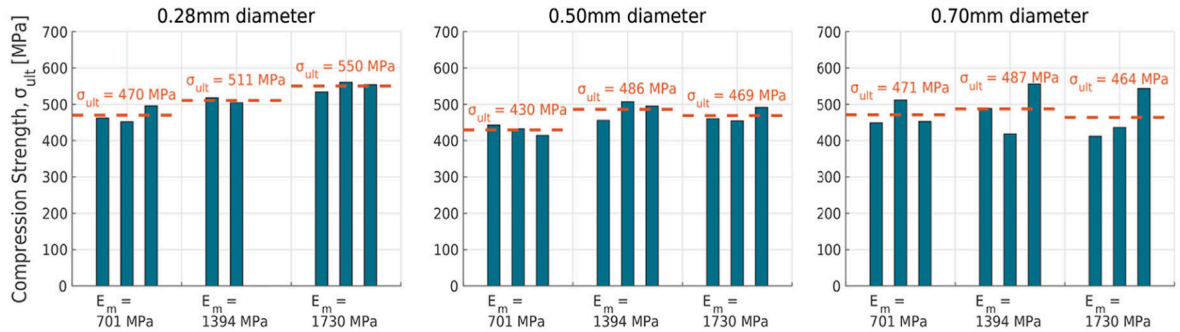

Figure 2.4: Compressive Strength of TMCs for micropultrusion diameters of 0.280, 0.500 and 0.700 mm. For each of these diameters, thre different secondary matrices have been used and the sample number for each of these is three[8].

2.1.2. Comparable Studies to Twin Matrix Composites

The studies of the previous subsection were about the researches that were done specifically on TMCs. This subsection represents studies that are done on composites that have comparable features to a TMC but still have not been considered as a TMC.

The first study to mention is the research of Baker and Rousseau [3]. The goal of their investigation was to develop a cost efficient stiffening approach for the hat stiffeners used in helicopter blades. Their method involved using pultruded rods inside the hat stiffeners. The diameter of these rods was 1.7 mm. These rods are held together via a synthetic adhesive. While they tried other stiffening methods as well, using composite rods embedded in an adhesive proved to be a simple, cost efficient and structurally efficient method to increase the stiffness and strength of the stiffened structure. However this option was not further investigated due to its low fiber volume and having several resin rich areas between the pultruded rods [3].
The next work to mention is the research of Potter and Wisnom [32]. They have categorized the composite that they have developed during the research as a composite with extreme anisotropy. This is because while the tensile to shear modulus ratio of typical carbon fiber UD composites is 30 to 1, this ratio is much higher for their developed composite. This feature could be essential to some applications. For example, the target application in Potter and Wisnom's case was to develop a flexbeam for bearingless main rotor of helicopters that can allow for relatively high twisting angles and at the same time, tolerate high bending loads. They proposed to create such composite by embedding pultruded rods (diameter of 1.7 mm) in a flexible matrix. Via finite element analysis, they tried several resin systems and compared the maximum and minimum specific modulus values of each matrix. Ultimately, they concluded that a blend of epoxy and polyurethane would lead to an ideal composite. Incorporating this (secondary) matrix and the composite rods, they managed to achieve a bending to shear modulus ratio of 108 to 1 with their composite. Additionally, they managed to construct beams with their composite that can twist up to 20^o without any permanent damage [32].
Another relevant study is the work of Cairns and Bundy [6]. The goal of their research was to investigate the use of carbon fiber pultruded rods as reinforcements for wind turbines. The diameter of their rods was 1.2 mm. Their secondary matrix was Bisphenol F, which is a stiffer and less flexible secondary matrix than the secondary matrix used in other studies. While their obtained composite had a lower total fiber volume (<50%), an advantage of their composite is that they managed to reduce carbon fiber waviness significantly. Their study focused on determining the best rod surface treatment method so that the best possible adhesion to the secondary matrix will be obtained. They tried several options such as erosion, abrasion and wet chemical oxidation. Their results indicated that the best surface treatment method is blast etching. With that method, the resultant composite had the highest shear strength which was equal to 90% of the shear strength of the pultruded rods. Acid etching on the other hand, reduced the shear strength of the composite the most [6].

The next study to mention is the work of Schmitz and Horst [36]. The target application of their investigation was morphing wings which means that their composite must have a high anisotropy as high bending strains are required for skin panels of a morphing wing. The composite that they had introduced consisted of bundles of stacked strips of glass fiber prepreg. These bundles, which are the light grey shapes in figure 2.5 had an elliptical shape with a major axis of 2 mm. These bundles were held together via a rubber foundation (ethylene–propylene–diene to be more precise); as shown in figure 2.5. A feature that makes their composite different from other composites discussed in this report is that at one side of each layer of bundles and rubber, there is a glass fiber reinforced laminate (as can be seen in figure 2.5). The purpose of having these reinforcements (from the laminate and the bundles) in the longitudinal direction is so that their composite will have a high bending stiffness in that direction and the purpose of the rubber matrix is to allow for the curvature of the wing. The goal of Schmitz and Horst's research was to investigate the compression failure of a morphing skin made from their composite. In their study they observed the (in-plane and out-of-plane) buckling of the bundles inside the rubber matrix and concluded that in-plane buckling causes the lower critical strains of the resultant composite.

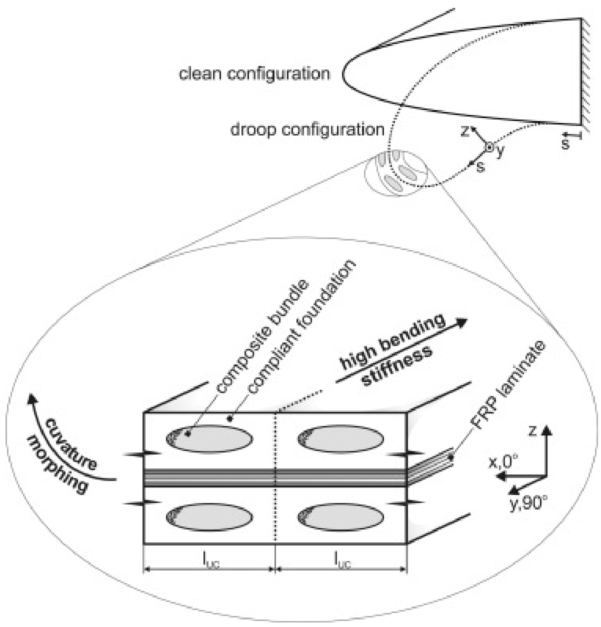

Figure 2.5: Sketch of the composite designed by Schmitz and Horst and its application in the leading edge of a morphing wing [36]

The last relatable study to mention is the work of Kim and Gardner in which created a twin matrix with a BAM architecture. The brick-like components of their composite are blocks of carbon nanotubes embedded in a toughened epoxy [26]. Then via filament winding and with the application of a BMI resin as the secondary matrix, these blocks are put together and the BAM structured composite is made. Note that this TMC is not the main composite of interest for their study. This TMC was in fact a benchmark and was made to be compared to another type of composite in their study. The latter composite is not a TMC but still has a BAM architecture. This composite is made from blocks of carbon nanotube embedded in a BMI resin. Once the blocks were obtained, they were put together via filament winding and additional BMI resin application and then lastly cured. The manufacturing scheme of both composite types can be seen in figure 2.6.
Kim and Gardner performed transverse tensile loading tests on both the TMCs (thus the one with blocks of toughened epoxy/CNT embedded in BMI resin and the other composite - the one with blocks of BMI/CNT embedded in BMI resin) [26]. Note that by transverse loading, the direction of load is along the width of the blocks. They observed that the TMCs performed significantly worse than the other composite system, both in terms of transverse tensile strain and strength. This can be seen in figure 2.7a. In this figure the graph labeled as TVT#1 belongs to the TMC made from toughened epoxy/CNT Roving embedded in BMI matrix. The rest of the samples in that figure are composites made from BMI/CNT rovings embedded in BMI matrix. What this figure shows is that the TMC sample has the lowest specific transverse tensile strength and strain. Figures 2.7b and c are SEM pictures of TMC failed due to transverse loading. What these two figures show is that TMC fails via pull out of the dry

epoxy/CNT block. The authors argue that the weakness of this composite arises from these dry region as the cracks propagate through there instead of going through the resin. Furthermore 2.7b shows that the cracks that initiate or propagate along the block/matrix interface, also go through the dry block.

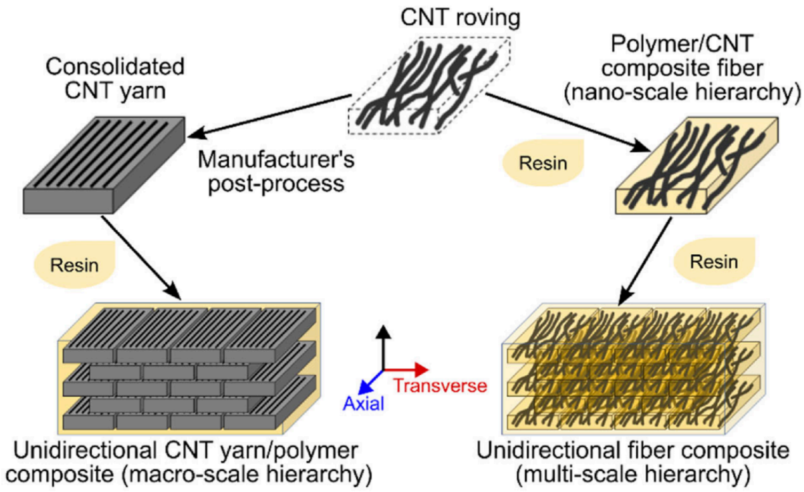

Figure 2.6: Build up scheme of composites with a BAM structure. The left side of the figure shows the build up of a TMC using blocks of carbon nanotube (CNT)/toughened epoxy and then filament wound in BMI resin. The right side shows a composite made from blocks of CNT/BMI embedded in additional BMI matrix [26].

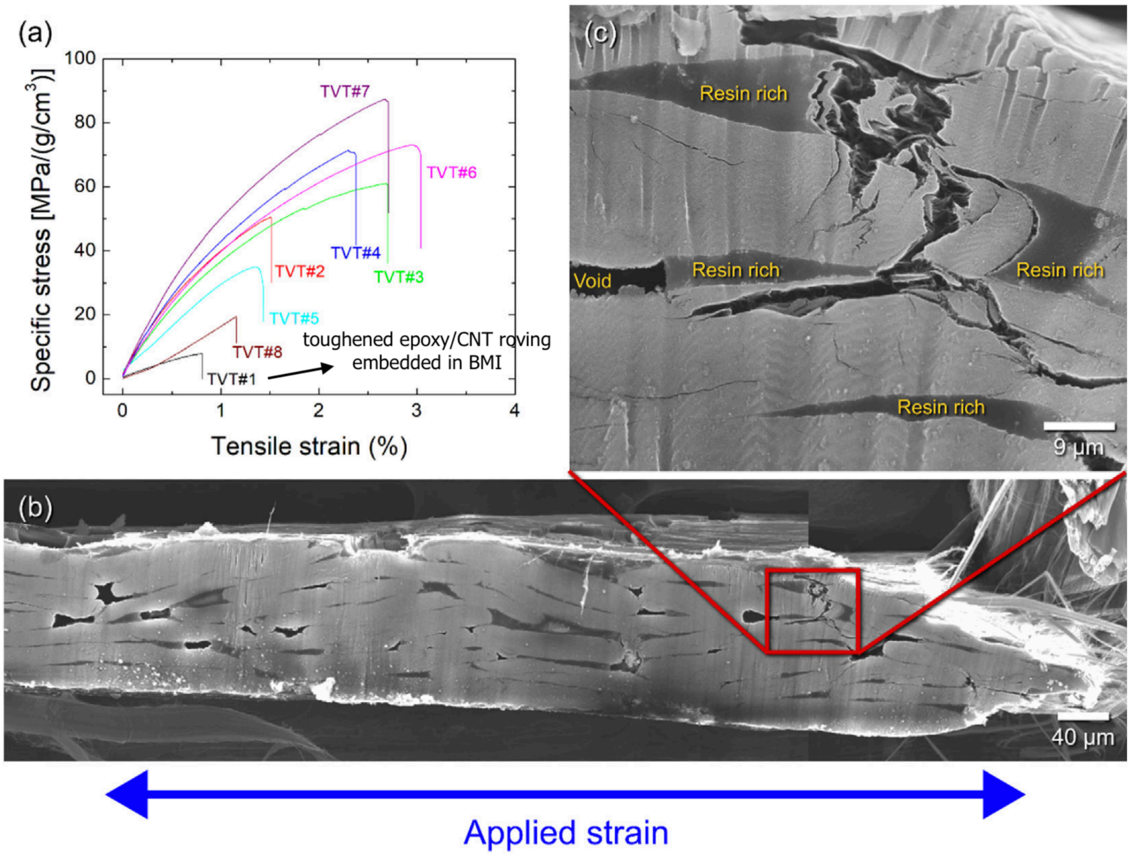

Figure 2.7: Figure a represents the specific transverse tensile stress-strain curve for several composites with a BAM architecture. The curve labeled with TVT#1 belongs to a TMC (epoxy/CNT roving blocks embedded in BMI) and the rest of the curves belong to other BAM structured composites (they are all made from BMI/CNT roving blocks embedded in BMI matrix). Figure b represents the cross section of the TMC after the loading and figure c zooms in the region of failure [26].

According to the results of Kim and Gardner, their CNT/toughened epoxy composite has a specific strength of 7.1 $\frac{MPa}{g/cm^3}$ and specific modulus of 1.25 $\frac{GPa}{g/cm^3}$ [26]. Given that composite had a density of 1.31 g/cm^3, that yields to transverse tensile strength of 5.15 MPa and transverse tensile modulus of 0.95 GPa. Comparing this to the TMC made by Vasiliev (shown in table 2.1), it can be seen that his TMC has a higher transverse tensile strength (46.7 MPa) and modulus (18.2 GPa). Furthermore, the epoxy/CNT roving/ BMI composite has a tensile strain of 0.69 % (also shown in figure 2.7 which is remarkably lower than that of Vasiliev's work (3.7 %).

2.2. Recyclamine Technology

The goal of using recyclamine technology is to create recyclable thermosets. These bio-based thermosets are made from the reaction of epoxy resin molecules with Recyclamine hardeners. Recyclamines are amine-based curing agents that have polyamine structures with amino end groups that form cleavable bonds during the formation of the epoxy matrix. Additionally, they contain acetal groups ($R_2C(OR')_2$ [43]) which are known to be degraded in an acidic solution. Due to this group, the resultant epoxy resin can be turned into recyclable and meltable thermoplastic under specific chemical reactions. The condition required to have a cleavage is an acidic environment and a 70-100^oC temperature [34]. Based on the literature study done on recyclable thermosets, recyclamine technology seems to be the easiest and most convenient method to create recyclable thermoset resins for a composite. What makes other (chemical recycling) methodologies more challenging is that they require the addition of several hardeners (or catalysts) [27] [49]. Despite being the most popular thermoset recycling technology, no industrial application of recyclamine technology has been yet found.
Figure 2.8 compares the general reaction mechanism for the bio-based epoxy thermosets made with Recyclamines (bottom side) with the formation of a typical thermoset epoxy (top side). This figure shows that thanks to Recyclamines, a network of polyamine bio-based epoxies are provided with cleavable points which further can be recycled to form thermoplastic.

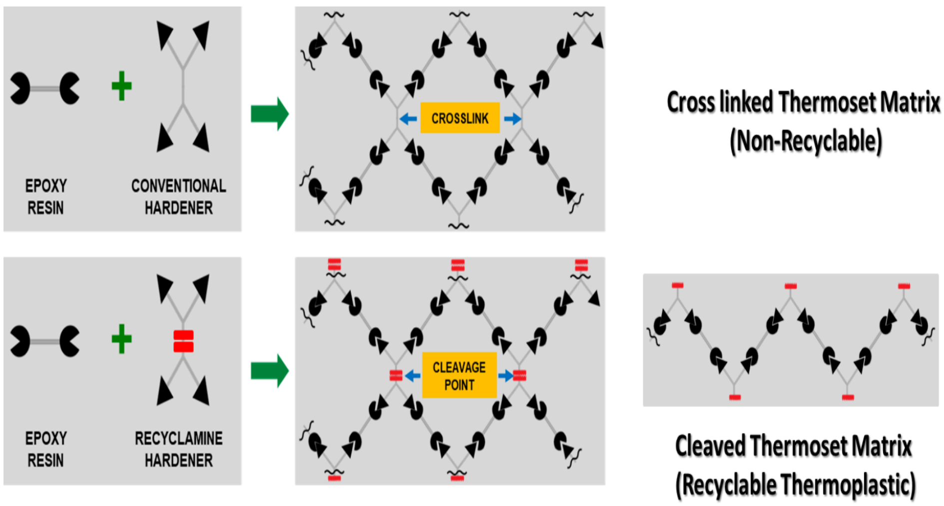

Figure 2.8: Comparison of the formation of bio-based epoxy versus the conventional composite epoxies [11]

The way recyclamine aids the recycling process of the thermoset composites is that once it is solved in an acidic solution during recycling, the bio-based thermoset resin network will be cleaved and converted into an epoxy thermoplastic. While this is happening and an epoxy-based thermoplastic is being developed, the thermoplastic is soluble in the acidic solution. This is because of the protonation of thermoplastic's polymer backbone. Furthermore, as a consequence any other extra component (composite rods in the case of this thesis study) can be extracted out [34].
To obtain the epoxy-based thermoplastic itself, the acidic acid solution is neutralized with a basic sodium hydroxide (NaOH) solution. This conversion of thermoset into epoxy thermoplastic can take from 30 minutes to several hours depending on the dimensions of the composites. The resultant thermoplastic is filtered out, rinsed and then dried [34]. It is possible to turn the obtained thermoplastic further into a more practical thermoplastic by adding equimolar amount of bisphenol and epichlorohydrin under

appropriate conditions [38].
The technology of recyclamines is a well approved method in the epoxy industry as it provides a broad spectrum of curing agents with a wide range of reactivity, latency, temperature application, chemical resistance and recyclability. An advantage of recyclamine technology over other general recycling approaches (such as mechanical recycling or recycling through the use of high temperatures) is that this method has shown to be the least energy-consuming method as well as being an environment friendly and cost effective recycling method for the recycling of thermoset composites [38].
There are different types of recyclamine available for different purposes which vary from each other in terms of recycling possibilities, suitability for different processes (for example whether it is wet lay-up or resin infusion) as well as other qualities such as temperature resistance or chemical compatibility with other polymers [12].

There have been several studies done on the recyclamine technology. The majority of these studies focused on the recycled epoxy based thermoplastic such as its characterization or how the manufacturing procedure of the bio-based epoxy affects the polymer before and after recycling [12] [10] [15] [46]. While the results of these studies are interesting, they go beyond the scope of this study and will not be addressed.
Despite that, there is one study that has relatable results that are worth mentioning. That is the works of Dubey and Mahanth in which they investigate how the glass fibers are affected by the recycling procedure [11]. They compared two sorts of composites with the same resin (bio-based epoxy with a recyclamine hardener) but different fibers. One type of composite is made with fresh glass fibers and the other one is made with recycled fibers. For both composites the fiber type is fabric, the manufacturing method is vacuum assisted resin transfer moulding and lastly both composites had a fiber volume fraction of 50-55%.
According to their results, the composite made from fresh fabric has a tensile strength of 536.5 MPa while the one made from recycled fabric has a tensile strength of 485.5 MPa (hence a 10 % reduction due to recycling). Furthermore, they obtained a tensile modulus of 25.91 GPa for composites made of fresh fabric and 23.49 GPa for the one made from recycled fabric (also a 10 % reduction). Lastly, the composite made from fresh fabric yields into a tensile strain of 2.63 % and the one made from recycled fabric has a strain of 2.60 %, meaning that recycling led to a 3 % increase in strain value.

A similar trend can be seen in the works of Fraunhofer Project Center for Composites in which they investigated the effect of recycling on the mechanical properties of a panel made from carbon fiber and a matrix system made from recyclamine hardener and a bio-based epoxy [17]. More specifically, they investigated how differently panels made from recycled carbon fibers behave compared to panels made with fresh fibers in terms of tensile and flexural loading. The result of their work can be seen in tale 2.3.

	Propety	Unit	Fresh	Recycled
Tensile	Modulus	GPa	97.60	99.10
	Strength	GPa	1.22	1.11
	Failure Strain	%	1.09	1.11
Flexural	Modulus	GPa	90.10	89.80
	Strength	MPa	1.51	1.43
	Failure Strain	%	1.75	1.60

Table 2.3: Tensile and flexural properties of the panels made from recycled or fresh carbon fibers. Both sample types have the same type of matrix: bio-based resin with recyclamine hardener. Furthermore for both of loading types, the load has been applied in the o^o direction [17].

The conclusion that can be drawn from this table is that recycling of the fibers has little effect on the tensile and flexural properties (either modulus, strength or failure strain) of the panel.
Another relatable study of Fraunhofer Project Center for this thesis study is when they decided to compare a composite made from recyclamine as hardener versus another composite made from a commercial hardener (Epikure) [31]. Both of these composites had the same Epikote resin and type of carbon fibers. They compared the panels in terms of tensile, compressive and ILSS properties. The results of their works can be seen in figures 2.9, 2.10 and 2.11. Figures 2.9 and 2.10 compare panels

made from commercial (Hexion Epikure) hardener versus panles made from recyclamine hardeners (either recyclamine 3382 or 3182) in terms of tensile and compressive properties respectively. A note about these two figures is that each of them include properties of panels with reinforcements placed in either 0^o and 90^o direction. That is indeed useful information because 0^o properties represent the fiber-based response of the panel and the 90^o properties represent the matrix-based response of the panel. Figure 2.11 compares panels made from the same materials but this time in terms of ILSS behaviour at two different temperatures, one is the room temperature and the other one is at 80^oC.

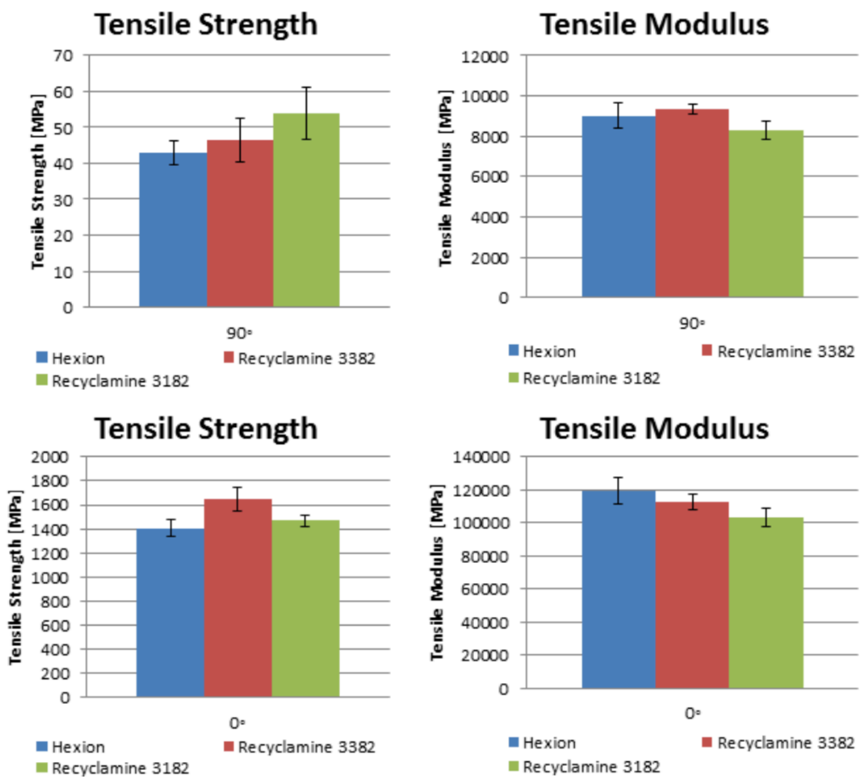

Figure 2.9: Tensile properties of composites made from commercial (Hexion Epikure) hardener versus composites made from recyclamine hardeners (either recyclamine 3382 or 3182). It can be seen that tensile properties both in the 0^o and 90^o are shown [31].

As figure 2.9 shows, in terms of tensile strength the panel made with commercial hardener has the lowest tensile strength (irrespective of the loading direction) while in terms of tensile modulus, the panel made from commercial hardener has a higher modulus than the ones made with recyclamine hardener (especially in case of 0^o loading direction).
Figure 2.10 displays a very similar pattern but this is for compressive properties. As can be seen there, using commercial hardener leads to obtaining lower compressive strength values but yields obtaining higher compressive modulus values. However note that there are few exceptions to this claim in case of panels loaded in 90^o degrees.

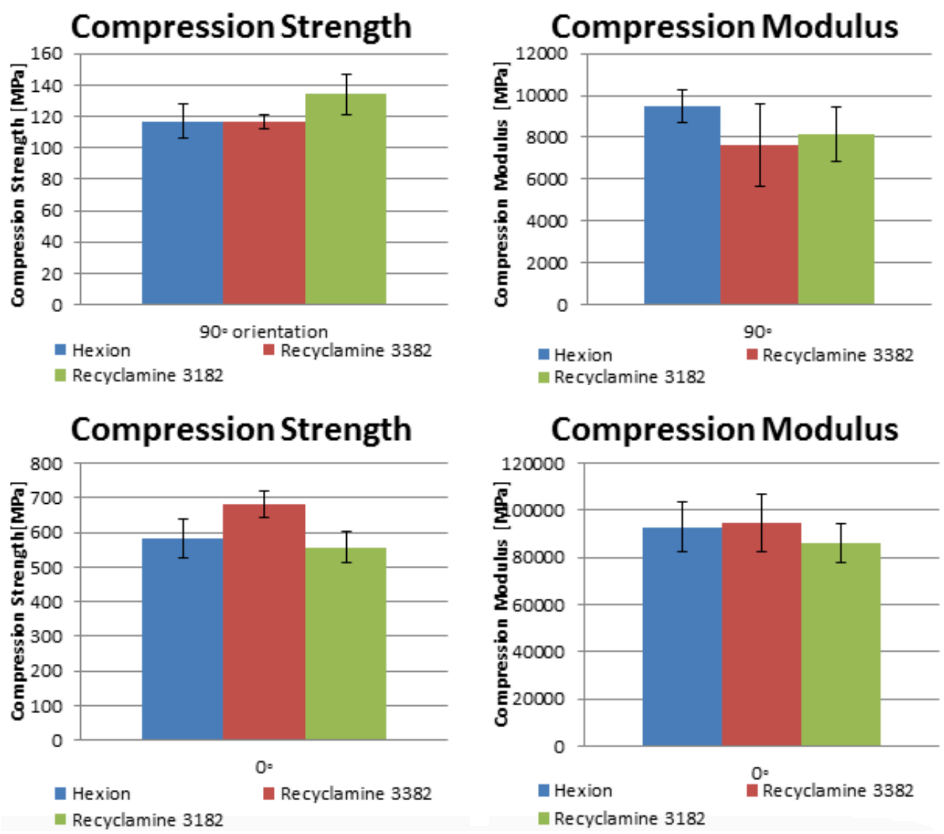

Figure 2.10: Compressive properties of composites made from commercial (Hexion Epikure) hardener versus composites made from recyclamine hardeners (either recyclamine 3382 or 3182). It can be seen that compressive properties both in the 0^o and 90^o are shown [31].

In terms of ILSS properties, figure 2.11 shows that at room temperature, there is an insignificant difference between ILSS values of composites made with commercial hardener and the ones made with recyclamine. Note that both of these panels have a $\pm45^o$ fiber orientation. This difference becomes more remarkable at a higher temperature (80 ^{o}C) as the panel made with commercial resin has a higher ILSS value.

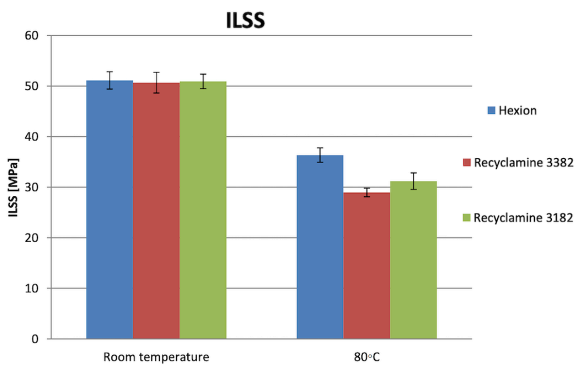

Figure 2.11: ILSS of composites made from commercial (Hexion Epikure) hardener versus composites made from recyclamine hardeners (either recyclamine 3382 or 3182). It can be seen that these ILSS properties are recorded in room temperature and 80^oC [31].

2.3. Conclusions on Literature Study

As mentioned in previous sections of this chapter, both the concepts of TMCs and Recyclamine Technology are only at the research and development and no record of their application in the industry has been found. That being said, the opportunities that these composites bring must not be neglected; in the case of TMCs, the main opportunity would be that the composite's functionality would be increased and in the case of Recyclamine Technology, the advantage is to break down the recyclamine-based matrix and extract the recycled fibers. Also, the fact the properties of composites made with recycled fibers are not significantly less than the composites made with fresh fibres is another motivating factor to pursue the application of recyclamine technology for this study.

As mentioned in section 2.2, recycling via acid treatment is known to be one of the cheapest recycling methodologies. Considering that in TMCs, pultruded rods will be used instead of fibers, that makes the recycling procedure even easier. That is because extracting rods would be easier than extracting individual fibers as fibers would be much smaller than the rods. On the other hand, given that typically composites are expected to operate in their designated role for more than 20 years [33], recycling a composite means that another 20 years will be added to its functional life. That is, of course, assuming that the initial properties of recycled composite will be similar to that of a fresh one. What would be even more interesting is if it is possible to recycle a composite multiple times and still obtain similar properties. That means that the functional life of the composite will be 60, 80 or even 100 years instead of 20 years. This leads to lower material consumption which yields several environmental and economical advantages.

Despite the environmental and economic advantages this combination could bring, the expected challenges should be mentioned too. A remarkable challenge is the low total fiber volume of TMCs (mentioned in section 2.1) with respect to other composites which could lead to lower mechanical performance properties. Another challenge is that because a recyclable TMC has been never made before, it is unknown whether the rods will be compatible with the recyclamine-based matrix or not. Based on the knowledge gathered during the literature study as well as the information gathered from the safety and technical data sheets of these components, no sign was found that could indicate any compatibility issues between the rods and the recyclamine-based matrix. Still, trial and error attempts are necessary to confirm complete compatibility between the rods and the recyclamine-based matrix. This lack of knowledge creates the research gap for this thesis study which will be mentioned in the next chapter.

3 Research Prospective

The literature study phase provided a platform of useful and guaranteeing knowledge regarding TMCs and the recyclamine technology. Based on this knowledge, it is decided to combine these two fields together and form a research study that focuses on the development and analysis of TMCs that have incorporated the recyclamine technology. More specifically it is decided to conduct a research study that focuses on the recycling aspect of TMCs. This chapter represents the research prospective that will serve this purpose and will be followed for the rest of this thesis. The first section of this chapter, section 3.1, lists the main research question, sub-research questions and the following sub-sub-research questions. Next, section 3.2 describes the research methodology which focuses on how main steps of this thesis will provide answers to the research questions and lastly, section 3.3 covers the expected outcomes and results of this study.

3.1. Research Questions

The main research question is:

How are interlaminar properties of Recyclable Twin Matrix Composites influenced by recycling?

- How are the surface properties of reinforcements in a Recyclable Twin Matrix Composite affected by recycling?
  - How are the surface properties of reinforcements in a Recyclable Twin Matrix Composite influenced after a recycling session?
  - How are the surface properties of reinforcements in a Recyclable Twin Matrix Composite influenced after multiple recycling sessions?
- How is the interlaminar shear strength of Recyclable Twin Matrix Composite affected by recycling?
  - How does a recycling session affect the interlaminar shear strength of a Recyclable Twin Matrix Composite?
  - How is the interlaminar shear strength of Recyclable Twin Matrix Composite affected after multiple recycling sessions?

3.2. Research Methodology

To find answers to the questions stated above, a research methodology must be defined. Before describing this methodology, it is important to remember that the only independent variable is the number of times rods have been recycled. Therefore, all efforts should be made to make sure it is only this variable that causes variations in results and nothing else.
Starting with focusing on the first sub-research question which focuses on the influence of recycling on the surface parameters of the rods, using Scanning Electron Microscopy (SEM) seems an ideal option. This technique will be used to study the surface topology of the composite rods before and after the recycling steps. More specifically, the intention of using SEM is to observe:

- How does treating the TMC (or essentially the composite rods) with acid affect the surface morphology of the composite rods?
- How does the number of acidic treatments affect the surface morphology of the composite rods?

The SEM investigation will be used to study and compare 5 types of composite rods: fresh rods, one-time recycled rods, two-times recycled rods, three-times recycled rods and four-times recycled rods. The reason for going up to four times of recycling is that this is rather a high number of recycling and will show if the rods can stand a high number of recyclings and if so, to what extent are they affected. Thus at the end of this SEM analysis, not only it will be understood how the rod surface will be affected by a recycling session, but it will also be learnt how multiple recycling sessions (up to an 'extreme' number) will affect it.

To have quantitative data about the rod surfaces and how they have been impacted by recycling, Water Contact Angle analysis for each rod type is performed. Water contact angle analysis clarifies how the surface hydrophobicity of a rod is changed with respect to the number of recycling trials. These results could be further used to understand how multiple times of recycling affects the roughness of the rod surfaces.
As in the SEM analysis, there will be 5 different types of rods studied in the water contact angle analysis (fresh, one-time recycled, two-times recycled, three-times recycled and four-times recycled). The outcomes of this investigation will be mainly shown in graphs that have contact angle measurements on the vertical axis and the number of recycling sessions on the horizontal axis.
These two measurement techniques (SEM and Water Contact Analysis) serve to answer the first sub-research question in section 3.1 which focuses on the surface properties of rod after one or multiple recycling sessions.
Additionally, it is useful to measure the weight of a rod before and after recycling sessions. Mass reduction of this rod is indicative of a possible reduction in its quality and performance in the TMC. As for SEM and water contact angle analysis, there will be 4 cycles of recycling performed on this rod and then, its weight will be measured. Doing so allows to understand how the mass loss of a rod is linked with the number of recycling cycles.

To answer the second sub-research question which focuses on the effect of recycling on the interface strength between the rods and the secondary matrix, interlaminar shear strength (ILSS) of TMCs is an appropriate parameter to focus on. For this ILSS analysis, three types of TMCs will be made and tested. One type will be the TMCs made from fresh and unrecycled rods. The second type will be the TMCs made from rods that have been recycled once. The last type will be the TMCs made from rods that have been recycled four times. Performing ILSS testing on these types of composites gives the following information:

- How does an original TMC perform during an ILSS testing (original meaning made from fresh rods)?
- How different is the behaviour of the TMC made from one-time recycled rods?
- How does a TMC made from rods that have been recycled multiple number of times, perform at ILSS testing?

The decision to initially not study the ILSS change of two or three-times-recycled TMCs is related to the expectation of recycling's limited effect on ILSS results; which further concludes that the number of recycling is not important (this expectation will be discussed more in detail in section 3.3). Otherwise, if there is a significant difference between the ILSS of four-times-recycled TMC and one-time-recycled TMC, the ILSS analysis of two or three-times-recycled TMCs can always be done.
Lastly, a fracture study will be done on the samples that have failed during the ILSS testing. These fractures will be obtained by a camera capturing every second of the ILSS testing. This analysis will serve to understand which failure mechanisms would occur during the ILSS testing of of the TMC samples and whether they have been impacted by the recycling of the rods.

3.3. Hypothesis

This section lays out the expected outcomes for this thesis study. It starts with describing the expected results for the SEM analysis, followed by expectations of Water Contact Analysis and then trends observed during weight measurements of the rods. Next it will be described what results are expected after the ILSS testing and how they are affected by recycling. Lastly, the predicted failure mode will be explained and stated whether it is expected that the failure mechanism be affected by recycling or not.

Starting with the SEM observations, it is expected these surfaces will be affected by each session of recycling. Since a recycling session includes the interaction of the rods with the acid, it is expected that these surfaces will be influenced. It is expected that after the first few recycling sessions (so the first or two recycling sessions for instance), the surface of the rods starts developing small defects such as small pits. These features are thought to be due to the degradation of the epoxy on the surface of the rods. After the next few recycling sessions (so the third or fourth recycling sessions for instance), it is expected that these defects will become bigger in size and depth. It is also expected that after these higher numbers of recycling sessions, damage to surface fibers will be observed. Such expected damages are distortion or discontinuation of these fibers.

Focusing now on the Water Contact Angle predictions, it is expected that the more often a rod has been recycled, the higher its contact angle will be. This increase in angle is expected to take place since the first time of recycling and will continue with each recycling session. That is because as mentioned in the above paragraph due to the initial recycling sessions, the surface epoxy is expected to be damaged and after the next recycling sessions, there will be additional dents and fiber distortions on the rod surface. All these parameters contribute to a rougher surface and therefore higher contact angles. It is expected that the trend line in the contact angle-recycling number graph will be a linear line with a positive slope. That is because it is expected each recycling will have a similar contribution to the roughness of the rod's surface.
Regarding the ILSS results, before stating the expectation of how recycling of the rods will affect the ILSS performance, first the expected general ILSS behaviour of the TMC should be stated. Since this material is also a composite, it is expected that it will have a brittle failure. That means that there will be a sudden drop in shear force (or stress) as soon as the ultimate shear force (or stress) has been reached. This behavior is expected to happen irrespective of how many times the rod has been recycled.
Regarding the effect of recycling on the ILSS performance of TMCs, it is expected that recycling will increase the ILSS performance of TMCs, but however this increase will be very minimal. The reason for this prediction is that it is expected that during each recycling, the surface of the rods will get rougher yielding into a better mechanical interlocking between the surface of the rods and the secondary resin. This increases the interface strength between these components and hence higher ILSS values.
Regarding the effect of number of recycling sessions on the ILSS properties, it is expected that the number of recycling sessions will not have an influence on the amount of rise in the ILSS properties (up to 4 recycling sessions). The reason is that as mentioned in the paragraphs about expectations of Water Contact Angle analysis, each recycling session is expected to contribute equally to the roughness of the rods. For the same reason, it is expected that each recycling session will contribute similarly to the improvement in the interaction of the secondary matrix and the rods. Therefore ILSS properties will increase linearly with the increase in the number of recycling sessions.

Lastly, in terms of failure mechanism, it is expected that the critical failure mode is delamination. This failure mode which will be caused due to interlaminar stresses, will happen at the secondary matrix/rod interface. It is expected that these interlaminar joints will be the weakest parts of a composite thanks to the mechanical properties mismatch of the matrix and rod. Therefore those locations are expected to be locations of crack initiation and propagation [48].

4 Materials Used for Manufacturing of Twin Matrix Composites

This chapter introduces the components that will be used to create TMC samples. These components are the composites rods which will be discussed in section 4.1 and the secondary matrix which will be discussed in section 4.2.

4.1. Composite Rods

The composite rods were purchased from a company called van Dijk Pultrusion Products (DPP) [1]. This company specialises in producing composite rod with different dimensions and profiles. It is interesting to mention the micro-pultrusions of Callens' [7] study were also provided by this company. The main reason for purchasing the rods from this manufacturer is that they claim their rods have exceptional resistance against acidic attacks and can maintain their integrity throughout thermal and chemical procedures. The matrix within this pultrusion is a high performance Bisphenol A Anhydride three component[2] epoxy system. It is suspected that because of using anhydride as a curing agent, these rods are resistant against chemical attacks [19]. The fiber filaments are TF700 (or a very similar carbon fiber according to DPP). Figure 4.1 represents a picture of these rods.

Figure 4.1: Two composite rods which will be used to create TMC samples

The pultrusions have the following the mechanical properties [3]:

[1] `https://www.dpp-pultrusion.com/en/`

[2] "Three Component" in this case means that in addition to the resin and the hardener, there is another component used in the production of the matrix of these rods. It is not specified by the manufacturer however what this tertiary component is.

[3] This list was obtained through contacting the company directly (https://www.dpp-pultrusion.com/en/contact/)

Property	Value	Unit
Fiber volume	63	%
Tensile strength	2500	MPa
Tensile modulus	140	GPa
Compression strength	1600	MPa
Ultimate tensile elongation	2	%
Glass Transition Temperature	120	^oC

Table 4.1: List of mechanical properties of pultruded rods provided by the DPP company

According to the manufacturer, the width and thickness of the used composite rods are 3.60 and 0.60 mm respectively. To be more precise, the length and width of the rod are 3.65-3.69 and 0.65-0.69 mm according to the measurements of the student (with a calliper).
While it was possible for the rod manufacturer to produce rods with different widths or thicknesses, it was decided to go with the 3.6 x 0.6 mm rods as they were the only ones available and making new rods with new dimensions would add costs and time. Also, remember that this thesis study does not focus on the variation of rod dimensions or the optimum dimensions and therefore, it was decided not to spend anymore thought or time on selecting any other dimensions. It is decided to have rods with rectangular (or strip like) cross sections as they lead to a BAM structure which has all the advantages discussed in appendix A.

4.2. Secondary Matrix

The secondary matrix is a bio-based epoxy matrix commercially known as Polar Bear [9]. The manufacturer of this epoxy system is a Spanish company called R∗Concept [4]. This resin system is based on the recyclamine technology (see section 2.2). It is worth mentioning that several papers that have been mentioned in the literature study so far have also used the epoxy system offered by this company [10] [15]. While this epoxy system is made specifically for compression moulding process, it is still an ideal matrix considering the manufacturing set up.
The mixing ratio for this resin system is 46:100 (this is a mass based ratio). Once the resin and the hardener are mixed, the pot life is 25 minutes at room temperature (25 ^0C). However, an assumption regarding this pot life time is that the mass of resin and the hardener together is 100 gr. If the total mass of resin and hardener is less than 100 gr, then the pot life will be longer than 25 minutes. Furthermore according to the manufacturer, the post curing temperature is 85 ^oC and its duration should be 15 minutes. That being said, after having several conversations with the manufacturer of the secondary resin system, it was understood that it is possible that with longer curing and at a higher temperature, one can reach the highest mechanical properties (in terms of strength and modulus) this epoxy system can offer. More specifically if one wishes to reach the highest mechanical properties, then it should cure the mixture first at 80^{o}C for 25 minutes and then at 140^{o}C for 4 hours. Doing so would yield the following properties:

Property	Value	Unit
Tensile Strength	65-75	MPa
Tensile Elongation	7-9	%
Tensile Modulus	2.5-3	GPa
Flexural Strength	110-130	MPa
Flexural Elongation	6-8	%
Flexural Modulus	2.8-3.2	GPa
Heat Distortion Temperature	85-95	^{o}C

Table 4.2: List of mechanical properties of the polar bear resin system cured first at 80^{o}C for 25 minutes and then at 140^{o}C for 4 hours

Later on in appendix B.1, it will be discussed that due to the lack of compatibility between the composite rods and the secondary resin as a result of (post-)curing at 140^{o}C for 4 hours, this curing cycle will not

[4]Company website: https://livingrconcept.com/

be followed. Instead, the general curing advice of the secondary resin manufacturer will be followed which is to cure the TMC at 85^{o}C for 15 minutes.
Unfortunately, no datasheet could be found that mentions any value regarding the mechanical performance of the secondary matrix cured at 85^{o}C for 15 minutes. However, it can be said that since this curing is at a lower temperature and the duration is significantly less, the degree of cross-linking is less. This leads to lower strength and modulus properties (for both tensile and flexural performance) and the same time higher elongation values (again for both tensile and flexural performance).

5

Manufacturing Recyclable Twin Matrix Composites

Given that this is a one of a kifnd composite, logically its manufacturing would also be rather unique. The manufacturing process of this thesis study is created after conducting several trial and error manufacturing sessions and improving the process along the way. This chapter represents the final preparation method of TMCs. To read about the trial and error attempts and how several manufacturing generations were made, refer to appendix B.
This chapter begins with section 5.1 which describes how the (main) mould for the TMCs has been made. One of the reasons why these TMCs are unique is because of how its reinforcing rods are placed next to and on top each other. This is thanks to the mould. Section 5.2 describes the lay-up of TMCs and explains why this lay-up has been chosen. Next, section 5.3 describes the recycling procedure that has been followed for TMCs. These initial sections are necessary as the lay the foundation for the main and last section of this chapter, section 5.4. This chapter describes the preparation schemes for all variants of TMC that will be tested and analyzed in this study.

5.1. Manufacturing the Mould For Twin Matrix Composites Via 3D Printing

Through this thesis, a few types of mould will be used depending on the type of TMC that is desired to manufacture (To know about mould types refer to section 5.4). Out of all these moulds, the most sophisticated mould is shown in figure 5.1. This mould makes it possible to align the rods next to each other in a highly organized manner and makes sure they stay in position once the secondary resin has been added. Considering the need for an accurate and precise mould, the best way to create it would be via 3D-printing. Making the mould via 3D-printing means that it should be first made as a CAD model and then sent to a printer. The CAD model is made via a software called FreeCAD [1].

[1] Information about the FreeCAD website: https://www.freecad.org/

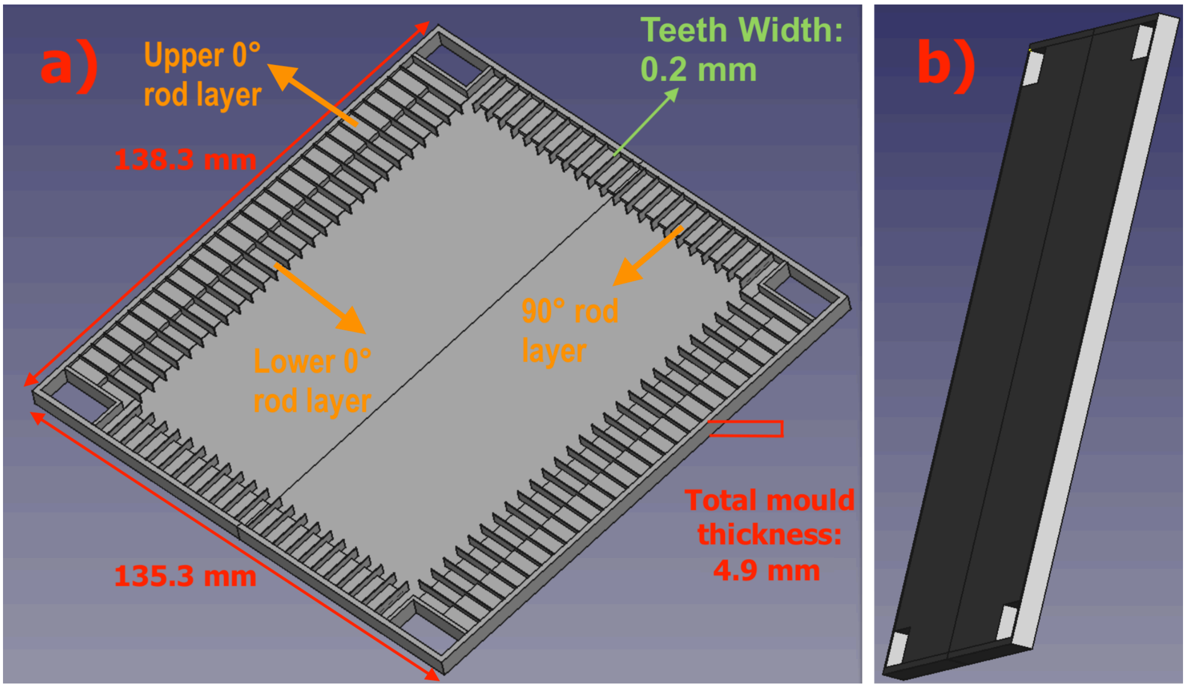

Figure 5.1: Pictures of the ultimate 3D printed mould. Figure a represents the top side upon which the TMC will be built. This figure includes the width, length and total thickness of the mould (written in red) as well as the width of its teeth (written in green). Additionally, this figure shows the orientation of the three rod layers that will be placed in this mould (written in orange). Figure b represents the rear side of this mould. A more detailed representation of this mould can also be seen in figure B.12.

This mould is equipped with 0.2 mm thick vertical walls (hereafter referred to as *teeth*) that separate the rods from each other and make sure they are at a constant horizontal distance from each other. The used 3D-printer (will be introduced shortly) has a resolution of 0.2 mm meaning that any part with lengths lower than that will be fragile, hence 0.2 mm is the limit width of the teeth. The reason for not having teeth wider than 0.2 mm is to make sure the rod volume will remain as high as possible.
Regarding the length and width of the mould (138.3 mm and 135.3 mm respectively, as shown in figure 5.1), the only limitation to these dimensions is the size of the printing bed of the 3D printer ,which is 14.5 by 14.5 cm [2]. It is decided to have the mould's length and width to be as large as possible so that as many TMC samples can be fit inside a mould.
Lastly, as figure 5.1 indicates, this mould allows for the placement of three layers of rods: At the bottom, there will be 0^o rods placed, in the middle 90^o rods will be placed and at the top, another 0^o rods will be placed. This yields a $0^o/90^o/0^o$ lay-up order for the resultant TMC (The reason for this lay-up selection will be mentioned in subsection 5.2).
For more information about the mould design and how it has been developed and optimized through out this study, refer to appendix B.

Selecting 3D Printing Features

Another matter worth mentioning is which 3D printing procedure has been selected to create these moulds. There exist several types of 3D printing such as Stereo-lithography printing (SLA), Selective laser sintering (SLS) or Fused deposition modelling (FDM). Since the mould of this thesis study requires a high resolution and detailing, SLA is chosen as it is the front-runner for this matter.
After selecting the printer type, the resin to create the mould should be selected. The available resins are Clear V4 [3] and Rigid 4000 [4]. After trial & error attempts with these resins, it was decided to go with the Clear V4 resin. That is because the mould made with the Clear V4 has a lesser amount of shrinkage and has a better compatibility with the release agent during the manufacturing of the TMC. Another advantage of the Clear V4 resin over the Rigid 4000 resin is that the Clear V4 resin is slightly

[2] Information about the print dimensions of the Form 3 printer: https://support.formlabs.com/s/article/What-is-the-build-volume-of-the-Form-2-and-Form-3
[3] Infromation about the Clear V4 resin `https://formlabs.com/store/materials/clear-resin/`
[4] Information about the Rigid 4000 resin`https://formlabs.com/store/materials/rigid-resin/`

less brittle for parts that are thin (such as the 2 mm thick teeth). The moulds printed with Clear V4 have proven to be stiff enough and maintain their integrity during the TMC manufacturing stages.
Once the mould is printed, it must be washed with isopropanol (for about 45 minutes) and then dried with a blower. Once dried, the next step is to cure it. It is decided to cure the mould only via UV. It is also possible to apply heat during the curing stage however it has been observed that curing only with UV leads to the least amount of mould shrinkage.

5.2. Lay-up Orientation of Twin Matrix Composite Samples

The lay-up of any composite is a function of several parameters such as its expected mechanical performance in a structure. Since this thesis study focuses more on the introduction of TMCs, its material and manufacturing perspectives will be dominant over how it will behave in a specific structural application when it comes to determining the layup order.
It is decided to have a 0^o - 90^o lay-up since for the ILSS testing, the difference in stiffness between these two orientations is the most. Since the specimens are flat plates, a symmetrical lay-up is preferred. Therefore a $0^o/90^o/0^o$ is selected.
A worthy note to make is whether it would be possible to add another angle (for example $\pm45^o$) to this lay-up. The challenge is that per each opposing sides of the mould, only one orientation can be put. So for instance, as can be seen in figure 5.1, two opposing sides are responsible for the 0^o direction and the other pair is responsible for the 90^o direction. If another orientation - for example $\pm45^o$- is added, one of the sides must be then updated. This is possible only by adding $\pm45^o$-oriented teeth on top, below or between 0^o or 90^o rods. Given how narrow and fragile each tooth is, doing so would add significant difficulties and risks to the current mould. Therefore it is concluded that with the current mould design, it is possible to have at most 2 orientations.

Regarding the number of layers, considering the thickness of rods and that there will be additional secondary resin around each layer, having three rod layers leads to a sufficient thickness of TMC samples. Any extra rod layers will increase the TMC thickness remarkably without adding any significant advantage. Another reason why having three layers is ideal is that the secondary resin's limited pot life (25 minutes as mentioned in section 4.2) is just enough for the hand lay-up of three layers.

5.3. Recycling Procedure Of Twin Matrix Composites

The purpose of this section is to clarify the general recycling procedure followed in this study. Just like the manufacturing stage, there are different types of recycling. However in this case there are only two recycling parts: one is recycling the TMCs and the other one is recycling only the composite rods. Fortunately, the difference between these two recycling variants is very small. In fact, the only difference is that in one case, the material to be recycled is the TMC and in the other case the material to be recycled is the rods. Further detailed information about the recycling variants will be mentioned in section 5.4.
Before mentioning the recycling steps, the safety measures must be pointed out. One is that the recycling shall occur in a fume hood. Also wear gloves, protective glasses and a lab coat and make sure there is a container into which the acidic waste can be disposed.
Now it is time to list the required components/devices. One is the acetic acid. The acetic acid used for this study is a Honeywell Acetic Acid (as shown in 5.2a). Another required fluid is Silicone oil (shown in figure 5.2b). The silicone oil used for this recycling step is manufactured by the company of Sigma-Aldrich. The last required liquid to mention is distilled water.
Regarding the testing equipment, 2 beakers are needed. The size of these beakers depends on the size of the specimens. One of these beakers will be the one that will contain the TMC and the acetic acid. Therefore make sure that this beaker will have sufficient length and width to contain them and there is no chance of spilling. The other beaker will be used to contain the first beaker, so it must have a higher radius than the beaker with acid in it.
The next equipment to mention is the magnetic stirring set (shown in figure 5.2c). This set consists of the magnetic stirrer which is also equipped with a thermometer mounted on top of the stirrer. Additionally, stirring magnet(s) are needed to stir the acidic solution.

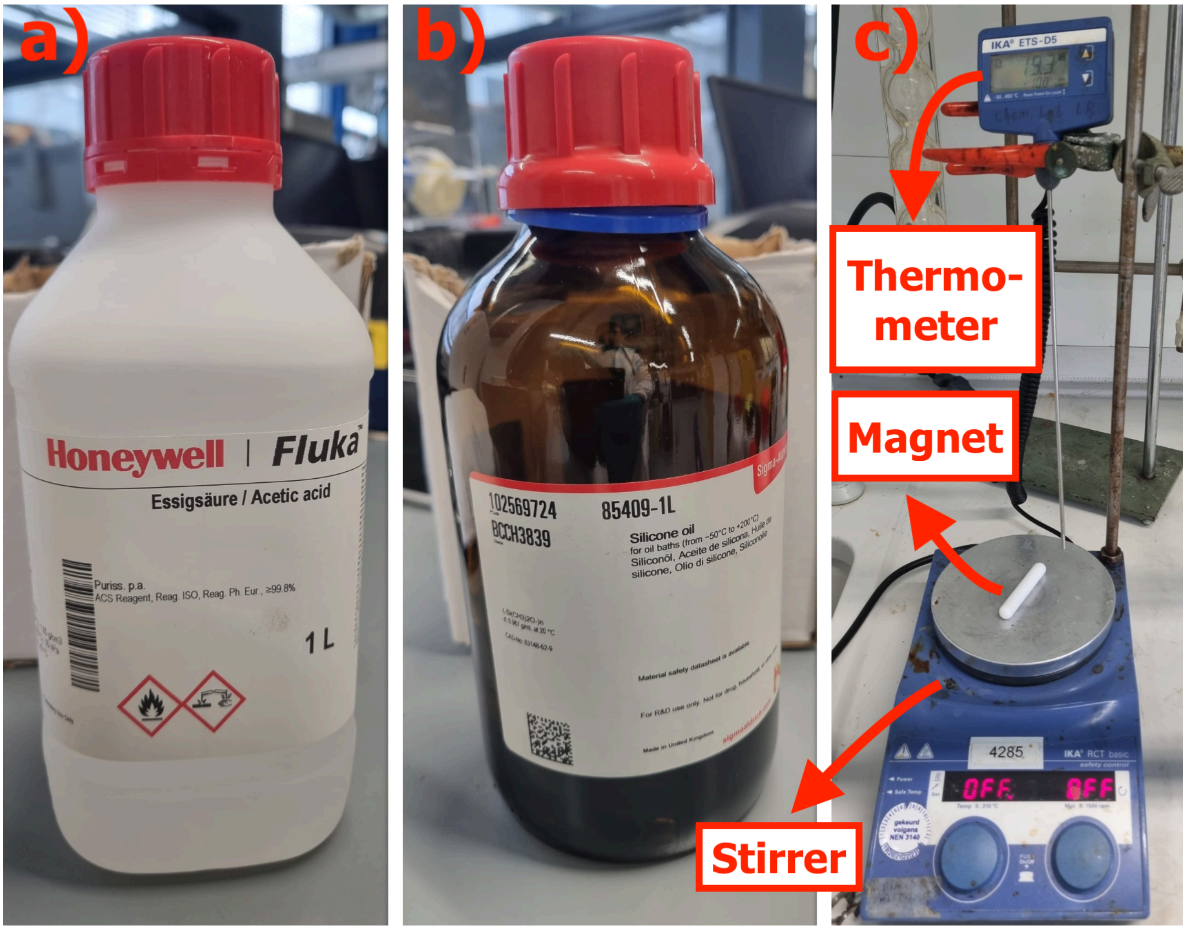

Figure 5.2: Pictures of the recycling equipment used: Figure a displays the acetic acid used, Figure b displays the silicone oil used and the Figure C Displays the components used for the stirring stage. In the later figure, the magnetic stirrer, stirring magnet and the thermometer can be seen.

Now that the equipment have been mentioned, it is time to describe the recycling procedure. Fill the wider beaker with silicone oil. Then fill in the smaller beaker with distilled water and acetic acid such that the resultant acidic solution will have a 50% concentration. Put the beaker with silicone oil on top of the stirrer and then the beaker with acidic solution inside the beaker with silicone oil.

The next step is to put the magnetic stirring bar and the composite inside the acidic solution. After that put the thermometer of the magnetic stirrer inside the oil bath. The job of this thermometer is to create a feedback loop for the stirrer to heat up the solution based on the temperature readings of the thermometer.

To have a better understanding of the recycling set-up, figure 5.3 has been made. Now that all components are in their position, it is time to start the recycling procedure. Set the stirring speed to 200 rpm and the stirring temperature to 90^{o}C.

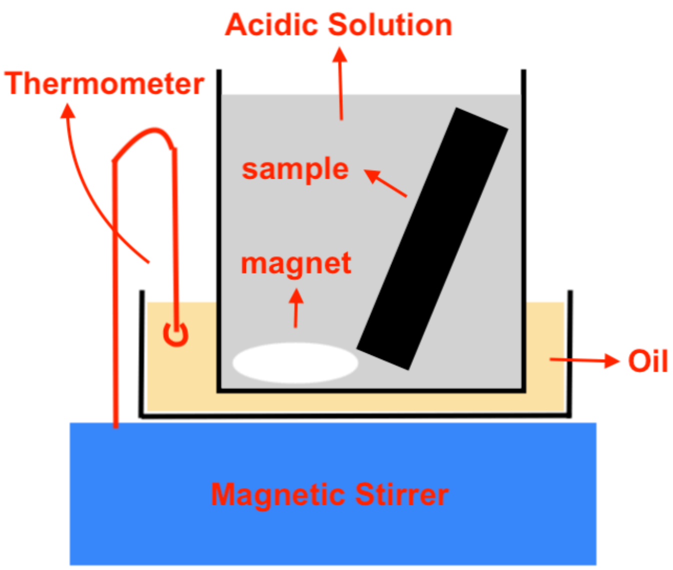

Figure 5.3: Sketch of the recycling set up of TMC or individual rods

If the sample to be recycled is the TMC, then obviously the secondary resin must be dissolved in order for the acid to interact with the rods. Once there is no sign of the secondary resin in the acidic solution, wait for the reaction to go on for another 2.5 hours. To have a good monitoring of whether all the secondary resin has been dissolved, it is recommended to pick out individual rods from the solution every now and then and observe if there are still any secondary resin attached to them. Figure 5.4 shows an example of a rod that still has secondary resin attached to it. It must be ensured that there is no more secondary resin attached to the rods; only after then the 2.5 hour period of recycling only the rods is counted and considered. Once this 2.5 hour period is finished, take out the rods with a tweezers and lay them to dry out.

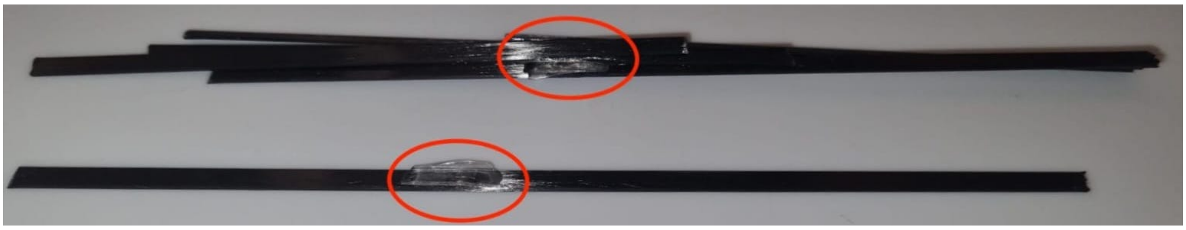

Figure 5.4: Recycled rods which still have secondary resin attached to them. The rod bunch on the upper side are still connected to each other because they are still via the secondary resin and the individual rod at the bottom still has secondary resin attached to it.

If the components to be recycled are the composite rods, then the recycling procedure will be shorter as there is no secondary resin to be broken. In that case, once the solution temperature reaches 90^0C, let it run for 2.5h and then the rods can be taken out with tweezers and laid next to each other.

Irrespective of the recycling variant, once the rods have been taken out from the acidic solution and are laid out, they should be dried with a cloth. Often towards the end of the recycling stage, several fibers (from the rods) are roaming around in the acidic solution, as shown in figure 5.5. These fibers are likely to stick to the rods' surface. Therefore it is necessary to use a cloth to make sure the rod surfaces are free from any fiber.

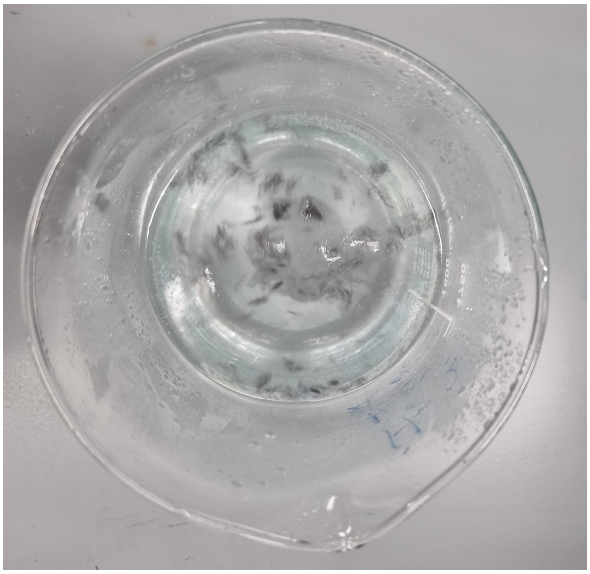

Figure 5.5: Top view of the acidic solution after the rods have been taken out. As can be seen in this solution, there are clouds of black fiber floating in the solution.

5.4. Preparation Of Twin Matrix Composite Samples

In this section the manufacturing steps of TMCs are discussed. Since there are different types of TMCs made in this thesis study, the manufacturing of each of them will be explained separately in the following subsections. In subsection 5.4.1, it is explained how TMC samples that are made from unrecycled rods are manufactured. Once these samples are made, they are ready for the ILSS testing. Next, subsection 5.4.2 describes the manufacturing of TMC samples that have been from one-time-recycled rods. Once made, these TMCs will also be tested. After that, in subsection 5.4.3 it is explained how the samples for the SEM, water contact angle and weight measurement analysis are prepared. Lastly, subsection 5.4.4 describes the production of TMCs that are made from four-times-recycled rods. As the initial two subsections, these TMCs are also to be tested after they are made.
Furthermore, in appendix B it is explained how the manufacturing procedure was developed and modified throughout this thesis study.

5.4.1. Preparation Of Samples With Unrecycled Rods

The first step to creating TMC samples that have been never recycled is to obtain their rods. In order to know about the lengths and quantity of these rods, it must be stated that the 3D printed mould (shown in figure 5.1) will be used. This mould will fit in 27 rods that are in the 0^o direction, 22 rods that are in the 90^o direction and lastly 27 rods that are oriented in 0^o direction and will be placed on top. The length of bottom layer rods (which will be in 0^o direction) shall be 110 $\pm$3 mm. The length of middle layer rods (which will be in 90^o direction) shall be 128 $\pm$3 mm. The length of top layer rods (which will be in 0^o direction) shall be also 128 $\pm$3 mm.

Once the rods are cut to the desired lengths, it is time to trim their edges so that they will fit in between the teeth of the mould. Experience has shown that not doing so will lead to a bad grip between the teeth and the rod and therefore, the rod will be tilted. Thus, the ends of each rod shall be trimmed as shown in figure 5.6. Once the rod edges have been trimmed and it is ensured they fit in their position in the mould, it is time to obtain an aluminium plate upon which the 3D-printed mould can stand. This mould is necessary as any extra secondary resin that will flow out of the 3D printed, will land there. In other words, this aluminium plate is necessary to make sure the secondary resin will not get on any other surface. The recommended dimensions of this plate are 400 x 400 cm.

Figure 5.6: A representation of ends of rods which must be trimmed so that they will fit within the teeth of the 3D printed mould.

The next item to get is a Teflon plate. This teflon plate will be placed on top of the TMC during the curing stage. The job of this plate is to apply a homogeneous pressure distribution on the upper surface of the TMC during the curing stage so that the resultant TMC will be as compact as possible and any excess secondary resin will be flown out. In terms of dimensions, the teflon plate should not be much larger than the mould. Given that the total length and width of the mould is 138.3 x 135.3 mm, the recommended dimension of the plate is about 160 x 160 mm.
The next step is to cleanse the rods, 3D printed mould, the aluminium and teflon plate with acetone. Acetone can be applied onto these surfaces with either a cloth or a (painting) brush. The next step is to apply a releasing agent on the 3D-printed mould, aluminium plate and teflon plate. The release agent selected for this work is Marbocoat 277 CEE [5]. Apply three layers of marbocote to these surfaces to ensure the easy release of the TMC batch.
Now it is time to start preparing the secondary resin solution. The first step is to warm up the epoxy resin component by putting it in a bucket of hot water (temperature around 75 ^{o}C) for about 40 minutes. The purpose of doing so is to break down any crystal blocks in the epoxy resin that could have been formed due to long storage times. If the hardener is mixed with an epoxy resin that has crystal blocks, the expected reaction will not happen as there will be fewer resin molecules available. This will lead further to the creation of voids in the resultant epoxy [13]. Once the resin component has been warmed up, the 75 gr of this resin shall be poured into a cup, which will be later put in the speed mixer (this device will be introduced soon). Once the specified amount of resin is poured into the cup, let it cool down to room temperature. Meanwhile, pour the hardener solution into another cup to the specified amount. This amount can be calculated by knowing the mass of the resin system and following the 100:46 ratio.
The next step is to mix the resin and the hardener together. Pour the obtained hardener into the cup with resin. Once the hardener is with the resin, mix these two with a wooden stick for about 2 minutes. Then put the resultant mixture into the Speedmixer. Mixing the hardener and the resin inside the speedmixer is an essential step as it not only ensures a sufficient mixing of these two components, but the fact that this mixing happens in an environment with a really low pressure leads to the removal of voids inside the solution. The name of the speedmixer used for this thesis study is DAC 400.2 VAC-P

[5] More information about this releasing agent: https://www.jacomp.fi/wp-content/uploads/2017/12/marbocote-227-v6.pdf

LR and is shown in figure 5.7a. The mixing program of this device is shown in figure 5.7b. As can be seen in that picture, this step will take about 7 and half minutes and the pressure drops to 40 mbar throughout the entire process. It can also be seen that mixing speed hovers around 1100 rounds per minute.

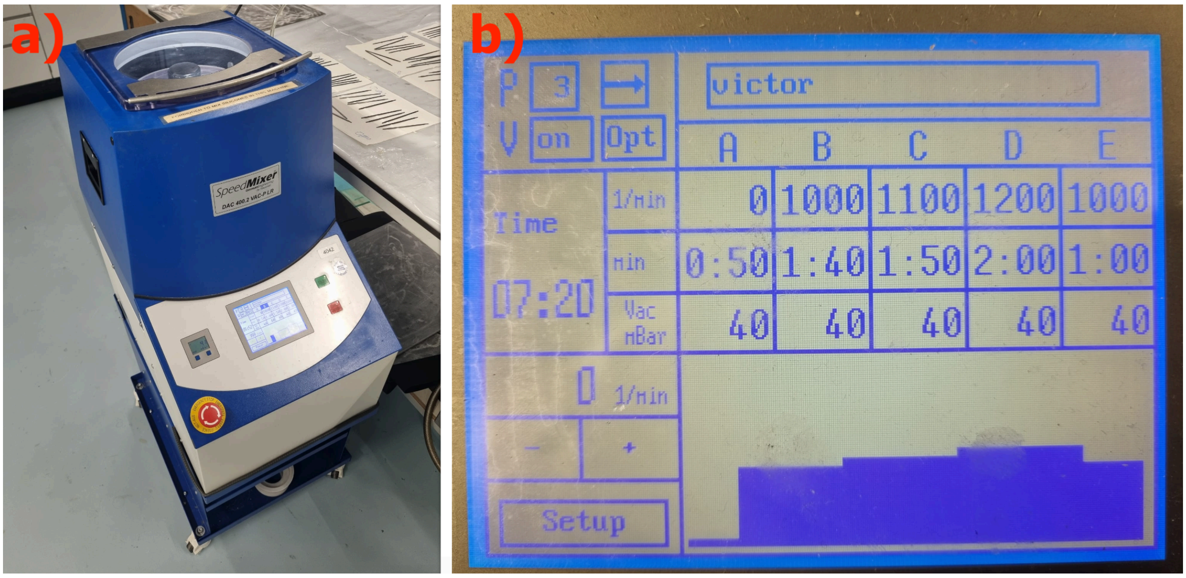

Figure 5.7: Speedmixer pictures: Figure a represents the machine itself (DAC 400.2 VAC-P LR) and Figure b represents the mixing program

Once the speed-mixing step is done, take out the secondary resin solution from the speedmixer. This cup is rather warm which increases the curing rate of the secondary matrix. Thus it is recommended to put the cup in a bucket of cold water so it cools down which increases the processing time of the secondary matrix. Then the secondary resin is ready to be used to create the TMC.

Now it is time to start making the TMC. Note this must happen as soon as the secondary resin is ready to be used. First, put the 3D-printed mould on top of the aluminium plate. Next, pour some of the secondary resin inside the 3D printer until all of its (inside) surface is covered with the resin. Once that is done, it is time to put the first layer of rods. These would be the 110 $\pm$ 3 mm rods that will be placed in the 0^o direction. Once these rods have been placed in their positions, apply more secondary resin until all of the first layers are covered. Push these first layer rods down (with fingers) into the 3D printed mould to make sure that the bottom most secondary resin layer is not unnecessarily thick. It preferred to push the rods down at their ends because once the pushing force is removed, the rods could bounce back upwards and that could leave a void in secondary resin.
Now it is time to put the 128 $\pm$ 3 mm rods in their 90 ^{o} direction. Again, once these rods are put in their position, apply the secondary resin until the rods are fully covered. Then push the 90 ^{o} rods inside.
It is time for the last layer of rods, the 128 $\pm$ 3 mm rods in their 0 ^{o} direction. Once these rods are in their position, apply the secondary resin and then push the rods inside. Make sure enough secondary resin is applied at the top so that its level will be higher than the mould's top side. Doing so should result in figure 5.8a.
Now it is time to put the teflon plate on top. This will cause any extra secondary resin that could make the composite thicker than the intended thickness to flow out. Figure 5.8b shows the set-up once this step has been done. It is advised to put small amounts of weight on top of the teflon, to make sure the pressure is applied as well as possible. The maximum mass (thus the teflon mass + mass of the weights) that has been tried in this thesis study is 3.5 kg and no defects due to excessive mass (such as bending of the teflon plate) have been detected.

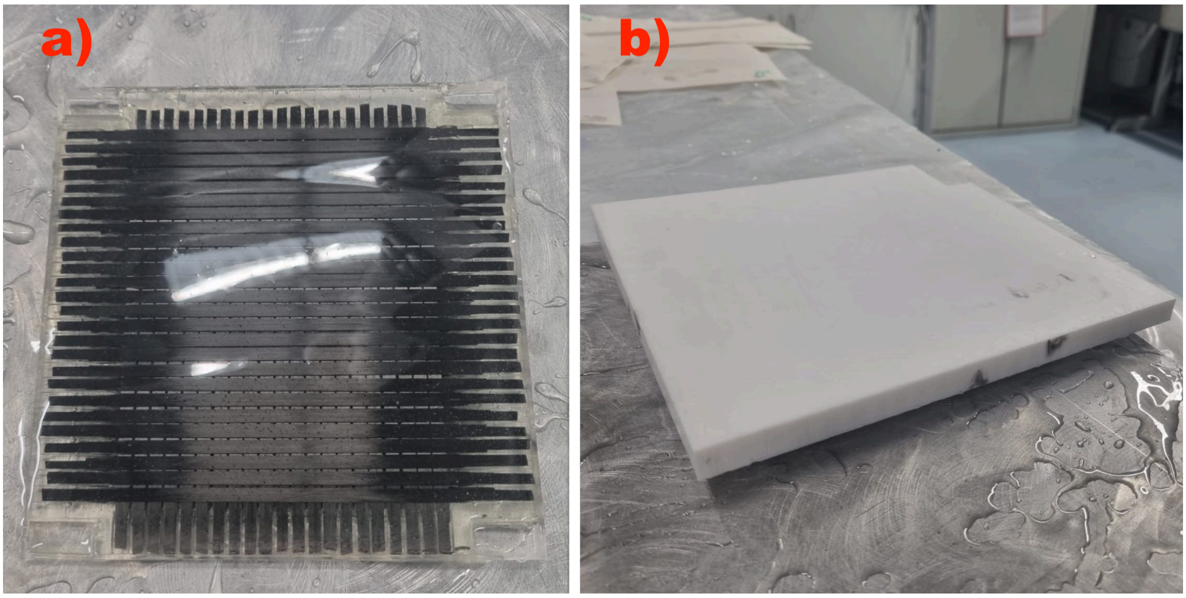

Figure 5.8: Figure a represents the TMC seconds after the last layer of secondary resin been applied. Figure b represents the set up after the teflon plate has been placed on the top of the TMC and the mould.

From now on, the curing process starts. Based on student's experience, the gel time of this composite is more than 5 hours. Therefore it is recommended to let the TMC cure at room temperature until the next day, which means that the given time for curing will be about 20 hours.
After curing, it is time for post-curing. For this step, the recipe of the manufacturer of the secondary matrix is followed and thus it is decided to post-cure the TMC for 15 minutes at 85^{o}C. The post-curing cycle for this TMC is shown in figure 5.9. As that figure shows both the warming up prior to the post-curing and the cooling down stage take a long time with respect to the actual post-curing duration. Such long durations are chosen so there will be no thermal shock introduced to the components inside the oven.

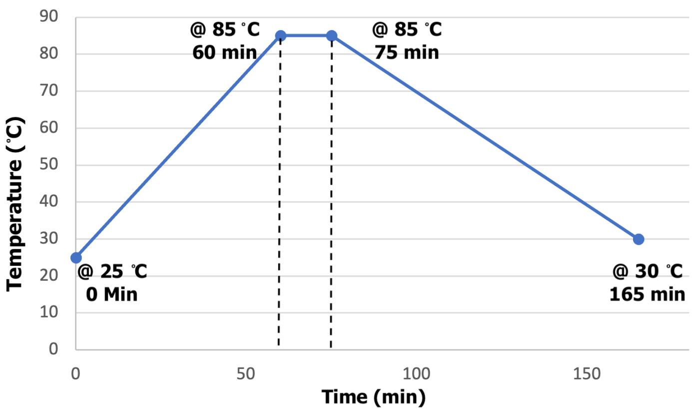

Figure 5.9: Post-curing cycle of the TMC

Once the post-curing stage is done, it is time for the demoulding. Thanks to the Marbocote, it should be easy to separate the teflon plate from the top side of the TMC. Similarly, it should be easy to separate the 3D printed mould from the aluminium plate. The only two components that will not be separated from each other is the TMC and the 3D printed mould. To separate these two, a diamond cutter is used to cut the TMC out of 3D printed mould. This machine is used to cut through the 3D printed mould with the desired TMC inside it in 4 lines; as shown in figure 5.10a. Once that is done, a TMC plate can be obtained.

While the above mentioned cutting was necessary to separate the TMC plate from the 3D printed mould, it is time for another cutting; this time its purpose is to cut the plate down to desired samples. To know the the dimensions of the samples, refer to subsection 6.4.1. Figure 5.10b represents a scheme on a TMC plate based on which the samples will be cut.
In order for the TMC samples to have the most similar rod volume, it is decided to make sure that the starting point for each sample will be similar. More specifically for all TMC samples, the cutting starts from the intersection of secondary resin boundary lines that are between the rods. Examples of these starting points are shown in figure 5.10b with light blue dots. Therefore, since the starting cutting point is similar for all samples as well as the sample dimensions, it can be expected that their rod volume will be similar as well.

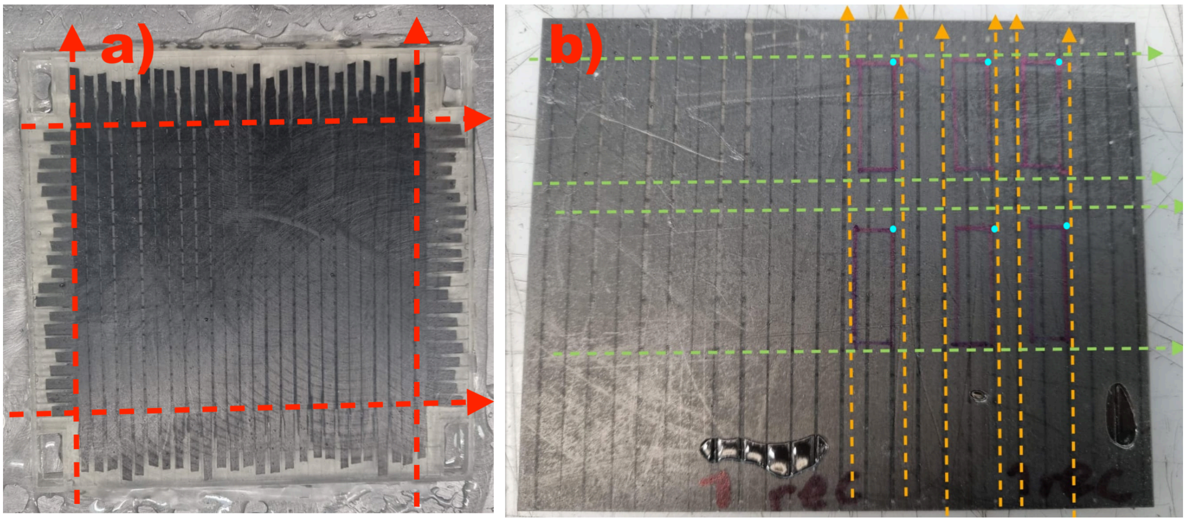

Figure 5.10: Cutting Plans of the TMC. Figure a represents the cutting plan for the first cutting, which aims to separate the TMC from the 3D printed mould. Figure b represents the cutting scheme to obtain the samples. The samples (marked with dark blue colour) lie between the cutting axes (shown with green and orange dashed lines). The light blue dots represent the starting points for each sketch, meaning that the lengths and widths of each sample starts measuring from there.

Once the sample sketches have been drawn, the next step is to use above mentioned second diamond cutter. The name of the cutter machine used for this purpose is Proth. This cutter is used to cut the TMC plate into samples that are to be tested.

5.4.2. Preparation of Samples With Once-Recycled Rods

The point of having these samples is to see how differently a TMC made with one time recycled rods performs with respect to the TMC with unrecycled rods. The composite of this subsection is to be made once, recycled, to be built once again and then tested.
The beginning of this manufacturing is same as the manufacturing of the TMC with unrecycled rods (subsection 5.4.1): Get 27 rods that will be placed in the 0^o direction (bottom layer), 22 rods that will be placed in the 90^o direction (middle layer) and lastly 27 rods that will be oriented in 0^o direction (top layer). Then same as the previous manufacturing, these rods will have to be trimmed in order for them to fit in the 3D printed mould.
Now it is time to create a TMC with these rods that is to be recycled. Because it will be first recycled once its made, TMC's quality will not be important. Therefore steps such as warming the epoxy resin, using the speedmixer or using the 3D printed mould will not be necessary to create this TMC for now. It is after recycling that these steps become essential.
Get the aluminium plate upon which the TMC will be built. Then get four wooden sticks which will be used to form a mould (example wooden sticks can be seen in figure 5.11). Now it is time to cut the wooden sticks so that they can form a mould with the desired dimension. Two requirements affect these dimensions. One is that is must fit the rods (so the length of the mould should be more than 130 mm) and the other one is that the resultant TMC should be able to fit in the beakers during the recycling stage. On this basis, the recommended mould size is 150 x 50 mm.

The next step is to cleanse the wooden sticks and aluminium plate with acetone. After that, it is time to treat them with Marbocote. The next step is to prepare the secondary matrix; for that the instructions given in subsection 5.4.1 can be followed. Note this time it is not necessary to use a speed mixer because the having voids will not be an issue for a TMC sample that is to be recycled.
Once the secondary resin mixture is made, take a painting brush and apply some of this secondary resin inside the wooden mould. Do that until the surface is covered with secondary resin. Now put the rods inside the mould and lay them up next to each other. Note it is not important how well organized these rods are next to each other because the resultant TMC will be recycled anyways.
Every time a layer of rods has been laid, apply more secondary resin. Do that until there are no more rods and the top side is filled with secondary resin. Once that has been done, the resultant set up should look like figure 5.11

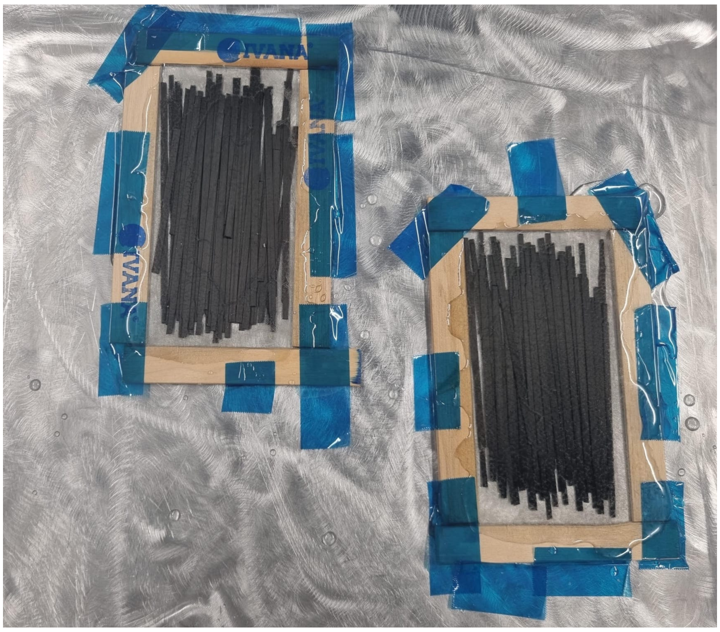

Figure 5.11: Set up of the TMC made to be recycled and then to be made again and then tested.

Now it is time for curing and post-curing. For both of these stages the curing instructions of subsection 5.4.1 can be followed as well. Once the curing stage is done, it is time for demoulding. This should be easy thanks to the releasing agent. That means that the resultant TMC must be separated from the wooden sticks and the aluminium plate.
Now it is time to recycle the TMC. This procedure has been already explained in section 5.3. Once the recycling has finished and the rods are taken out with tweezers and dried up, they can be used again to create a TMC which will be tested. That means that this time the quality of TMC matters. This implies that from this point onwards, to create this TMC the entire manufacturing plan described in subsection 5.4.1 should be followed. In other words, with these recycled rods and the manufacturing plan of subsection 5.4.1, the TMC of this stage should be built.

5.4.3. Preparation of Samples For Scanning Electron Microscopy, Water Contact Angle Measurements and Weighing Analysis

The purpose of this subsection is to describe the preparation of rods that will be used for SEM, water contact analysis and weight measurement of the rods. As mentioned in section 3.2, the samples to perform these studies are rods that have never been recycled or have been recycled once, twice, three times and four times.
First obtain 8 rods, each with a length of approximately 80 mm. Additionally, obtain another rod that has a length of 50 mm. The 80 mm rods will be used for the SEM and Water Contact Angle analysis and the 50 mm rod will be used for the weight measurement analysis. Unlike the rods of subsections 5.4.1 and 5.4.2, these rods do not need any trimming at their edges. To create the first TMC from these

rods, follow the instructions of the first half of subsection 5.4.2 until the point where the recycled rods have been extracted out of the acidic solution.
Once the first recycling is done, take out 2 rods. These 2 rods will be used to perform SEM and water contact angle. Also, take out the 50 mm rod and measure its weight (for the weighing procedure, refer to subsection 6.3). Once that is done, bring it back to the remaining rods.
With the remaining rods, do this process all over again. So make the composite using wooden sticks and an aluminum plate. Cure and post-cure the resultant TMC. Demould it and then recycle it. Then take out 2 more rods and classify them as rods that have been recycled twice for the SEM and water contact angle analysis. Then, measure the weight of the 50 mm rod and then bring it back to the remaining rods.
Repeat this process two more times until rods that have been recycled 3 and 4 times have also been obtained. That means that by the end of this manufacturing routine, there will be 4 sets of recycled rods. Each of these sets will have at 2 samples and each set will be different from each other in terms of the number of times it has been recycled. Another outcome of this manufacturing will be the 50 cm rod that has been recycled 4 times has its weight recorded after each recycling.

5.4.4. Preparation Of Samples With 4 times Recycled Rods

The TMCs manufactured in this subsection will be used to show how does a TMC with rods that have recycled 4 times compare to other variants of TMC. As the title suggests, what makes these TMCs unique is the fact that its rods have been recycled 4 times. However, an important note to make is that this means the rods are treated 4 times with acid; not that they have been used 4 times to create TMCs and then recycled each time. The reason for not making a TMC 4 times by recycling its rods between each manufacturing session is that it takes a lot more time than treating the rods 4 times with acid only.
The rods of this subsection should be prepared in the same way as subsection 5.4.1 and 5.4.2. That means that 27 rods with the length of 110 $\pm$3 mm (these will be placed in the bottom layer in 0^o direction), 22 rods with the length of 130 $\pm$3 mm (these will be placed in the middle layer in 90^o direction) and 27 rods with the length of 130 $\pm$3 mm (these will be placed in the top layer in 0^o direction). The edges of these rods should then be trimmed (as shown in figure 5.6).
The next stage is to treat these rods with acetic acid 4 times. Prepare the acidic solution (as prescribed in section 5.3). Drop the rods in the acidic solution and let the recycling process go on for 2.5 hours once the acidic solution reaches 90^oC. Once that is finished and the rods are taken out by tweezers, give them 30 minutes to dry out. Meanwhile, renew the acidic solution so that it will be ready for the next treatment for rods.
Once the rods have been dried up, drop them in the new acidic solution and repeat the acidic treatment of 2.5 hours at 90^oC. Then take them out and let them dry for about 30 minutes while renewing the acidic solution. Once that is done, repeat this acidic treatment step 2 more times so that at the end, all rods have been treated with acetic acid 4 times.
The next step is to manufacture the TMC with these rods. Since this TMC will be mechanically tested, its quality is important. Therefore from this point onwards, it will have the same manufacturing procedure as described in subsection 5.4.1; the only difference will be that in this case instead of unrecycled rods, rods that have been 4 times recycled will be used.

6

Testing Re-usable Twin Matrix Composites

This chapter introduces testing and analyzing procedures that will be carried out to gather desired information about TMCs and whether they will be affected by recycling. This chapter starts with section 6.1 describing the set up and the measurement plan for the SEM analysis. Section 6.2 which describes the same thing, but for the water contact angle measurement. After that, section 6.3 describes the set up which will be used to understand how recycling affects the weight of a rod. Lastly, section 6.4 introduces the ILSS set-up and all the steps to obtain meaningful and constructive data to understand interlaminar strength of TMCs and whether they will be affected by recycling.

6.1. Scanning Electron Microscopy

The purpose of this section is to describe the SEM set-up which aims to understand recycling's effect on rod surfaces. In total, there are 5 sets of rods that will be analyzed via SEM analysis: the unrecycled rods, one time recycled, two times recycled, three times recycled and four times recycled rods.

From each set, take a rod which will be used the perform the SEM analysis. Cut this rod into smaller samples that will fit in the sample holder of SEM. That length can be at most 2 cm, so cut the sample for a length of around of 1.5 cm. The next step is to apply a gold coating on top of the sample. The purpose of doing so is to make the rod's surface conductive which further enhances the reflection of secondary electrons from this surface [40]. Figure 6.1 shows a gold-coated sample placed in sample holder, ready to be put into the SEM machine.

The name of the SEM machine is JSM-7500F and the name of the gold coating machine is Quorum Q300t D. There are several SEM modes available, however the best one would be SEI (In-lens upper secondary electron detector), as this is the mode used to study the surface morphology of composites [18].

Figure 6.1: A gold coated rod sample placed on top of a sample holder. This will be then put into a SEM machine to study the rod surface

In terms the magnification, it is decided to have the same magnifications for all samples so that a fair comparison between them will be made. It is decided to have 4 magnifications per samples. The first one will be x25 which is the least magnification value and aims to show the entire rod surface. Next is magnification x75 which shows a more detailed view of the surface and points to any unique surface features (such as freckles, holes, fiber pull outs etc). Next magnification is x130 which has a more detailed view on the surface, specially the region picked out via the x75 magnification. The last magnification is x300 which is the most detailed magnification of this analysis and zooms in the regions picked out by x75 and x130 magnification.

In addition to observing any surface irregularities, each SEM analysis also aims to capture representative pictures of each rod. The results of SEM analysis can be found in section 7.1 and appendix C.

6.2. Water Contact Angle Measurements

Same as in the SEM analysis, the samples for the water contact angle analysis are obtained from the manufacturing procedure described in subsection 5.4.3. Since one of the three rods of each set has already been used for SEM, the second rod of each set can be used for water contact angle analysis. That means for this analysis, the following sets must be prepared: Unrecycled rods, one-time-recycled rods, two-times-recycled rods, three-times-recycled rods and four-times-recycled rods.
The name of the machine used for the water contact analysis is KSV Cam 200 and the corresponding software to read the measured angles is Attension Theta. To have the results comparable to other studies, the ASTM D7334 − 08 [41] is adopted as a procedure. According to this standard, the size of the water droplet must be 20 μL. However, based on the experiences of running this test, it was observed that getting an exact droplet volume of 20 μL is impossible [1]. Therefore based on several trial and error sessions and the frequency of resultant volumes, it was decided to have an accuracy of ± 5 μL.
Furthermore, the temperature and the humidity of the room are also checked to be in accordance with the standard. The water droplet can be dropped onto the rod surface via a pipette.
Regarding the sample number per each configuration, in order to have valid and trustworthy results, it was decided to have 3 readings per rod. While these 3 readings will belong to the same rod, their location along this rod will be different. For instance, one recording may be on the left side of the rod, one can be on the right side and the other one can be measured from the middle of the rod.
Before performing the analysis on each rod, treat it with alcohol so that any debris or unrelated material will be gone. Once the alcohol on the surface has been dried up, the analysis can begin. Put the rod on the sample holder of the machine and make sure the position, aperture and focus of the camera are optimum for the analysis. Now use the pipette to extract distilled water. Make sure that the droplet size of the pipette is set to 20 μL. Once the water is in the pipette, drop a droplet on the rod.
As soon as the droplet hits the rod surface, wait 20 seconds and then press record on the surface. Doing so captures a picture based on which the software will perform the analysis. Then the software should evaluate the captured picture. The results of this evaluation are the magnitudes of the left and right angles of the water droplet on the surface and the volume of the observed droplet.
The results of the water contact analysis can be found in section 7.2 and Appendix D.

6.3. Weight Measurement of Rods

Same as SEM and water contact angle analysis, weight measurements will be carried out to understand how the rods are affected by recycling. More specifically, the purpose of this analysis is to understand how the weight of a rod is affected after each recycling.
The only necessary information about the set-up of this testing is that the scale used to measure rod's weight must be up to 0.1 mg accurate and the rod's surface must be cleansed with alcohol before weight measurement. Given that there are 5 rod types (un-recycled, recycled one time, recycled two times, recycled three times and recycled four times), 5 weighing tests must be done. Note that all these tests will be carried on the same rod, so that way the only varying factor between each test will be the number of recycling trials. Regarding the preparation of this sample, the method of manufacturing has been already explained in subsection 5.4.3 (which is the same for the SEM and water contact angle measurements).

6.4. Interlaminar Shear Strength Testing

This section aims to describe the ILSS testing procedure on TMC samples as well as the outcomes of these tests followed by the post processing of these outcomes. The results of these testings and post processing will be shown later in section 7.4.

[1] the volume of the water droplet is obtained from the Attension Theta software. This software estimates the volume based on the picture it takes

6.4.1. Type of Interlaminar Shear Strength Testing

There exist several tests that can be applied to investigate the rod-secondary matrix interface strength. Examples of these tests are Short Beam shear testing, Double Cantilever Beam (DCB) testing, single fiber push-out testing [37] or tests that involve the bending of notched specimens. However because this type of TMC has never been made before and there are many uncertainties regarding the preparation possibilities of the TMC samples, it is decided to choose the test type that requires the most simple samples and yet delivers valuable information about the interface strength of the TMCs. That would be the short beam shear Testing.

The next thing to decide is the test standard for the short short beam shear testing. There are two possible test standards for short beam shear testing of composites, ASTM D2344-00 [24] and ISO 14130 [42].
The sample dimensions for both tests is based on the composite thickness. For the ASTM testing, the length must be 6 times the thickness and the width must be 2 times more. For ISO testing, the length of samples must be 10 times the thickness and the width must be 5 times it. That means that ASTM will be smaller than the ISO samples. The smaller size can be advantageous in case manufacturing steps do go not according to the plan. This has proven to happen many times during the TMC manufacturing. An examples is when a part of TMC becomes unavailable due to inadequate cutting. On the other hand, a disadvantage of smaller sizes is that handling smaller TMCs is harder than the bigger samples. The last remark worth mentioning is that While looking at studies that have performed short beam testing on composites, it was noticed that ASTM D2344-00 standard was followed more than ISO 14130.
Based on the comparison above it is decided to select ASTM D2344-00 as the testing standard; mainly because it offers more free TMC material to be used in case if some samples are damaged for whatever reason.

Figure 6.2 represents a sketch of the short beam shear testing. As it can be seen there, short beam shear testing is in essence a 3-point bending test in which the sample length is relatively small with respect to the thickness. Because of this dimension ratio, the dominant loading mode would be shear loading [24], although the role of other loading modes should not be ignored. One of these loading modes would be flexural loading which leads to tensile stresses on the lower side of the sample and compressive stresses on the upper side of the sample.

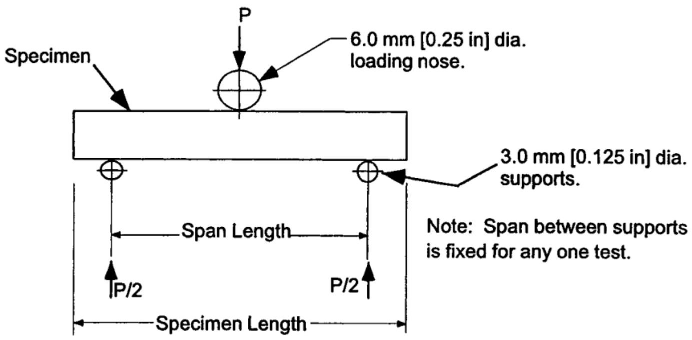

Figure 6.2: A sketch of Short Beam Shear testing which follows the ASTM D2344-00 standard [24].

Aside from the loading mode, there are other parameters that could contribute to the results of a short beam shear test. One is the thickness (or the number of plies). For example, Whitney and Browning observed that in case of 50-ply carbon fiber/epoxy composite, the composite fails due to compression close to the load application support [47]. However, while testing a 16 ply composite, they observed that the composite fails due to interlaminar shear loading at the upper quarter of the sample.
Typically during short beam shear testing, the interlaminar shear failure occurs at the upper corners, but it has been observed that this failure has also happened near halfway across the thickness of the composite. In that case, the short beam shear results are the most accurate representations of the

shear strength of the composite [39].
According to the beam theory the maximum shear stress shall occur at half way of the composite's thickness. This theory however has proven to be not applicable to most composites. Following the elasticity module proposed by Whitney and Browning, the maximum shear stress will happen at the upper half of the composite and will follow a skewed trend [47]. He expanded this conclusion by stating that the maximum shear stress during short beam shear testing is different for each point along the length of the specimen. This can be seen in figure 6.3 which shows at a location close to the loading nose (location C), a higher stress is seen than the other locations that are further from the loading nose (locations A and B).

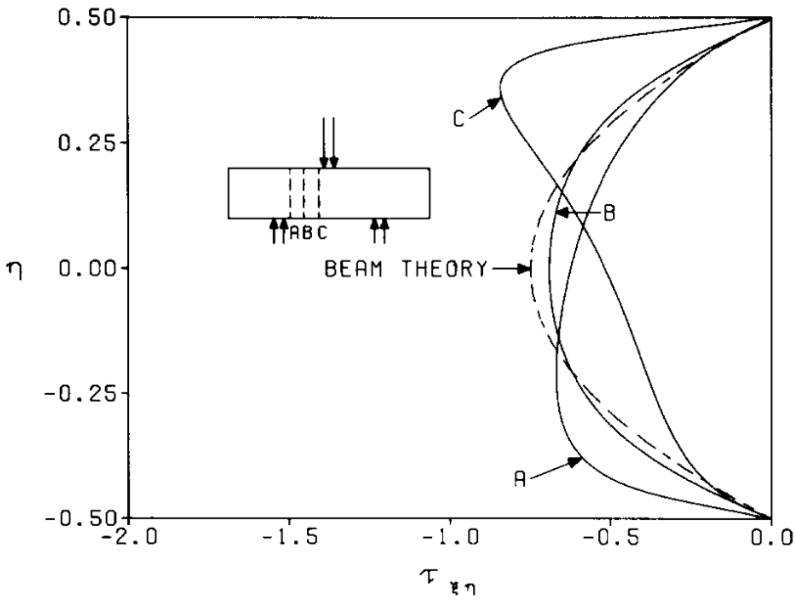

Figure 6.3: Variation of ILSS ($\tau_{\zeta\eta}$) across the thickness of the composite (η). The dashed curve represents the variation of ILSS according to the beam theory and solid lines represent the variation of ILSS according to Whitney and Browning. Curve C represents the ILSS recorded at a location close to the loading nose, curve A represents the ILSS recorded at a location close to the support nose and curve B represents the ILSS recorded at a location between locations A and C [47].

Now that a few theoretical considerations about composite failure in short beam shear testing have been mentioned, it is time to describe further details about this test. The span length should be 4 times the thickness. The diameter of the loading nose should be 6 mm and the diameter of the support noses should be 3 mm. The testing speed should be 1 mm/min (this is the speed at which the loading nose comes downward). According to the standard, there must be at least 5 samples for each configuration of samples. Therefore, there will be 5 samples with unrecycled rods, 5 samples with one-time recycled rods and 5 samples with four-times recycled rod.

6.4.2. Equipment For Interlaminar Shear Strength Testing

First and foremost, the set-up should include the 3-point bending fixture prescribed in subsection 6.4.1. Make sure all components of the fixture are set up accurate and firmly. The name of the software that is linked with this set-up and records data is TestExpert II and is from ZwickRoell, which is the manufacturer of this test set up machinery [2]. Use a caliper to make sure all lengths such as the span length or the distance between the sample edges of the supports are accurate.
Additionally, a camera will be used that will take pictures of each test every second. These pictures can provide valuable confirmation of the order of test events, for instance, what fracture modes are present in the failure of the TMC samples. Figure 6.4 shows a sample picture of a TMC specimen taken before

[2]Link to the website of the TestXpert II of ZwickRoell: `https://www.zwickroell.com/accessories/testxpert-testing-software/`

the ILSS starts.

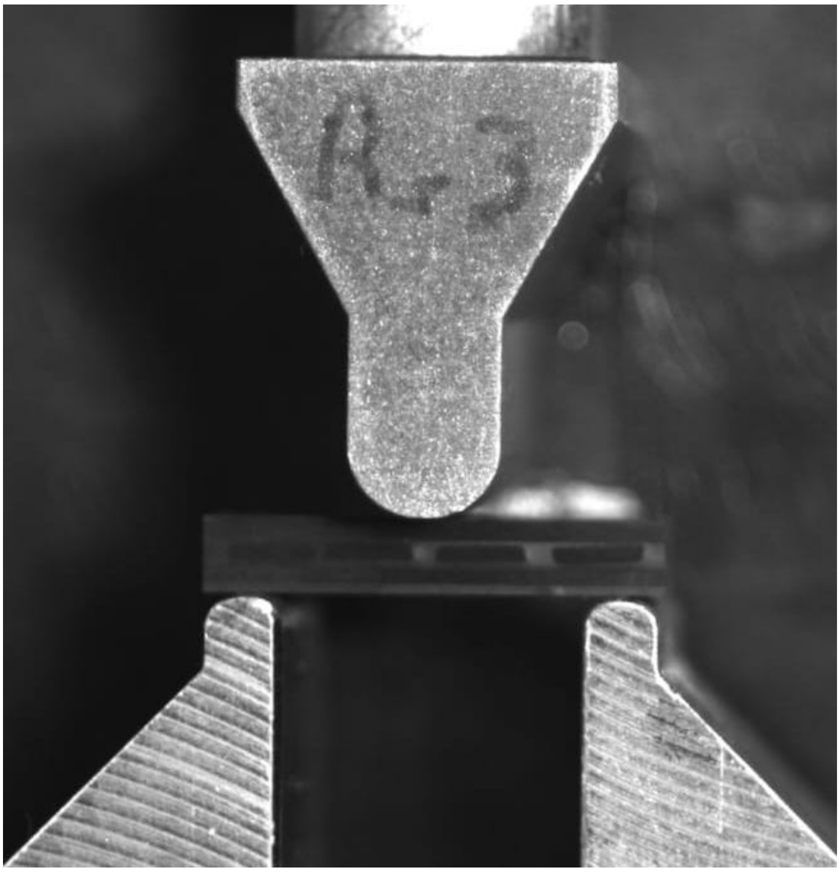

Figure 6.4: A TMC sample in the short beam testing set up

The output of this machine will be a force-displacement graph for each sample. The next step is to post-process these graphs so that a valid comparison between recycled samples can be made.
Once the test is started for each specimen, the force-displacement graph starts inclining upwards. It will be continued until there is a sudden jump in the force-displacement graphs (as shown in figures E.1, E.2 and E.3 of appendix E.). After this point, the testing is stopped and the sample can be removed.

6.4.3. Post Processing Interlaminar Shear Strength Results

In this subsection, the post-processing steps are described. The purpose of these steps is to have a fair comparison between the TMC samples and make sure that the number of recycling sessions is the only controlled parameter that could affect the performance of TMCs.

Interlaminar Shear Stress Values

The reason why Force-Displacement graphs cannot be used to compare ILSS samples together is that it is likely there will be variations in the dimensions of samples, and both the force and displacement will be affected by such differences. Therefore, parameters must be used that are per unit dimension (for example width and thickness) or area.
The first post-processed data is the Interlaminar Shear Stress. To obtain this value, the formula proposed by ASTM D2344-00 is used [24]:

$$\tau = \frac{0.75 * P}{t * w} \tag{6.1}$$

Where t is the sample's thickness, P is the applied load and w is the sample's width. It would be interesting to note that this equation is based on the beam theory introduced in subsection 6.4.1. Despite the mentioned disadvantages of this theory, equation 6.1 will still be used because all studies using this standard have applied it.

Rod Volume in TMCs

Another property that will be affected by the differences in dimensions is the rod volume in the TMC. For example if a TMC is thicker than another TMC, this extra thickness will be only due to the extra secondary resin (as the thickness of the rods will remain the same anyways). That means thicker samples will have a lower rod volume than the thinner samples and a fair comparison cannot be made between them. Therefore, to have an accurate understanding of how TMC's performance is affected by recycling, the effect of extra secondary resin must be accounted for. To that, the obtained ILSS values must be divided by rod volume, V_r.

To obtain the V_r for each sample, microscopic captures of its side with the thickness and width as well as the side with length and thickness are taken, as shown in figures 6.5 and 6.6.

Since the TMC is made from three layers (0^o/90^o/0^o), to calculate the TMC's V_r, it is decided to calculate the V_r per layer and then take the average of these three V_rs. For each layer, the dimensions of its rods must be measured (whether they are completely inside the TMC sample or only a portion of them is inside it). The width and thickness of (whole) rods are considered to be 3.63 and 0.65 mm respectively. The lengths of incomplete rods, can be found by looking at the pictures.

The software used to measure the lengths of the rods and secondary resin layer for each cross-section is Software ImageJ.

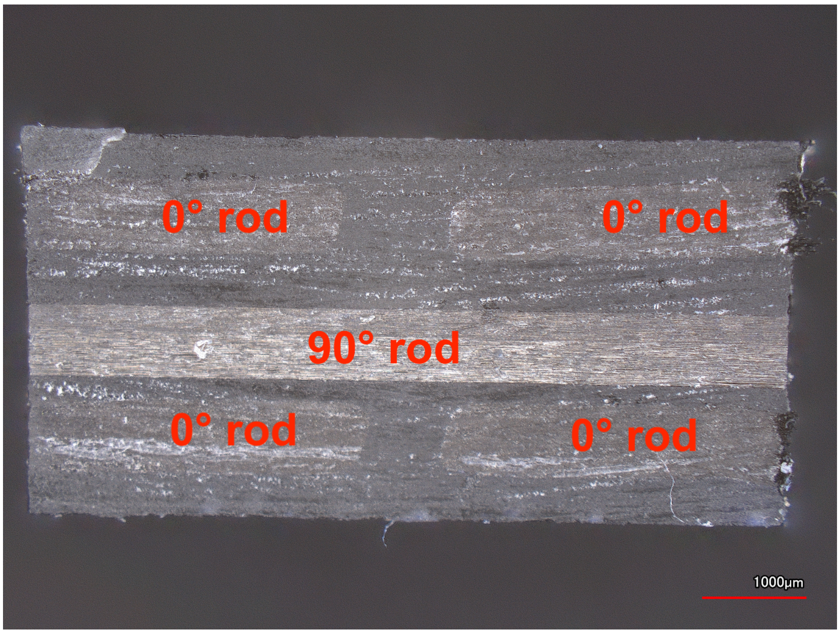

Figure 6.5: Cross section of a TMC in longitudinal direction. This picture will be used to obtain the height of each level of the TMC.

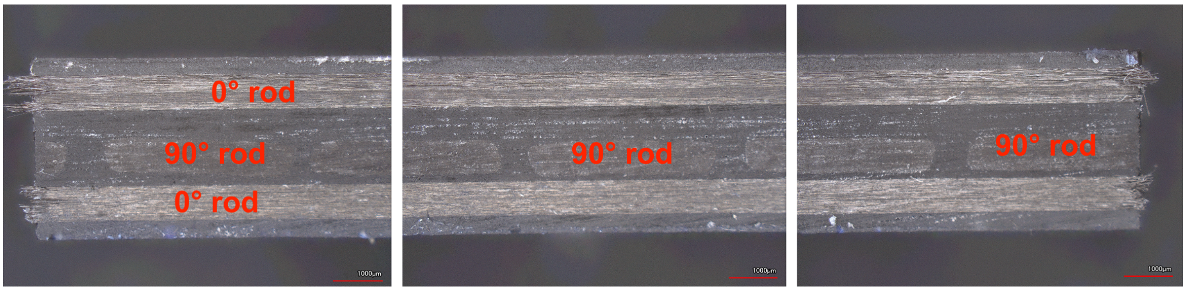

Figure 6.6: Cross section of a TMC in the transverse direction. These pictures will be used to count how many rods 90^o are in a TMC, based on which the V_r in the 90^o level (level 2) can be found.

To have a more clear explanation of V_r calculation, a mathematical expression is made based on figures 6.7 and 6.8. Starting with figure 6.7, it can be seen that layer 1 extends from TMC's top to the (upper) surface of the 90^o rod. Height of layer 1 is shown with $L1_H$ and its width is equal to TMC's width. Similarly, layer 3 starts from the (lower) surface of 90^o rod and goes until the bottom of the TMC. The height of layer 3 is shown with $L3_H$ and its width is also equal to TMC sample's width. Regarding layer 2, as figure 6.7 indicates, the height of this layer will be equal to the rod's thickness which will be 0.65 mm. That means this layer is considered to be as thick as the rods and the only secondary resin of that layer is the secondary resin between the neighbouring 90^o rods.
In figure 6.7, widths of rods in layer 1 is labeled with $L1_{r1}$ and $L1_{r2}$. If a complete rod can be seen in the cross section, then the corresponding $L1_{r1}$ or $L1_{r2}$ value would be 3.63 mm. The same applies to the rod lengths of layer 3. Since the height of layer 2 is known, the only parameter of that layer that is yet to be determined is the number of complete 90^o rods and the width of the incomplete ones. For that, figure 6.8 can be used. Once again, ImageJ software must be used to determine the width of incomplete rods. For the complete rods, their width can be considered to be 3.63 mm. It is worth mentioning that layer 2 of most TMC samples, just like the one shown in figure 6.8 consists of 4 complete rods ($L2_{r2}$ - $L2_{r5}$) and two incomplete rods at each end ($L2_{r1}$ and $L2_{r6}$).

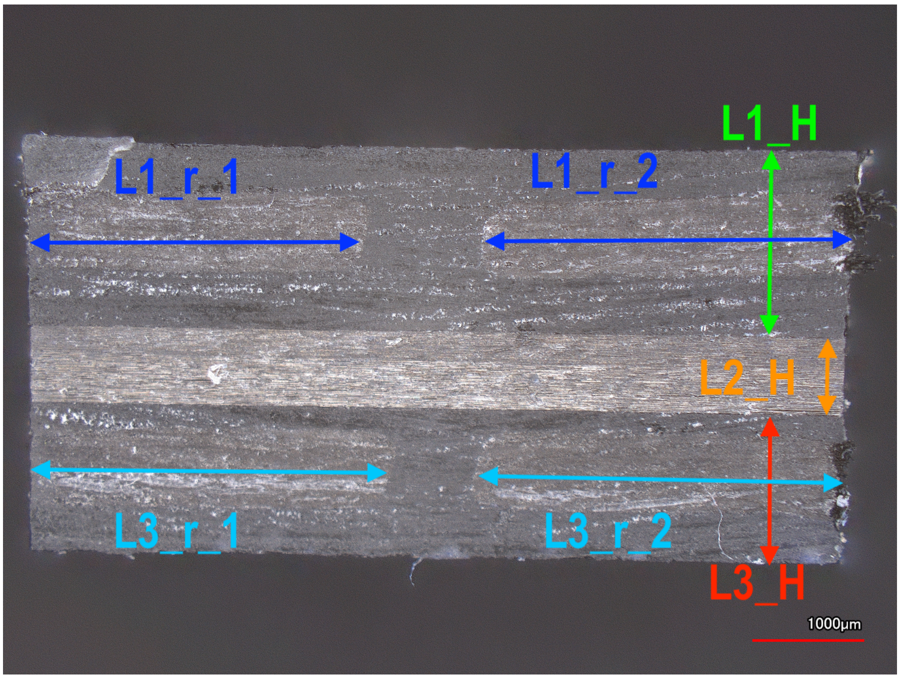

Figure 6.7: A modified representation of figure 6.5 including labels such as level heights ($L1_H$, $L2_H$ and $L3_H$) and rod width values ($L1_{r1}$, $L1_{r2}$, $L3_{r1}$ and $L3_{r2}$)

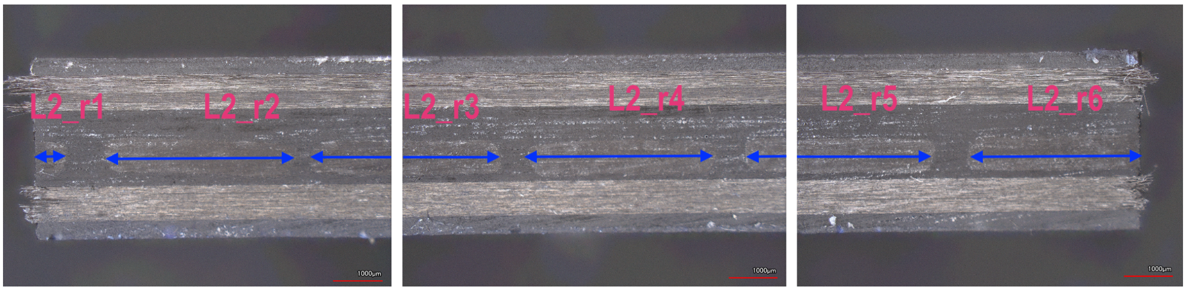

Figure 6.8: A modified representation of figure 6.6 including labels for the width values of rod ($L2_{r1}$, $L2_{r2}$, $L2_{r3}$ etc)

Now that parameters needed to create an expression to obtain V_r have been introduced, it is time to represent these expressions. As said earlier, first the expressions of each layer must be presented. In these equation, TMC's width and length are represented as w and l respectively. Equation 6.2 produces the rod volume for the first layer (V_{r1}). Equation 6.3 produces the rod volume for the second layer (V_{r2}). Lastly, Equation 6.4 produces the rod volume for the first layer (V_{r3}). All these equations are obtained by following the logic that the rod volume of each layer is obtained by dividing the rod area by the total area of that layer.

$$V_{r1} = \frac{(L1_{r1} + L1_{r2}) * 0.65}{L1_H * w} \tag{6.2}$$

$$V_{r2} = \frac{(n_{complete\,rods} * 3.63 + L2_{r1} + L2_{r6}) * 0.65}{0.65 * l} \tag{6.3}$$

$$V_{r3} = \frac{(L3_{r1} + L3_{r2}) * 0.65}{L3_H * w} \tag{6.4}$$

Now that the rod volumes for all levels are obtained, it is time to draw an expression that calculates the total rod volume of each TMC sample. As explained in a few paragraphs above, this is done by taking the average of rod volume of each level while considering their portion of the total TMC thickness. This is done in equation 6.5.

$$V_{r_{Total}} = \frac{1}{t_{TMC}} * (V_{r1} * L1_H + V_{r2} * L2_H + V_{r3} * L3_H) \tag{6.5}$$

7

Results & Discussion of Testing Twin Matrix Composites

This chapter displays all the results and outcomes of testing and analysis that have been done on TMC samples (or its reinforcing rods) during this thesis study. Section 7.1 presents and discusses the SEM results and section 7.2 presents and discusses the water contact angle measurements. Next, section 7.3 shows how recycling has affected rod's weight and lastly, section 7.4 shows and discusses the raw and processed ILSS values that are based on the ILSS testing.

7.1. Scanning Electron Microscopy Results

In this section, the observations made from the surface of the composite rods via SEM are shown. As described in section 3.2, SEM is used to compare the surface of 5 types of composite rods; non-recycled, one-time-recycled, two-times-recycled, three-times-recycled and four-times-recycled rods. This section presents the results obtained from the SEM analysis by showing pictures of the surfaces of each type of rod.
As mentioned in section 6.1, each type of rod has had pictures taken of it with magnifications of 25, 75, 130 and 300. Given that there are 5 types of rod and there are 4 magnification sizes per each type, presenting them all in this section would take a significant amount of space. Therefore, it is decided to show only the figures that are sufficient to present essentially how the recycling trials affect the rods. More specifically only pictures with x75 magnification will be shown as this magnification size shows a vision that is detailed enough but also presents a broad view of the rods' surface. The rest of magnification sizes can be seen in appendix C.
Before showing the results, one remark to make is that if there are any deep cuts in the images, these are due to slicings that have occurred to obtain these samples. Given that the samples must be short in length to fit in the SEM machine (< 20 mm) slicing a rod will most likely create cuts along the length of the specimen. These cuts could occur for any type of composite rod and is irrespective of the number of recycling times. Therefore in this analysis, no attention will be given to them. An example of these cuts can be seen in figure 7.2 or figures C.1, C.5 and C.9 in appendix C.

Now focusing on the results, the most general result observed is recycling has very little impact on the surface of rods. This can be confirmed especially by comparing the surface of a rod that has been never recycled (figure 7.1) with that of a rod that has been recycled 4 times (figure 7.5).
With that being said, there are still a few changes due to recycling that are worth mentioning. One is that after one time recycling, several dark coloured freckles appear on the surface of the rod. These dark-coloured freckles, which can be seen in figure 7.2, can be linked to the light-coloured freckles on the surface of unrecycled rod (figure 7.1). It is expected that due to recycling, these freckles become less attached to the rod surface and that is why they are observed with a different colour in SEM observations. Furthermore, it is expected that these freckles will fully detach and dissolve away during the second recycling session which would explain not seeing them anymore after the second recycling.
In addition to the disappearance of surface freckles, another trend that can be seen is that rods with

higher recycling sessions have a higher number of surface defects. An example of such defects is when a fiber or a bundle of fibres emerge out of the surface of the rod. Examples of such phenomenon can be seen in figures 7.4 and 7.5. Another defect is the creation of dents on the surface of rods, as shown in figure 7.2) and 7.5.

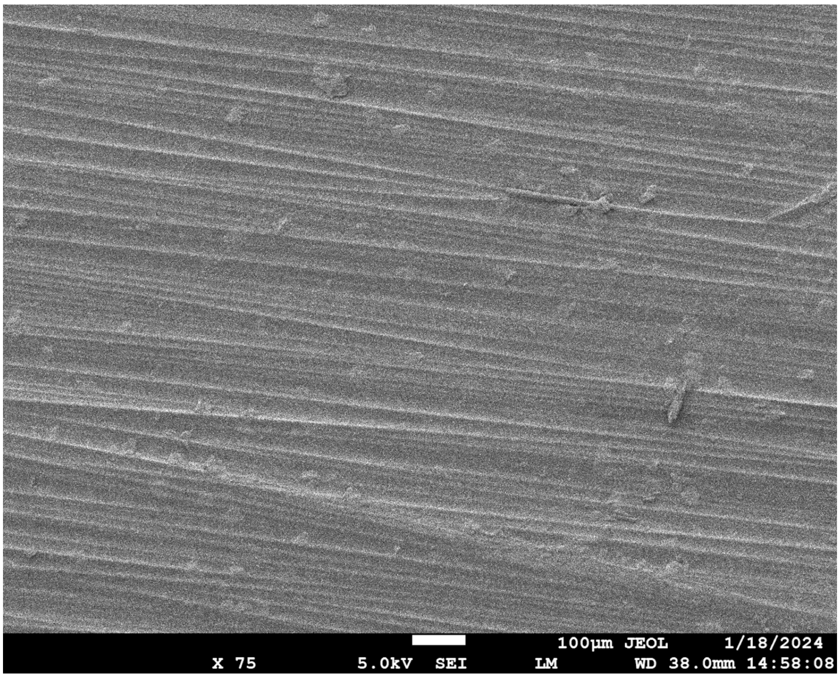

Figure 7.1: SEM figure of an unrecycled rod.

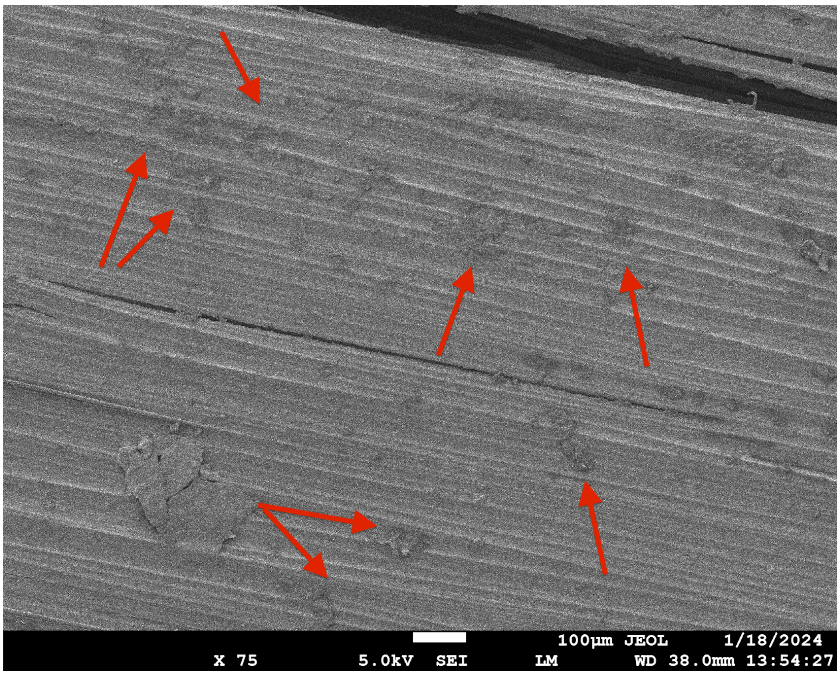

Figure 7.2: SEM figure of a rod that has been recycled once. The red arrows indicate freckles that exist on the surface of the rod.

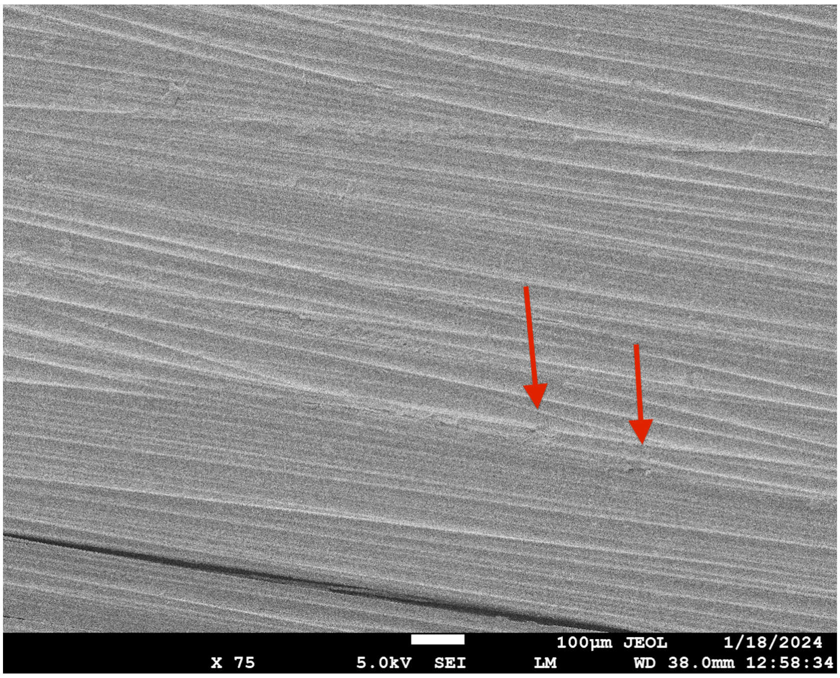

Figure 7.3: SEM figure of a rod that has been recycled twice. The magnification size is 75. The red arrows indicate (rather small) holes on the surface of the rod.

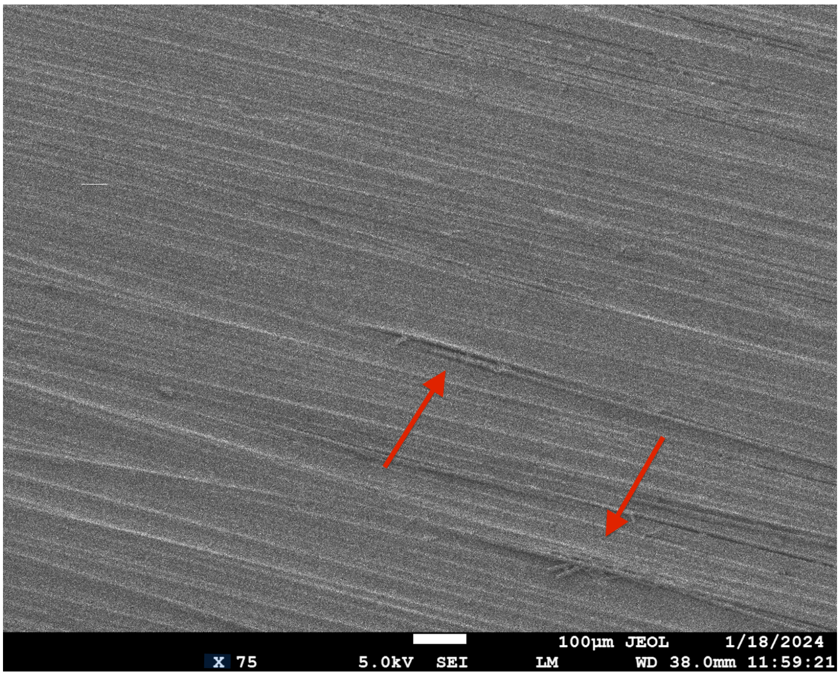

Figure 7.4: SEM figure of a rod that has been recycled three times. The magnification size is 75. The red arrows indicate fibers that come out of the rod surface.

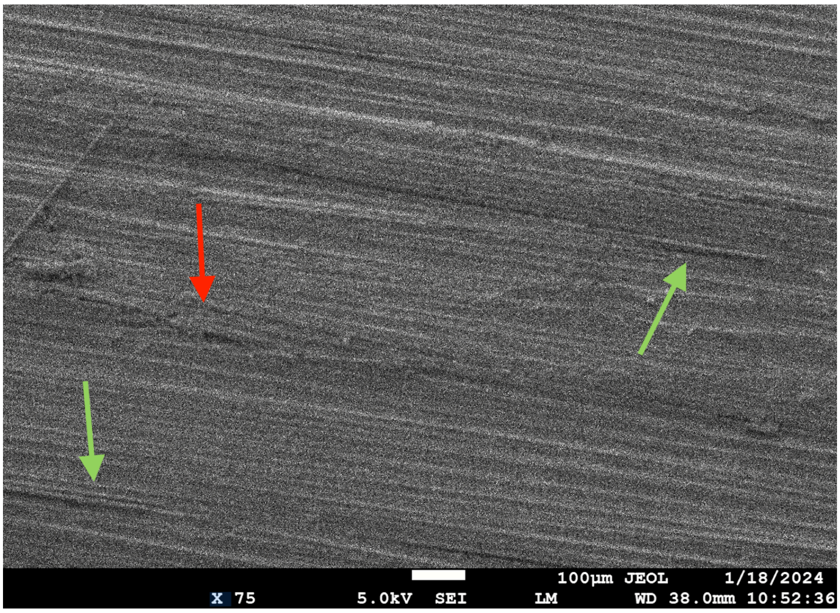

Figure 7.5: SEM figure of a rod that has been recycled four times. The magnification size is 75. The red arrow indicates a dent that is created due to the shifting of the fibers. Green arrows point to fibers merging out of the rod surface.

An important note to make is that there was no observation concluding that recycling increases the severity of defects. Thus for example the dents observed after two-times recycling are as deep as after four-times recycling. How recycling has shown to affect these defects is that the more recycling sessions the rod has gone through, the higher the number of defects will be. So for example, comparing the two-times recycled rod with a four-times recycled rod, it can be seen the four-times recycled has a rougher surface in the sense of having more surface dents or individual fiber pull-outs.

Comparing these results with the expected outcome mentioned in section 3.3, it can be said the hypothesis of SEM results is not far from reality as it was predicted recycling affects the rod surfaces. While this has proven to be true, the influence of recycling seems to be smaller than what had been expected. It was also expected that after high numbers of recycling, the defects would become more severe (for example deeper surface dents) however in reality, it was shown that the number of recycling has no effect on the severity of defects but it will impact the chance of their occurrence.

To have a final conclusion of this section, even though comparing figures from unrecycled to recycled 4 times indicates that the rod surfaces get rougher with each time of recycling, it can still be stated that these effects are still not very significant and there are not any severe changes happened to the rod surface. It can also be concluded that according to SEM results, the change in rod's surface before and after an individual recycling is very negligible. Differences are more likely to be noticed after several times of recycling.

7.2. Water Contact Angle Measurement Results

As mentioned in section 3.2, via water contact angle analysis it can be understood how recycling affects a rod's surface roughness. This section presents the results of this analysis.
In section 6.2 it was described that for each rod type, 3 recordings will be made. Each water droplet will have two angle measurements, the angle values for its left and right sides. Once the angle values for each recycling configuration are measured, the average of the left angle measurements as well as the average of the right angle measurements are taken. Table 7.1 represents these average values. Additionally, the last column of this table represents the average of the left and right side averages. To see all the angles measured during the water contact analysis, refer to table D.1 in appendix D.

Number of recycling	Left angle average (^{o})	Right angle average (^{o})	Average of both sides (^{o})
0	58.82	57.16	57.99
1	65.47	64.98	65.22
2	66.61	65.76	66.19
3	66.72	66.73	66.73
4	79.16	78.59	78.88

Table 7.1: Table of average values of the angles measured for each recycling occasion in the water contact analysis. The second and third columns represent the average angle values for the left and right side of the water droplets. The last column represents the average of the left and right average values.

What the above table displays is that after each recycling session, the value of contact angles increase for both the left and right sides as well their average. While this raise is rather small between the second and third recycling, it can be seen that the magnitude of this raise is much larger between the un-recycled rod and once recycled rod as well as between the three times recycled and four times recycled rod. This can also be seen in graphs which have been made based on table 7.1. These graphs are shown in figures 7.6a and 7.6b.

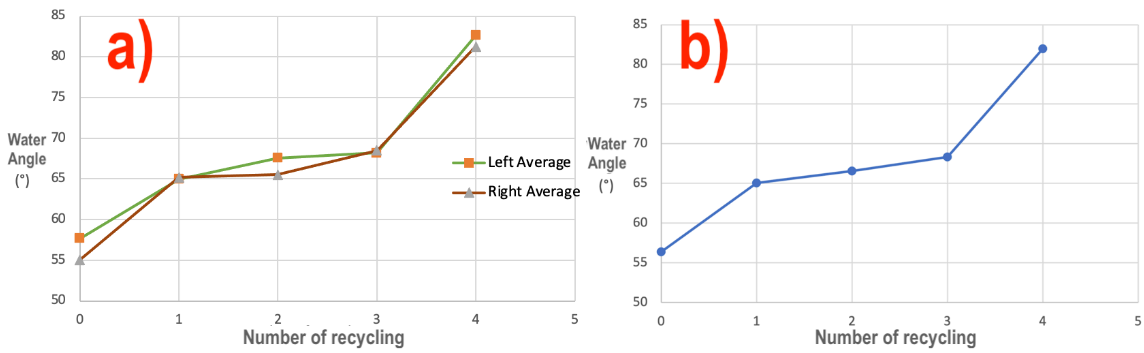

Figure 7.6: Variation of water contact angles after each recycling session. Figure a shows the average values for the left and right sides of the water droplets after each recycling session. Figure b shows the average of these two averages for each recycling session.

As it can be seen in figures 7.6, the average water contact angle increases per each recycling session. The increase in angles becomes the highest after the fourth recycling (about 12^o). The second highest increase in water contact angle is after the first time recycling (about 7^o). The second and third recycling show to have significantly lesser effects. Figure 7.6a shows that both the left and right averages follow rather similar trends and there is no significant difference in their slope. This means it is safe to draw conclusions based on figure 7.6b which has taken the average of the left and right sides.
To explain the high amount of angle change due to the first recycling, it is hypothesized this is linked to the freckles (shown in figure 7.1) that became less attached to the rod surface during this procedure. Therefore having less attached-to-surface freckles is expected to make the rod surface rougher, leading to higher water contact angles.
Due to the removal of these freckles after the second recycling (mentioned in section 7.1), one could expect that the surfaces would get smoother. However as shown in figures 7.6, the contact angle after the second recycling is increased; though by a small margin. This rise can be attributed to the creation of surface defects (such as dents or fiber pull-outs) due to recycling. The same logic is expected to apply to getting higher angles after the third and fourth recycling. It is suspected the reason why recycling four times increases the water contact angle by the greatest amount, is that the number of surface defects after four-times-recycling increases the most leading to the highest rise in the roughness.
This outcome is in line with the hypothesis described in section 3.3, as it was expected that the water contact angles would increase with higher numbers of recycling. The surprising outcome is that angles increase the most after the first and fourth recycling. This is in contrast with the expected outcome as it was expected that the angle-number of the recycling graph would be a linear line which is not the case as shown in figure 7.6.

7.3. Rod Weight Measurement Results

As mentioned in section 3.2, the purpose of measuring the weight a rods after each recycling session is to understand how its mass is affected by each recycling. The initial mass of the rod is 259.2 mg. Table 7.2 represents the masses of the rod after each session of recycling.

Recycling number	0	1	2	3	4
Rod mass (mg)	259.2	259.0	258.5	257.0	255.6
Percentage mass loss (%)	0	0.07	0.27	0.85	1.40

Table 7.2: Mass of the rod with respect to each number of recycling and the corresponding mass loss percentage with respect to initial mass

As it can be seen from the above table, with each session of recycling the mass of rod decreases. This reduction becomes more significant towards 4 times recycling. So for example the mass reduction after the first recycling is 0.2 mg (0.07% of the initial mass), the mass reduction after the second recycling is 0.5 mg (0.27% of the initial mass), the mass reduction after the third recycling is 1.5 mg (0.85% of the initial mass) and the mass reduction after the fourth recycling is 1.4 mg (1.40% of the initial mass). This trend can also be seen in the graph shown in figure 7.7.

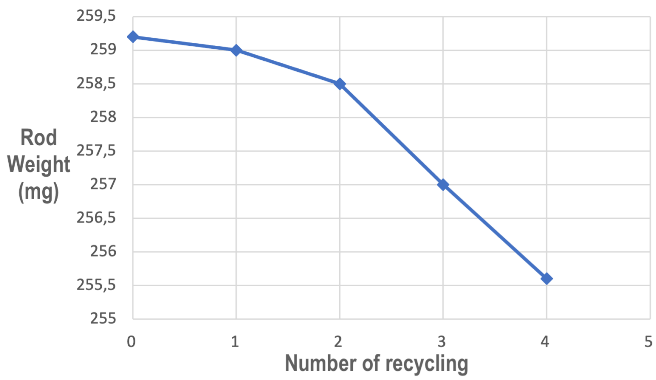

Figure 7.7: Graph of variation of rod's weight after each recycling session

It is suspected that mass reduction is due to the loss of surface epoxy as well as surface fibers during each recycling session. To prove that fiber loss is a factor for mass reduction, a reference to figure 5.5 can be made which shows the existence of floating (short) fiber filaments in the acidic solution at the end of a recycling session. To prove the loss of surface epoxy, reference to SEM pictures (shown in section 7.1) can be made which shows the degradation of surface epoxy components due to recycling. Despite this mass loss, it is worth reminding that the rod has lost only 1.4% of its initial mass due to four times recycling. Considering this negligible mass variation and that SEM pictures reveal there is no remarkable difference between the surface of unrecycled rods and four-times-recycled rods, it can be hypothesized that its structural integrity is most likely not impacted after four recycling trials.
This outcome is in line with the hypothesis mentioned in section 3.3 as it was expected that recycling leads to a reduction in rod's mass. However, what was different from the hypothesis is that it was expected that the rod weight-number of recycling graph would seem like a linear line however as shown in figure 7.7, this is not the case and the graph is rather a curve with a higher slope towards the end.

7.4. Interlaminar Shear Stress Testing Results

This section aims to show and discuss the result of the ILSS testing described in section 6.4. As mentioned in that subsection 3 types of samples have been tested, TMCs with fresh rods, TMCs with one-time-recycled rods and TMCs made with four-times-recycled rods. The first subsection of this section, subsection 7.4.1 compares the interlaminar shear strength of TMC samples. Next, subsection 7.4.2 represents results on how the fracture has happened in TMC samples and whether it was influenced by recycling.

Additional information on the results of ILSS testing can be found in appendix E which includes all relevant information about each TMC as well as its force-displacement curve.

7.4.1. Interlaminar Shear Strength Values

The most important method to have a measure on how recycling has influenced interlaminar behavior of the TMC samples, is to compare their interlaminar shear strength values. These values are obtained from the maximum shear force data obtained from the testing machine, sample dimensions (following equation 6.1) and the guidelines of ASTM D2344-00 standard (discussed in subsection 6.4.1). These results are shown in figure 7.8.
However, before looking at this graph, an important matter should be reminded and that is TMC samples made from four-times-recycled rods have the highest thickness with an average thickness of 3.40 mm and the TMC samples made from unrecycled rods have the lowest thickness with an average thickness of 3.10 mm. TMC samples made from one-times-recycled rods lie in between with an average thickness of 3.36 mm. As discussed in subsection 6.4.3, thicker samples will have less rod volume because any extra thickness will lead to only additional secondary resin. According to this logic, TMCs made from unrecycled rods must have the highest rod volume, TMCs made from four-times-recycled rods must have the least rod volume and TMCs made from one-time-recycled rods must have a rod volume value that is in between the other two rod volumes. To check this hypothesis, the rod volume is calculated for each TMC sample (the instructions are given in subsection 6.4.3). The results show that the average rod volume for TMCs made from unrecycled rods is 56 %, the average rod volume for TMCs made from one-time-recycled rods is 48 % and the average rod volume for TMCs made from one-time-recycled rods is 46 %. This confirms the hypothesis that thicker samples will have less rod volume.

Since it is the rods that will take up the majority of loads during the short beam bending test, it is expected that TMCs with unrecycled rods will have the highest ILSS (because they have the highest rod volume) and the TMCs made from four-times-recycled rods will have the least ILSS (as they have the least rod volume). However note that in this statement the effect of recycling is neglected. Of course, recycling should be considered as the entire purpose of this study is to analyze recycling as an influencing factor. That means that in figure 7.8, there are ultimately two independent valuables: Rod volume and recycling.

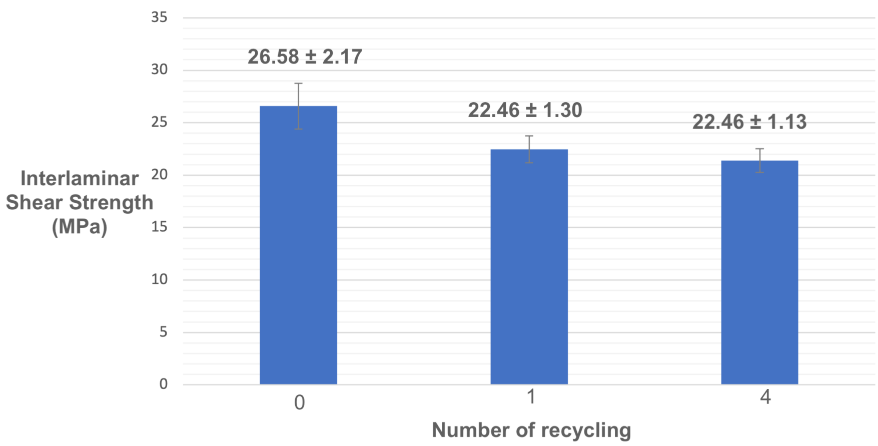

Figure 7.8: Variation of average ILSS values for TMCs based on the number of recycling of rods.

In author's opinion, the most useful and solid information that can be obtained from figure 7.8 is that the benchmark value for the ILSS of a recyclable TMC would be 26.58 $\pm$2.17 MPa, which represents the category of TMCs made from fresh rods. An interesting note about this category is that all samples in this case have the same thickness. That means that the TMCs made from fresh rods have similar rod volume and there is no need to divide the ILSS values by the rod volume. This means further that the 26.58 $\pm$2.17 MPa value is a reliable benchmark value for the ILSS of TMCs.
To be able to have a fair comparison between different categories of TMC and have a solid conclusion on whether recycling has affected ILSS values, the ILSS value of each sample is divided by its rod

volume. Once that is done, the average ILSS per rod volume (hereafter referred to as ILSS$_{rod}$) is obtained for each TMC category. Figure 7.9 represents the results of this step for all three categories of TMC.

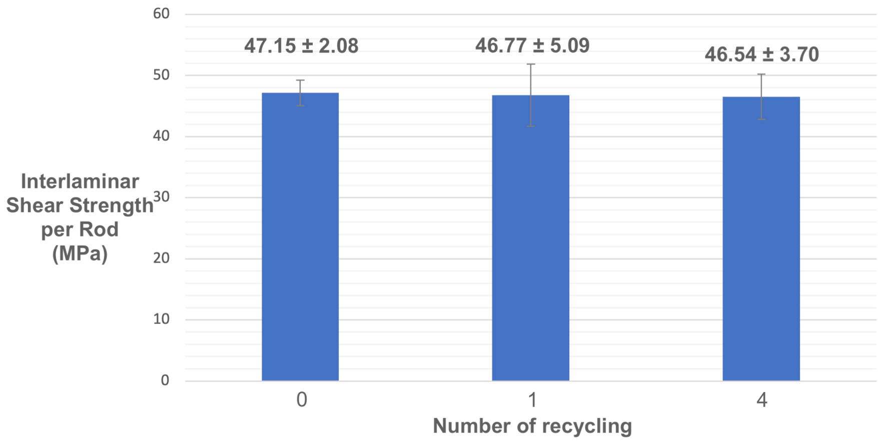

Figure 7.9: Variation of average ILSS$_{rod}$ values for TMCs based on the number of recycling of rods. ILSS-per-rod-volume in this case means the ILSS values of figure 7.9 divided the average volume for each type of TMC.

As it can be seen in this figure, TMC samples made with unrecycled rods have an ILSS$_{rod}$ of 47.15 $\pm$2.08 MPa, TMC samples made with one-time-recycled rods have an ILSS$_{rod}$ of 46.77 $\pm$5.09 MPa and TMC samples made with four-times-recycled rods have an ILSS$_{rod}$ of 46.54 $\pm$3.70 MPa. That means that the reduction in average ILSS$_{rod}$ after one recycling is around 0.8% and after four times recycling is 1.3 % (both percentages are with respect to the TMC made from fresh fibers). Therefore one could say that there is a small reduction in the average ILSS$_{rod}$ value due to the increase in the number of recycling trials.
However considering the error bars and the fact that for example, the lowest ILSS$_{rod}$ value of TMCs with four-times-recycled rods (46.54 - 3.70 = 42.68 MPa) is higher than the lowest ILSS$_{rod}$ of TMCs with one-time-recycled rods (46.77 - 5.09 = 41.68 MPa), one can also conclude that the change in ILSS$_{rod}$ values due to recycling is negligible and recycling has almost no influence on ILSS$_{rod}$ properties of TMC samples. This conclusion becomes more favorable considering that the TMC samples made from four-times-recycled rods (meaning rods that have been recycled multiple times) have a very similar average ILSS$_{rod}$ value to TMC samples made from fresh rods.
These ILSS results are quite opposite to what had been predicted in section 3.3. As mentioned there, it was expected that because the rod surface would get rougher due to recycling, the interface strength between the secondary matrix would get higher leading to higher ILSS values for TMCs that are made from rods that have been recycled a higher number of times. This is obviously in contrast with the results shown in this subsection as it has been shown that recycling has almost no influence on the ILSS values of the TMC samples.

7.4.2. Fracture Study

The fracture study will be done by looking at pictures taken as soon as there is a drop in the force-displacement graph of the ILSS testing. As mentioned in subsection 6.4.2, these pictures are taken every second by a camera in hope of having a glimpse of how TMC samples fail initially and whether these failures are affected by the number of recycling sessions.

First and foremost, looking at fracture figures of all samples, it has been observed that all samples have similar fracture figures and they all look similar to figure 7.10. That means that recycling has no effect on the failure mechanisms of the TMC samples. As Figure 7.10 shows, there are multiple fracture types that are created in this TMC. For instance, it can be seen that there has been a sliding movement between the secondary resin and bottom-most 0^o rod layer (shown with an orange arrow). That means that delamination has occurred at this interface which can be further interpreted as an interlaminar shear failure. Another delamination that points to interlaminar shear fracture is shown with a red arrow in Figure 7.10. For a better view of these delaminations, please refer to Figure 7.11. Apart from delamination, another failure mechanism can be seen in Figure 7.10, which is the crack that runs through the 90^o rod (shown with a green arrow) as well as the secondary matrix. This points to the failure of the 90^o rod and the secondary matrix.

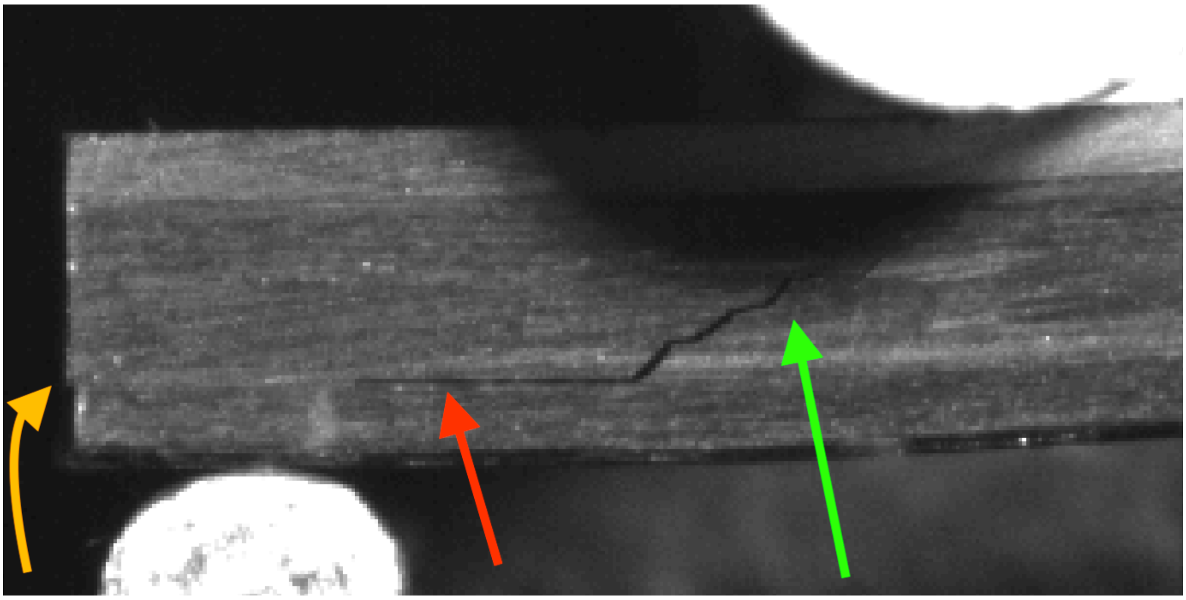

Figure 7.10: The first captured picture of fracture initiation and growth in a TMC made from one-time recycled rods. The red arrow points to an interlaminar fracture which is at the interface between the bottom-most 0^o rod layer and the secondary later. The green arrow points to a crack that has gone through a 90^o rod. The orange arrow points to the sliding of the bottom-most 0^o rod layer with respect to the rest of TMC sample.

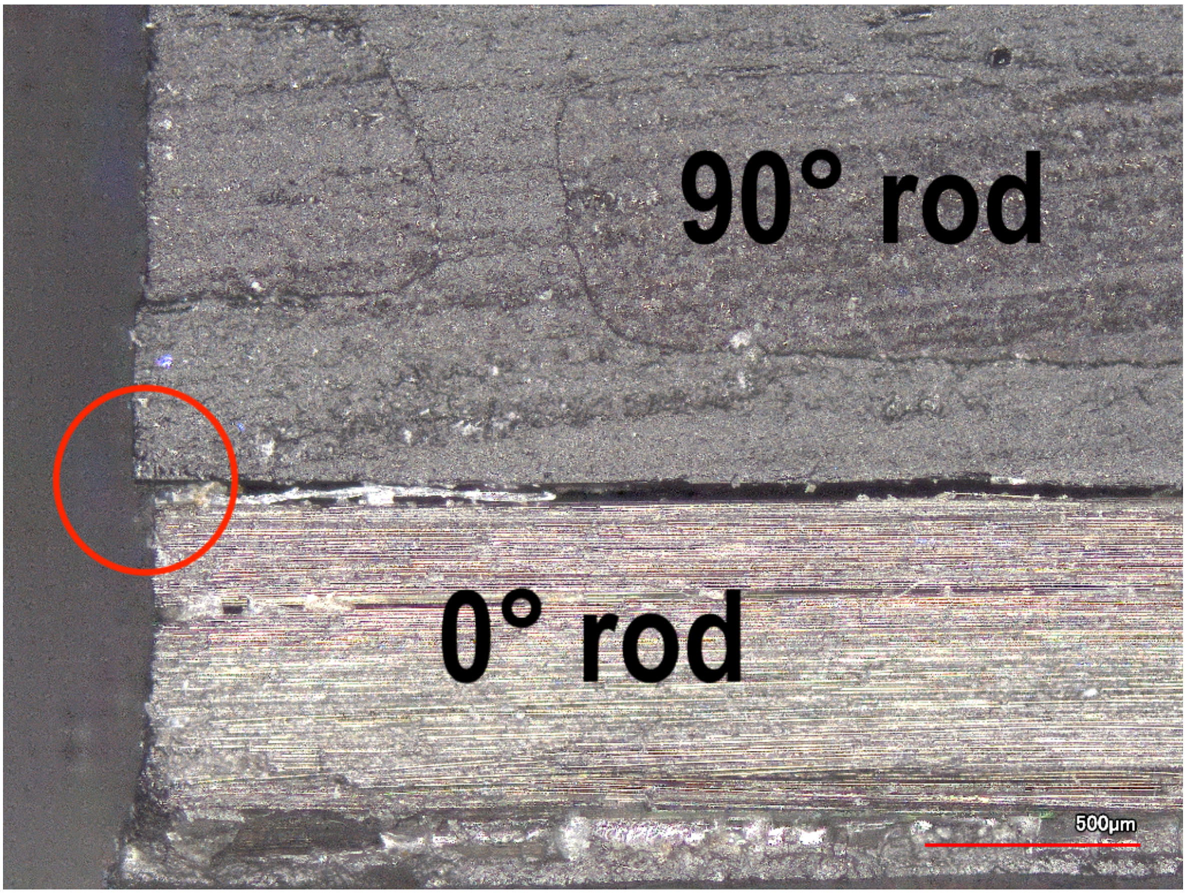

Figure 7.11: A zoomed-in view of the delamination in the sample of Figure 7.10. Additionally, the sliding movement of the secondary resin with respect to the bottom-most rod has been shown with a red circle. Note that it is suspected that the magnitude of sliding in this figure is smaller than the one shown in Figure 7.10 because in that figure, the layers are loaded and therefore are moving with respect to each other.

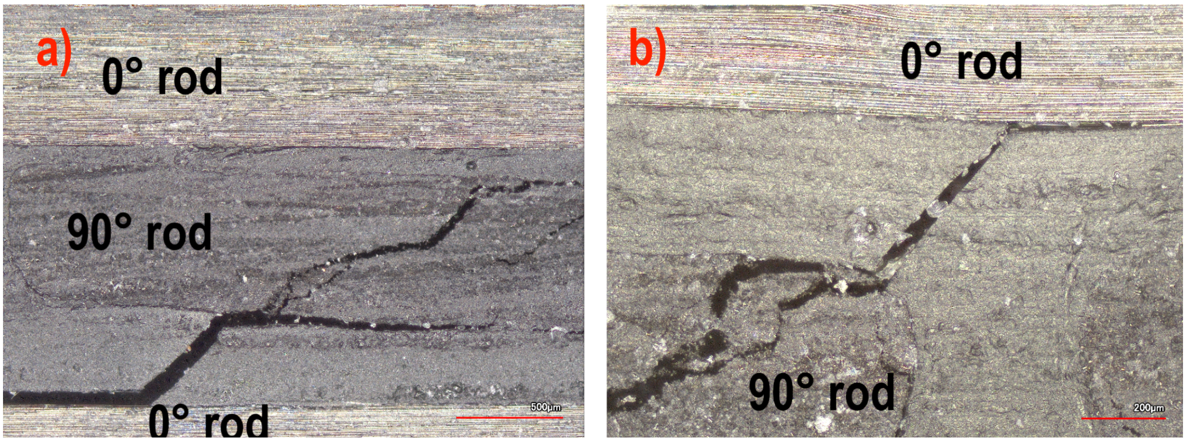

Figure 7.12: A zoomed-in view of the propagation of fracture crack through the secondary matrix and 90^o rod. Figure a belongs to the sample shown in Figure 7.10 and Figure b belongs to another sample. The reason for selecting the latter picture is because this picture represents the crack path in the upper region of the 90^o rod better. Note that the delamination crack at the bottom of the 90^o rod in Figure A happened several seconds after the initial failure mechanisms and that is why it cannot be seen in Figure 7.10.

Because the delamination, fracture at the 90^o rod and fracture through the secondary matrix all happened within the same second when this picture was taken, it is not possible to conclude what is the exact failure mode of the TMC in this test. Still, this analysis presents interesting results. One is that the crack goes through both the secondary matrix as well as the 90^o rod which indicates that the transverse shear strength of the rod is similar to the shear strength of the secondary matrix. If for instance, the crack went around the 90^o rod instead of going through, it could have been interpreted that the transverse shear strength of the 90^o rod is higher than the secondary matrix's shear strength.

It is worth mentioning this outcome is in line with how a cross-ply composite (given that its 90^o reinforcements are in the middle axis) is expected to perform in an ILSS test. This expectation is represented in Figure 7.13a which shows that the crack propagates in a diagonal manner through the 90^o reinforcements. Rodriguez and Costa obtained similar fracture results while performing ILSS tests on composite samples with a [45^o/0^o/-45^o/90^o]$_{ns}$ lay up [16]. According to their fracture result, which is shown in Figure 7.13b, there is a crack in every 90^o layer and delamination cracks between off-axis layers. Both of these phenomenons have also occurred for the TMC samples (as discussed above and shown in Figure 7.10). Additionally, they had smaller cracks within $\pm$45^o layers however this phenomenon is not of interest for this study because $\pm$45^o layers have not been applied in the case of TMCs.

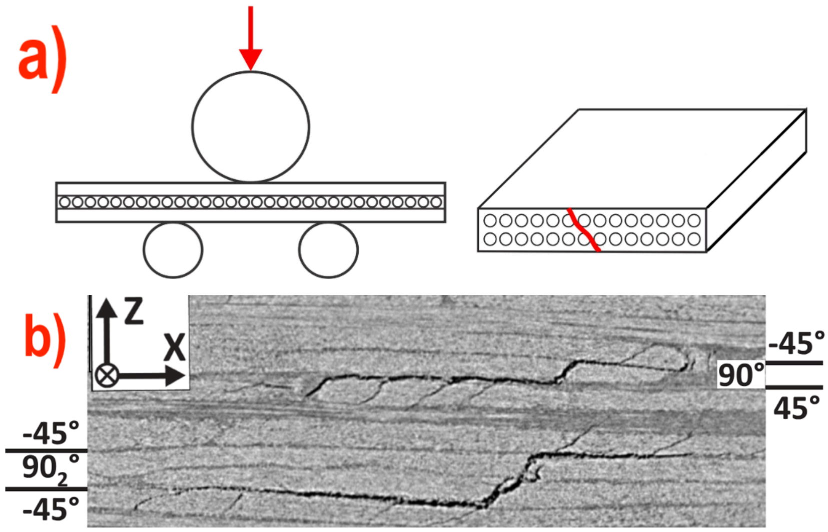

Figure 7.13: ILSS Performance of composites with lay ups consisting of 90^o reinforcements. Figure a represents the expected crack propagation in a 0^o/90$_2$^{o}/0^o composite. Figure b represents the failure mechanism in a composite with [45^o/0^o/-45^o/90^o]$_{ns}$ lay up [16].

As mentioned in section 3.3, it was expected that the TMCs sample would have failed via delamination and that the crack would propagate only along the 0^o rod/secondary matrix interface. Looking at the fracture figures of this subsection, it can be seen that this hypothesis is not accurate as the crack has gone through the 90^o rod as well as the secondary matrix. That being said, a hypothesis that has been proven to be more or less correct is that the number of recycling sessions does not affect the type of failure mechanisms that occur during ILSS testing of TMC samples.

8
Recommendations

In this section, the TMC made in this thesis study will be evaluated and several recommendations will be given on different aspects of the TMC. Section 8.1 represents the most important challenge to overcome regarding this thesis's TMCs and gives recommendations on how to overcome it. Section 8.2 gives recommendations to other aspects of TMC manufacturing to be investigated. Lastly, section 8.3 covers other remaining recommended matters on which recyclable TMCs can be investigated.

8.1. Evaluation and Recommendations on the Quality of Twin Matrix Composite Samples

In the author's opinion, the most important and critical matter to evaluate and improve is the thickness of secondary resin layers. In fact, this matter was the reason for developing several manufacturing generations (more about these generations can be read in appendix B). The goal throughout this phase (phase of optimizing the manufacturing procedure) was to find a way to obtain TMC samples with a homogeneous distribution of secondary resin across the cross section and that there will be no regions with an excess amount of resin along the sample thicknesses.

While this problem was ultimately solved at the end of the manufacturing procedure development phase, a new challenge was spotted during during the phase of manufacturing samples to be tested. The problem is that the cross section of batches are not completely consistent with each other. This problem has already been addressed few times through out this thesis study, for example in subsections 6.4.3 and 7.4.1.

In those subsections, it was said that the difference in cross section between samples should be taken into account while comparing TMC samples. This difference in cross section of batches can be seen by comparing figure 8.1 (representing TMCs made from unrecycled rods) with figure 8.2 (representing TMCs made from one-time-recycled rods) and figure 8.3 (representing TMCs made from four-time-recycled rods). An example of these cross sectional differences is that the distance between the topmost 0^o rod and the 90^o rod in case of unrecycled rod is 0.22 mm (figure 8.1) whereas this distance is 0.08 mm in case of one-time-recycled TMC (figure 8.2) and 0.43 mm in case four-times-recycled TMC (figure 8.3).

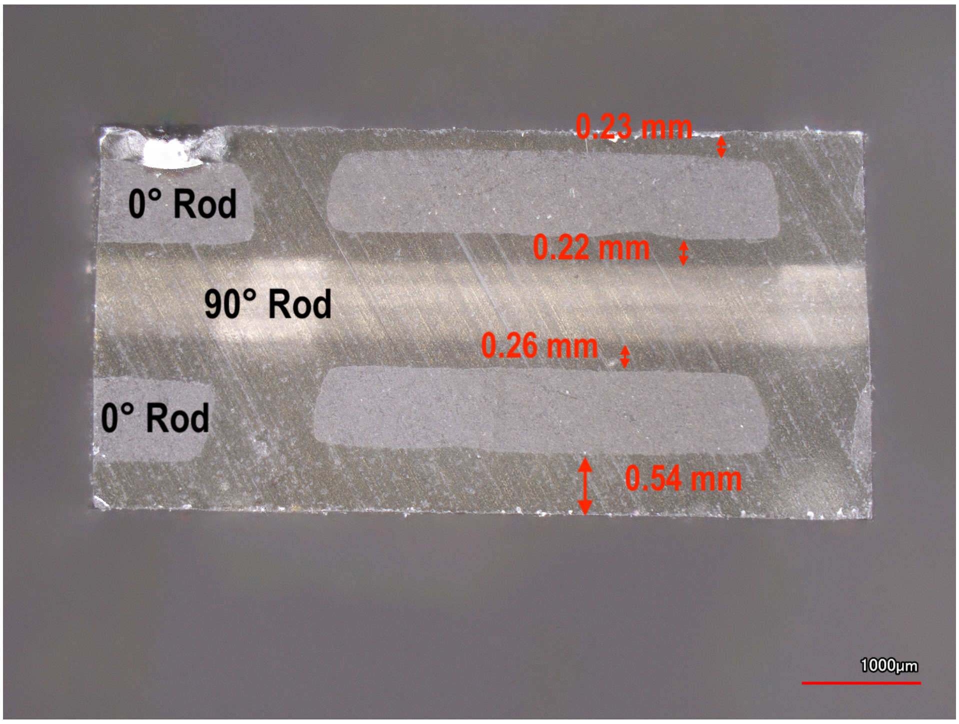

Figure 8.1: Cross section of a TMC sample made from unrecycled rods including the thickness of secondary resin layers.

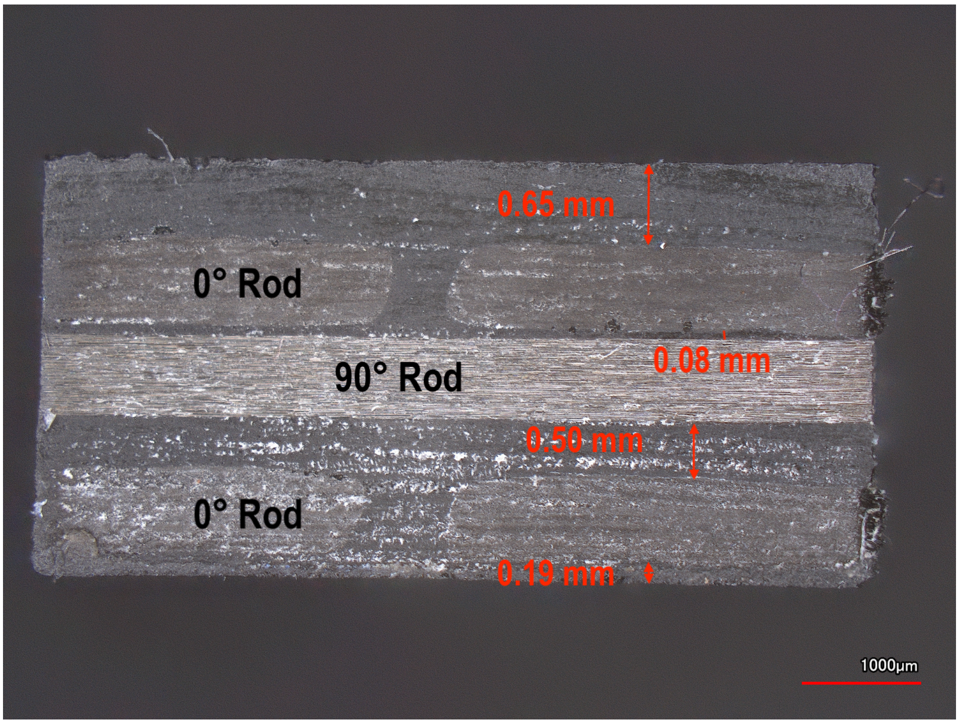

Figure 8.2: Cross section of a TMC sample made from one-time-recycled rods including the thickness of secondary resin layers.

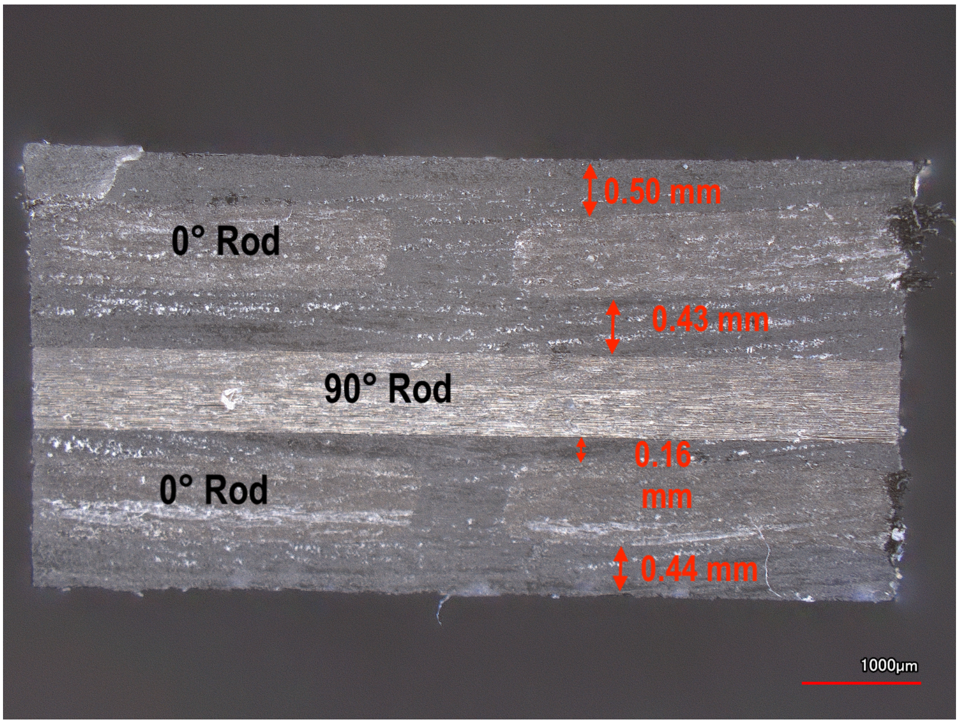

Figure 8.3: Cross section of a TMC sample made from four-times-recycled rods including the thickness of secondary resin layers.

It is therefore recommended to strive for more consistent cross sections among TMC samples. This means the following two goals:

- To make sure that all TMC samples will have the same total thickness leading to similar rod volumes (V_r). Once that is obtained, there is no need to divide strength values by V_r to have a fair comparison between the samples. It is expected that this goal will be achieved by applying more pressure (in other words, more weight) on the teflon cover plate during the curing step. The applied weight on top of the teflon plate to manufacture TMC samples of this thesis study is 3.5kg. It is now suggested to try heavier weights such as 10kg or 15kg and see their influence on obtaining samples with the same thickness.
- To make sure that the thickness of each secondary resin layer will be similar to that of the other samples. So for example, it is desired that the thickness of the secondary resin layer between the topmost rod layer and the middle rod layer should be similar for all TMC samples. To achieve this goal, it is suggested to come up with a mechanism that makes sure the rods will be held in their place tightly during the manufacturing stages (such as secondary resin application or curing) and the total thickness will be constant for all samples.

While the above mentioned remarks are focusing on having consistencies among TMC samples, there is another feature which should be considered and improved. That is the total fiber volume of the TMC samples. As shown in tables of appendix section E.1, the rod volume of TMC samples ranges from 44 - 58%. Considering that each rod has a fiber volume of 63%, that means that the total fiber of these TMC samples will range from 28 - 36%. This total fiber is less than the total fiber volumes that Callens (42-49%) [7] or Vasil'ev and Salov (51%) [45] have obtained.
Based on this comparison, an appropriate goal to set is to strive for creating TMCs with higher total fiber volume fractions. This can be achieved by creating TMCs with a higher packing density of rods within the TMC cross section. This can be done by getting rid of any excess secondary resin that lies between the rod layers or is on top of the topmost rod layers or below the bottom-most rod layer. Manufacturing via the filament winding can be an interesting route to achieve higher total fiber volume however the high viscosity of secondary resin could introduce challenges.

8.2. Exploring Other Possibilities In Manufacturing Twin Matrix Composites

In author's knowledge, this is the first study on recyclable TMC. There are many ways these composites can be varied and their new properties to be studied. List below describes such possibilities:

- Exploring other lay-up orientations: The lay-up order in this composite is 0/90/0. Note that the reason for this lay-up selection has already been discussed in section 5.2. It is recommended to explore the possibility of increasing the number of orientations in TMC's lay-up by for example adding $\pm 45^o$ oriented rods. In this case, however, a third lay-up angle must be added which calls for fundamental modifications made to the mould design such as that it allows for three directions.
- Exploring other lay-up numbers: The lay-up number in this thesis study is 3 which resulted into TMC samples of thicknesses 3.1 - 3.4 mm. Adding another rod layer would increase thickness by at least 0.75 mm (that is because the rods are 0.65 mm thick and the additional secondary resin will be at least 0.1 mm thick). That means with the addition of a layer, the thickness of the resultant composite will be at least 3.85 mm. This is a high a value for a composite's thickness considering that a conventional ply is 0.125 mm thick [23] (3.85 mm is roughly 30 layers of ply). If it is yet desired to explore TMCs with a different number of lay-up layers, it is better to select rods with lower thicknesses. This is explained in the next point.
- It is recommended to manufacture and investigate TMCs that are made from rods with different geometries than the one used in this thesis study. This variation in rod's geometry can either happen via change in the general profile (for example it could change from rectangular to circular or triangular) or the dimensions of cross section (rod's thickness and width) can change. It would be interesting to see how different geometries will affect the performance of TMCs and whether the TMC will impacted differently due to recycling for different geometries. DPP (the manufacturer of composite rods) offers a great variety of rod profiles and geometries, therefore obtaining rods with different cross section should be no challenge.
- It is recommended to explore the possibility of modifying the secondary resin. There are two ways the secondary resin needs to be improved. One is that the gel time can be increased leading to a rise in the processing time of secondary resin which allows for the manufacturing of bigger and more complicated samples. The other way the secondary resin can be improved is to have its mechanical properties such as shear strength increased. This can happen by either adding additives to the secondary resin mixture or having a curing procedure at higher temperatures and longer times (as recommended by the secondary resin manufacturer - mentioned in section 4.2).

8.3. Other Recommendations for Future Studies

There are many ways in which the research on recyclable Twin Matrix Composites can be continued. Section 8.1 and 8.2 have already listed several ways that the TMC samples can change. This section lists other aspects of recyclable TMC that are yet to be investigated:

- More mechanical testings: So far, the only mechanical testing done on TMCs is the ILSS testing. There is room for many other mechanical testings, examples are tensile, compression, flexural, fracture toughness, impact testing etc. It is also recommended to use a >1000 fps camera to capture the initial failure mode of the TMCs during each of these tests. All of these tests contribute to gathering more information about recyclable TMCs and whether their performance will be affected by recycling.
- Load application before recycling: While this study has shown that TMCs have a high potential to be applied in sustainable composite-based industries, it has neglected an important factor. This factor is that in any application, the TMCs will be first used (to serve their operational purpose) and then will be recycled. However, in this study, the TMCs are recycled right after they have been created. Therefore, to make TMCs more industrially relevant it is recommended that for future studies, consider loading TMCs before recycling. This includes putting the TMC under either static loads (such as tension, compression, bending, shear etc) or dynamic loads (such as harmonic or non harmonic loads) before recycling and investigate how a recycled and used TMC compares to a fresh one.

- Simulation tools: It would be very useful to create simulation models that represent the TMC of this study. Based on the given geometries and material properties of the ingredients, a TMC sample model can be made. A challenge however is that there would be several parameters that are yet unknown and must be determined in order to create an accurate model. An example of these are parameters are that linked to cohesive behaviour between the rods and the secondary matrix. To determine these parameters, it is recommended to perform experiments and tune the unknown model parameters such that the model gives the same output as the real experiment. Of course, it should be ensured that all unknown influencing parameters are considered and the assumptions are fair and valid. Once the model is made, the effects of changing several parameters (such as change in the dimensions of the rods, change in secondary matrix properties or varying the lay up order) can be studied.
- Economical, industrial and environmental aspects: The fact this composite is recyclable adds economical advantages for the user because now its reinforcing component can be used again or sold for a comparable price as their performance is not affected greatly due to recycling. In addition to economical benefits, there will be environmental advantages too because thanks to the reusing of rods, less reinforcement will be used. Therefore, it is suggested to perform a study on the economical, industrial and environmental aspects of recyclable twin matrix composite and ultimately find their role in a circular economy.

9
Conclusion

In this thesis study a state of art recyclable twin matrix composite (TMC) has been created and analyzed. The reinforcements of these TMCs are composite rods and are made from carbon fibers embedded in a bisphenol A epoxy resin. These composite rods will be used together with another resin (referred to as secondary resin) to create the TMC samples. The secondary resin of this study is the result of mixing bio-based epoxy resin and an amine based hardener, labeled recyclamine. What makes the TMC of this thesis study unique is that it is recyclable. This is thanks to the secondary resin's ability to decompose in an acidic solution and the composite rods' resistance against acidic solution. That means the resultant TMC offers the possibility of recycling as its reinforcing rods can be used multiple times (each time with a new dosage of secondary matrix).

The goal of this thesis study is to investigate whether recycling affects the properties of TMCs and if so, to what extent. The properties that have been studied, fall into two categories: one is regarding the surface properties of the reinforcing rods and the other category is regarding the interlaminar strength of the TMC. Regarding the first category, the change in surface features was studied via secondary electron microscopy (SEM) and water contact angle analysis. To investigate the effect of recycling on the interlaminar strength of TMCs, interlaminar Shear Strength test (ILSS) tests have been done on the samples. To understand the effect of recycling and whether this effect will be the same after a large number of recycling sessions, it is decided to compare three types of TMC samples: TMC samples made from rods that have been never recycled, TMC samples that are made from rods which have been recycled once and lastly, TMC samples made from rods that have been recycled four times.

The lay up order of samples is $0^o/90^o/0^o$ and they are made via the method of hand lay up. Thanks to a mould that has been specifically made for these composites, the reinforcing rods can be placed next to each other in an organized manner. In case a sample is to be recycled, the TMC batch will be dropped in an acetic acid solution which will result into the full decomposition of the secondary resin and the possibility of extraction of recycled rods. These recycled rods will be then used again to create a new TMC with a new secondary resin.

Results of the SEM analysis indicate that there is no remarkable change made to the rod surface due to recycling; this has shown to hold true also in case of high numbers of recycling. However, it has been observed that recycling leads to the creation of very small surface dents as well as fiber bundles emerging out of rod's surface. With increasing the number of recycling sessions, it becomes more probable to see these features. Results of the water contact analysis on the other hand showed that the water contact angles increase with the increasing the number of recycling sessions. This means that the surface of the rods becomes rougher with increasing the number of recycling sessions. This is in line with the SEM results and putting these two conclusions together, it can be concluded that recycling contributes to a less smooth rod surface while still, there will be no significant damage to rod's surface and structure.

Results of ILSS indicate that there is no significant change on interlaminar shear strength of TMC samples due to recycling. Note that in order to have a fair comparison between the ILSS performance of

TMC samples, the ILSS values of each of them must be divided the rod volume. The reason for doing so is that there are thickness differences between TMC samples and these differences lead only additional secondary resin and no change in the amount of rods. Therefore, instead of ILSS values, ILSS value per rod ($ILSS_{rod}$) must be compared. The average $ILSS_{rod}$ of TMCs made from unrecycled rods is 47.15 $\pm$2.08 MPa, while that of TMCs made with one-time-recycled rods is 46.77 $\pm$5.09 MPa and the average ILSS of TMCs made from four-times-recycled rods is 46.54 $\pm$3.70 MPa. If one only looks at the measurement values and ignores the absolute uncertainties, it can be concluded that there is a slight reduction in $ILSS_{rod}$ properties due to recycling but considering the absolute uncertainties, the conclusion would be that there would be no significant reduction in $ILSS_{rod}$ of TMC samples.
If one wishes to know the reference ILSS value of TMC samples (thus not the $ILSS_{rod}$), that value would be 26.58 $\pm$2.17 MPa. This value is the average ILSS value of samples made from unrecycled rods, thus there is no influence of recycling in this value. Also, because all samples in this category have the same thickness, there is no need to divide the ILSS numbers by the rod volume which makes the above-mentioned ILSS value a trustworthy value.
Another information provided by the ILSS testing was the failure mechanisms that had occurred during this tests. It was observed that these fracture mechanisms are not affected by the number of recycling sessions and are the same for all TMC samples. For all these samples, the observed fracture mechanisms are delamination between the secondary matrix and the 0^o rods as well as the failure of the 90^o rods and the secondary matrix around these 90^o rods as cracks are observed to go through them.

Given that this is a rather novel composite, there are many aspects of this composite that are new and have never been done before. For example, there were many trials and error attempts for the designing and manufacturing of this composite. Despite making several progresses on different aspects, there is still plenty of room to improve. In the author's opinion, the two most critical aspects to improve are obtaining samples with the same thickness and achieving more consistent cross sections among TMC samples. As said above, because not all samples had the same thickness in this study, that meant the rod volume would not be the same which meant further that the total fiber volume would not be the same. Had all samples had the same thickness, this would not have been necessary. Therefore, it is recommended to strive to have samples with the same thickness as well as very similar cross sections.

This thesis study has taken many initial steps in creating and understanding recyclable twin matrix composite. Thanks to this study, there is now the knowledge that the physical properties and mechanical performance of TMCs is affected only by a negligible margin by the recycling procedure and this statement holds for high numbers of recycling. This advantage is expected to be an attractive feature for future studies to continue this research field and expand the knowledge on recyclable TMCs.

References

[1] Kenneth Alambra and Nicholas Swanson. *Beam Deflection Calculator*. Apr. 2024. URL: https://www.omnicalculator.com/construction/beam-deflection.

[2] A. V. Azarov et al. “Development of a two-matrix composite material fabricated by 3D printing”. In: *Polymer Science - Series D* 10 (1 Jan. 2017), pp. 87–90. ISSN: 19954220. DOI: 10.1134/S1995421217010026.

[3] Donald J. Baker and Carl Q. Rousseau. “Analysis and test of repair concepts for a carbon-rod reinforced laminate”. In: American Institute of Aeronautics and Astronautics Inc., 2000. DOI: 10.2514/6.2000-1596.

[4] F. Barthelat and H. D. Espinosa. “An experimental investigation of deformation and fracture of nacre-mother of pearl”. In: *Experimental Mechanics* 47 (3 June 2007), pp. 311–324. ISSN: 00144851. DOI: 10.1007/s11340-007-9040-1.

[5] Francois Barthelat. “Designing nacre-like materials for simultaneous stiffness, strength and toughness: Optimum materials, composition, microstructure and size”. In: *Journal of the Mechanics and Physics of Solids* 73 (Dec. 2014), pp. 22–37. ISSN: 00225096. DOI: 10.1016/j.jmps.2014.08.008.

[6] Douglas S. Cairns and Bryan C. Bundy. “The application of pre-cured carbon fiber/epoxy pultrusions as reinforcement in composite wind turbine blades”. In: vol. 14. 2007, pp. 9985–9993. ISBN: 1563478900. DOI: 10.2514/6.2007-821.

[7] Sebastien Callens. *MSc Thesis Development and Evaluation of Twin Matrix Composites*. URL: http://repository.tudelft.nl/..

[8] Sebastien J.P. Callens and Otto K. Bergsma. “Two-matrix composites: Carbon fiber micropultrusions embedded in flexible epoxy matrices”. In: *Composites Part A: Applied Science and Manufacturing* 114 (Nov. 2018), pp. 1–12. ISSN: 1359835X. DOI: 10.1016/j.compositesa.2018.08.008.

[9] R Concept. *POlar bear: Biobased Compression Molding Epoxy System*. https://livingrconcept.com/wp-content/uploads/sites/7/2020/04/TDS_POLARBEAR_bio.pdf.

[10] Sandro Dattilo et al. “Full Recycling and Re-Use of Bio-Based Epoxy Thermosets: Chemical and Thermomechanical Characterization of the Recycled Matrices”. In: *Polymers* 14 (22 Nov. 2022). ISSN: 20734360. DOI: 10.3390/polym14224828.

[11] Pradip K. Dubey et al. “Recyclable epoxy systems for rotor blades”. In: vol. 942. IOP Publishing Ltd, Oct. 2020. DOI: 10.1088/1757-899X/942/1/012014.

[12] Pradip Kumar Dubey and Satish Kumar Mahanth. *Recyclamine ®-novel amine building blocks for a susitainable world*. URL: www.epotec.info.

[13] Getting rid of bubbles in epoxy. *TotalBoat*. https://www.totalboat.com/blogs/totalboat/getting-rid-of-bubbles-in-epoxy. Sept. 2022.

[14] Ömer F. Erkendirci and Bazle Z. Haque. “Quasi-static penetration resistance behavior of glass fiber reinforced thermoplastic composites”. In: *Composites Part B: Engineering* 43 (8 Dec. 2012), pp. 3391–3405. ISSN: 13598368. DOI: 10.1016/j.compositesb.2012.01.053.

[15] Francesca Ferrari et al. “Fully recyclable bio-based epoxy formulations using epoxidized precursors fromwaste flour: Thermal and mechanical characterization”. In: *Polymers* 13 (16 Aug. 2021). ISSN: 20734360. DOI: 10.3390/polym13162768.

[16] S. M. García-Rodríguez et al. “Experimental demonstration of the in-situ effect under transverse shear”. In: *Composites Part A: Applied Science and Manufacturing* 138 (Nov. 2020). ISSN: 1359835X. DOI: 10.1016/j.compositesa.2020.106047.

[17] Ginger Gardiner. *Recyclable epoxy proven in HP-RTM*. Aug. 2016. URL: https://www.compositesworld.com/articles/recyclable-epoxy-proven-in-hp-rtm.

[18] Laboratoire Georessources. *Scanning Electron Microscopes*. https://georessources.univ-lorraine.fr/en/content/scanning-electron-microscopes. Sept. 2017.

[19] Jeff Gotro. *Epoxy Curing Agents – Anhydrides, Long Pot Life and Exceptional Properties*. Aug. 2022. URL: https://polymerinnovationblog.com/epoxy-curing-agents-anhydrides-long-pot-life-and-exceptional-properties/.

[20] Fabrizio Greco et al. “Mechanical behavior of bio-inspired nacre-like composites: A hybrid multiscale modeling approach”. In: *Composite Structures* 233 (Feb. 2020). ISSN: 02638223. DOI: 10.1016/j.compstruct.2019.111625.

[21] Madeleine Grossman et al. “Hierarchical Toughening of Nacre-Like Composites”. In: *Advanced Functional Materials* 29 (9 Feb. 2019). ISSN: 16163028. DOI: 10.1002/adfm.201806800.

[22] J. Henry and S. Pimenta. “Increasing damage tolerance in composites using hierarchical brick-and-mortar microstructures”. In: *Journal of the Mechanics and Physics of Solids* 118 (Sept. 2018), pp. 322–340. ISSN: 00225096. DOI: 10.1016/j.jmps.2018.06.003.

[23] E. V. Iarve and D. H. Mollenhauer. “Mesh-independent matrix cracking and delamination modeling in advanced composite materials”. In: Elsevier Inc., Aug. 2015, pp. 227–264. ISBN: 9780081003428. DOI: 10.1016/B978-0-08-100332-9.00009-8.

[24] ASTM International. *Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates*. 2022. URL: https://www.astm.org/d2344_d2344m-22.html.

[25] Bram C.P. Jongbloed et al. “A study on through-the-thickness heating in continuous ultrasonic welding of thermoplastic composites”. In: *Materials* 14 (21 Nov. 2021). ISSN: 19961944. DOI: 10.3390/ma14216620.

[26] Jae Woo Kim et al. “Multi-scale hierarchical carbon nanotube fiber reinforced composites towards enhancement of axial/transverse strength and fracture toughness”. In: *Composites Part A: Applied Science and Manufacturing* 167 (Apr. 2023). ISSN: 1359835X. DOI: 10.1016/j.compositesa.2023.107449.

[27] Matthieu Lejeail and Hartmut R. Fischer. “Development of a completely recyclable glass fiber-reinforced epoxy thermoset composite”. In: *Journal of Applied Polymer Science* 138 (3 Jan. 2021). ISSN: 10974628. DOI: 10.1002/app.49690.

[28] Performance Composites Ltd. *Mechanical Properties of Carbon Fibre Composite Materials, Fibre / Epoxy resin (120°C Cure)*. http://www.performance-composites.com/carbonfibre/mechanicalproperties_2.asp. July 2009.

[29] “Numerical analysis of resin-rich areas and their effects on failure initiation of composites”. In: *Composites Part A: Applied Science and Manufacturing* 117 (Feb. 2019), pp. 125–133. ISSN: 1359835X. DOI: 10.1016/j.compositesa.2018.11.016.

[30] JEC Organization. *Recycling thermoset composites*. July 2011. URL: https://www.jeccomposites.com/news/spotted-by-jec/recycling-thermoset-composites/.

[31] S Pastine et al. *Higher Tg recyclable high pressure resin transfer molding (hp-rtm) epoxy properties and how they compare to a commercial system*.

[32] K. D. Potter and M. R. Wisnom. “Composites of extreme anisotropy initial experiments”. In: *Plastics, Rubber and Composites* 31 (5 2002), pp. 226–234. ISSN: 14658011. DOI: 10.1179/146580102225005108.

[33] R.P.L.Nijssen. “Composite Materials: an Introduction”. In: *Materials Under Extreme Conditions: Recent Trends and Future Prospects* (2015).

[34] Angela D. La Rosa et al. “Innovative chemical process for recycling thermosets cured with recyclamines® by converting bio-epoxy composites in reusable thermoplastic-an LCA study”. In: *Materials* 11 (3 Feb. 2018). ISSN: 19961944. DOI: 10.3390/ma11030353.

[35] Josef Schlacher et al. “Micro-scale fracture toughness of textured alumina ceramics”. In: *Journal of the European Ceramic Society* 43 (7 July 2023). ISSN: 1873619X. DOI: 10.1016/j.jeurceramsoc.2022.06.028.

[36] A. Schmitz and P. Horst. “Buckling of multiple discrete composite bundles in the elastomeric foundation of a curvature-morphing skin”. In: *Composite Structures* 134 (Dec. 2015), pp. 1014–1023. ISSN: 02638223. DOI: 10.1016/j.compstruct.2015.09.004.

[37] J. J. Sha et al. “Measurement and analysis of fiber-matrix interface strength of carbon fiber-reinforced phenolic resin matrix composites”. In: Sage Journals, 2013. DOI: 10.1177/0021998313485264.

[38] Varad Shahane. *Development of Short Bamboo Fiber Reinforced Recyclable Epoxy Composites*. URL: http://repository.tudelft.nl/..

[39] Short Beam Shear. *Adams and Lewis on assessing shear teset methods 175 Experimental Results*. URL: http://asmedigitalcollection.asme.org/testingevaluation/article-pdf/25/2/174/7135608/10_1520_jte11475j.pdf.

[40] Manhattan Gold & Silver. *Gold Coatings for Scanning Electron Microscopy*. https://www.mgsrefining.com/blog/gold-coatings-for-scanning-electron-microscopy/. Sept. 2017.

[41] “Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement 1”. In: (). DOI: 10.1520/D7334-08R22. URL: http://www.copyright.com/.

[42] ISO International Standardization. *Fibre-reinforced plastic composites Determination of apparent interlaminar shear strength by short-beam method*. 2023. URL: https://www.iso.org/standard/23642.html.

[43] Entela Treska. *Acetal Group Formation Structure and Mechanism*. https://study.com/academy/lesson/acetal-formation-mechanism.html. 2023.

[44] V V Vasil and V A Salov. “Development and examination of a two-matrix glass fiber composite with high transverse strain”. In: *Prikl. Mat. Mekh., 1* 22 (1 1979), pp. 3–174.

[45] Valery V. Vasiliev. *Composite Pressure Vessels: Design, Analysis, and Manufacturing*. https://books.google.nl/books/about/Composite_Pressure_Vessels.html?id=oF-oWPmKU4UC&redir_esc=y. 2009.

[46] Jerry E. White et al. “Poly(hydroxyaminoethers): a new family of epoxy-based thermoplastics”. In: *Advanced Materials* 12 (23 Dec. 2000), pp. 1791–1800. ISSN: 09359648. DOI: 10.1002/1521-4095(200012)12:23<1791::AID-ADMA1791>3.0.CO;2-A.

[47] James M Whitney. *Elasticity Analysis of Orthotropic Beams under Concentrated Loads*. 1985.

[48] Burak Ogun Yavuz, Levend Parnas, and Demirkan Coker. “Interlaminar tensile strength of different angle-ply CFRP composites”. In: vol. 21. Elsevier B.V., 2019, pp. 198–205. DOI: 10.1016/j.prostr.2019.12.102.

[49] Kai Yu et al. “Carbon Fiber Reinforced Thermoset Composite with Near 100% Recyclability”. In: *Advanced Functional Materials* 26 (33 Sept. 2016), pp. 6098–6106. ISSN: 16163028. DOI: 10.1002/adfm.201602056.

A

Composites With Brick And Mortar Architecture

As mentioned few times already in this report, the TMC will have a brick and mortar (BAM) structure. In this case, the brick-like component will be the composite rods and the mortar-like component will be the secondary matrix. Such architectures have been shown to provide structures that have high shear strength, stiffness and fracture toughness simultaneously [5]. The BAM architecture is able to dissipate (fracture) energy in a stable manner, specially if the brick like reinforcements are ordered in a hierarchical and organized structure. This type of architecture ensures that cracks propagate throughout the composite before leading to stress concentration and damage localization. This results in a non-linear stress-strain graph which leads to a 'warning' before failure [22]. Thanks to this stable energy dissipation mechanism, BAM composites have relatively higher fracture toughness values. This has been shown in a study done by Kim and Gardner who observed that the Mode-1 fracture toughness of their BAM composite was 0.670 kJ/m^2, which according to them is a high number for a structural composite [26]. Another advantage of a hierarchically ordered BAM composite is that it is less sensitive to imperfections such as the misplacement of reinforcements [22].
The BAM structure is an architecture which can be seen in several natural structures. For instance, mollusk shells have a nacreous-layered structure consisting of inorganic platelets ordered in a BAM formation. The platelets connected to each other via mineral bridges and nano-asperities and the mortar like resin would be a bio-polymer matrix. These bridging and deflection mechanisms [21] as well as the platelet movement mechanisms control the sliding movement within the BAM composite [5]. Similar to conventional composites they have higher tensile strengths and strain in the longitudinal direction than in the transverse direction[4]. In addition to composites, nacre-like organisms have also inspired the development of metal-based components (such as metallic glasses or toughened steel alloys) and ceramics (zirconia-based ceramics) [21].

In a study done on extrinsic and intrinsic toughening mechanisms of Nacre-like composites by Grossman and Pivovarov [21], they came up with a composite made in the BAM formation with Alumina platelets acting as brick components and epoxy (or a combination of epoxy and PEI) polymer acting as the mortar. Additionally in their case, they had also used mineral bridges distributed along the polymer to connect the platelets. The reason for using these bridges was to enhance intrinsic toughening however as this tactic is not very relatable to the scope of this thesis study, the effect of mineral bridges will not be discussed.
Back to the discussion of relevant findings of this study, the authors compared two BAM composites each with different polymer characteristics; one with a DGEBA resin mixed by hardener known as D320 resulting into a stiff matrix and while the other BAM composite's matrix is made from DGEBA resin mixed by another hardener known as D400 resulting into a softer matrix (the difference between these matrices is within the cross linking density). Their results showed that the BAM composite with the softer matrix has an elastic modulus of 101.4 GPa and fracture strength of 241.2 MPa while the BAM composite with a stiffer matrix had an elastic modulus of 102.3 GPa and fracture strength of 234.1 MPa. Thus it can be seen that these properties were not affected much with the change in polymer's

stiffness. Additionally, the authors learned that the fracture toughness is also not impacted by this change and remains in the 5-6 MPa $\sqrt{m}$ range (which is almost twice of a lone alumina platelet) [35]. The proportionality of the behavior of BAM composites with soft and stiff matrices with respect to each other changes for different thicknesses of matrix. For example it was found that increasing this thickness leads to a larger energy dissipation during fracture for BAM composites with softer matrices. In other words in case of BAM composites with softer matrices, increasing the matrix thickness has a greater toughening impact than in BAM composites with the stiff matrix. Other properties that vary differently for BAM composites with soft and stiff matrices based on matrix thickness are fracture strength and modulus. Such differences can be seen in figure A.1 which compares BAM composites with different matrices in terms of their response to changes in matrix thickness. As can be seen, the fracture toughness of the BAM composite with a stiff matrix reduces more significantly than the one with soft matrix. As figure A.1 shows, their initial strengths were similar while the final strength of the BAM composite with the soft matrix was higher than that of the stiff one. Regarding the fracture modulus, it can be seen that in case of BAM composite with the soft matrix, the modulus does not change remarkably with changing matrix thickness while the modulus of the BAM composite with the stiff matrix reduces remarkably with increasing the matrix thickness.

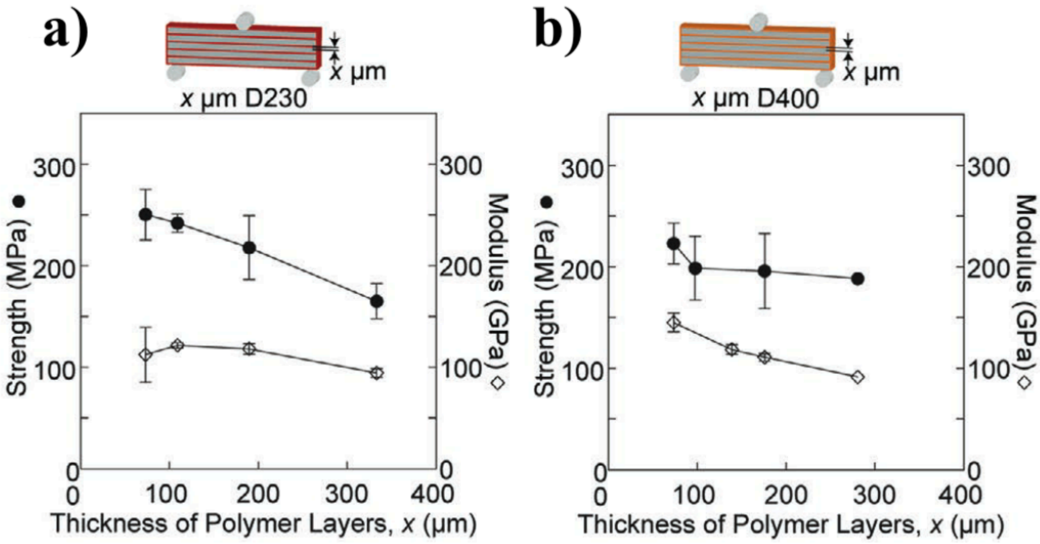

Figure A.1: Variation of fracture strength and modulus of BAM composites with respect to matrix's thickness. The reinforcement (bricks) are Alumina platelets and the matrix polymer made from a) epoxy resin with D320 hardener (stiff) and b) epoxy resin with D400 hardener (soft) [21].

Another study that has useful information is done by Greco and Leonettia [20] which aims to investigate the flexibility and penetration stiffness (penetration stiffness can be interpreted as fracture toughness in this case [14]) of BAM composites. One of the outcomes of this study was to determine the influence of reinforcing bricks' aspect ratio and their volume fraction on bending and penetration stiffnesses. Results of their study are shown in figures A.2. Figures A.2a and c indicate that increasing the platelet's aspect ratio leads to higher bending and penetration stiffnesses, though these rises seem to have low slopes. Also by looking at figure A.2a, notice that at high volume fractions, bending stiffness is affected more by the variation of platelet's aspect ratio. Figures A.2b and d indicate that increasing the platelet volume fraction on the other hand has shown to cause more-than-linear rises in bending and penetration stiffnesses. To put it more generally, the authors found that flexibility of BAM composite decreases with increasing either the aspect ratio or volume fraction of platelets. Also, it is found that the BAM composites become stiffer at higher platelet aspect ratios and volume fractions. However it must be mentioned that the variation of volume fraction seems to be more influential than the variation of aspect ratio.

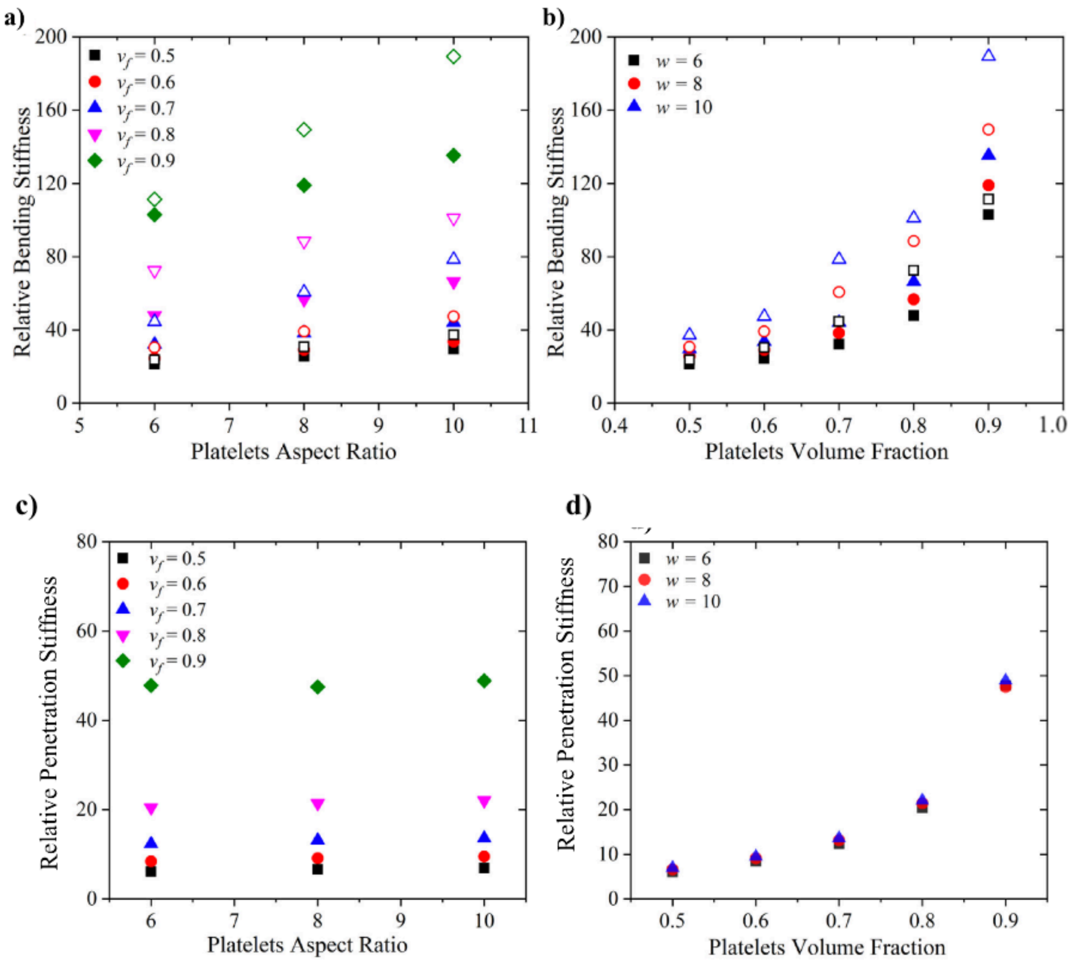

Figure A.2: The variation of relative bending stiffness with respect to reinforcing platelet's a) aspect ratio and b) its volume fraction as well as the variation of the relative penetration stiffness with respect to reinforcing platelet's c) aspect ratio and d) its volume fraction[20]. Several notes must be made regarding these figures; one is that for figures a and b, the empty cells would be un-bent samples and full cells are for the bent samples (bending angle = 15^o). For the sake of this thesis, looking at the empty cells shall suffice. Other note is to explain 'relative' in relative bending stiffness or relative penetration stiffness refers to the corresponding stiffness of the BMA composite sample normalized to that of its polymer

It is worth mentioning that according to Barthelat, in order for the BAM composites to have their unique characteristics, the brick-like reinforcements have to be at least 5 times stronger than the surrounding matrix [5]. Typically speaking, the volume fraction of brick like components in BAM composites is around 95% meaning that the volume fraction of mortar like components would be 5% [20].

B

Development of Manufacturing Procedure

Since this is a novel composite and has been never made before for any study, first it must be determined how to make an acceptable TMC. An acceptable TMC shall have the following properties:

- All sides of the TMC must be flat and free of any curvature. To check this requirement, the thickness of the middle, left and right sides of each sample will be measured and compared to the other two sides of that sample.
- The thickness along any part of a TMC sample shall be within $\pm$ 5% of its mean thickness. This requirement is inspired by a regulation of ISO 14130; a test standard that is mentioned further in detail in 6.4.1.
- All surfaces of the composite rods must be covered with the secondary resin with a minimum thickness of 0.1 mm. This requirement is checked by looking at the microscopic views of all sides of the samples.
- The distance between the lower surface of the first-layer rod to the bottom surface of the TMC must be at most 0.3 mm. Any distance more than that would be a waste of space and make the TMC unnecessarily thicker.

In addition to these hard requirements, there are also several preferences that are influential in evaluating of the manufactured batches or selecting the samples to be tested. One is about the amount and the size of the voids. The fewer and smaller voids a batch/sample has, the more preferred it is. This preference is applied especially when selecting the locations to cut the samples from. That means that even if a manufactured batch has voids, the samples that are to be cut will be selected from regions with the least amount of voids.
Another preference is that the rods should be flat instead of being tilted. This is however hard to observe until the batch has been cut to give out samples. Only then it is possible to observe whether the cut samples have any tilted rods. The only way to observe whether there are any tilted rods in a batch before the cutting stage is to look at the top or bottom surface and the sides of the TMC.

B.1. First Generation of Twin Matrix Composite Manufacturing

Developing the first generation of TMC manufacturing was the most time-consuming phase of this thesis study. The reason is that while the development of the next few generations will mostly involve improvements in the mould design, the development of the first generation involves other stages of the production as well as the mould development.
Starting off with developments in the secondary resin, initially it was thought that mixing the epoxy resin with the recyclamine hardener would be sufficient to create the secondary matrix with an acceptable quality. However, doing so resulted into a secondary matrix with a significant number of voids, as shown in figure B.1a. After having multiple discussions with the manufacturer of the epoxy resin and recyclamine hardener and multiple trial and error trials, it is decided to put the epoxy resin solution into

hot water (74 ^oC) for about 40 minutes. As already mentioned in subsection 5.4.1 doing so breaks any crystal blocks in the epoxy resin which could potentially prevent the reaction of the epoxy chains with the recyclamine molecules. Another lesson learnt from these trial and error trials is to use the speed mixer (shown in figure 5.7a). Doing so has shown to lead to a remarkable reduction in the number of voids in the secondary matrix, as shown in figure B.1b.

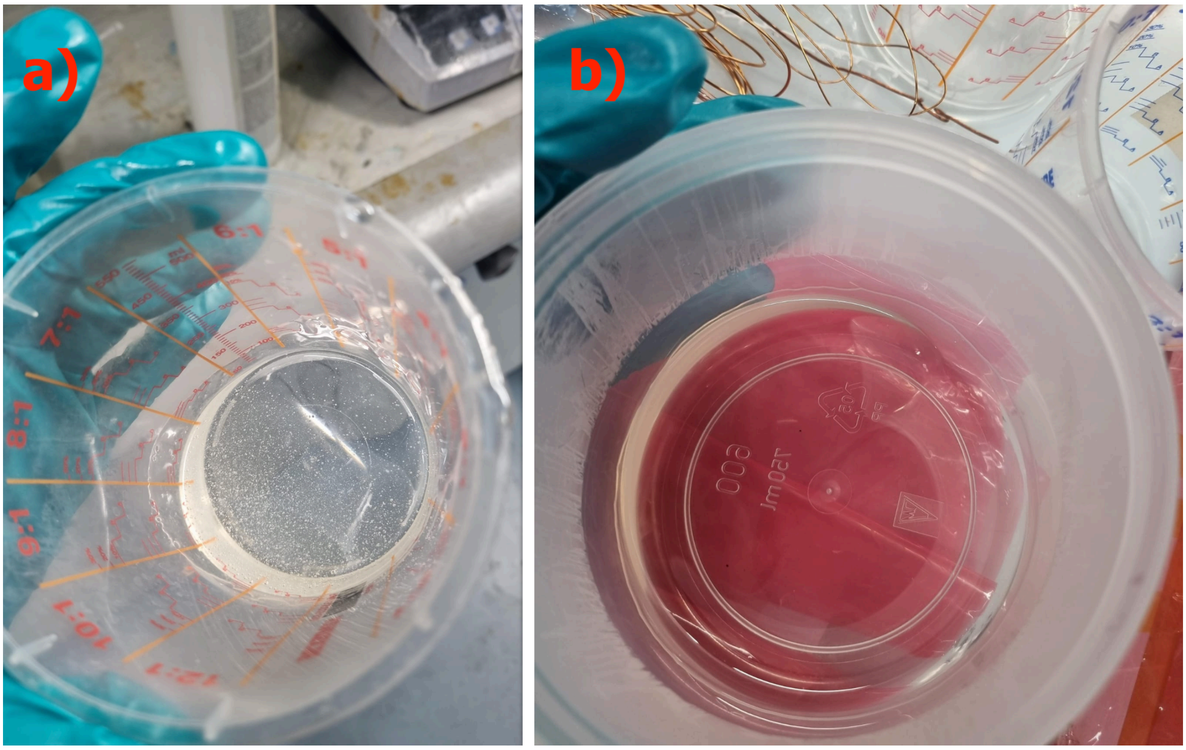

Figure B.1: Comparison of the effect of using the speed mixer. Figure a represents a secondary matrix for which the speedmixer has not been used and therefore has voids. Figure b represents another secondary matrix solution that has no voids thanks to the usage of the speedmixer

Now, referring back to table 4.2 in subsection 4.2, it was promised to explain why curing at 140^oC for 4 hours was not an option for this TMC while according to the manufacturer of the secondary resin, this would be an ideal curing cycle to obtain the strongest secondary resin. Figure B.2 represents a TMC that has been made with this cycle. At the end of post-curing cycle, the secondary resin breaks into smaller components. Some of these components remain attached to the composite rods and the other ones become totally loose. Separating the rods from each other becomes then very easy and that is how figure B.2 has been obtained. The author suspects that this phenomenon occurs due to the difference in the thermal expansion coefficient of the rods versus that of the secondary matrix. Furthermore, it is suspected that the expansion coefficient of the secondary matrix would be higher than the rods' expansion as they have shrunk more.

Figure B.2: Consequence of curing at 140^{o}C for 4 hours on TMC

To overcome this issue, it is suggested to investigate the addition of additives to the secondary resin. However ultimately, it was decided not to pursue this path as it would consume a significant amount of time of the thesis study and lifts the focus off the recyclability matter. Therefore it is decided to stick to the general advice of the secondary resin manufacturer and post-cure the TMC at 85^{o}C for 15 minutes. Focusing now on the developments of the 3D printed mould for this generation, this was first started by investigating which material would be best to make the mould. The process and results of this investigation are already mentioned in section 5.1. Once that was selected, it was time to find the optimum mould design. The initial design can be seen in figures B.3. These figures represent the top and bottom of the ultimate mould designed for the first generation. As it can be seen in figure B.3a, the distance between the teeth are 3.8 mm, which is 0.11 - 0.15 mm more than the width of the rods given that their width is 3.65-3.69 mm. The reason for having X-shaped reinforcements at the bottom of the mould (can be seen in figure B.3b) is that without them, the mould had shown to have curvature (due to the thermal kickback after printing). Adding this X-shaped reinforcement showed to reduce the curvature of the mould; though still there was some curvature.

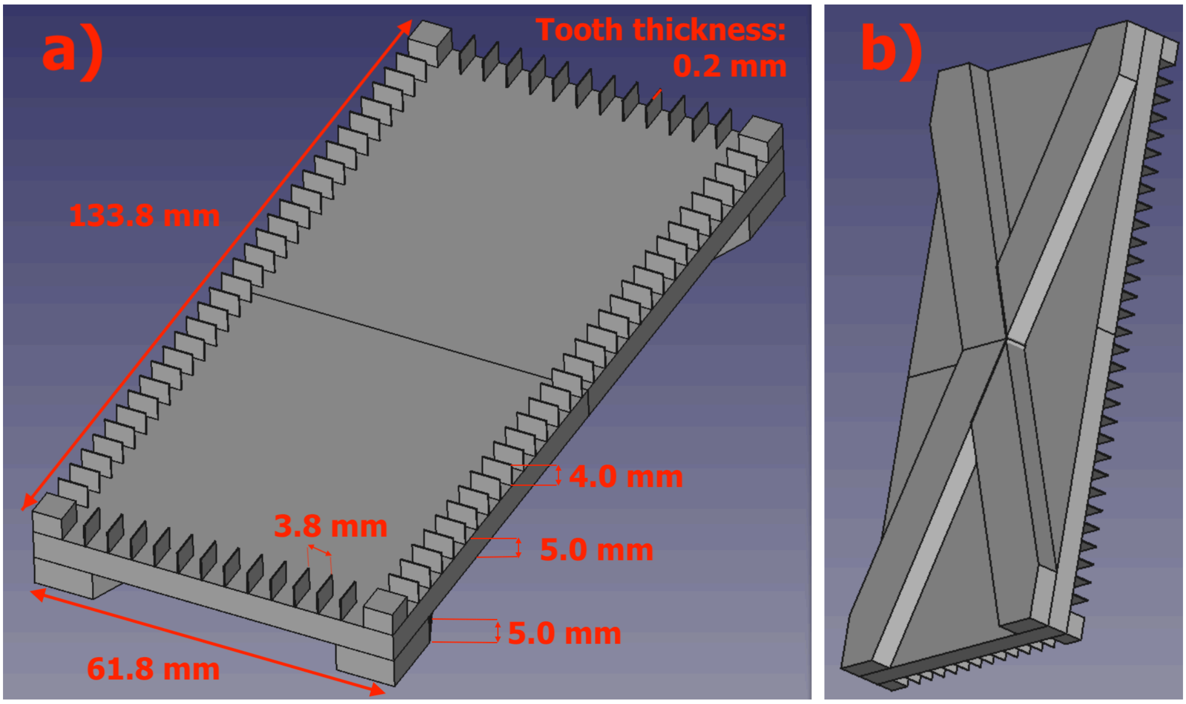

Figure B.3: Pictures of the ultimate mould for for the first generation of TMC manufacturing. Figure a represents the top side of the mould as well as the dimensions of components. Figure b represents the bottom side of the mould.

Once the TMCs were made with this mould and then de-moulded, large voids were observed at the bottom of the TMCs. The dimensions of these voids could as big as 20 x 20 mm. It is suspected that these voids were created during the curing stage in which the secondary resin flowed out of the mould through the gaps between the teeth. This phenomenon must have created regions under the first layer rods with no secondary resin, hence the creation of voids there. To overcome this issue, it can be proposed to add walls around the mould so that no secondary resin can flow out of the mould and thus no void be created at the bottom of the TMC.
A question could be raised on why not have these walls from the very beginning? The answer is that because having walls would cause a limitation to the placement of rods between the teeth. Having no walls means that the rods can extend out of the mould. In that case there is a better *biting* and grip between a rod and its neighbouring teeth. In fact, the first generation has shown to be the best manufacturing generation in terms of having no twisted or tilted rods within the TMC (this will be seen in the upcoming subsections). Having no walls allow the rods to be as close as possible to each other without being bent or twisted. Such (horizontal) placement yields into a maximum rod volume in a cross section of TMC. Figure B.4 displays a cross section of the TMC made in this generation. The advantage of having no walls in terms of having a higher rod volume becomes more clear when comparing to TMC cross sections of other generations.

That all being said, solely because of having big and unacceptable voids at the bottom of TMC, a new generation of TMC must be introduced.

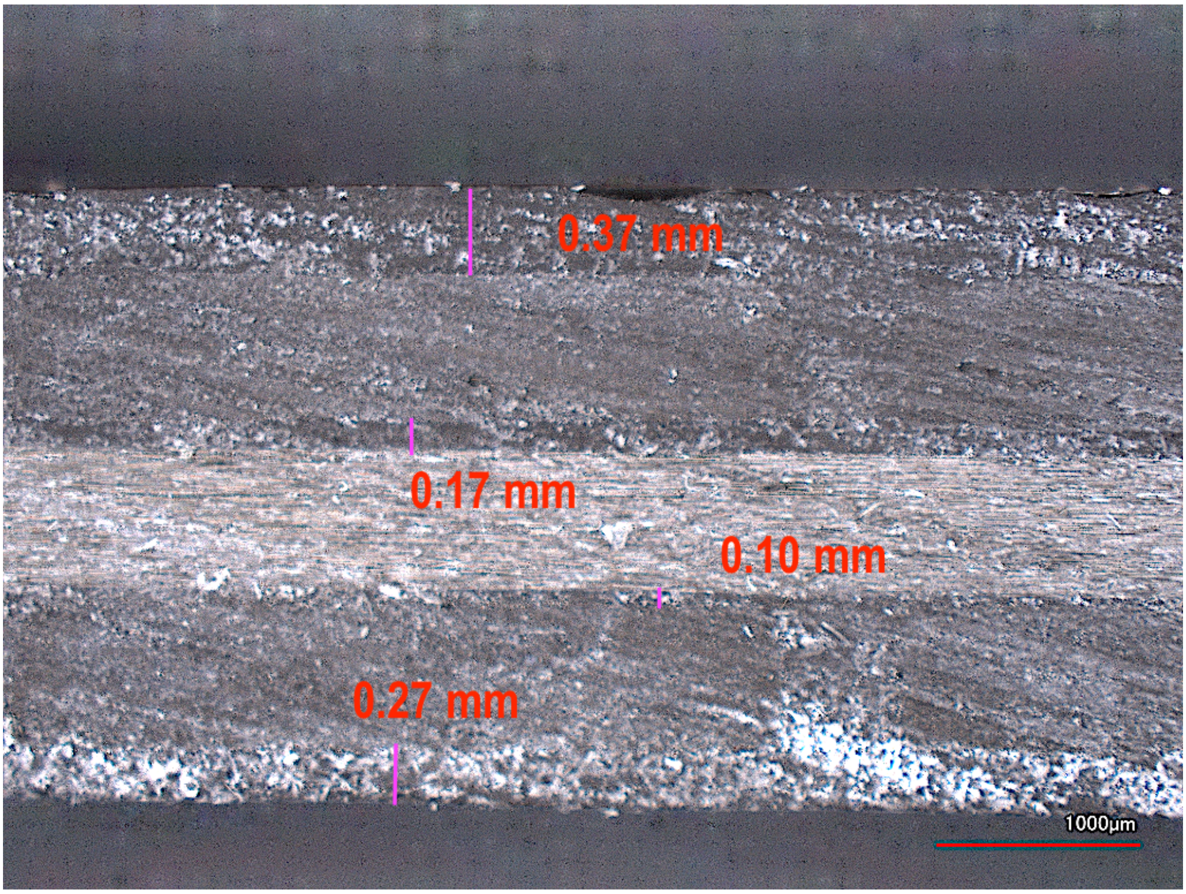

Figure B.4: Picture of the cross section of a first generation TMC including the differences between each rod and its upper and lower boundaries.

B.2. Second Generation of Twin Matrix Composite Manufacturing

The second generation had been started with sole purpose of having no unacceptable voids at the bottom of the TMCs. To overcome this issue, the only update applied is to add walls to the surroundings of the mould. The result can be shown in figure B.5. As that figure shows, a 3 mm thick wall has been added to prevent the flow of the secondary resin outside of the mould.

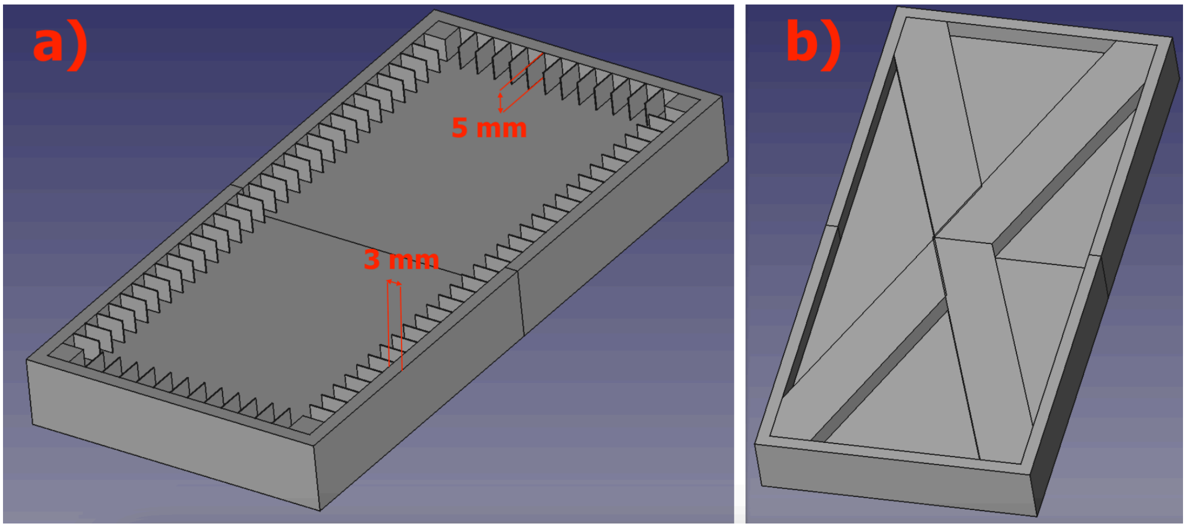

Figure B.5: Pictures of the mould designed for the second TMC manufacturing. Figure a represents the top side of the mould and Figure b represents the bottom side of the mould. Except the wall surrounding the mould, all components have the same dimension as the mould for the first generation TMC manufacturing (Figure B.3). The wall is 3 mm thick and extends to 5mm higher than the surface upon which the TMC will be made.

A challenge that this update creates, is that fitting the rods between the teeth becomes harder. The reason is that because of the added wall blocking the extension of rods towards the outside of the mould, the biting and grip between each rod and its neighbouring teeth has weakened. That means that now if one wishes to place a rod between its neighbouring teeth, the rod will not fit properly and thus will be titled. To overcome this challenge, two solutions can be proposed: One is to increase the distance between the teeth so that each rod would have more distance and will have no problem laying flat. The other solution is to taper both ends of each rod, as already shown in figure 5.6. Doing so allows the rod to fit between the teeth more easily and thus to obtain flat laying rods. It was decided to choose the second option because choosing the first one (rods laying further from each other) would mean a TMC with a lower rod volume.
After manufacturing the TMC, it was observed the addition of walls to the mould has served its purpose; there was a significant reduction in the number and size of the voids at the bottom of TMC. The remaining surface voids are small and do not create any issues because while cutting the samples out of the batch, regions with these voids will not be included in the samples.
While evaluating the obtained TMC, another challenge has been detected. It was observed that these TMCs are too thick, which is unacceptable. Range of thicknesses of the TMCs obtained in this generation varied from 4 to 5 mm. Considering that a TMC is made from 3 layers of rods each with thickness of 0.6 mm, total thickness of 4-5 mm is indeed too much. This can be also seen in figures B.6a and B.6b. Furthermore figure B.6a shows that the thickest part of second generation TMCs is the top most secondary resin layer (2.51 mm). Figure B.6b shows that the bottom most secondary resin layer is also significantly thick (0.99 mm).

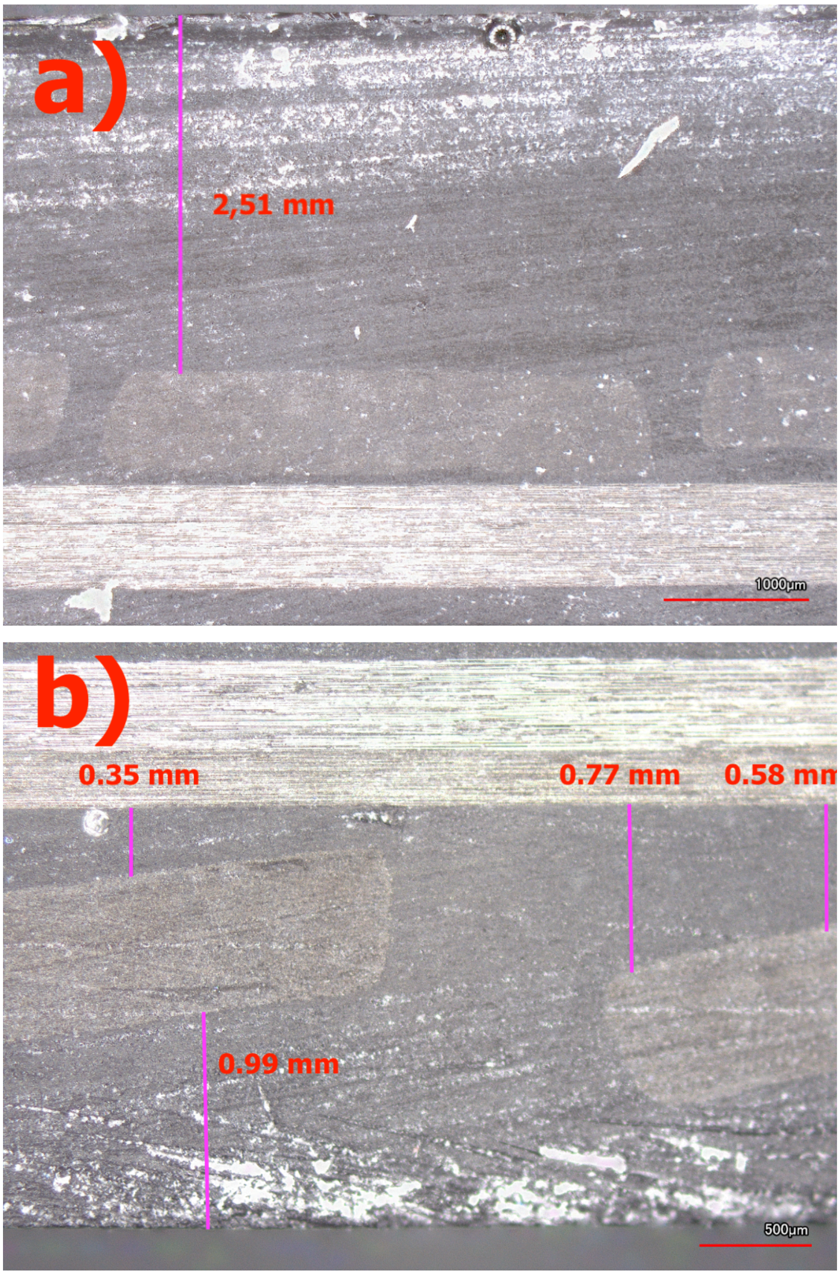

Figure B.6: Pictures of the cross section of the TMCs made via the second generation. Figure a represents the upper half and Figure b represents the lower half. Note that these two pictures are from different samples, hence the difference in lighting and scale. Figure a aims to show the thick top secondary resin layer and Figure B aims to show the thick bottom secondary resin layer as well as the tilted rods.

Figure B.6b highlights another issue of this generation. As can be seen there, rods are titled and not flat. Note that this issue has also been observed in the upper side of the TMC, though figures B.6 does not indicate this phenomenon particularly. Such mis-orientations also contribute to higher TMC thicknesses and lower rod volumes. As said earlier, it is suspected that the rods are titled because of the bad grip between each rod and its neighbouring teeth. This is an issue that must be solved through the next generation. Additionally, next generation should also target to solve the problem of having thick layers of the secondary resin at the top and bottom of TMC.

B.3. Third Generation of Twin Matrix Composite Manufacturing

The third generation is needed to solve the problem of having thick secondary resin layers and tilted rods (as addressed in the above subsection).

To solve the problem of having a thick secondary resin layer at the top, it is decided to decrease the height of the wall. Note that wall height starts from the base surface upon which the TMC is made, as shown in figure B.5. The plan is to reduce this height to the thickness of TMC. So for example, for this generation the intended TMC thickness is 2.70 mm. In that case, the height of the wall should be also 2.70 mm, as shown in figure B.9. It is advised however to have the teeth to be longer than the walls though, in other words longer than the desired TMC thickness. The reason is that longer teeth help the rods stay in their place. This has proven to be a very helpful feature because it is easy for rods to float in the secondary resin (especially when the viscosity of the secondary resin is at its lowest) and thus it would be likely for the top layer rods to float on the top side surface if the teeth are not higher. Based on trial and errors practices, it is learnt that it is sufficient for the teeth to be 0.20 mm higher the wall.
To solve the problem of having a thick secondary resin layer at the bottom of the TMC, it is proposed to have the first layer rods laying 0.2 mm higher than the surface on which the TMC batch will be built; as shown in figure B.7. In other words, the intended distance between the first layer rod and the bottom of TMC will be 0.2 mm.
Adding the steps of 0.2 mm for the first layer rods inspired the addition of steps for the other two rod layers. The initial thought was to see if with adding these steps, thickness of the secondary resin between these layers can be controlled or not. Therefore, it was decided to add the second step for the second layer rod such that distance between the first step and the second step is 0.8 mm. In other words, the distance between the second step and the top side of first layer rod would be 0.2 mm (assuming that the rod thickness would be 0.6 mm). This feature can also be seen in figure B.7.
The same procedure was applied to the third layer rods. That means the intended height difference between the third and second step should be 0.8 mm and thus the distance between the third step and the top side of second layer rod would be 0.2 mm (assuming that the rod thickness would be 0.6 mm). Up to now (from the bottom of first secondary resin layer to the top of third rod), the resultant thickness is 2.4 mm. Now considering that the intended TMC thickness of this generation is 2.7 mm, the top layer of secondary resin shall have a thickness of 0.3 mm (as shown in figure B.7).

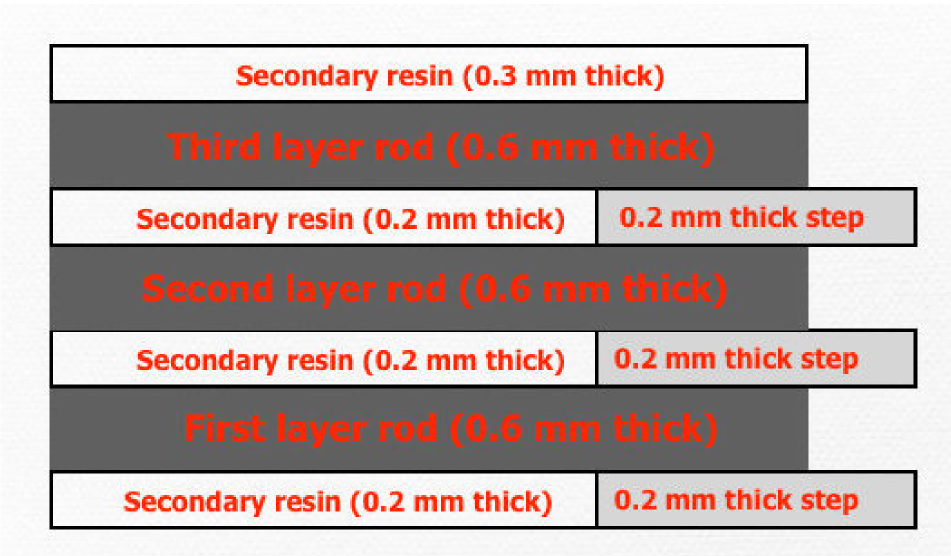

Figure B.7: Sketch of the intended layer thicknesses to obtain in the third TMC generation. Note that picture does NOT wish to represent the desired TMC cross section as it does not show the difference between the first and third rod layers (in the 0^o direction) and the middle rod layer (in the 90^o direction).

To solve the problem of titled rods and making them flatter, it is proposed to increase horizontal distance between the mould teeth. To do so, it is decided to increase the gap length between the teeth from 3.8 to 4.0 mm.
The resultant mould is shown in figures B.8a, B.8b and B.9. As it can be seen in these figures, the general dimensions have changed in comparison to previous generations. The mould used for the previous two generations was 133.8 by 61.8 mm with a total thickness of 14.0 mm while the mould used for this generation is 138.3 x 135.3 mm with the total thickness of 4.6 mm. The reason for this

change of dimensions is to make the resultant mould completely flat and free of any curvature. Despite these changes, there was no reduction in the amount of mould's curvature. Another idea implemented to make the mould flat, was to clamp the mould to an aluminum plate during the TMC production stage. Doing so led to obtaining a completely flat mould.

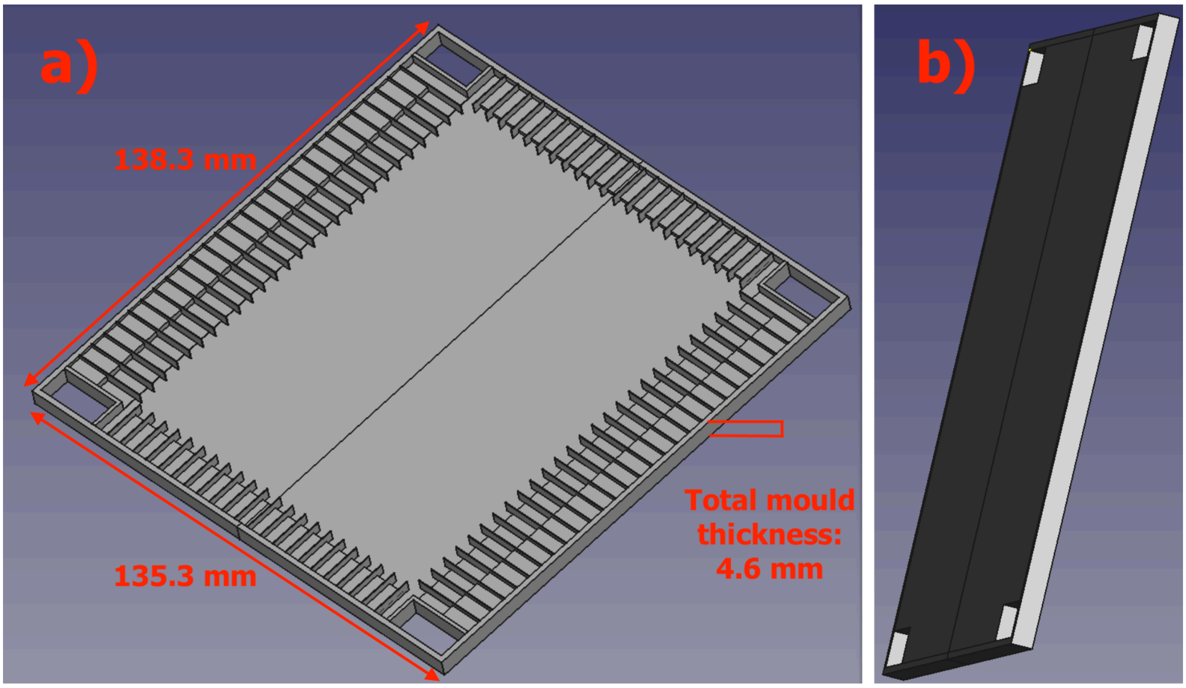

Figure B.8: Figures of the mould designed for the third generation of TMC manufacturing. Figure a represents the front side of the mould with its (total) dimensions. Figure b represents the rear side of the mould.

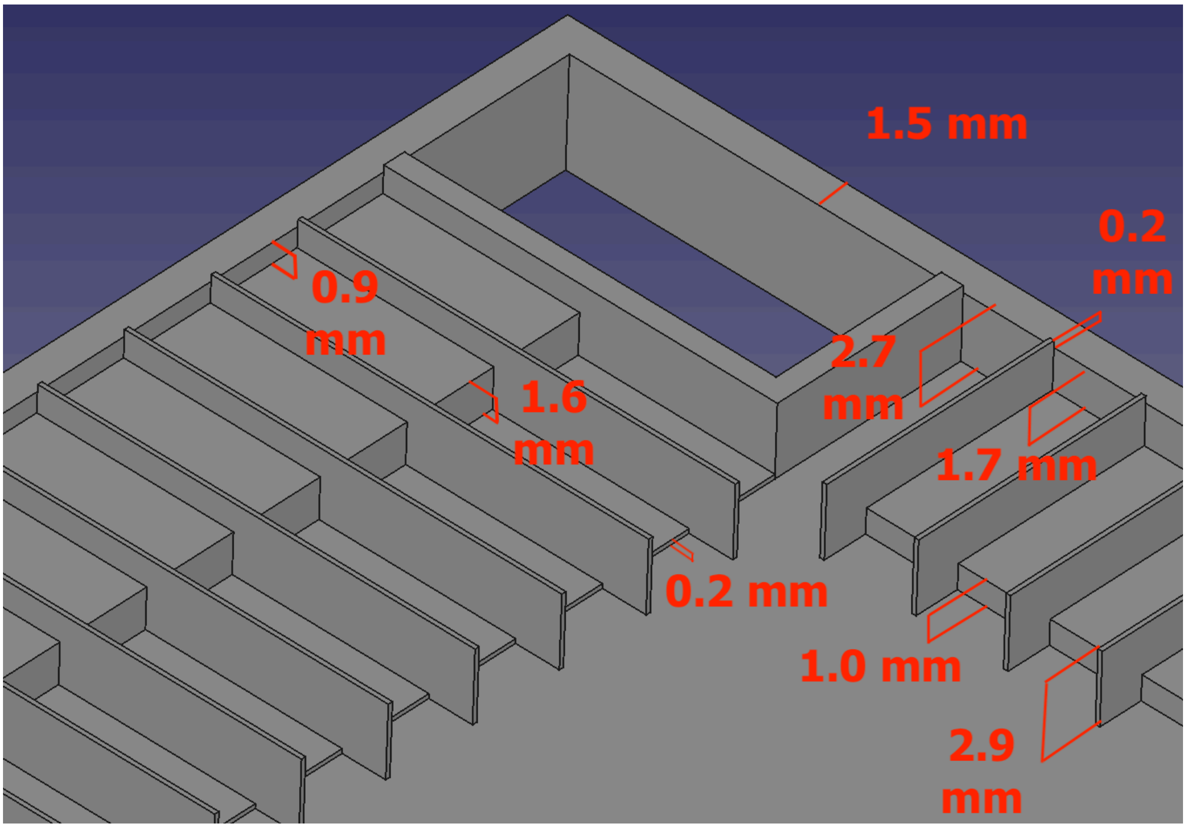

Figure B.9: Zoomed in view of the mould designed for the third generation of TMC manufacturing. This figure represents the heights of the steps with respect to each other and the base on which the TMC will be made. These heights can also be seen in figure B.7.

Now that the development of the third generation of TMC manufacturing has been described, it is time to evaluate the ultimate TMC obtained via this method. Figure B.10 represents a microscopic view of the cross section of the ultimate TMC obtained from the third TMC manufacturing generation. As this figure displays, the top secondary resin layer is 1.0 mm thick. While this thickness is too thick and unacceptable, it is still thinner than the previous generation (comparing with figure B.6 for example). This means that lowering the height of the wall (so that it will be on the TMC's top level) has worked but not sufficiently. Another issue that has not been solved yet is that there is still variations in the total TMC thickness value along different regions of a batch. These thickness variations are ± 0.2 mm. So for example, if the average thickness of a batch is 3.8 mm, then it is possible to obtains samples from this batch that are as thick is 4.0 mm or as thin as 3.6 mm.

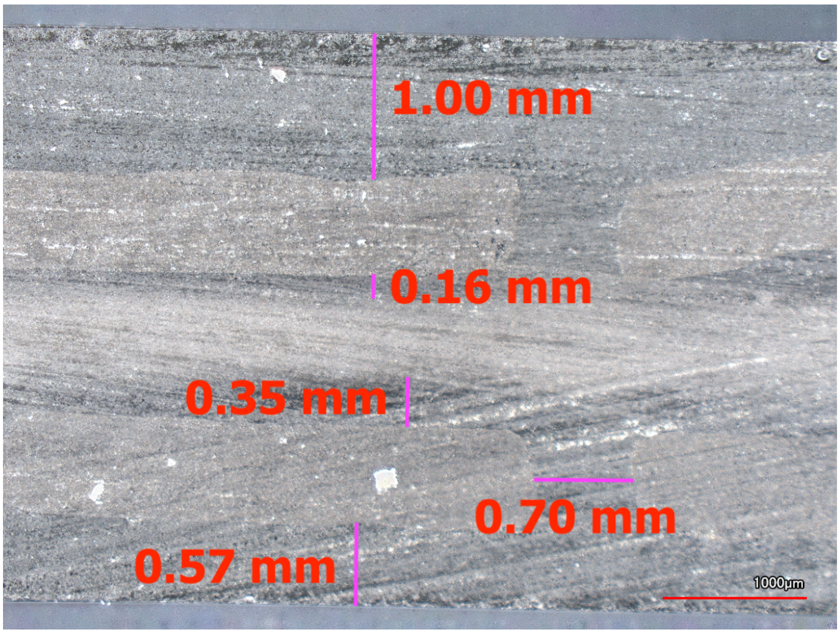

Figure B.10: Picture of the cross section of ultimate TMC made in the third generation.

Regarding the issue of having titled rods, it seems that increasing the distance between the teeth has solved the issue of having tilted rods for the bottom layer rods but not for the top layer rods. It is indeed surprising that increasing the horizontal distance between the upper layer rod has not helped their tilting issue. It is suspected that by applying an equally distributed force over the entire top surface of the TMC batch, this problem can be overcome.
Regarding the thickness of the bottom-most secondary resin layer, this value has reduced in comparison to the previous generation. While this is an improvement, it is expected that this value can decrease further. To achieve this, it is recommended to press down the first layer rods with a (hand) force and make sure they have sunk inside the mould as much as possible before laying the next layer of rods.
A lesson learnt from this generation is that not only the first rods must be pressed inside after they have been laid in their positions, but the other two rod layers must be also pressed down right after each one of them has been laid down. That means that in total, there should be three phases of pressing down; one per each rod layer. Pressing down the rods has shown to be a vital step for the sake of obtaining thinner TMC thicknesses and without it, the rods will 'float more' in the secondary resin. It is recommended to not press down the layers in their center, but at their edges (thus close to mould walls). The reason is that once the force is removed, the rods could exhibit some kind of a kickback and deflect outwards. This could lead to the creation of voids in the TMC. If that is so, the best place to have these voids is at the edges of the TMC batch, where it is certain that the samples will not be taken.

B.4. Fourth Generation of Twin Matrix Composite Manufacturing

The fourth generation of TMC is developed with the purpose of achieving a more constant total TMC thickness for a given batch, having thinner layers of secondary resin and fewer tilted rods at the top side of the TMC.
As said in the above subsection, it is believed that many of these issues are expected to be solved with applying pressure on the TMC during the curing stage. This can happen by putting a plate on top of the TMC and then put weights on top as soon as the curing step begins. Putting a plate on top of TMC has some challenges however. One is that it could disrupt the order of the top layer rods laying next to each other. This issue however is not very likely to happen as long as there is sufficient space between the plate and the top layer rods. This extra space can be provided by creating more 'room' for the secondary resin by making sure that the thickness dedicated to that layer will be thicker than other layers. To monitor whether the composite rods will be displaced or not due to the placement of the plate on top, the plate should be transparent. Poly-carbonate plates are therefore selected initially

as they are known to be transparent thermoplastic components. The plan was that if poly-carbonate would not work, an aluminium plate could be placed on top of the TMC instead. If aluminium does not work either, teflon plates will be tried. All of these three materials are known to have release-free surfaces for epoxy and at the same time, be rigid enough to provide an equal pressure for the epoxy under them.
Another challenge regarding the addition of the cover plate is demoulding. In fact, the only reason why having a plate on top of the TMC during the curing stage has not been tried yet, was the concern that the plate would stick to the TMC and could not be separated. Despite this concern, it is necessary to have this plate on top in order to solve the above-mentioned issues. To make the demoulding as easy and likely as possible, the plate will be treated with Marbocote 4 times. This can happen at the same time when other components (such as the 3D printed mould) are also being treated with marbocote.
Regarding the mass of the weights that will be placed on top of the TMC batch, note that the mass of the cover plate must be considered too. During the development of the fourth manufacturing generation, up to a total weight of 3.5 kg has been tried out (Other weights that have been tried were 1 kg and 2.5 kg). The results indicated that within these weight ranges, variation of the weights does not make any significant change to the TMC's total thickness or its cross section. That being said, as mentioned in section 8.1, it is recommended that higher weights should be tried as well.
Now it is time to describe how the mould itself is updated for this generation. The total length and width of the mould will remain unchanged; so it will have the same length and width dimensions as in figure B.8a and B.8b. What will change, is the height of the wall with respect to the base on which the TMC will be made. It is decided to increase this height from 2.7 mm (as it was for the third generation mould shown in figure B.9c) to 2.9 mm. However, this does not mean the desired the TMC thickness will be 2.9 mm. The desired TMC thickness for this generation is in fact, 3.2 mm. The remaining 0.3 mm will be provided by the teeth as they will be 0.3 mm higher than the wall, as shown in figure B.11. Because of this, the poly-carbonate plate will lay on the teeth instead of the wall and thus the height difference between the plate and the wall be 0.3 mm. Any extra secondary resin that will cause the TMC to be thicker than 3.2 mm, will flow out the mould through these 0.3 mm high channels, as shown by the orange arrow in figure B.11. This is how the height of the TMC is intended to be 3.2 mm.

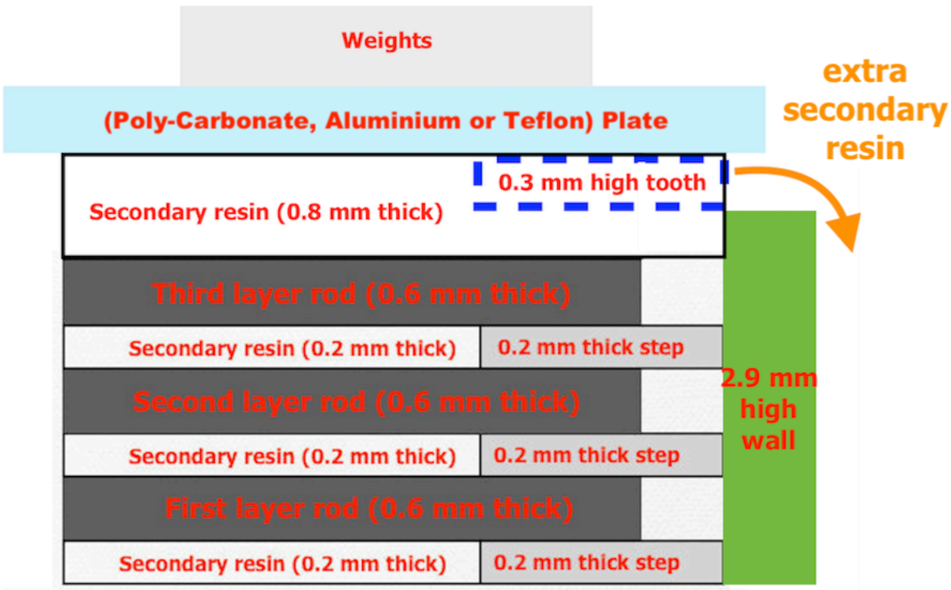

Figure B.11: Sketch of the intended layer thicknesses to obtain in the fourth TMC generation. Note that picture does NOT represent the desired TMC cross section as it does not show the difference between the first and third rod layers (in the 0^o direction) and the middle rod layer (in the 90^o direction). In this figure blue dashed rectangle represents a tooth upon which lays the plate (blue coloured rectangle). This plate can is made from either Poly-carbonate, Aluminium or Teflon. The green rectangle represents the wall and the light grey rectangle represents the weight that will be put on the poly-carbonate plate.

Based on the above description and sketch, the mould of the fourth TMC manufacturing generation has been obtained. The result is shown in figure B.12. This figure displays a corner of this mould, showing how the height values have changed. The total thickness of this updated mould is 4.90 mm (excluding the extra 0.3 mm that the teeth emerge from the top).

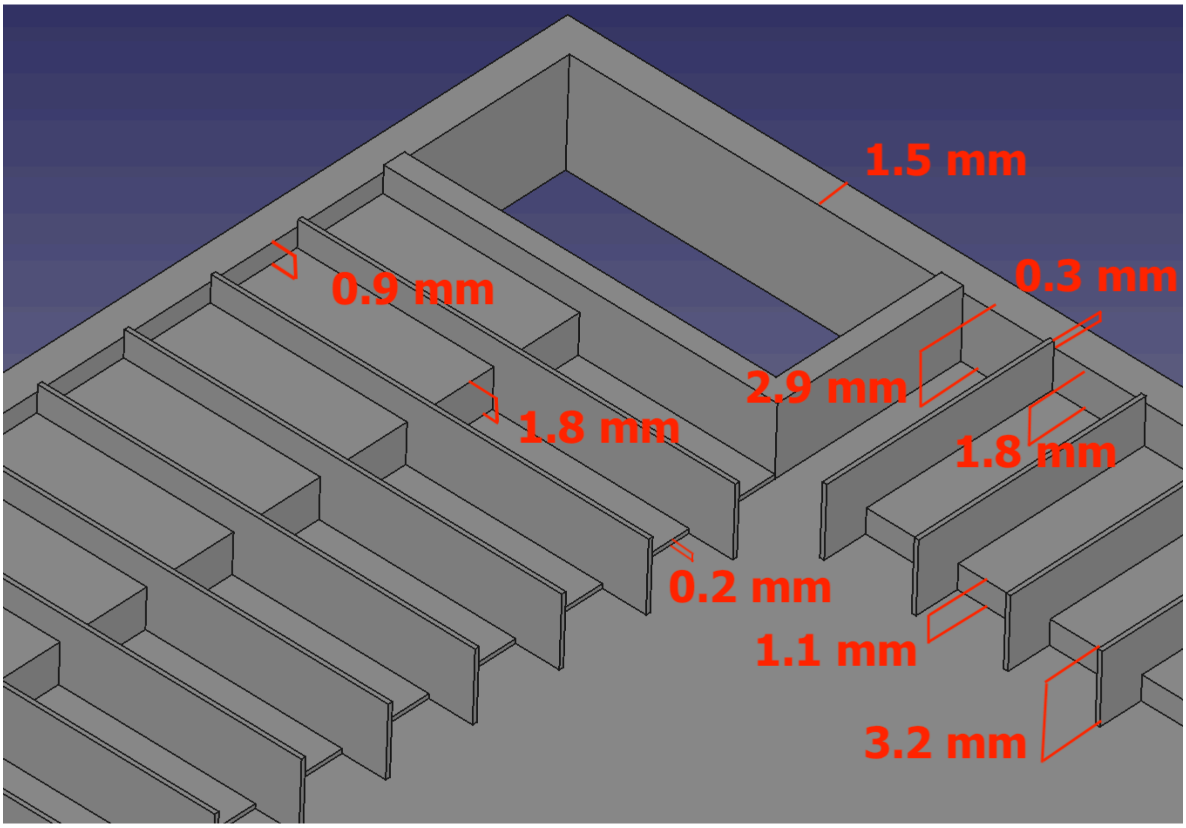

Figure B.12: Figure of a corner of the mould used for the fourth generation TMC manufacturing. To see a figure representing the whole mould, refer to figure 5.1.

A note about figure B.11 is that this figure does not wish to state that the top secondary resin is intended to be 0.8 mm thick. One reason why this picture cannot be applicable in reality is that as discussed in in subsection 4.1, the thickness of rods is not really 0.60 mm but it varies from 0.65 to 0.60 mm. Another reason that makes this sketch not applicable for reality is that in every batch made so far, it was observed that the neighbouring rods are not exactly on the same level and the height difference between neighbouring rods can get up to $\pm$ 0.1 mm. Following the student's experience, getting the neighbouring rods on the same level required more advanced equipment, for example grippers that hold the rods exactly at their intended place. This of course, goes beyond the scope of this thesis study.

Few paragraphs above, it was mentioned that it is recommended to have the upper secondary resin thicker than other secondary resin layers. The reason was that once the upper plate is placed on top, it will not touch the upper rods and disturb their orientation. Therefore, this extra room was created. There is actually another reason for this extra space and it can be seen in figure B.13. As this figure displays, there is a tilted upper rod that is less than 0.16 mm away from the upper side of the TMC. The other end of that tilted rod is 0.51 mm away from the surface (which is not shown in that figure). If the top secondary resin layer did not have this extra space for the upper corner of the tilted rod, these upper corners would pop out of the top side of the TMC and therefore the TMC would not have a flat surface.

Throughout all the samples made via the fourth manufacturing generation, the highest distance observed between (the top side of) an upper rod and the top side of its TMC is 0.56 mm and the least distance observed between these two is 0.1 mm.

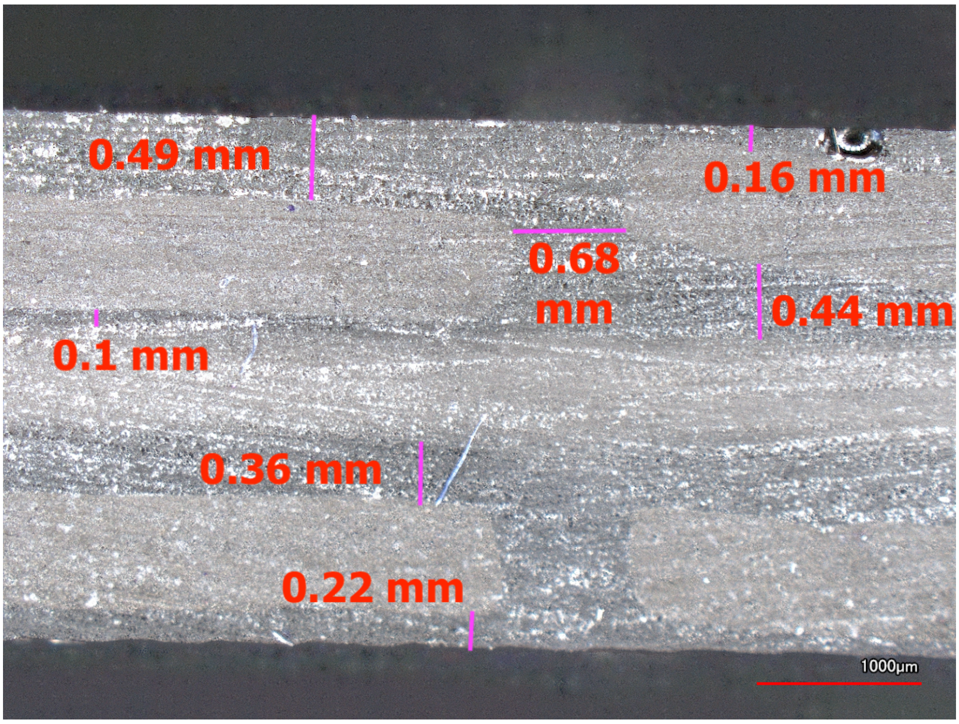

Figure B.13: Microscopic view of the cross section of a TMC manufactured via the fourth generation manufacturing

Now it is time to decide whether to use poly-carbonate, aluminium or teflon as the upper plate. All three materials have been tried out. Out of these three, teflon is the best candidate because it is the only one that the secondary resin does not attach to. An example of such resin attachment is shown in figure B.14b which shows cured resin attached to the poly-carbonate plate after the demoulding. This of course defects the resultant composite (as shown in B.14a) and makes it unacceptable. The same problem happened with using Aluminium plate and the results can be seen in figure B.15a and b. Therefore, teflon is the only remaining candidate.

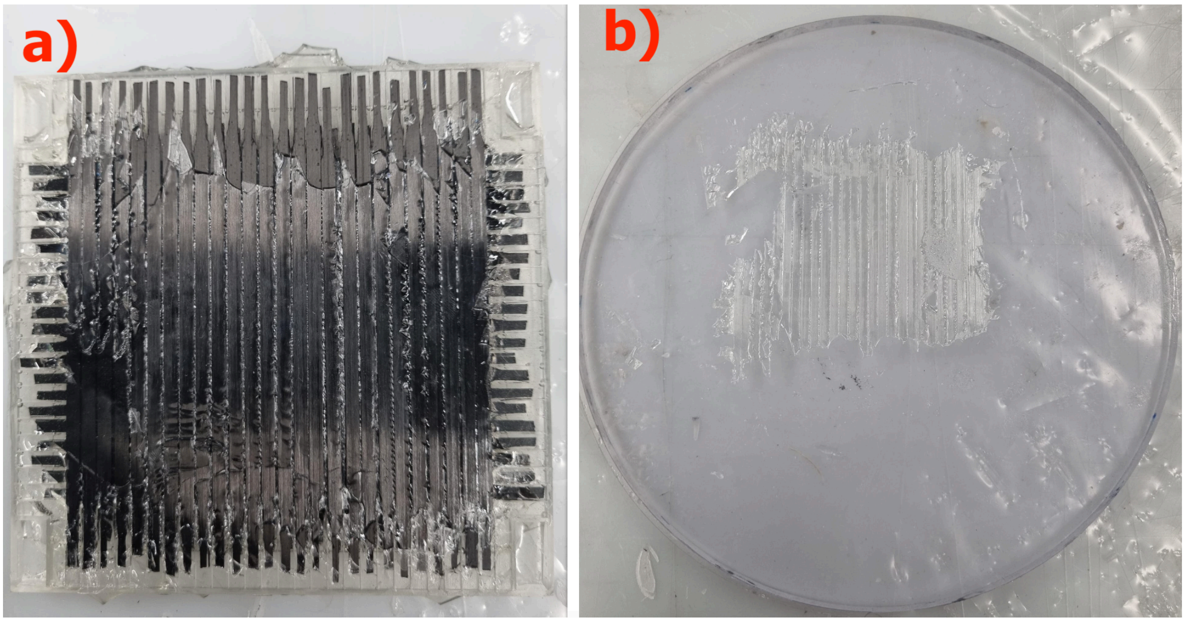

Figure B.14: Result of removing the poly-carbonate plate off the cured TMC. Figure a represents the top side of the TMC and Figure b represents the face of the poly-carbonate plate that has been on the TMC.

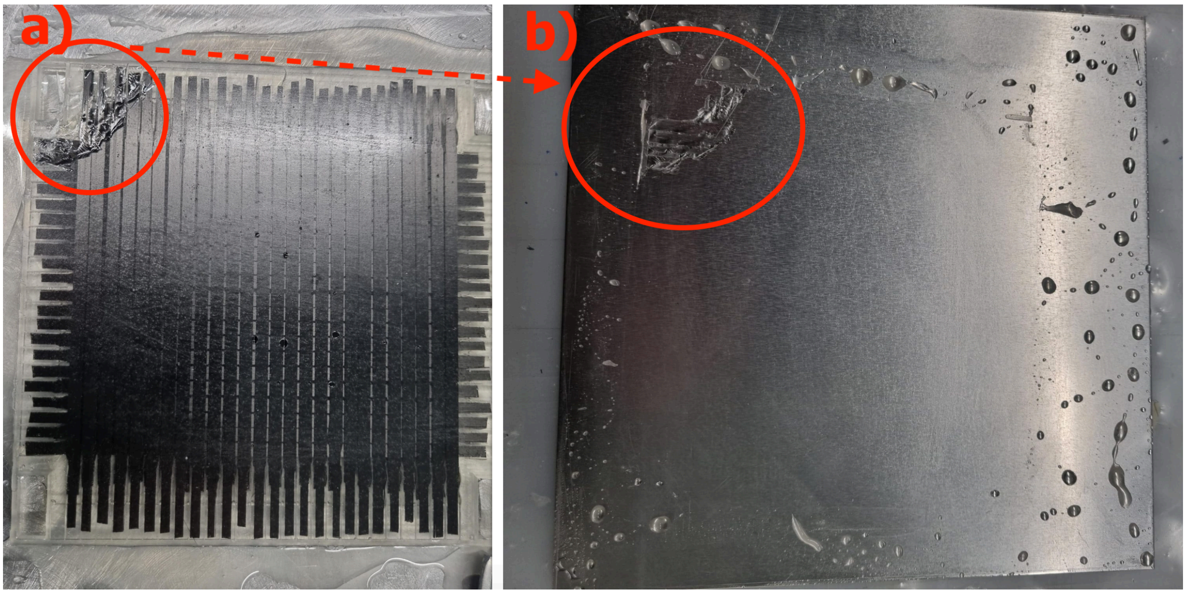

Figure B.15: Result of removing the aluminium plate off the cured TMC. Figure a represents the top side of the TMC and Figure b represents the face of the aluminium plate that has been on the TMC. The red circles indicate the matching locations on the TMC and the plate where the damage has occurred.

C
Scanning Electron Microscopy Figures

This appendix shows the figures captured via SEM analysis from the surface of the rods. As mentioned in section 6.1, per each number of recycling occasion there are 4 different magnifications (x25, x75, x130 and x300). Given that there are 5 possible numbers of recycling occasions, that means that there are 20 SEM observation trials. This appendix displays a figure from each of these 20 observations.

C.1. Figures Of Non-Recycled Rod

This section aims to show pictures of the surface of non recycled rod.

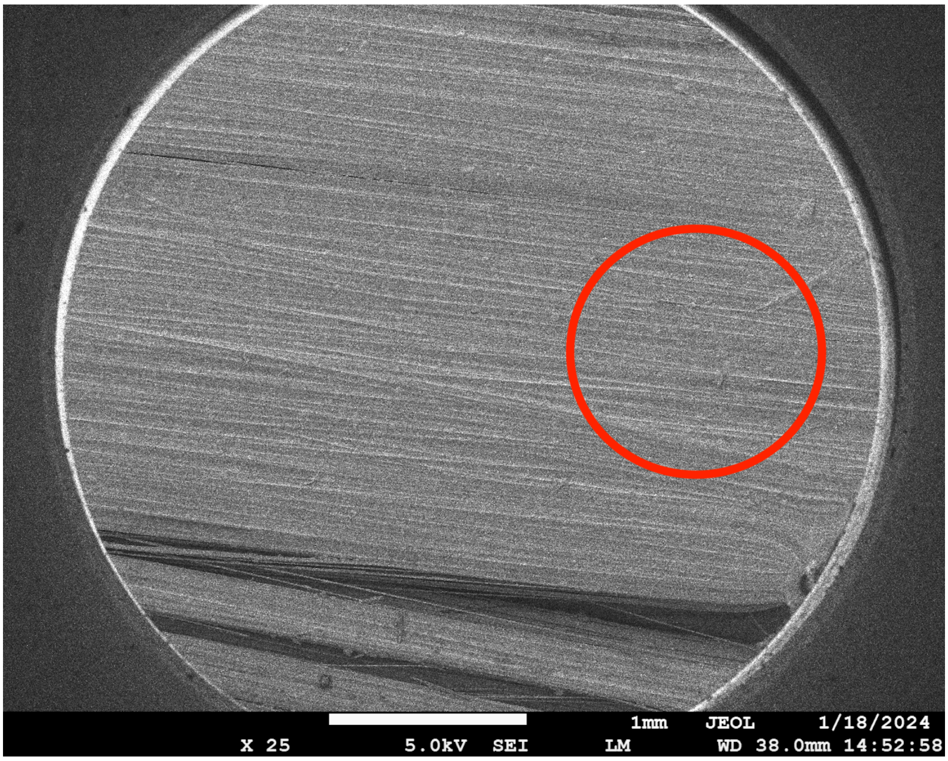

Figure C.1: SEM view of the surface of a non recycled rod. The magnification is x25. The red circle shows the region that will be shown in more detail in figure C.2.

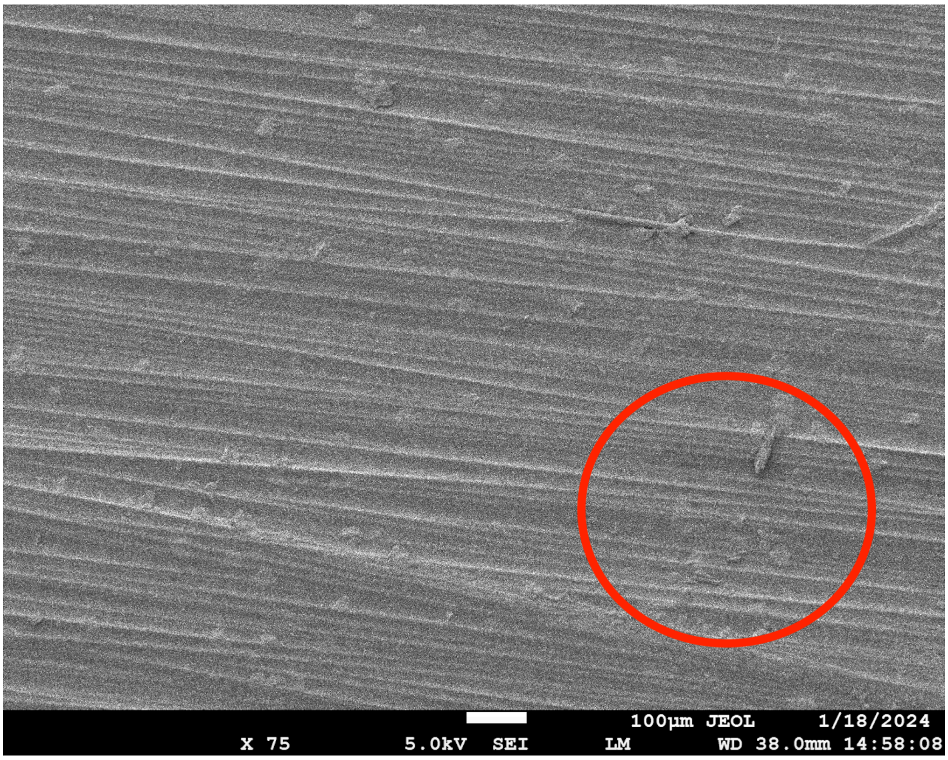

Figure C.2: SEM view of the surface of a non recycled rod. The magnification is x75. This view is a zoomed in version of figure C.1. The red circle shows the region that will be shown in more detail in figure C.3.

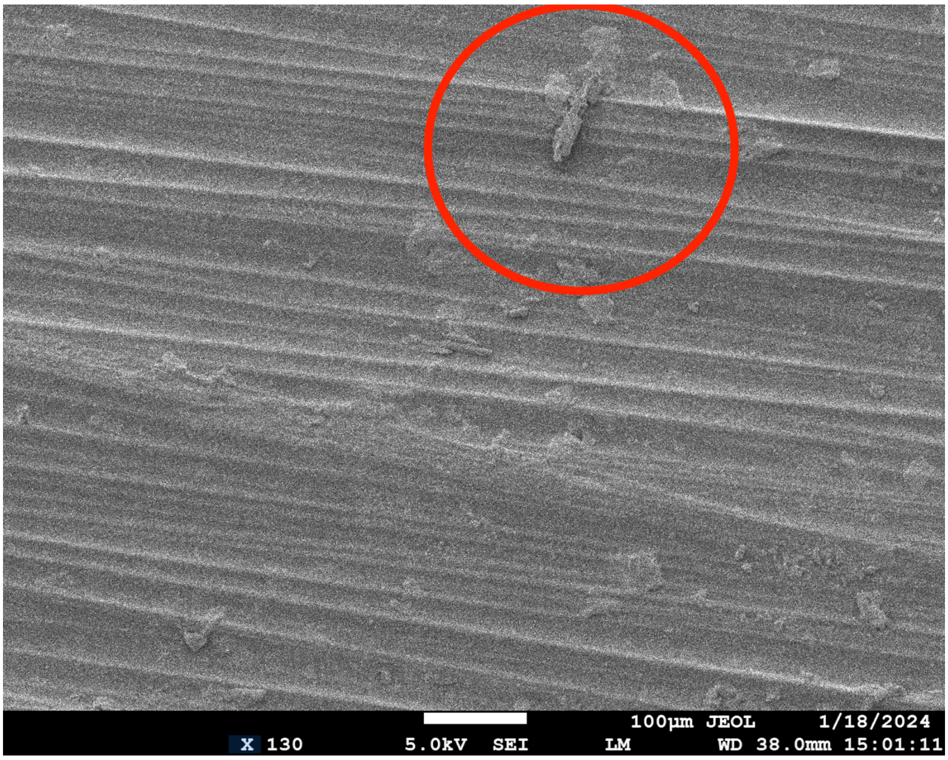

Figure C.3: SEM view of the surface of a non recycled rod. The magnification is x130. This view is a zoomed in version of figure C.2. The red circle shows the region that will be shown in more detail in figure C.4.

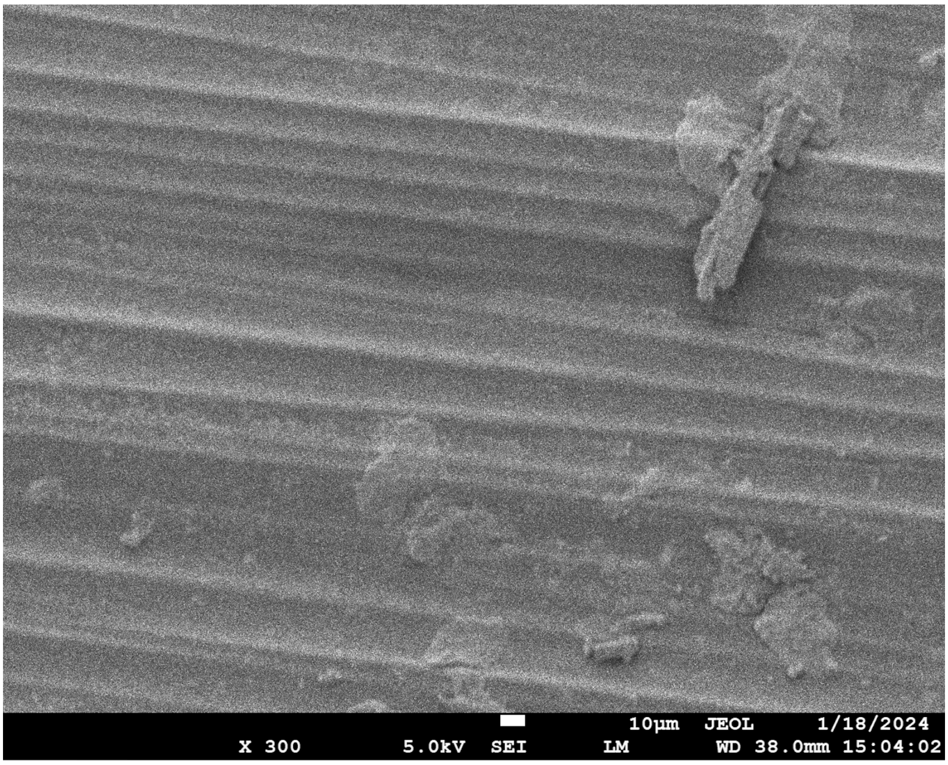

Figure C.4: SEM view of the surface of a non recycled rod. The magnification is x300. This view is a zoomed in version of figure C.3.

C.2. Figures Of One-time Recycled Rod

This section aims to show pictures of the surface of the rod that has been recycled once.

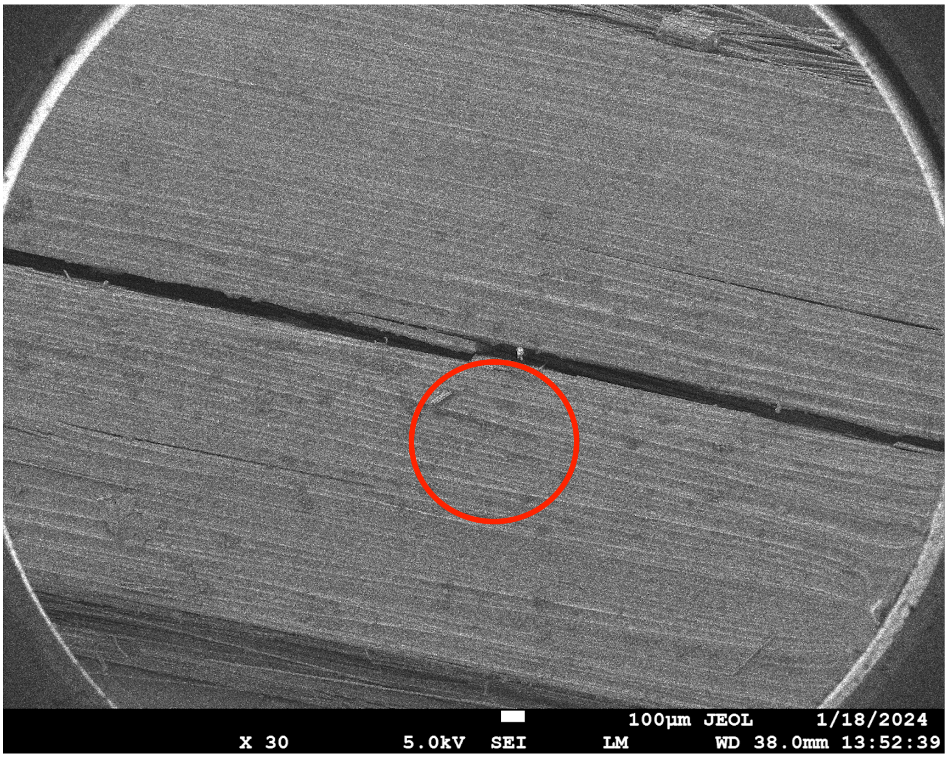

Figure C.5: SEM view of the surface of a rod that has been recycled once. The magnification is x25. The red circle shows the region that will be shown in more detail in figure C.6.

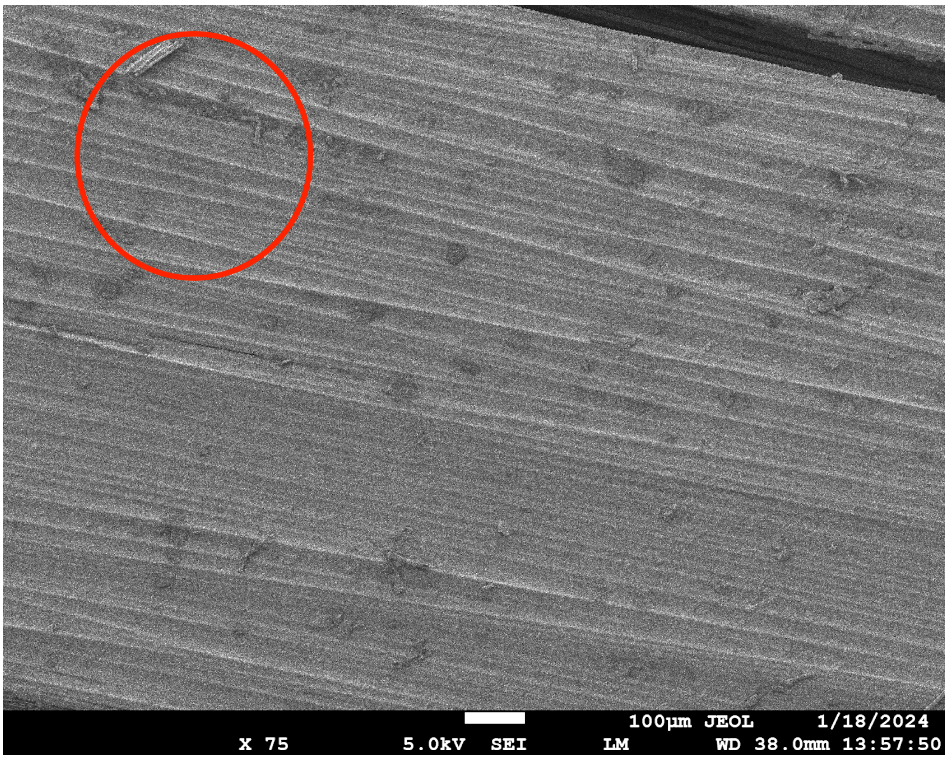

Figure C.6: SEM view of the surface of a rod that has been recycled once. The magnification is x75. This view is a zoomed in version of figure C.5. The red circle shows the region that will be shown in more detail in figure C.7.

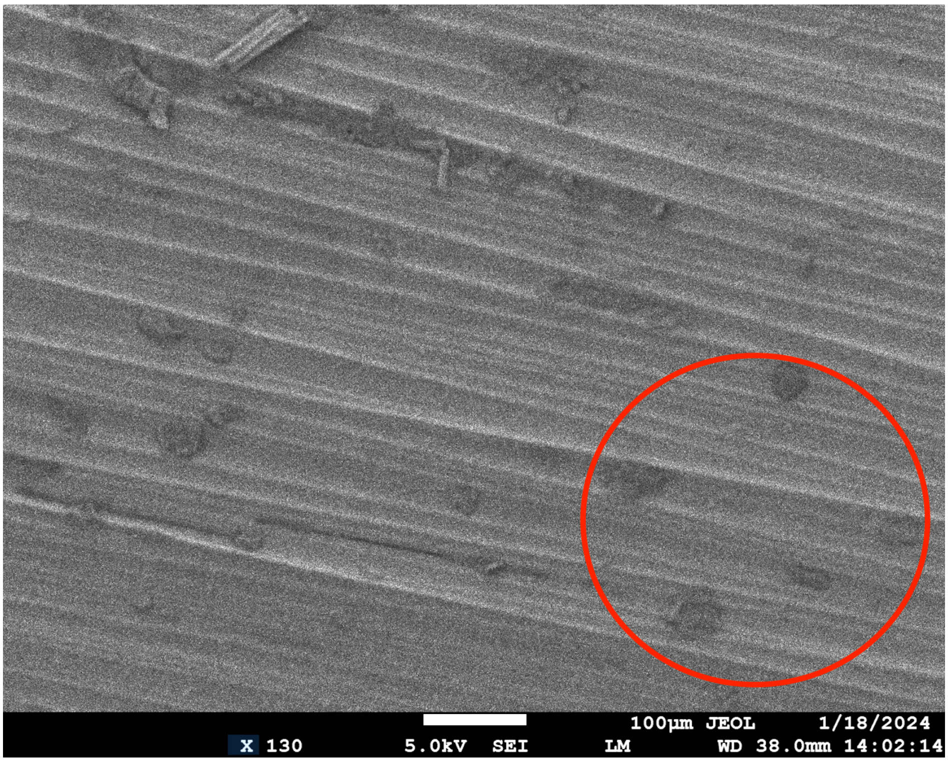

Figure C.7: SEM view of the surface of a rod that has been recycled once. The magnification is x130. This view is a zoomed in version of figure C.6. The red circle shows the region that will be shown in more detail in figure C.8.

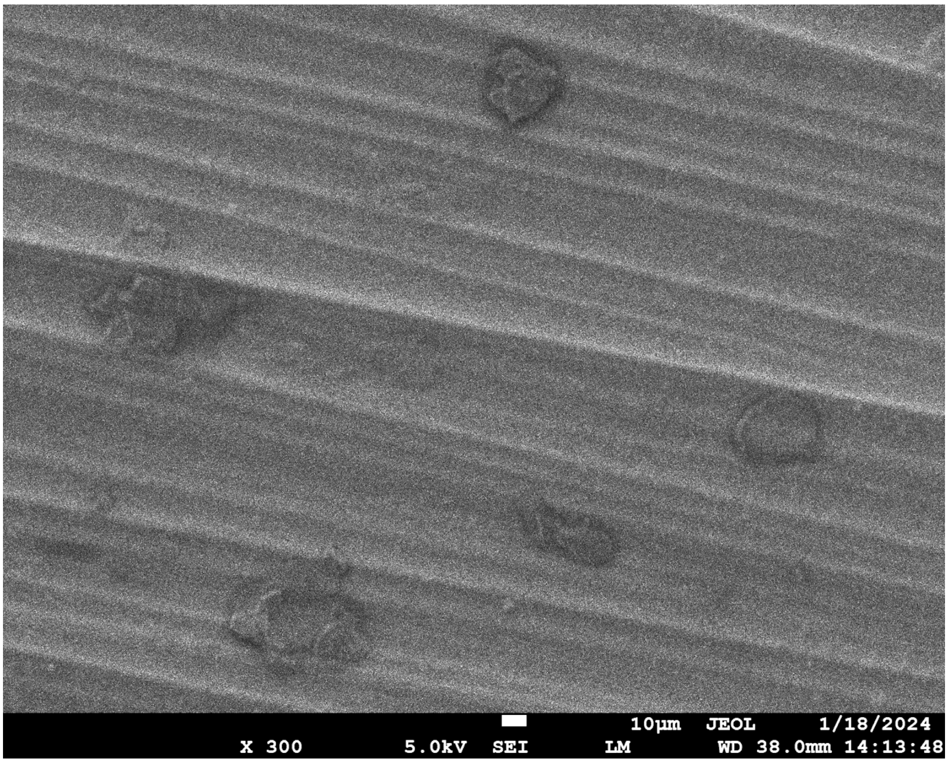

Figure C.8: SEM view of the surface of a rod that has been recycled once. The magnification is x300. This view is a zoomed in version of figure C.7.

C.3. Figures Of Two-times Recycled Rod

This section aims to show pictures of the surface of the rod that has been recycled twice.

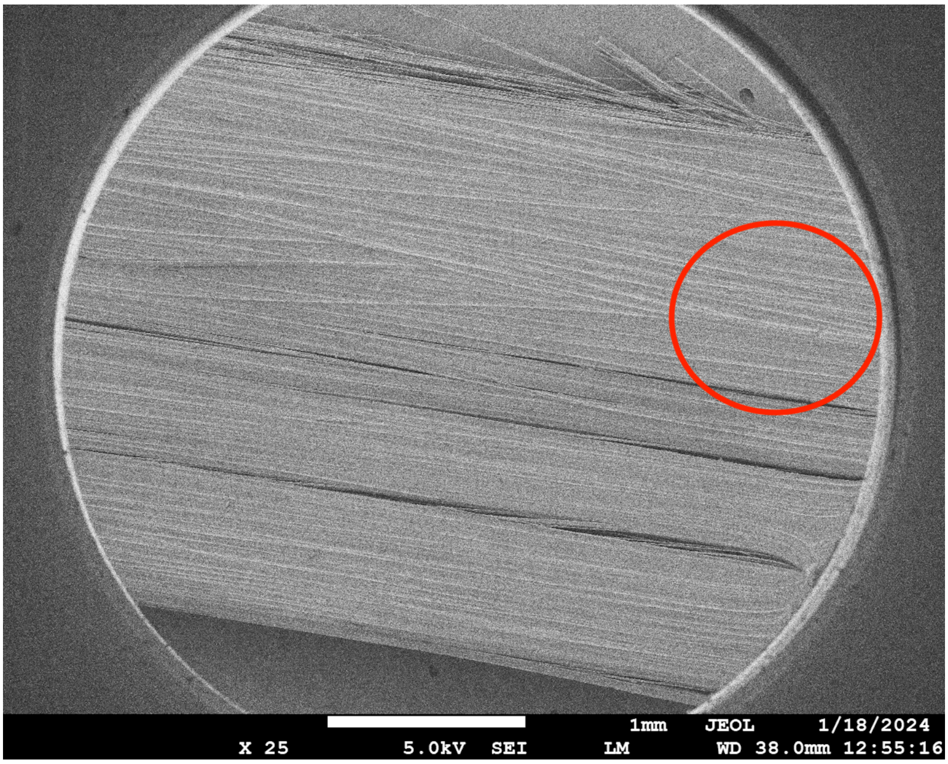

Figure C.9: SEM view of the surface of a rod that has been recycled two times. The magnification is x25. The red circle shows the region that will be shown in more detail in figure C.10.

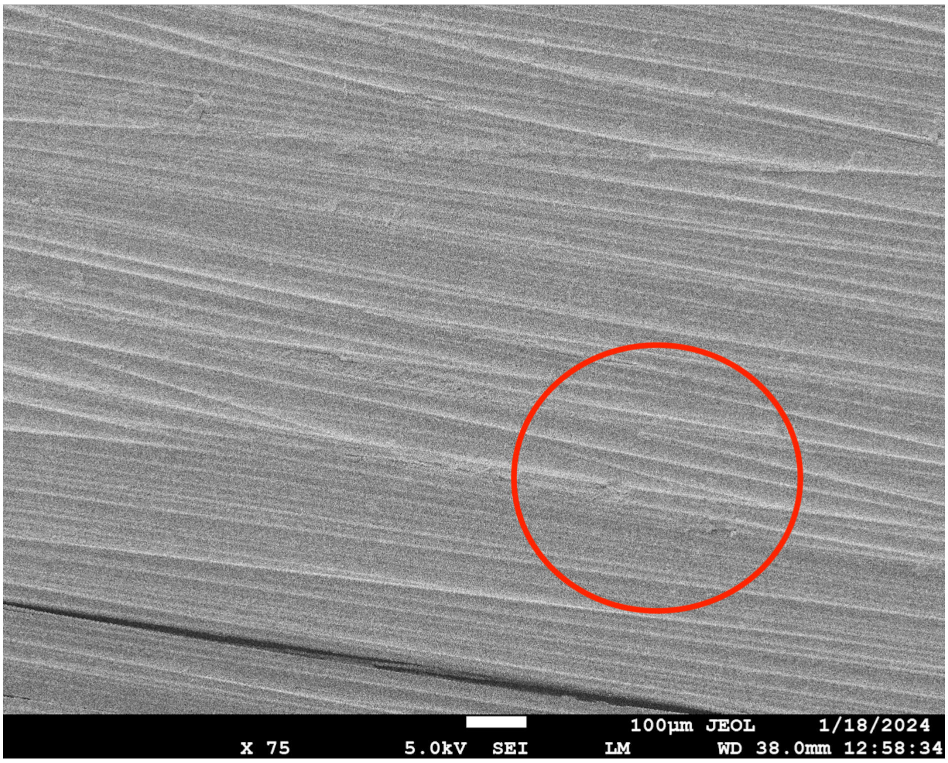

Figure C.10: SEM view of the surface of a rod that has been recycled two times. The magnification is x75. This view is a zoomed in version of figure C.9 The red circle shows the region that will be shown in more detail in figure C.11.

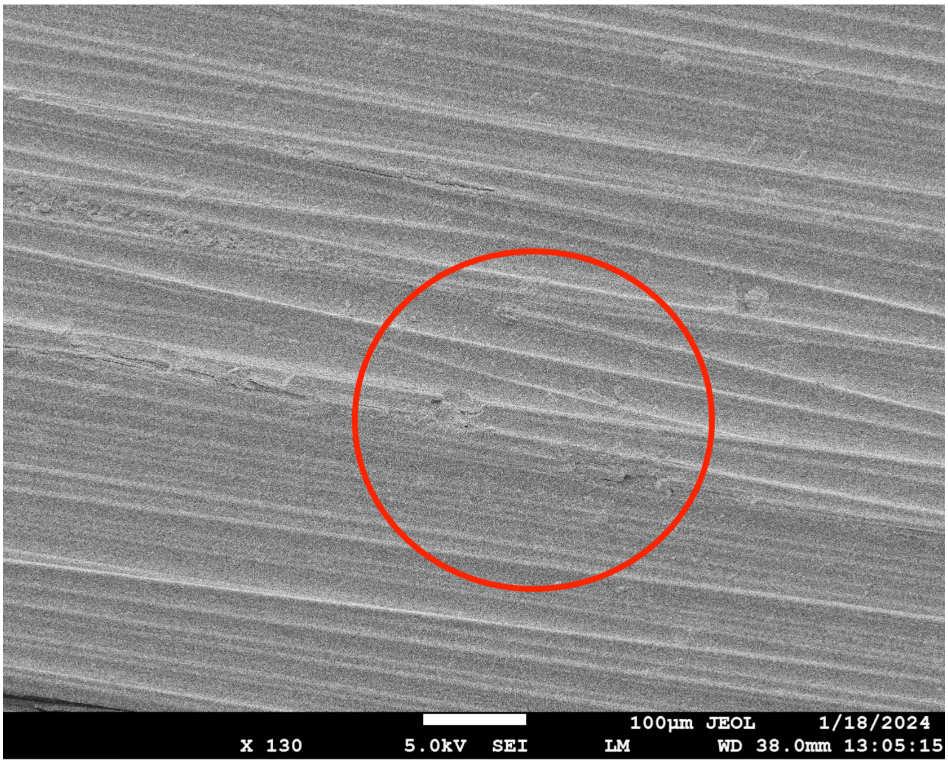

Figure C.11: SEM view of the surface of a rod that has been recycled two times. The magnification is x130. This view is a zoomed in version of figure C.10. The red circle shows the region that will be shown in more detail in figure C.12.

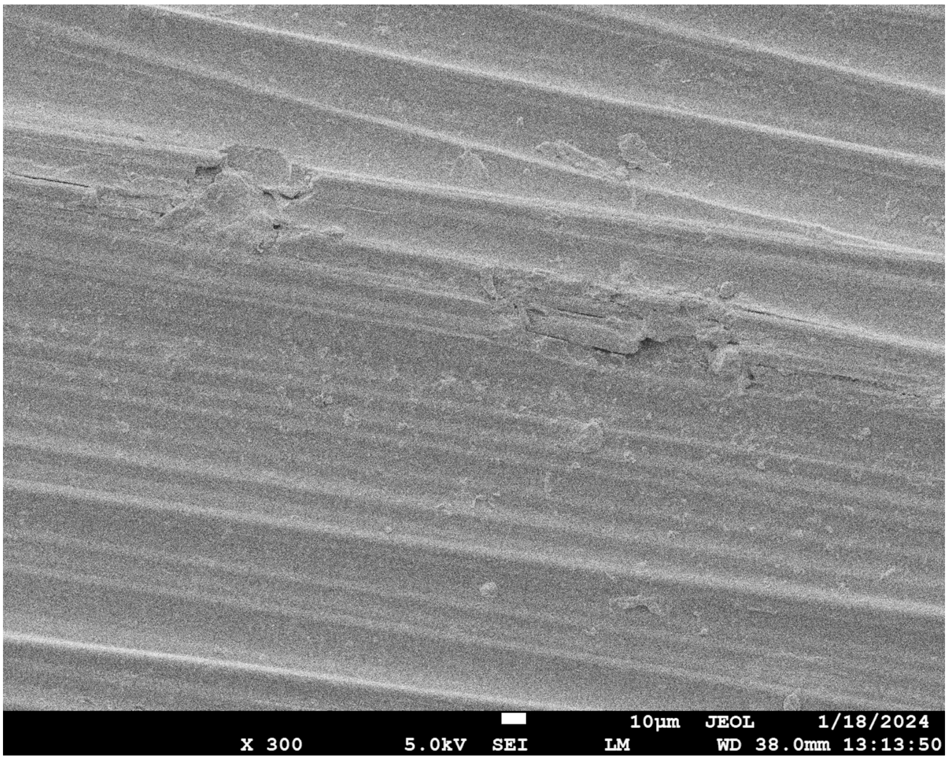

Figure C.12: SEM view of the surface of a rod that has been recycled two times. The magnification is x300. This view is a zoomed in version of figure C.11.

C.4. Figures Of Three-times Recycled Rod

This section aims to show pictures of the surface of the rod that has been recycled three times.

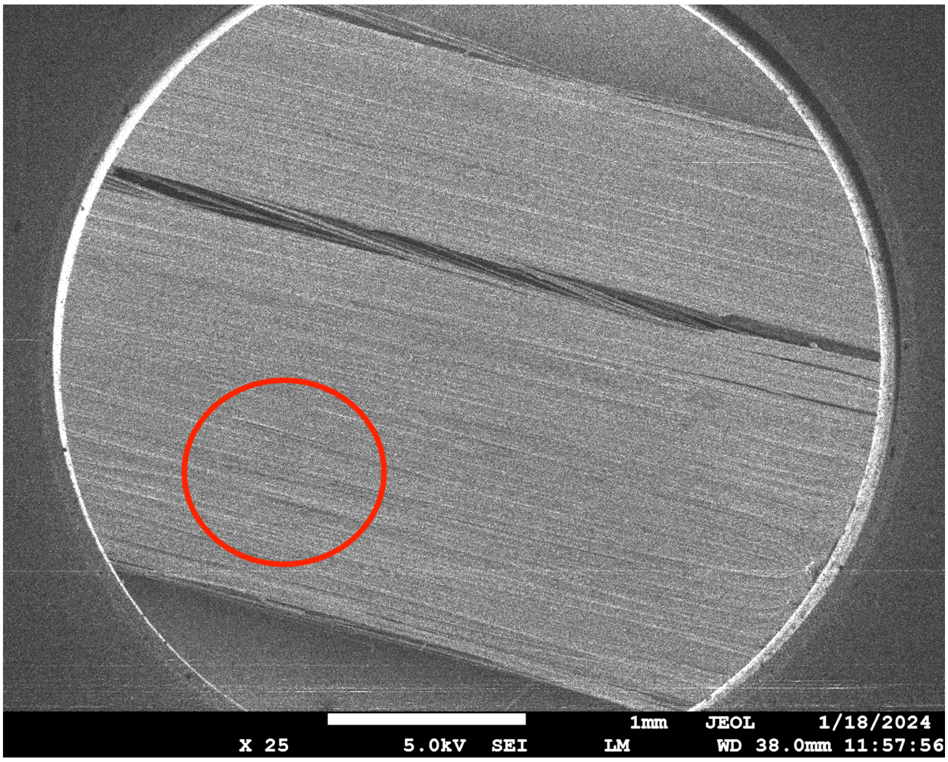

Figure C.13: SEM view of the surface of a rod that has been recycled three times. The magnification is x25. The red circle shows the region that will be shown in more detail in figure C.14.

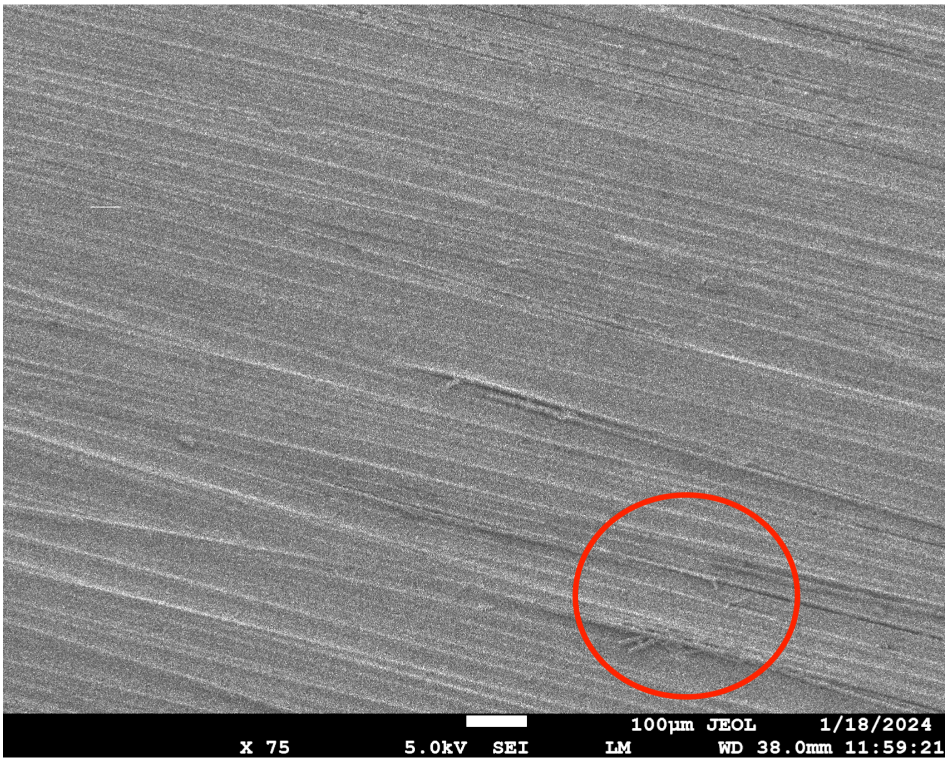

Figure C.14: SEM view of the surface of a rod that has been recycled three times. The magnification is x75. This view is a zoomed in version of figure C.13 The red circle shows the region that will be shown in more detail in figure C.15.

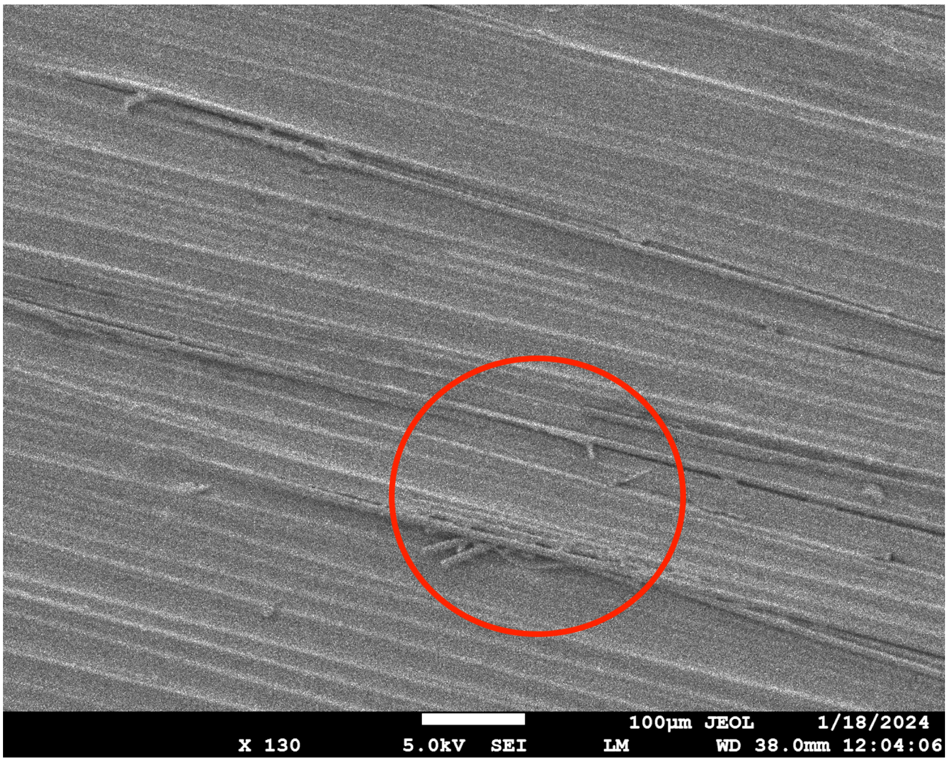

Figure C.15: SEM view of the surface of a rod that has been recycled three times. The magnification is x130. This view is a zoomed in version of figure C.14. The red circle shows the region that will be shown in more detail in figure C.16.

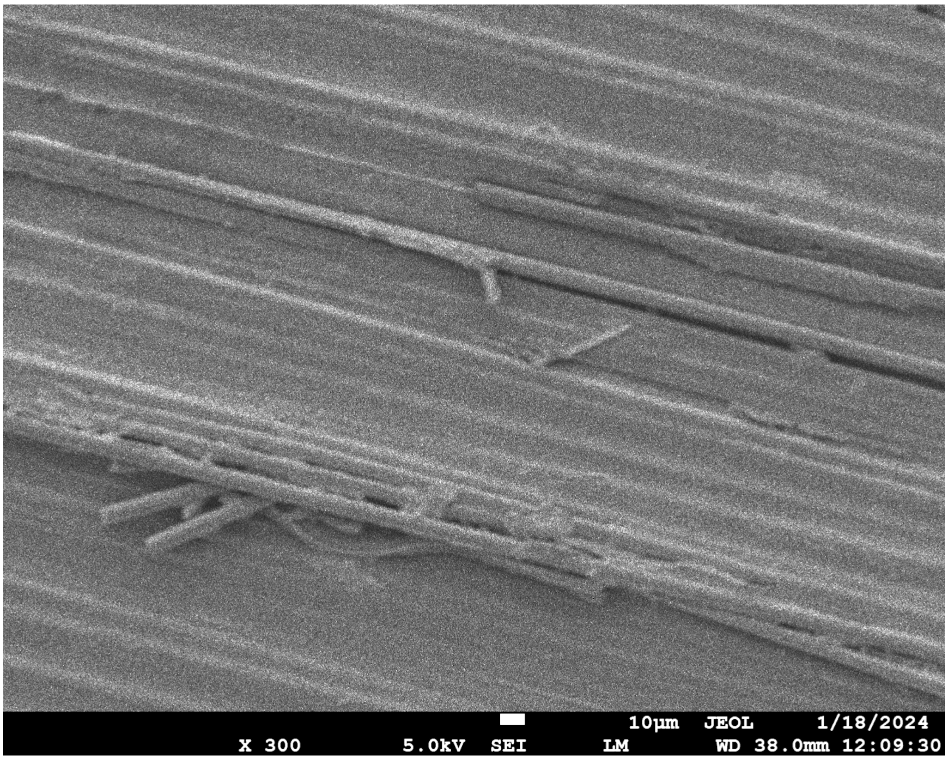

Figure C.16: SEM view of the surface of a rod that has been recycled three times. The magnification is x300. This view is a zoomed in version of figure C.15.

C.5. Figures Of Four-times Recycled Rod

This section aims to show pictures of the surface of the rod that has been recycled four times.

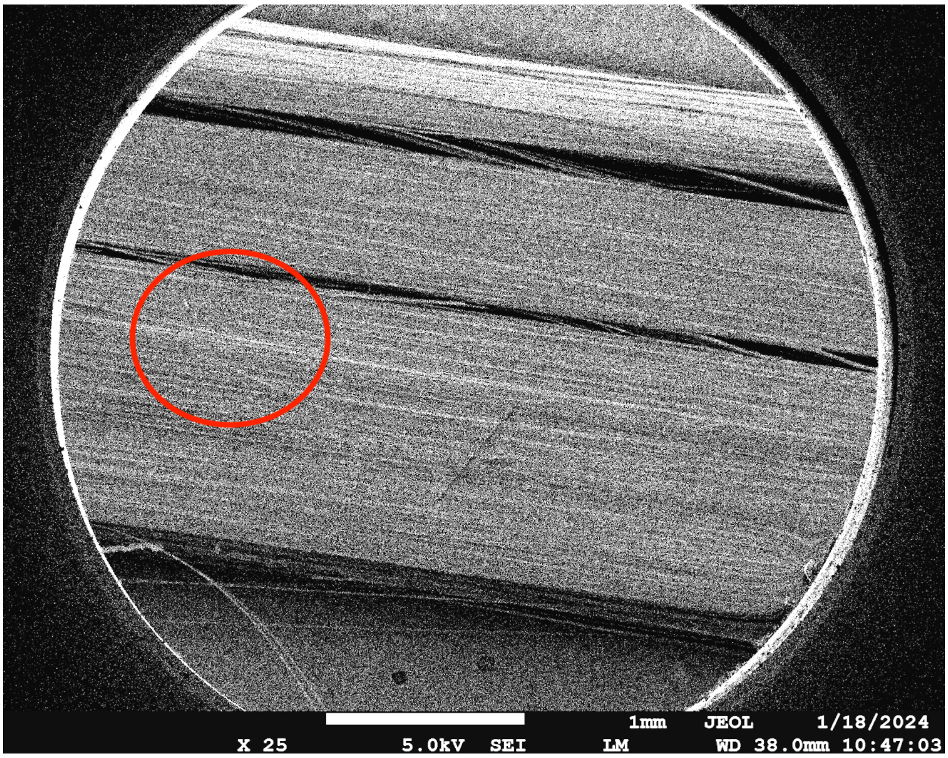

Figure C.17: SEM view of the surface of a rod that has been recycled four times. The magnification is x25. The red circle shows the region that will be shown in more detail in figure C.18.

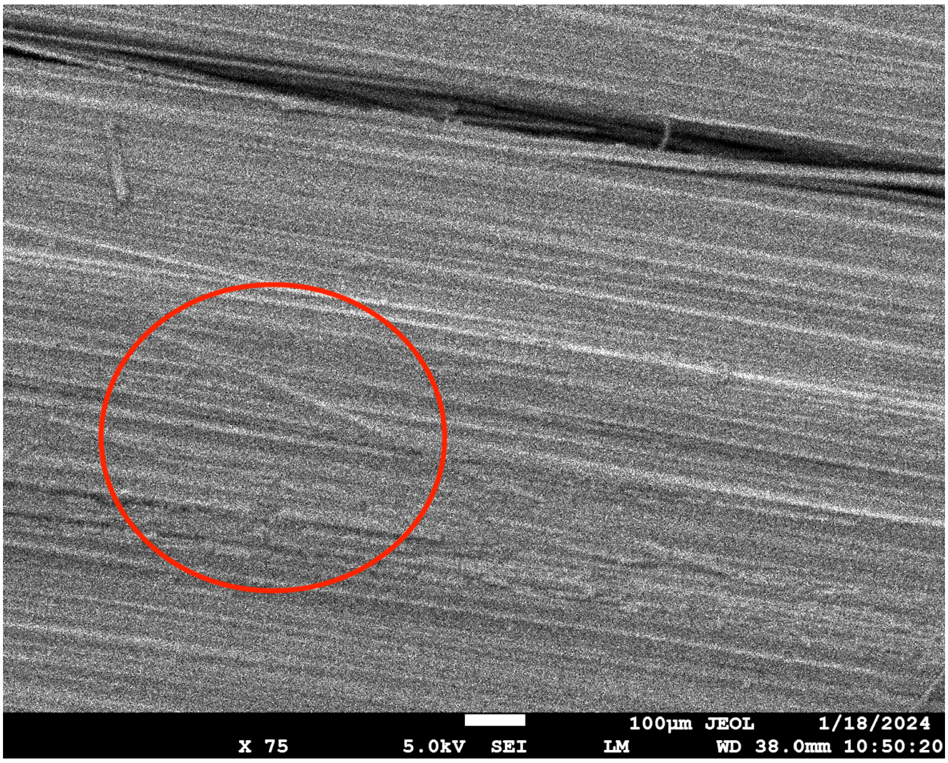

Figure C.18: SEM view of the surface of a rod that has been recycled four times. The magnification is x75. This view is a zoomed in version of figure C.17 The red circle shows the region that will be shown in more detail in figure C.19.

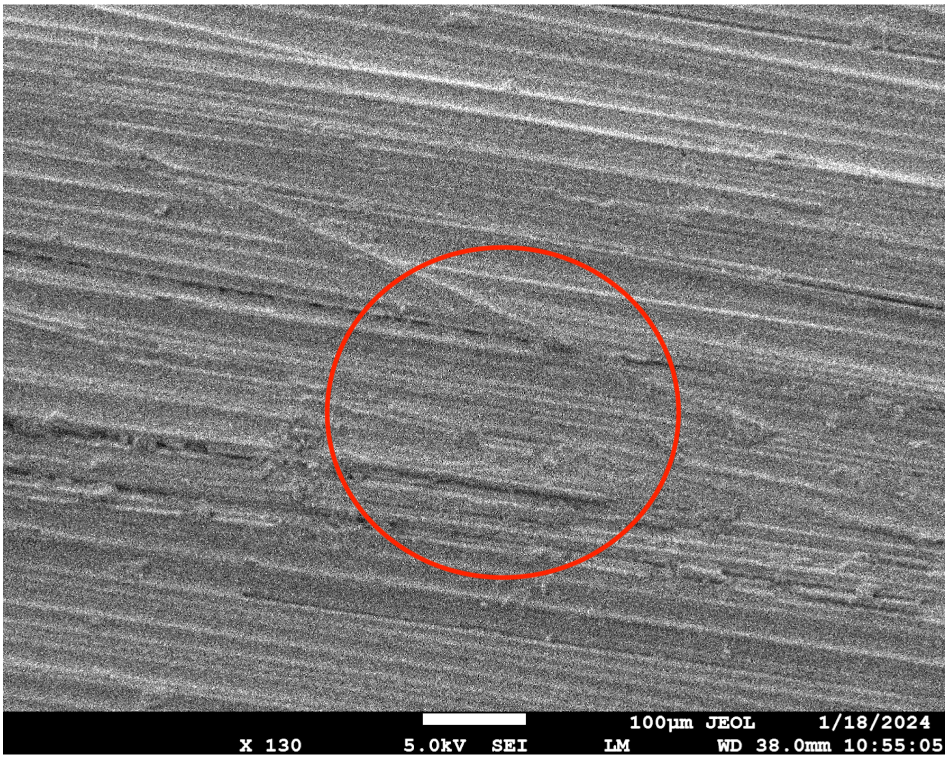

Figure C.19: SEM view of the surface of a rod that has been recycled four times. The magnification is x130. This view is a zoomed in version of figure C.18. The red circle shows the region that will be shown in more detail in figure C.20.

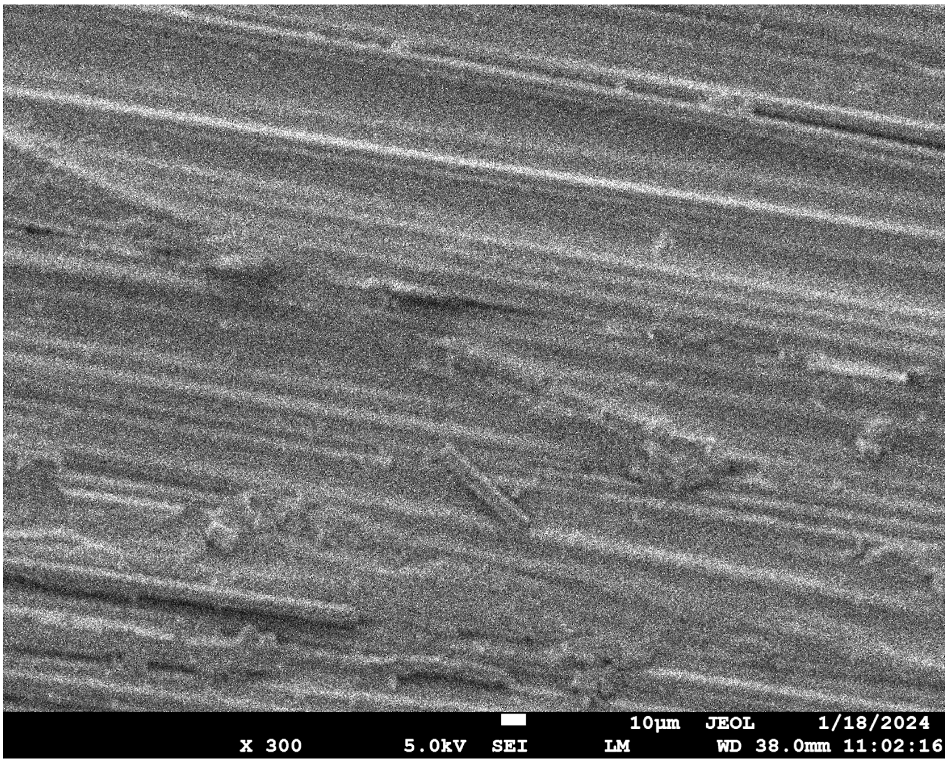

Figure C.20: SEM view of the surface of a rod that has been recycled four times. The magnification is x300. This view is a zoomed in version of figure C.19.

D

Water Contact Angle Measurements

This appendix represents additional data regarding the water contact angle measurements. Starting with table D.1, this table represents all the angles that have been measured after each number of recycling. These are the right and left side angles of each water droplet. Additionally, this table also shows the water droplet size for each trial. As mentioned in section 6.2 , it is decided to only record water droplets that have a recorded volume of 20 $\pm$ 5 μL.

Number of recycling	Left angle (^{o})	Right Angle (^{o})	Water Volume (μL)
0	54.48	55.11	23.99
0	60.36	59.52	20.15
0	61.61	56.85	23.99
1	64.89	65.25	24.39
1	62.81	62.81	17.54
1	68.70	66.88	18.65
2	63.33	62.16	19.25
2	68.58	69.33	19.21
2	67.93	65.79	18.75
3	69.64	70.75	19.23
3	64.32	63.71	21.09
3	66.21	65.73	21.08
4	76.42	76.90	19.22
4	77.26	77.41	19.22
4	83.80	81.47	24.47

Table D.1: Table of the angles measured in the water contact analysis. This table displays the left and rights angles of each trial for all recycling occasions. Additionally this table shows the corresponding droplet volume detected by the software for each trial.

Graphs shown in figure D.1 are made based on above table. Figure D.1a represents the angle values of the left side of each water droplet after each recycling time. Figure D.1b does the same but this time for the right side.

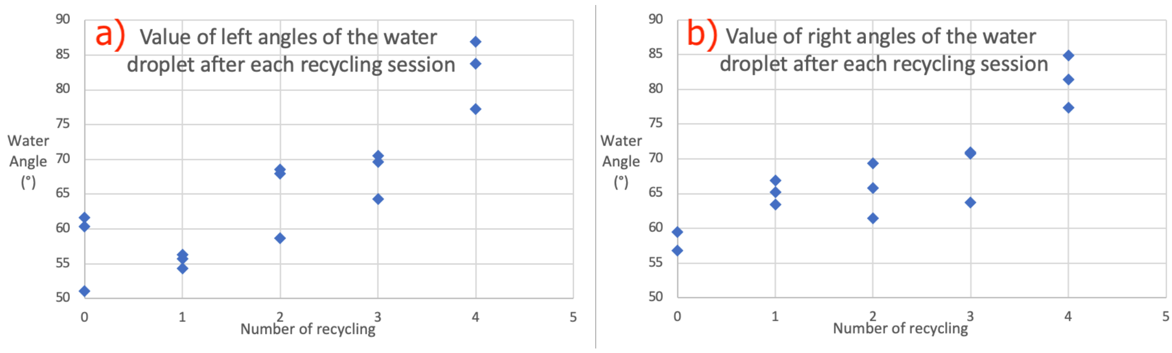

Figure D.1: Variation of water contact angles after each recycling for each side of the water droplet. Figure a represents the left side and figure b represents the right side.

Lastly, each of the figures D.2 - D.6 represents a screen shot of the Attension Theta software for a trial of each recycling time. Each of these figures include the left and right angle dimensions as well as the water volume size for that specific trial.

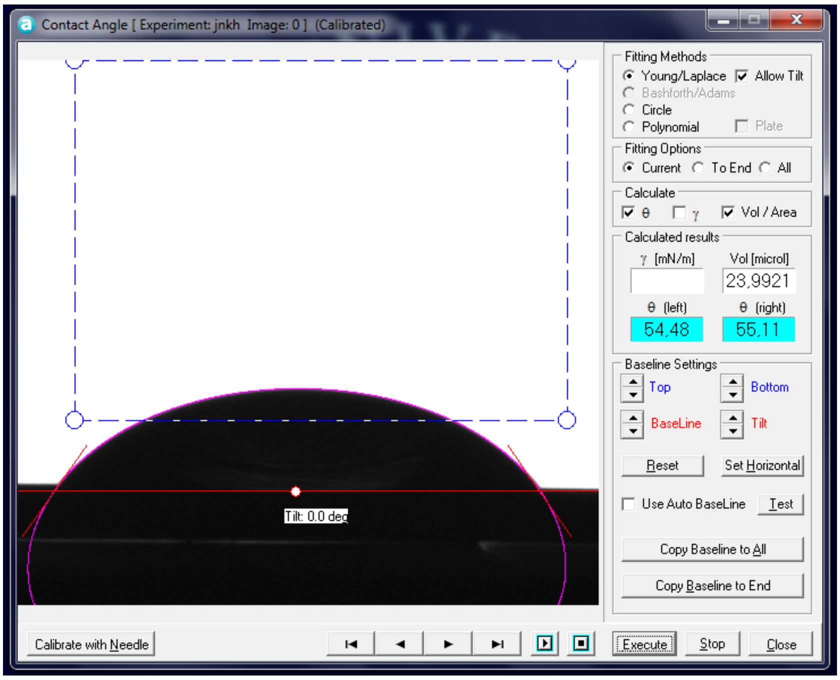

Figure D.2: Screenshot of the water contact angle analysis performed on rod that has been not recycled. The values of this reading can be also found in the first row of table D.1.

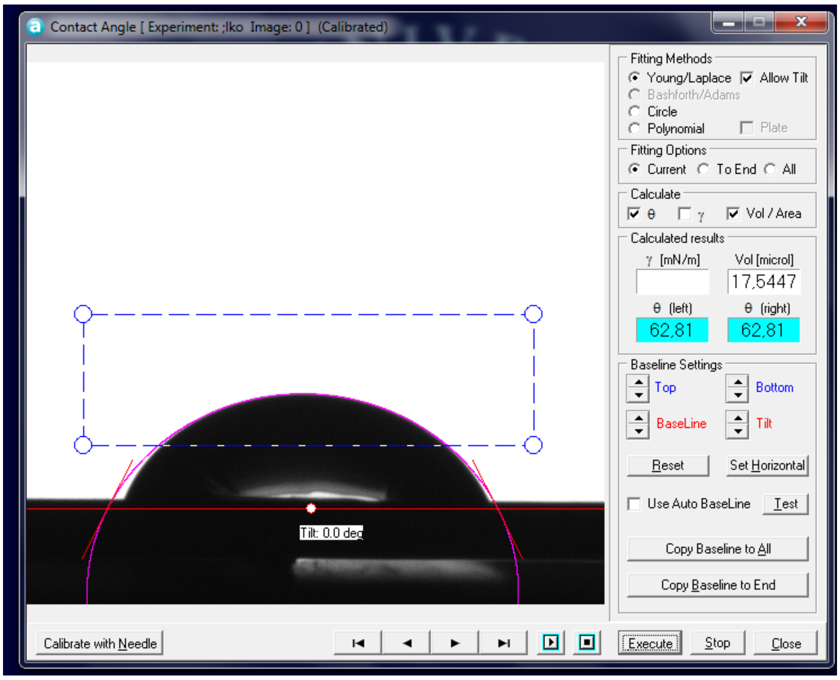

Figure D.3: Screenshot of the water contact angle analysis performed on rod that has been recycled once. The values of this reading can be also found in the fifth row of table D.1.

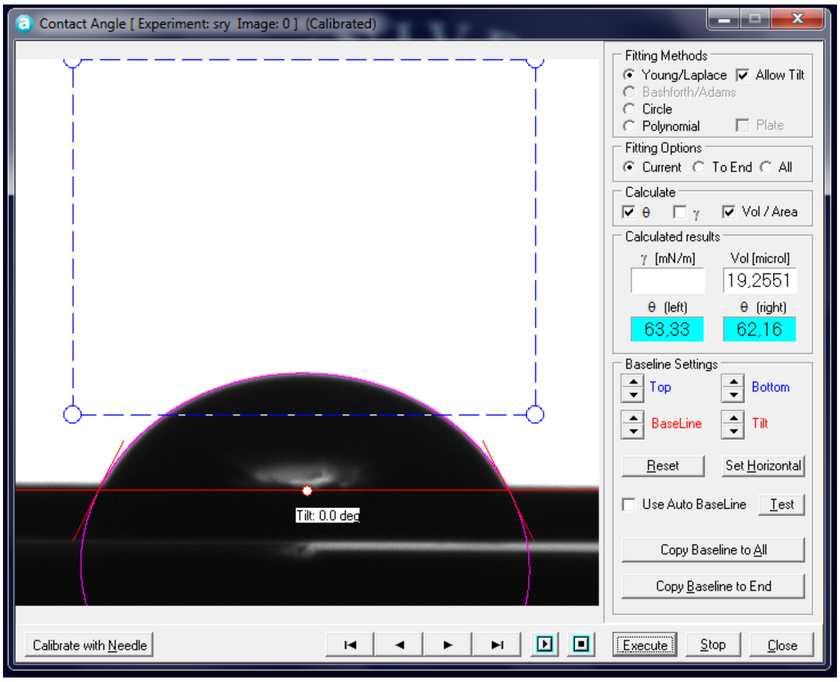

Figure D.4: Screenshot of the water contact angle analysis performed on rod that has been recycled twice. The values of this reading can be also found in the seventh row of table D.1.

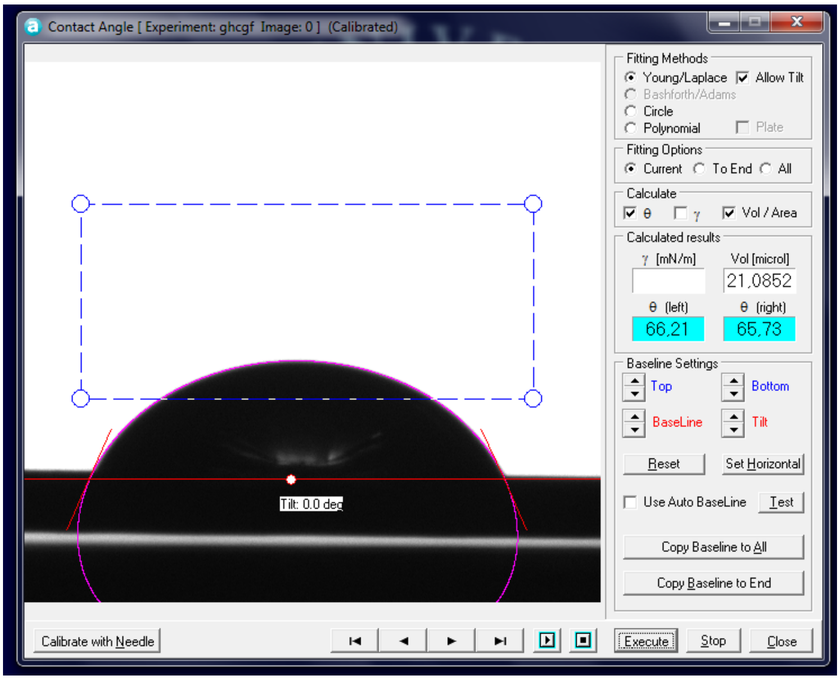

Figure D.5: Screenshot of the water contact angle analysis performed on rod that has been recycled three times. The values of this reading can be also found in the twelfth row of table D.1.

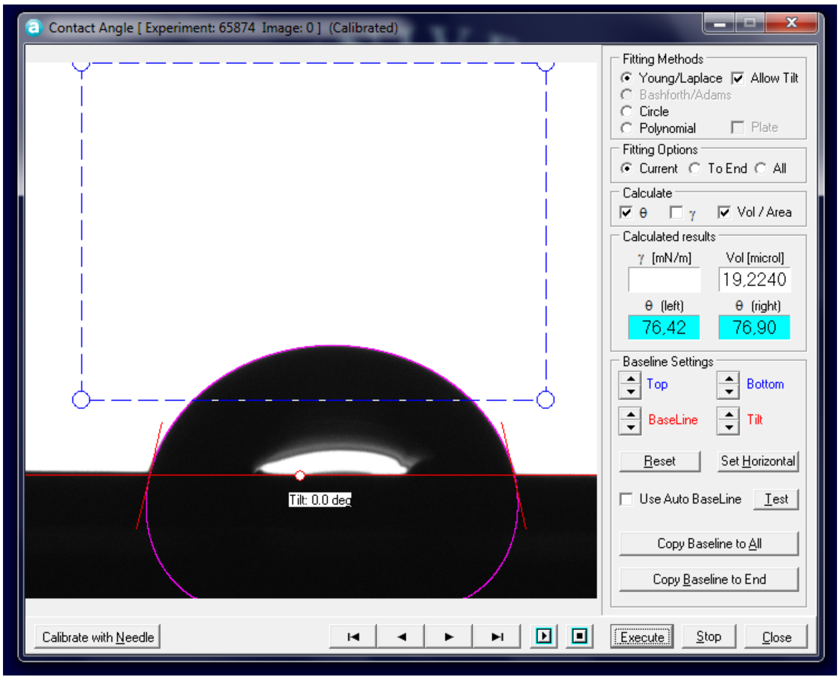

Figure D.6: Screenshot of the water contact angle analysis performed on rod that has been recycled four times. The values of this reading can be also found in the thirteenth row of table D.1.

E

Additional Data on Interlaminar Shear Stress Testing

This appendix represents additional data regarding the ILSS testing of TMC samples. This starts with section E.1, representing lists of the most relevant and important information about each sample and then section E.2 representing the force-displacement graphs for each of these samples. Lastly, section E.3 represents calculation attempts to estimate the bending stiffness of TMC samples.

E.1. Properties of Twin Matrix Composites Samples for the Interlaminar Shear Testing

Tables below represent the information about TMC samples that have undergone ILSS testing. Each table starts with listing the dimensional parameters such as length or thickness and then moves on to listing the rod volume for each sample. Next it mentions the maximum shear force recorded by the machine. Next row is for the interlaminar shear strength which can be obtained by inputting maximum shear force into equation 6.1. The row after is for the vertical deflection at the moment when the maximum force has been obtained. The last row displays the ILSS per rod volume for each sample.

	Unit	Sample 1	Smaple 2	Sample 3	Sample 4	Sample 5
Thickness (t)	mm	3.1	3.1	3.1	3.1	3.1
Width (w)	mm	6.7	6.7	7.4	7.4	7.9
Length (l)	mm	19.2	18.4	18.0	19.4	18.6
Rod Volume (V_r)	-	0.53	0.54	0.58	0.57	0.60
Maximum Force (F_{Max})	N	690.61	690.61	815.93	872.11	943.10
Maximum Interlaminar Shear Strength (τ_{Max})	MPa	23.91	24.94	26.67	28.51	28.88
Displacemnt at maximum force (δ_{max})	mm	0.31	0.31	0.34	0.33	0.37
Maximum Interlaminar Shear Strength per rod volume ($\tau_{Max_{Vr}}$)	MPa	45.50	46.35	46.33	49.54	48.22

Table E.1: Test data and processed results of ILSS testing of TMCs made with unrecycled rods.

	Unit	Sample 1	Smaple 2	Sample 3	Sample 4	Sample 5
Thickness (t)	mm	3.4	3.3	3.3	3.4	3.4
Width (w)	mm	6.8	6.9	6.8	6.7	6.8
Length (l)	mm	19.8	19.8	19.9	19.8	19.8
Rod Volume (V_r)	-	0.50	0.49	0.45	0.45	0.52
Maximum Force (F$_{Max}$)	N	674.99	665.88	741.59	663.83	673.77
Maximum Interlaminar Shear Strength (τ_{Max})	MPa	21.90	21.93	24.79	21.85	21.86
Displacemnt at maximum force (δ_{max})	mm	0.28	0.30	0.32	0.29	0.29
Maximum Interlaminar Shear Strength per rod volume ($\tau_{Max_{V_r}}$)	MPa	43.44	45.50	54.77	48.35	42.28

Table E.2: Test data and processed results of ILSS testing of TMCs made with one-time-recycled rods.

	Unit	Sample 1	Smaple 2	Sample 3	Sample 4	Sample 5
Thickness (t)	mm	3.4	3.4	3.4	3.4	3.43
Width (w)	mm	7.0	6.9	6.9	6.85	6.9
Length (l)	mm	21.3	21.4	21.3	21.4	21.4
Rod Volume (V_r)	-	0.48	0.48	0.45	0.45	0.44
Maximum Force (F$_{Max}$)	N	675.15	669.56	634.33	644.71	733.47
Maximum Interlaminar Shear Strength (τ_{Max})	MPa	21.27	21.41	20.28	20.76	23.24
Displacemnt at maximum force (δ_{Max})	mm	0.29	0.30	0.30	0.33	0.33
Maximum Interlaminar Shear Strength per rod volume ($\tau_{Max_{V_r}}$)	MPa	44.51	44.13	44.60	46.55	52.94

Table E.3: Test data and processed results of ILSS testing of TMCs made with four-times-recycled rods.

E.2. Force - Displacement Graphs of Interlaminar Shear Testing of Twin Matrix Composites

This section represents the force-displacement graphs resulted from the ILSS testing of TMC samples. These graphs are the (raw) output of testing machine. Graphs shown in figure E.1 belong to TMC samples made with unrecycled rods where as graphs shown in figure E.2 belong to TMC samples made with one-time-recycled rods and graphs shown in figure E.3 belong to TMC samples made with four-times-recycled rods.

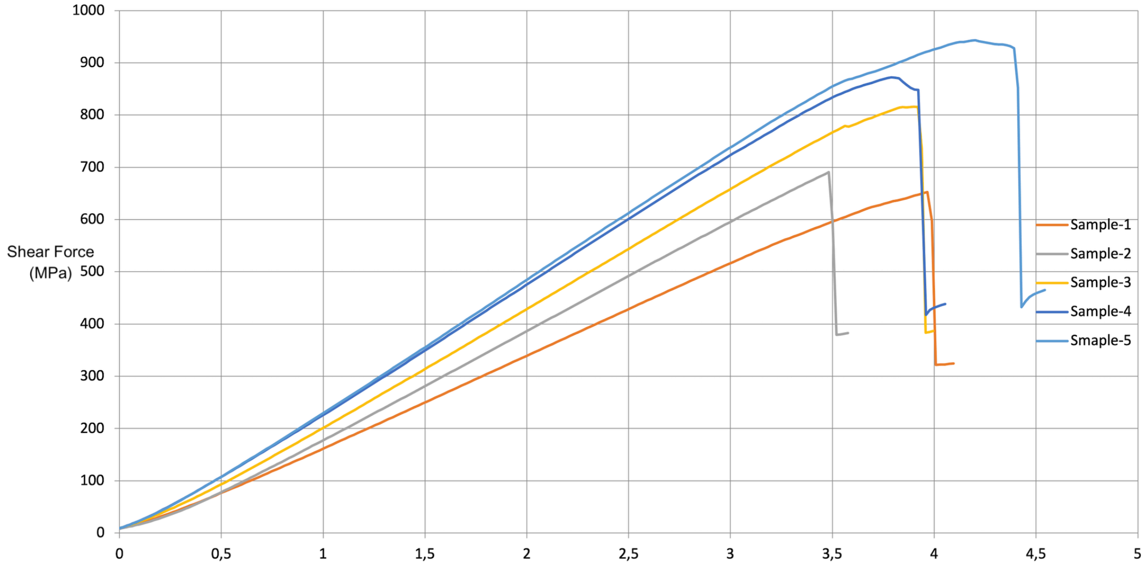

Figure E.1: Force-Displacement graph of ILSS testing of TMC samples made from unrecycled rods

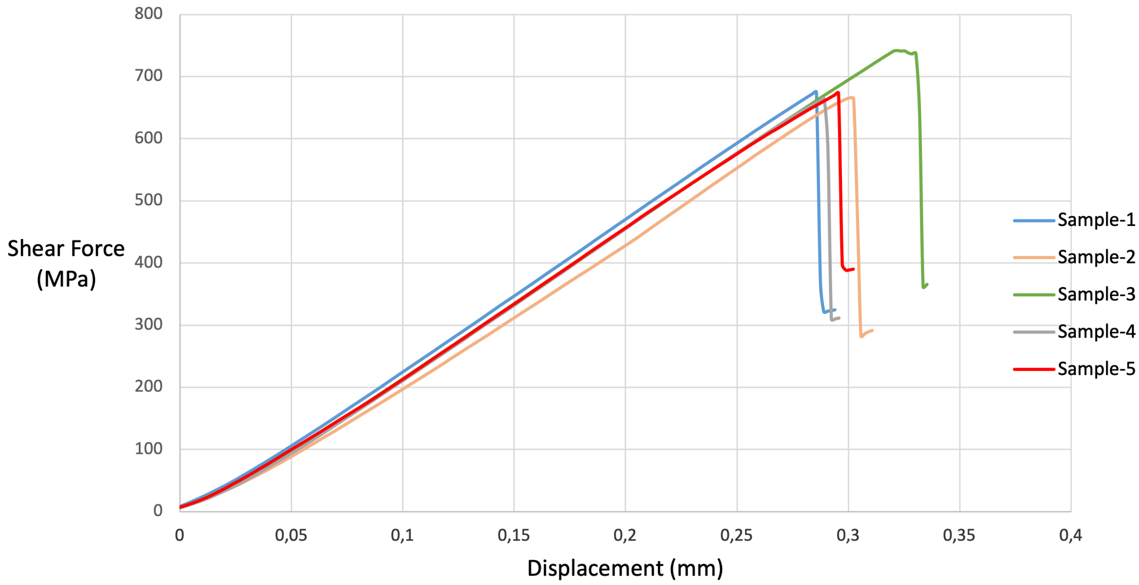

Figure E.2: Force-Displacement graph of ILSS testing of TMC samples made from one-time-recycled rods

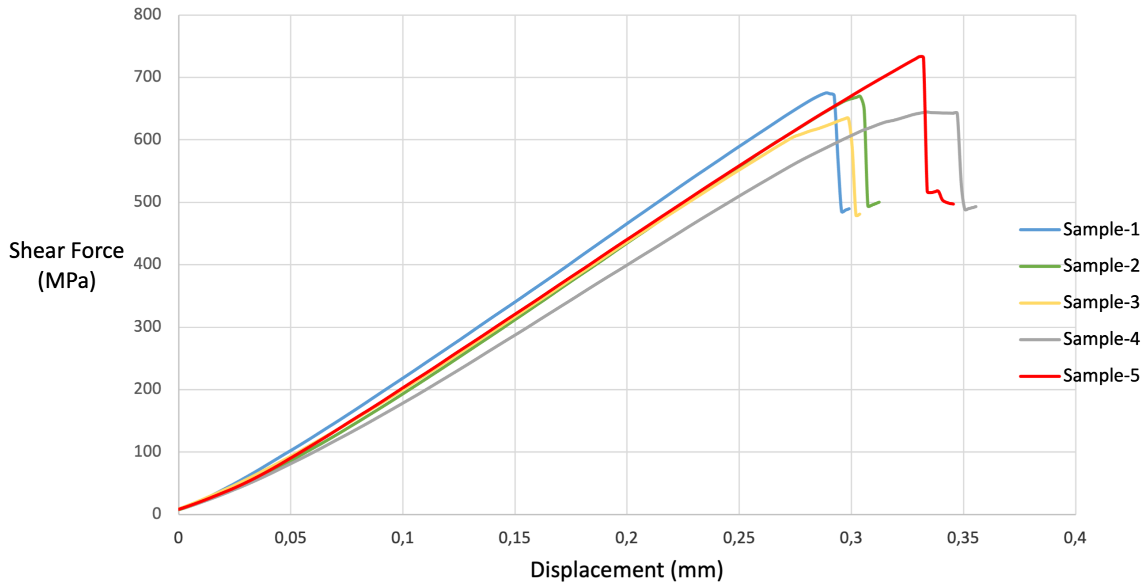

Figure E.3: Force-Displacement graph of ILSS testing of TMC samples made from four-times-recycled rods

E.3. Theoretical Calculations on Bending Performance of Twin Matrix Composites

This section presents two different approaches to analyse the bending performance of the TMCs. For both approaches, there are several assumptions and discussions that could affect the accuracy of the results. Therefore it is decided not to have recycling as an influencing factor and only look at TMCs that are made from unrecycled rods. Both approaches are based on the Euler–Bernoulli beam theory and assume pure bending, which would mean neglecting the additional shear force the TMC samples were experiencing.

Before describing either of these approaches, other common assumptions must be mentioned. One is that the contribution of the 90^o rod to TMC's stiffness is neglected. This is a safe assumption because composites are known to be remarkably less stiff in the transverse direction than in the longitudinal direction. Additionally, because the stiffness of the secondary matrix is remarkably less than that of the 0^o rod, only the contribution of the 0^o rods to the beam's stiffness will be considered. The next assumption is that the TMC cross section is symmetric with respect to the middle axis. Looking at microscopic figures of TMC samples, it can be seen that none of the samples are completely symmetrical. Despite that, assuming symmetry simplifies the calculations greatly. One last assumption that applies to both approaches is that if there are two rods next to each other within the same layer, these rods can be assumed as one together. This assumption serves also to make the calculations easier.

All of the above-mentioned assumptions have been shown in figures E.4. In these figures, w_{rx} represents the width of the rods and d_{rx} represents the distance values between the neutral axis of the 0^o rods and the neutral axis of the TMC. As it can be seen, the 90^o rods are neglected and it is assumed that all 0^o rods have the same distance to the neutral (x-axis). Lastly, it can be seen that 0^o rods that are next to each other, combine to form a whole rod. The width of 0^o rods (in figure E.4a) is the average of the actual rods (in figure E.4b).

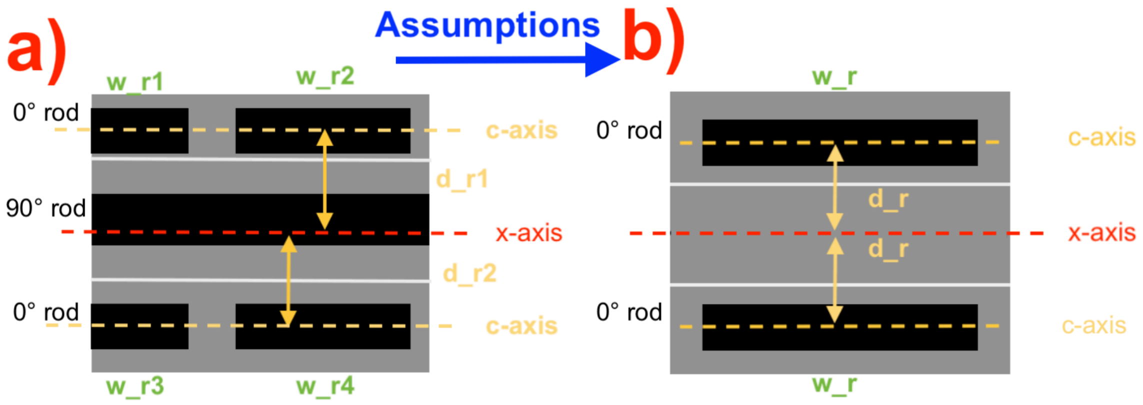

Figure E.4: Simplifications made to the rod cross section to assist bending calculations.

Now that the assumptions for these two approaches are mentioned, it is time to introduce them:

Approach 1:
This method is based on an approach that aims to calculate the elastic modulus of a beam that is simply supported on both ends and has a vertical force applied in its middle, as shown in figure E.5. The formula to obtain the elastic modulus in this case is $E = \frac{P*l^3}{48*I*\delta_{Max}}$.

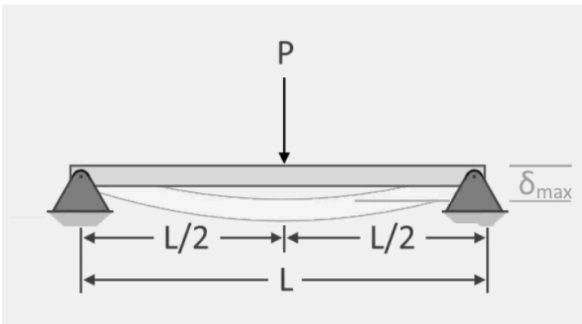

Figure E.5: Sketch of a simply supported beam load under a transverse load [1].

An important assumption in this approach is that the beam under bending is isotropic, which is contrary to the case of TMCs. To solve this issue, it is decided to only focus on the contribution of 0^o rods to the bending of the TMC sample. That means more specifically that only $I_{0^o rods}$ will be considered and $I_{90^o rod}$ and I_{matrix} will be neglected. This is an acceptable assumption because the 0^o rods are remarkably stiffer than the 90^o rod and the secondary matrix. Therefore the formula to obtain the elastic modulus is updated to equation E.1.

$$E = \frac{P * l_{span}^3}{48 * I_{rods} * \delta_{Max}} \quad \text{(E.1)}$$

The P and δ_{max} values are obtained from the tests results. It is decided to use the data of sample 2 in table E.1 (note that all TMC samples in this table are made from unrecycled rods). The reason for selecting this sample is that most of its parameters (such as P, δ_{max} or rod volume) are 'average' with respect to other samples in that table. That means that P = 690.61 N and δ_{max} = 0.31 mm. Note l_{span} is not the same as the sample length, but it is the distance between the supports. In this case, l_{span} is 14 mm. I_{rods} is the sum of second moment of area of the upper and lower 0^o rods. The equation to calculate I_{rods} is as follows:

$$I_{rods} = 2 * (\frac{w_r * t_r^3}{12} + w_r * t_r * d_r^2) \quad \text{(E.2)}$$

Looking at the microscopic view of sample 2's cross-section, it is observed that w_{r1} = 1.39 mm, w_{r2} = 3.63 mm, w_{r3} = 1.17 mm and w_{r4} = 3.63 mm. That means that the average rod width would be w_r =

4.91 mm. d_r is also the average of d_{r1} and d_{r2} which are 1.10 mm and 0.90 mm. That leads to d_r = 1.00 mm. t_r is the thickness of the rod which is always 0.63 mm (as discussed in section 4.1). Applying all these numbers leads to I_{rods} = 6.39 mm^4.
Referring back to equation E.2 and plugging in all the required parameters, an elastic modulus of 19.93 GPa is obtained.

Approach 2:
This approach is based on a method that was used in a paper with the goal of finding an expression to obtain the effective bending stiffness, E$_b$, of a composite ply with a uniform fiber distribution by using the mechanical properties of its components. The advantage this approach holds over the first approach is that this one does not assume a homogeneous material and considers the differences between the rods and the secondary matrix properties. According to this model, the effective bending stiffness parameter can be obtained by dividing the bending stiffness for the composite cross section, $\hat{D}$ over the second moment of area of the TMC sample. $\hat{D}$ is obtained by following equation E.3.

$$\hat{D} = 2 * \sum_{n=1}^{N} (E_m * I^i_{x|m} + E_r * I^i_{x|r}) \tag{E.3}$$

In this equation, N represents the number of 0^o rod layers above the neutral axis of the TMC and $I^i_{x|m}$ and $I^i_{x|r}$ are the moments of area of of the secondary matrix and the 0^o rod with respect to the neutral axis. To calculate $I^i_{x|r}$ and $I^i_{x|m}$, equations E.4 and E.5 are followed.

$$I^i_{x|r} = \frac{w_r * t_r}{12} + w_r * t_r * (\frac{2 * n - 1}{2})^2 * d_r^2 \tag{E.4}$$

$$I^i_{x|m} = (\frac{w * \frac{t}{2}}{12} - \frac{w_r * t_r}{12}) + (w * \frac{t}{2} - w_r * t_r) * (\frac{2 * n - 1}{2})^2 * d_r^2 \tag{E.5}$$

Given that there is only one layer of 0^o rods, N = 1. A note about the above two equations is that for the sake of simplicity, it is assumed the centroid of the secondary matrix aligns with that of the 0^o rod and is equal to d_r. Same as the first approach, it is decided to use sample 2 as an example to find its bending stiffness. That means that w_r = 4.91 mm and d_r = 0.63 mm. w and t are the width (=6.7 mm)and thickness (=3.1 mm) of the sample respectively. Inputting all these values, leads to $I_{x|r}$ = 0.86 mm^4 and $I_{x|m}$ = 3.81 mm^4
The next step is to plug the calculated moments of areas in equation E.3. E$_r$ is 140 GPa (mentioned in table 4.1) and the value for E$_m$ is 2.5 GPa (mentioned in table 4.2 [1]). Doing so yields a $\hat{D}$ value of 259.85 GPa*mm^4. To get the effective bending stiffness, equation E.6 is followed. In this equation, I is the moment of area of the whole sample.

$$E_b = \frac{\hat{D}}{I} = \frac{\hat{D}}{\frac{w * t^3}{12}} \tag{E.6}$$

By inputting the required parameters into equation E.6, the resultant effective bending stiffness is 15.62 GPa.

Conclusion:
Thus according to Approach 1, the effective stiffness that the 0^o rods display during the ILSS bending test is 19.93 GPa and according to Approach 2, the effective bending stiffness of TMC sample is 15.62 GPa. It can be argued whether these parameters represent the same phenomenon and can be compared. In the author's opinion, they can be compared because the bending strength of the TMC comes mainly from the 0^o rods. The fact that E modulus from approach 1 (19.93 GPa) is not so far off regarding the E modulus from approach 2 (15.62 GPa), can be a confirmation of this hypothesis.
Note that Approach 1 is based on the performance results of the TMC sample and Approach 2 is based on material properties of its rods and secondary matrix. The fact that E modulus values calculated based on these two different approaches are still comparable is quite interesting. Nevertheless, it can be concluded that based on the mentioned assumptions, the (effective) bending stiffness of TMCs is in the range of 15.62 - 19.93 GPa.

[1] According to that table, the young modulus of the second matrix is 2.5 - 3 GPa. The reason for selecting the lower bound is that the secondary resin was not cured at the highest possible temperature. More about that can be read in subsection B.1