Impact resistance of a twin matrix composite material through quasi-static testing

Msc. Thesis

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by

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Alberto Bombace
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Summary

Composites consist in combining two or more separate and distinct components within a structure to create a new material with different properties from those base components. Reinforced plastics are one family of this order of materials that often exhibit high specific properties, making them attractive for lightweight applications. Polymers reinforced with fibres however have different strength and stiffness values depending on the direction of the reinforcements, which can make their application difficult in some circumstances. Twin-matrix composites were originally designed to improve the failure strain in the transverse direction of unidirectional laminae without compromising the strength in the fibre direction. The concept works by impregnating fibre bundles in a stiff polymer matrix, providing stiffness and strength, and subsequently embedding the bundles in a flexible matrix for the transverse properties. The concept can be applied to introduce other functionalities as well, like allowing new manufacturing methods or recycling the reinforcements.

Another weakpoint of fibre reinforced plastic composites is their low interlaminar shear strength, as the thin layer of matrix between the laminae has relatively low strength compared to the rest of the material. This means that even under a low energy impact the laminae might de-bond, compromising the laminate strength. Having a resilient and tough polymer between the laminae should therefore help to prevent delamination from occurring or growing as fast. Because of this reason twin-matrix composites should present a favourable impact behaviour thanks to their flexible secondary matrix. This thesis work is a first step to investigate whether this is true. The twin-matrix composite in this project is made by embedding commercially available carbon pultrusions in a partially cured vitrimer secondary matrix, and then tested under quasi-static indentation to simulate a low energy impact. Several ways to make the TMCs were attempted, but at the end it was set to continue with casting the vitrimer on the pultrusions, and the laminates' quality was examined optically with a microscope to measure the interlaminar resin layer thickness and the distance between the pultrusions, as well as to make observations on other defects. A traditional carbon fibre composite made with vacuum infusion is used as a benchmark to compare the performance, and finally the delamination area is measured thanks to the aid of ultrasonic non-destructive testing. The study concluded that indeed a TMC would present a lower delamination area compared to a traditional composite subjected to the same impact energy, but impact resistance can be a nuanced topic, so more research is encouraged.

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Nomenclature

Abbreviations

Abbreviation	Definition
4-AFD	4-Aminophenyl disulfide
BDE	1,4-Butanediol diglycidyl ether
DOC	Degree of cure
QSI	Quasi-static impact/indentation
SEM	Scanning Electron Microscope
TIM	Thermal interface material
TMC	Twin matrix composite/ Two matrix composite
UTM	Universal testing machine
VIP	Vacuum infusion process

Symbols

Symbol	Definition	Unit
a	plate radius	[mm]
D	plate bending stiffness	[Nmm^2]
E	elastic modulus	[MPa]
F	force	[N]
h	thickness	[mm]
T_g	glass transition temperature	[$°C$]
y_{max}	displacement in the middle of the plate	[mm]
ν	Poisson's ratio	

1 Introduction

Fibre reinforced plastics are a class of material which often presents very high specific properties, and because of this are often used in the aerospace, automotive, and civil engineering sectors. The most common polymers employed are thermosets for their strength, stiffness, and versatility in manufacturing, however they also present inherent limitations, like low repairability of the parts, their difficult recyclability, their low impact resistance, and the fact that unidirectional composite laminates exhibit lower strength in the transverse direction.

Twin matrix composites are a relatively new and under-researched class of composite materials, which promise to improve the failure strain in the transverse direction of unidirectional composite laminates. This is important to improve the cyclic strength of the laminate, or in case of gas tanks, to prevent the vessel from leaking[1]. Other applications might include scenarios where it is required that the structure undergoes high deformations while preserving the material's strength. Morphing wings are one example, and Schmitz and Horst researched a comparable composite structure for this specific application[2].

Twin matrix composites are still in their infancy from a research perspective, with Vasil'ev and Salov[1] being the firsts to create the concept and investigate the transverse tensile properties, Callens[3] having investigated the compression behaviour in the longitudinal direction, Moghaddam[4] exploring their potential as a recyclable material, while Azarov and Antonov[5] researched the application of twin matrix composites in 3D printing, as they appear to be less susceptible to damage during the printing stage. At the moment however, there are no actual industrial uses for twin-matrix composites due to manufacturing processes that are not yet matured, and the fact that very little is known about the behaviour of this class of composites.

This research's objective is to develop a vitrimer based twin-matrix composite, to test study its behaviour under low-energy impact through quasi-static indentation, and to compare it with a traditional fibre reinforced plastic. A plate similar to the one developed by Moghaddam[4] will be used, although a vitrimer based second matrix and slightly different manufacturing processes are selected in an attempt to achieve better fibre volume fraction than their research, as this would translate in better properties. Additionally, a vitrimer-like matrix can address other limitations of thermoset based composites, mainly the recyclability and repairability of parts made with these new polymers while also maintaining the ease in manufacturing parts that characterise fibre reinforced thermosets, although this research will only focus on the impact resistance.

2 Literature study

This chapter presents a synthesis of some of the works previously done on Twin-Matrix composites and on impact testing using quasi-static indentation method.

2.1. Studies on Twin-matrix composites

Vasil'ev and Salov are credited to be the first to come up with the idea of twin-matrix composites to allow for higher transverse failure strains in unidirectional composite cross-ply laminates while maintaining sufficient strength and stiffness in the fibre direction. In order to do so, they impregnated bundles of glass fibres in a stiff epoxy resin, which makes sure that the stress is distributed well among the fibres and to achieve better strength in the their direction, and after the resin was fully cured, encased them in a soft and flexible secondary matrix to achieve the larger transverse failure strain[3]. In their case, the flexible polymer was made by modifying an epoxy resin with liquid SKN rubber[1] and achieved a strain at failure of 120%. The resulting twin-matrix composite had a fibre volume fraction of around 50% but achieved a strength of 1420 MPa in the fibre direction, which is slightly less than a traditional composite they tested against it made by glass fibres and the same stiff matrix they used for the bundles, which achieved a strength of 1470 MPa. On the other hand, the transverse failure strain of the twin matrix composite was 3.0%, while the regular composite achieved 0.2%[3].

Callens instead of impregnating fibre bundles employed pre-made carbon micropultrusions and used a flexible secondary matrix made by mixing two different epoxies, achieving a strain at failure of at most 35%. His research was focused on understanding the behaviour of twin-matrix composites during compression, and to do so circular specimens were made by differently flexibilised matrices encasing different sized micropultrusions. His research concluded that the primary failure mode for twin matrix composites reinforced with thin micropultrusions is fibre kinking, and there is no significant variation in the strength of the material when the diameter of the reinforced changed, but not when the secondary matrix properties change. It is hypothesised that this is due to the fact that smaller micropultrusions are more susceptible to buckling, but are not as defect sensitive. Larger reinforcement on the other hand would provide more resistance to buckling, but are harder to manufacture with consistent quality and are therefore are susceptible to different kind of failures. The strength was also influenced by the modulus of the secondary matrix, with stiffer matrices achieving higher compressive strengths as they could better resist the lateral movement of the pultrusions. Callens made his twin-matrix composites with filament winding, and achieved a fibre volume fraction between 40 and 50%, but in his process the alignment of the reinforcement made it so that resin rich zones were observed, as well as voids between the micropultrusions[3].

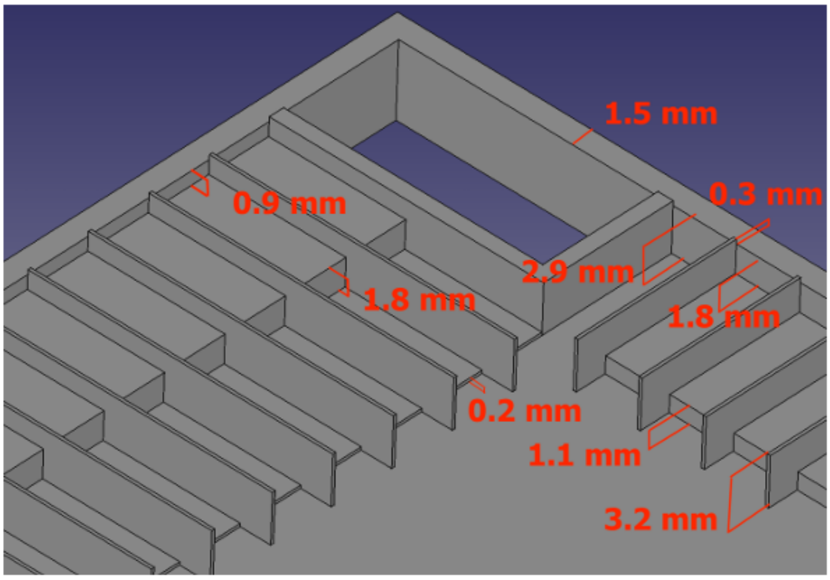

Figure 2.1: Detail from Moghaddam's mould[4]

Combining two different matrices can be done to give new functionalities to the composite material other than improved transverse elongation. Moghaddam's research was focused on the possibility of achieving recyclable composites using the structure of a twin-matrix composite. The idea is to use a soluble secondary matrix to recover the reinforcements, which can then be impregnated again. To prove the concept, carbon pultrusion were encased in a secondary matrix and then subjected to an interlaminar shear strength test to cause cracks in the secondary matrix, which was then dissolved and the pultrusions were employed to make new specimens. The pultrusions are rectangularly shaped, and the embedding resin was a commercial recyclamine one called Polar Bear. This resin presented an ultimate strain of 7-9% and could be dissolved in an acetic acid solution. Analysis with a scanning electron microscope (SEM) proved that the recycling process caused minimum damage to the reinforcements, but the manufacturing process in this case gave less consistent quality in the manufacturing of specimens. Moghaddam used a 3D printed mould to align the fibres and then cast the resin onto them, and applied pressure from the top. Despite the mould design counting on some teeth to hold the reinforcements in place, perhaps due to tolerances that the printer could not achieve or due to thermal expansion of the mould, this process resulted in inconsistent resin thickness in between the pultrusions. His reason to select this method of manufacturing is that the resin employed had a very short pot life at room temperature (only 25 minutes).

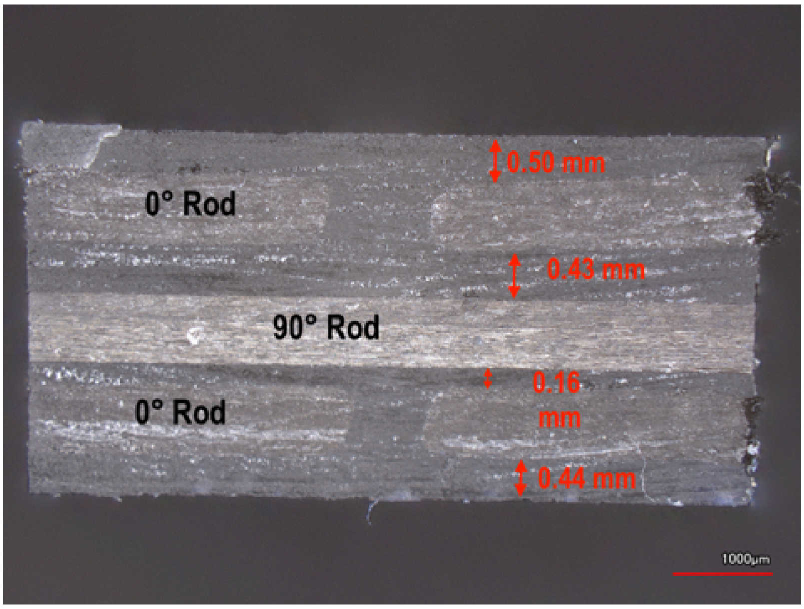

Figure 2.2: Microscopy image of a one time recycled sample from Moghaddam's research[4]

Azarov et al., as well as Liu et al., used the structure of a twin-matrix composite to create a 3D printable composite for use in additive manufacturing. Thermoset polymers are not indicated for this process, as once cured they do not adhere to one another, and thermoplastics on the other hand would require higher pressure at the nozzle to extrude, have usually worse properties than thermosets in terms of stiffness and strength, and tend to be more viscous, which results in poor impregnation of the fibres. The researchers combined bundles of impregnated and cured fibre reinforced thermoset with a secondary thermoplastic matrix. The thermoplastic polymer protects the bundles, which provide the stiffness, and supplies adhesion so that the structure can be created. The secondary matrix also provides a slightly better impact resistance, given the viscous fracture behaviour of thermoplastics[5][6][7].

Li et al.[8] combined different polymers on the same piece by developing a method to ensure that specific sections of reinforcement are impregnated by different polymers. Their process was inspired by Chinese sugar art, and the first step consists of creating a mixture of sucrose and water. The solution is allowed to hydrolyse and the water is consequently evaporated, leaving a low viscosity slurry that is used to impregnate the reinforcements through resin transfer moulding, and left to solidify. This temporary matrix is dense enough to fully cover the fibres without leaving voids or cracks, and it has a melting point around 150°C, which is compatible with many epoxy resins. The sucrose resin is then dissolved leaving fibres exposed in predetermined areas that are impregnated with a polymer matrix while the remaining sucrose prevents the other areas to make contact with the epoxy. The process is then repeated for the areas that have to be impregnated with a different polymer. The researchers made a bendable structure by using soft silicon between areas impregnated by an epoxy system. This made it so that the flexible polymer could act as hinges to make a foldable structure. They argue that a process like this might also be used for different polymers to create bendable and auto-deployable fibre reinforced structures using memory shape polymers, or to give the structure secondary properties in key areas by using matrices thermal and electric traits.

A structure similar to a TMC can also be used in microelectronics to create thermal interface materials (TIM) that possess better heat transfer properties and resilience than the polymer TIMs currently used. The ones available offset the poor conductivity of polymers by dispersing conductive particles in them, which create channels from where the heat can escape. Because of this process the thermal conductivity of TIMs can have a random distribution, and increasing the amount of fillers in the polymer also has the disadvantage of increasing residual stresses due to the different thermal expansion of the materials, as well as stress concentration points. Shao et al.[9] made a structure using carbon fibres, platinum catalyst, an acetylenic cyclohexanol inhibitor, and thermally conductive silicone rubber to create a new TMI to solve this problems. The idea is to use carbon fibres to drive off the heat, while the flexible matrix contours the shape where the heat has to be transferred from and provides additional resilience, as well as helping with damping of vibrations to cushion and shield electric parts.

Finally, embedding fibre reinforced polymer pultrusions in a second matrix is something that has been researched in civil engineering extensively. Concrete has a high compressive strength, but its tensile strength is usually just a fraction, prompting engineers to develop ways to improve the tensile properties. This has commonly being done with the use of steel rebars as reinforcements. These rods have the task of bearing unfavourable stresses and give the concrete much needed tensile strength[10], but are susceptible to corrosion and fatigue, which can alter the structure's loading capabilities. Composite rebars made by glass or carbon reinforced plastic have gained popularity because of their corrosion resistance and fatigue properties, with the additional advantage of being lighter than steel, allowing for taller constructions[11]. In the case of carbon rebars, they tend to be stiffer than the steel ones and do not need a protective environment around them, meaning that higher volume fractions of the reinforcement in the concrete are easy to achieve[12].

2.2. Studies on impact and quasi-static impact on composite materials

Low impact resistance is one of the factors to limit the extensive use of thermoset based fibre reinforced composite materials. The brittle nature of these resins and the most common fibres like glass and carbon, makes it so that these materials can only absorb energy from an impact in their elastic state[13]. The response of the material is influenced by the speed of the projectile and its contact time with the material. For long impact times, generally caused by large masses at low velocity, the response will be governed by transverse waves and the material will deflect as in static loading. Small masses at low speeds result in shorter impact times and cause transient waves to form, so the response will be mostly controlled in shear and flexure[13][14]. Finally, short impact times caused by high speed projectiles don't allow regions of the material far from the impact site to absorb the kinetic energy, so the response of the material is governed by through-the-thickness waves[15].

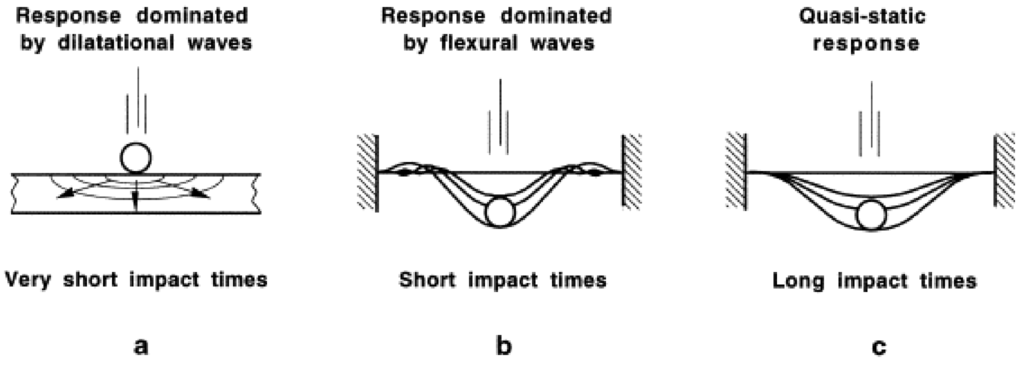

Figure 2.3: Different responses of composite materials to impact[15]

Beside the materials and type of impact, the strength of the composite is also influenced by the layup[16] and fibre architecture. Woven fabrics provide better strength than unidirectional fibres, with 3D woven fabrics being especially noteworthy for their ability of providing fibres capable to give a contribution in the transverse direction, which in the two other architectures is entirely left to the matrix. Stitching is another architecture that improves the impact resistance, as it results in decreased delamination area when compared to an unstitched laminate at the same impact energy.

The geometry also has an effect on the impact strength. The overall thickness of the laminate is a key parameter and can influence the energy absorption mode. Thicker laminates are reported to be less susceptible to damage, and having a higher energy threshold for both delamination onset and penetration than thin laminates[13].

The shape of the impactor is another factor to take in consideration when evaluating the impact resistance of composite laminates[13]. Mitrevski[17] conducted a study to establish the influence of the impactor's geometry at low velocities by comparing the damage and damage area of carbon fibre hit by a spherical, an ogival, and conical impactor, all having a 12 mm diameter. They found that as the impactor becomes blunter, the composite will absorb more energy and the damage area will be bigger. In fact, as the contact area increases, the delamination becomes the favoured damage mode. Sharper impactors on the other hand cause localised fibre breakage, and will penetrate the laminate at lower energies.

Additionally, as composite materials are often susceptible to environmental condition, their impact response will also change depending on moisture and temperature. Polymer matrices can absorb and diffuse water in humid environments, creating local defects and causing an expansion of the matrix, which in turn creates residual stresses that can result in premature failure[13]. Given the different thermal expansion of the materials constituting composites, temperatures far from the one at which the laminae were created can also create similar residual stresses. The cold is particularly dangerous as it embrittle the matrix, thus the laminate will present a bigger damage area after being hit[18].

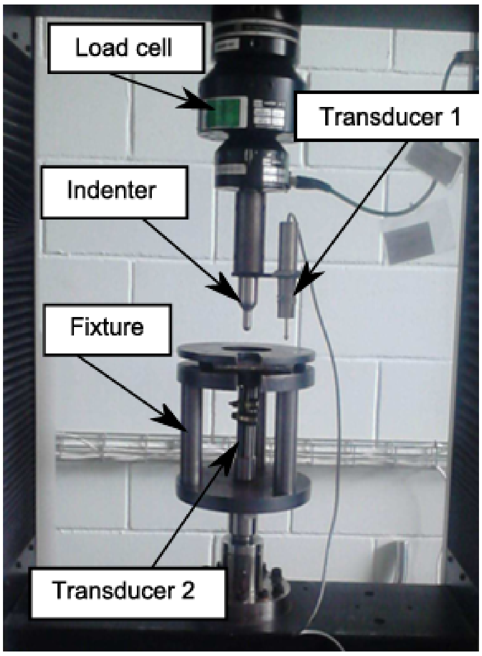

Figure 2.4: QSI setup used by Wagih[19]

To test for impact resistance, one of the most common methods is through an impact tower, however the set-up of this tool is often complex and does not allow to easily gather a large amount of data. For these reasons, researchers have tried alternative means to recreate impact events. Because of the static response of laminates subjected to long impact times, a proposed way to test collisions from larger masses is quasi-static impact testing, sometimes referred as quasi-static indentation (QSI). The setup usually consists in an indenter driven into a plate, which is clamped in a similar way to drop-weight test. The displacement of the plate in the centre of the cut-out is measured by a linear transducer, and the force by a loadcell.

QSI testing is not an exact replica of a large mass impact, as it ignores effects based on vibrations and strain rate sensitivity, but it can still provide useful information about the way a composite fails[20]. For thick laminates in particular, the force-displacement response during loading of a low velocity impact and a quasi-static one are almost identical[20][21]. QSI can also be used to analyse the onset of delamination. Sutherland[22] compared the response of glass fibre laminates of different thicknesses during quasi-static impact loading and several low velocity impacts, and observed that thick laminates exhibited a bilinear behaviour, where the knee point coincided with the onset of delamination, and that this point coincided for both kind of tests. Moreover, Sutherland observed that the force-displacement response of the laminates remained the same until the stiffness drops several times as the fibres begin to fail and the material is penetrated. This phenomenon appeared sooner in QSI tests, suggesting that maybe fibre failure is more strain sensitive than the growth of delaminations. Leroy[23] compared the low velocity impact and QSI responses of plastic reinforced with flax fibres, which is less strain sensitive than glass and carbon fibres, and obtained force-displacement curves between tests that were closer than Sutherland's. Additionally, Sutherland observed that thin laminates did not exhibit the same behaviour as the thick ones, as they did not present the knee point caused by the onset of delamination, but instead their stiffness appears unchanged until fibre failure occurs. It is hypothesised that membrane effects are predominant in this case, and that prevents the stiffness of the laminate to drop significantly until fibre failure. Sutherland suggests a plate diameter to laminate thickness of 15 to estimate if a laminate will behave as "thick" or "thin".

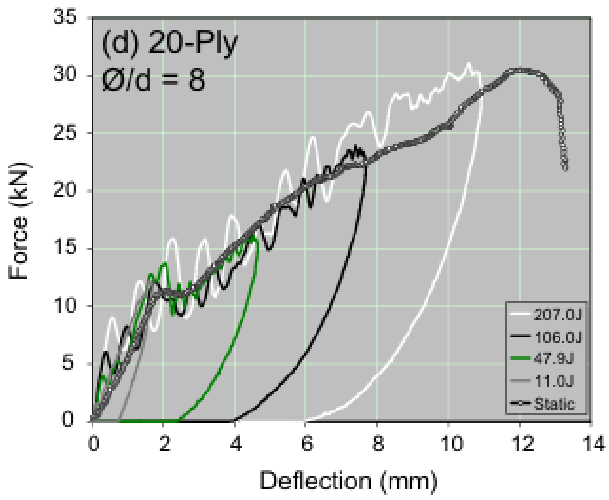

Figure 2.5: Curves obtained by impact and QSI testing by Sutherland[22]

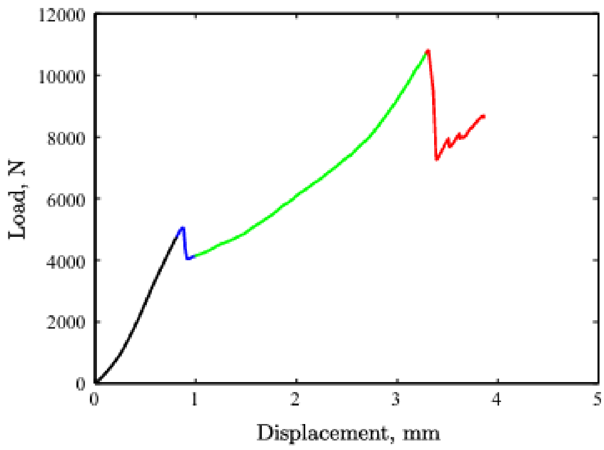

Figure 2.6: Curve for one of the samples obtained by Wagih[19] using QSI

Wagih[19] studied the damage sequence in detail using quasi-static indentation. For their analysis a 25 mm radius plate was used, and the specimens' thickness was 2.4 mm, meaning that the laminates are comparatively thick according to Sutherland's observations, and in fact the load-displacement curves present similarities despite the different materials employed by the researchers. Wagih observed that upon loading the laminates (Figure 2.6), it reacted linearly until there was a sudden drop (in blue) in the load carrying capabilities caused by sudden cracking of the matrix inside the plies at a 45° angle with respect to the surface normal. The plies closer to the indenter are the first one to fail. As the indenter keeps going forward, the cracks grow and meet the resin layer between the plies, and grow there causing delaminations (green). In this stage the stiffness of the laminate changes, and it is lower than when it was undamaged. The final stage (red) marks the point where the fibres begin to break, and it is characterised by several drops in the load bearing capability of the composite. This is caused by the fact that there are two different damage mechanisms. One is the tensile failure of plies at the bottom of the laminate, which interests approximately one third of the entire thickness. On the other hand, the remaining two thirds see the formation of a shear cone. Figure 2.7 illustrates the damage sequence.

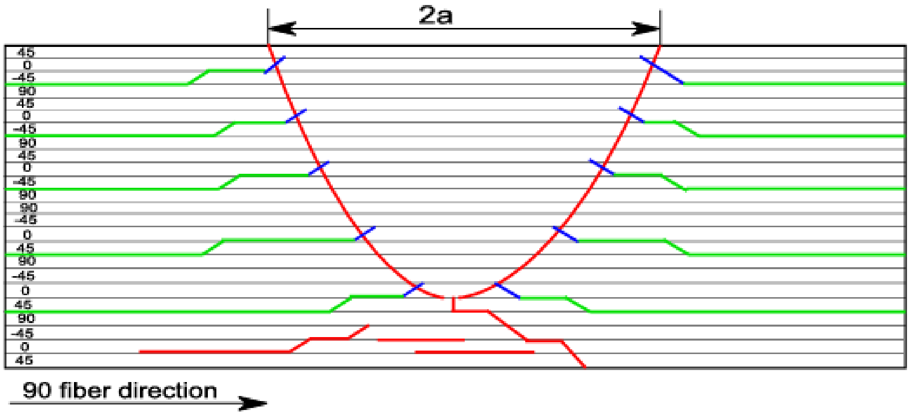

Figure 2.7: Schematisation of the damage sequence as observed by Wagih[19]

3
Material selection

Here the materials constituting the TMCs are described, as well as the reason they were selected. At first, the pultrusions acting as reinforcement are presented, followed by a brief explanation on the secondary matrix and a brief elucidation on the mechanisms behind vitrimers.

3.1. Reinforcement

As part of the reinforcement, Callens used commercially available carbon fibre micro-pultrusions instead of manufacturing bundles like Vasil'ev and Salov did. Moghaddam followed suit by employing carbon pultrusions. In this thesis project, the same pultrusions used by the latter constitute the reinforcement for the twin matrix composite (Figure 3.1). One reason is convenience, as the pultrusions were already in the laboratory as they were leftover from their research, and they are also easier to align than micro-pultrusions.

The pultrusions are manufactured by van Dijk Pultrusion Products (DPP), and are made by TF700 carbon fibres reinforcing a Bisphenol A Anhydride epoxy system. They have a rectangular profile with sizes reported by the manufacturer measuring 3.6 mm by 0.6 mm, however Moghaddam measured them to be between 3.65 and 3.69 mm, and between 0.65 and 0.69 mm. DPP also reported the pultrusions to have a fibre volume content of 63%, which results in stiffness and elongation at break in the fibre direction of 140 GPa and 2% respectively. Additionally, the tensile and compressive strength in the fibre direction is 2500 MPa and 1600 MPa, and the resin has a glass transition temperature of 120°C[4].

3.2. Secondary matrix

The secondary matrix has to be compatible with the reinforcement, impregnate them adequately, possess high elongation, and ideally low processing time. High failure strains are achieved by polymers that are comparatively less cross-linked, and have chains that can rotate and slide past each other to allow the material to stretch[24].

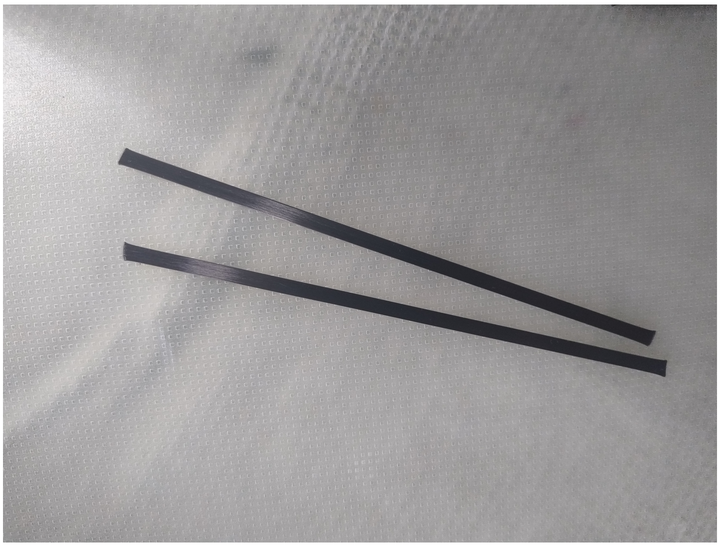

Figure 3.1: Chopped pultrusions used for the project

Thermoplastic materials often possess ultimate failure strains over 100%[25], however they do not usually adhere well to thermosets because of their low surface energy and polarity[26]. Additionally they possess high melting point at which the thermoset plastic of the pultrusions might be damaged, and their high viscosity when melted can make impregnation of the reinforcement challenging without significant pressure. For these reasons thermoplastic materials were ruled out. Elastomers also usually possess high viscosity. Finally, thermosets are the most versatile when it comes to processing, but they do typically exhibit high stiffness and low elongation. It is however possible to control the final structure of the network by using specific curing agents to decrease the amount of cross-links and increase chain mobility. Amongst these agents are polyamides, polyetheramines and urethane modifiers. Some examples of commercially available formulations include Ancamine 910, Ancarez 2364 and Jeffamine D-400. These solutions were also disregarded at the end because most of the products had cure cycles that lasted a week or more, which was considered excessively long for the time allocated for the project to allow to produce enough plates to try and perfect the manufacturing process, examine them, and then test them, in conjunction to the fact that some of the substances are not available for the European market.

At the end, a vitrimeric formulation was chosen for the secondary matrix. This class of polymers is notorious for its ability to be initially processed like a thermoset, except that the covalent bonds between the atoms can be rearranged under special conditions, for example by imparting heat to the material[27][28]. For this reason, the use of a vitrimer can also mean that a twin matrix composite will have great potential for manufacturing purposes and additionally during the material's operational life, given the healing capabilities of the polymer, as well as for recycling at the end of life of the product. These aspects however will not be covered in this master's thesis. For this project, the application of vitrimers is warranted for their above average elongation[27] and ease and speed of manufacturing.

For the composite plate, the selected polymer is a disulfide exchange vitrimer made

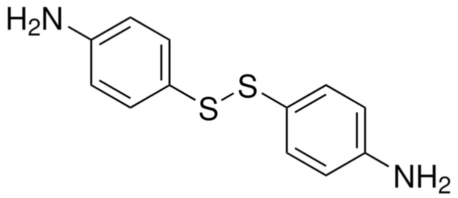

Figure 3.2: Molecule of 4-Aminophenyl Disulphide

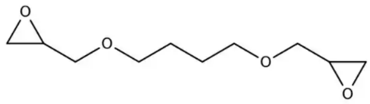

Figure 3.3: Molecule of 1,4-Butanediol Diglycidyl Ether

by combining 1,4-Butanediol diglycidyl ether and 4-Aminophenyl disulfide in a 1 : 0.625 ratio by weight of BDE to 4-AFD. The 4-AFD (3.2) is an aromatic amine curing agent that presents two amine groups and a disulfide bond between the aromatic rings. The disulphide covalent bonds are weaker than C–C and C–H bonds[29], but they have the property of being reversible as they can be cleaved and reformed under specific conditions of temperature[30]. BDE (3.3) is used as an epoxy resin monomer as it possess two epoxy groups that will react with amine groups present in 4-AFD. BDE is commonly used as a crosslinking agent for dermal fillings because of its biocompatibility and degradability[31], or employed as a reactive diluent for other epoxy systems due to its low viscosity[32].

The formulation was prepared by first melting the hardener at 87°C, which is slightly higher than its melting point but it is necessary to ensure that the 4-AFD will remain liquid when handled outside the oven. Once fully melted, the BDE is poured in the same vessel and they are mixed by hand. The formulation is then spun under 50 mbar of pressure in a speed mixer and then completely degassed under vacuum before being stored in the freezer or used. In the former case, the resin would be degassed once again in the speed mixer before being employed.

The fully cured polymer, although presenting a relatively high failure strain when compared to most thermosets, could not be elongated nearly as close as the secondary matrix in the original publication of Vasil'ev and Salov, and was relatively too stiff. In order to obtain an even higher elongation and a lower elastic modulus, the resin was partially cured to reduce the amount of crosslinks, and had tensile properties tested and compared to fully cured resin by mechanical testing. More specifically, 5 tensile samples were manufactured with a degree of cure of 0.8 to ensure that the glass transition temperature is around 40°C, above room temperature (Figure 3.5). This should mean that there is not a big variation in the stiffness of the polymer during subsequent tests. The formulation takes a very long time to cure at room temperature, but the samples were still stored in a freezer at -18°C until testing to minimise the loss of elongation. This batch of samples was therefore cured at 130°C for 1 hour to achieve the degree of cure of 0.8, while the cured specimens were cured at 120°C for 2 hours, followed by 3 hours at 150°C. As shown in Figures 3.6 and 3.7 the samples are virtually indistinguishable from one other at first sight, except for the fact that the partially cured ones present a rubbery texture. The tensile samples' elongation and modulus were tested using a universal testing machine (UTM) where the force exerted was measured by a 1 kN loadcell and length of the samples using the machine's extensometer. The

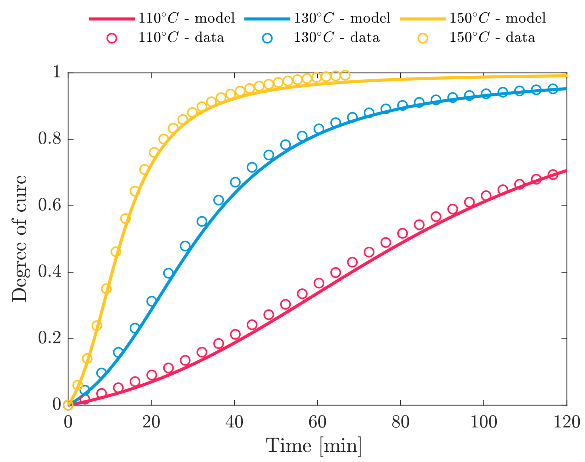

Figure 3.4: Curing behaviour of the formulation[33]

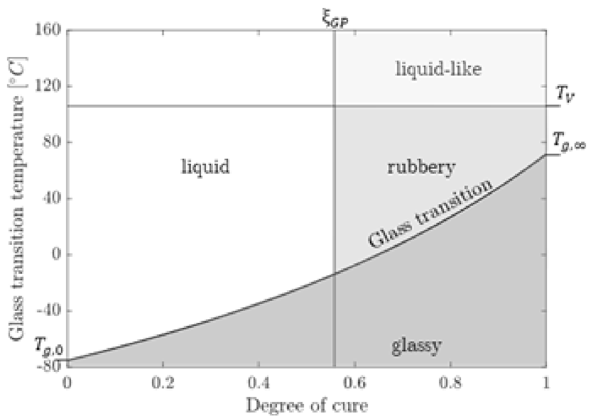

Figure 3.5: Glass transition temperature change as the degree of cure increases[33]

Figure 3.6: Fully cured samples

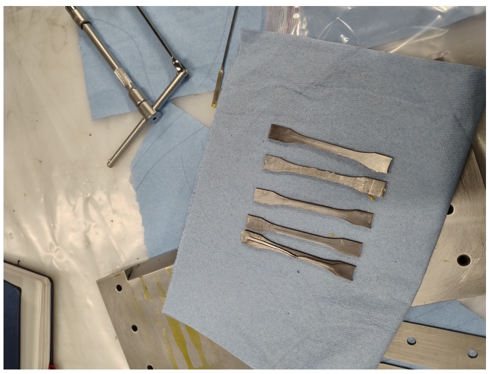

Figure 3.7: Samples cured at a DOC of 0.8

results are presented in figures 3.8 and 3.9.

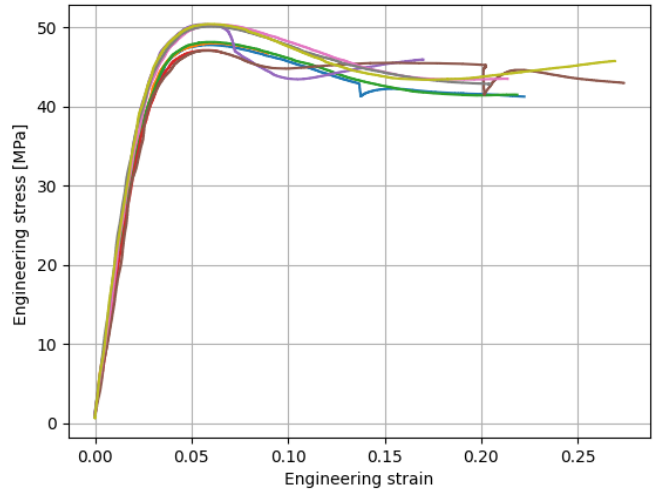

Figure 3.8: Stress strain curves of the fully cured samples

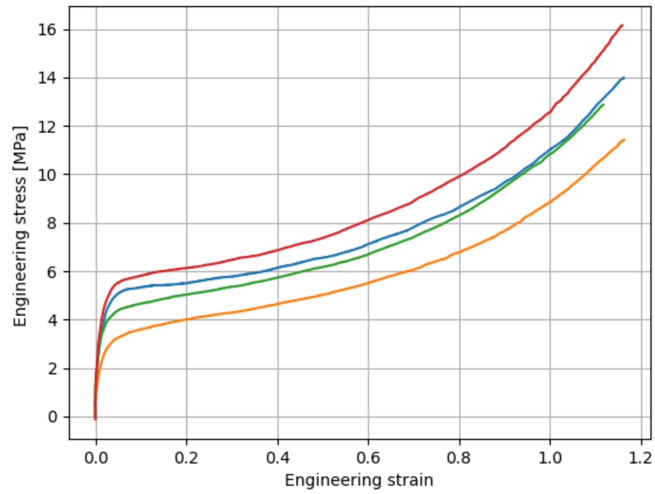

Figure 3.9: Stress strain curves of the partially cured samples

More fully cured samples were tested because the material becomes brittle, and more sensitive to defects, causing in turn more scatter in the results for their strength and ultimate strain values. As for the partially cured samples, only 4 curves are shown as the first specimen slipped from the clamp after reaching an elongation of about 70%. To prevent the other samples from slipping, they were clamped with high grip paper. The stiffness of the fully cured samples is very consistent across all specimens but, as previously said, the material is brittle and is sensitive to defects, causing significant scatter at the elongation at which the samples failed. No specimen had an elongation higher than 27%, with an average of 19%. The samples with a DOC of 0.8 on the other hand presented more consistent results. In figure it is possible to see how the partially cured resin presents a low elastic modulus, and a large elongation at break, around

Figure 3.10: Three tested and one intact partially cured tensile samples. Despite the fact that they broke at nearly the same elongation, it is possible to see that the two that were left on the table have already begun to shrink down, while the one that was just tested is considerably longer

118%. These characteristics make it a good secondary matrix candidate, and it was decided to use the formulation with the DOC of 0.8 to make the twin-matrix laminates. An additional property of the formulation is that it has remarkable memory shape. Despite being subjected to enormous elongation, the samples returned to their original size after a couple of minutes left at room temperature, which could help even further the case for the repairability of vitrimer based twin-matrix composites. Memory shape is a property shared between several other vitrimeric formulations using aminophenyl and diaminophenyl disulfide as hardeners[34][35][36].

4 Manufacturing

At the moment of writing this thesis, there are no actual applications of twin-matrix composites, thus there are no standard manufacturing processes for this kind of material. Ideally, the method has to allow an acceptable fibre volume fraction which means that, given the nature of twin-matrix composites where two matrices have to be combined and in the right amount, achieving a value as high as composites used in aerospace can be challenging but acceptable levels such as the twin matrix composite created by Vasil'ev and Salov are possible. Of course, the manufacturing process must also be compatible with the two matrix systems, which have to adhere to each other, and have a compatible processing temperature. Additionally, in applications where the laminate's transverse failure strain is important, the amount of defects that could cause the onset of cracks has to be minimised. These defects include voids, as well as pultrusions touching each other, which would prevent the secondary matrix to adequately impregnate them.

4.1. Double weaving the pultrusions

To prevent the pultrusions to come in contact with each other and to make laying up the layers easier, the idea of binding several pultrusions together with a spacer in between them was immediately considered, rather than processing them one by one by hand. This however adds a layer of complexity, as the binder, be it mechanical or chemical would need to be compatible with the manufacturing process. One of the simplest solutions, and the one adopted for the project, was to use a thread to tie the reinforcements at the edges and then cut them out. A double weave pattern ensures that each pultrusion is touched by the thread on all sides, meaning that it should not be possible to be touched by another one, and the different layers should also be separated as well. This distance is dictated by the diameter of said thread.

Several options for the binder were considered, most of them commercially available for time convenience. Polymeric threads offered many possibilities. Common products that have a diameter between 0.07 and 0.2 mm are made of polyethylene or Dyneema, which have a melting point too close to the secondary resin's cure temperature of

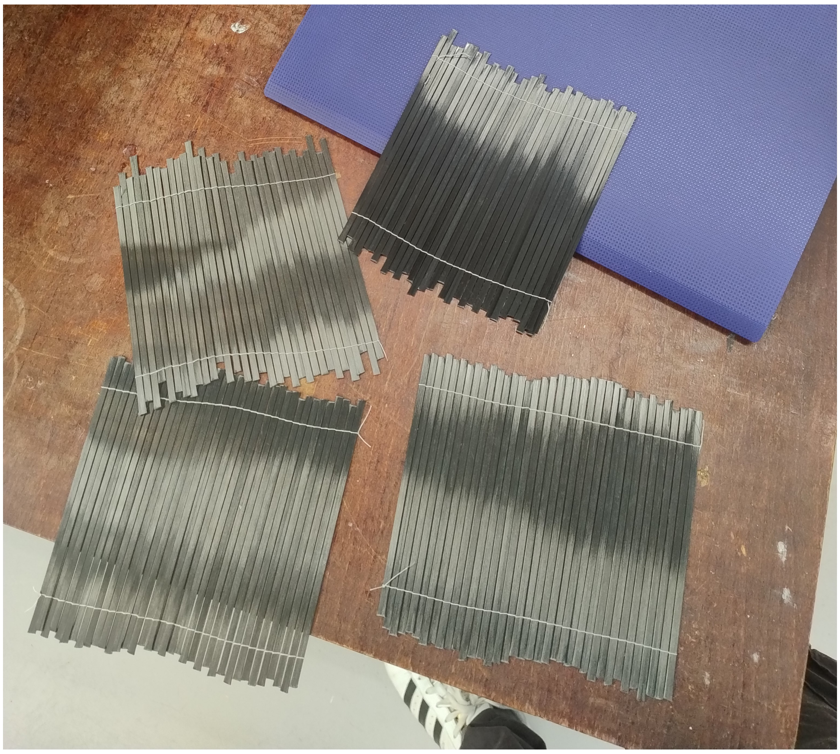

Figure 4.1: Reinforcement layers tied by the cotton thread

130°C, meaning they could melt and mix with unknown consequences. On the other hand, threads made by Nylon, Dacron and ultra high molecular density polyethylene were discarded because no product was found to have a low enough diameter. Metal wire were also considered, but the smallest size available at the faculty's laboratory was 0.2 mm, and it has the disadvantage that it is harder than polymers, meaning that a metal thread could bite into the pultrusions damaging them when the layers are compressed together. Thinner threads already available were glass and carbon fibres, but they would snap when bent at the required curvatures. At the end, the choice fell on a cotton thread, given that its degradation temperature is far higher than 130°C and is soft, which means it does not damage the reinforcement when compacted (figure 4.1).

4.2. Manufacturing of twin-matrix composites

Several manufacturing processes were considered. Vasil'ev and Salov[1] used filament winding, which is also the method chosen by Callens[3]. It allows for a relatively high fibre volume fraction, but as Callens observed it is hard to prevent the reinforcement to come in contact with each other. Moreover, this method is not the best when it comes to manufacture flat plates, which is the shape more indicated for the QSI test. Vacuum infusion was initially considered given the low viscosity of the secondary resin, but controlling the resin layer thickness is complicated. Moreover, the vacuum bag could press the reinforcement together, and the method described in section 4.1 to space apart the pultrusions can't be used with this process because the vacuum bag would press them in the middle of the laminate. It could be perhaps used in a resin transfer moulding process, but the mould design would be very complex. Finally, 3D printing was immediately discarded as the chosen secondary matrix is incompatible with this method. At the end, it was decided to cast the resin on the pultrusions, where the interlaminar resin layer thickness is determined by the distance between the reinforcement layers. To determine the amount of resin to be cast, a possible method is to calculate the volume of the mould left unoccupied by the pultrusions, which have known measurements, but it would also be necessary to account for the shrinking of the vitrimer as it cures. Another possible solution is to dip the pultrusions in the secondary matrix and then lay them up in the mould, which could allow for more conservative thicknesses, as well as less voids forming as the resin is not directly poured in the mould, and therefore should incorporate less air.

The mould is made by three pieces: a male part, a female and a middle piece. The reason behind this choice is that the composite plate would normally be stuck inside the female, so it is necessary to put holes inside the female to push and eject the plate, but in turn, these holes are points where the resin might flow out of the mould so they need to be covered. During the manufacturing phase, this was done using teflon tape, and the middle piece was positioned on top to guarantee a smoother finish and to protect the plate when it was ejected. The plates have a [0/90/0] layup, and the mould is machined to manufacture plates with a thickness of 2.4 mm and are sized 14x14 cm. The edges are then cut to remove the bindings.

The first plate was manufactured by dipping the pultrusions layers in the resin and subsequently laying them up in the preheated mould. Given that the resin has a viscosity of just 14 cP at room temperature, it would just drip off of the reinforcements, so the dipping was done with a batch of previously degassed resin directly out of the freezer, as the formulation is thicker when cold. Still, the resin returned quickly to its watery consistency so obtaining a uniform coating for the third layer was challenging. At the end, the resin coating might have been too thin, as when the plate was demoulded there were zones of irregular shape that were not covered by resin, likely because it shrank during the curing process an left the reinforcements exposed (Figures 4.2 and 4.3). The second plate was manufactured simply by casting the resin inside the preheated mould loaded with the pultrusions. This plate, seen in Figures 4.4 and 4.5, yielded a better result as there was more resin in the mould, however both plates presented zones of thinner resin in between the reinforcements (Figure 4.6), and the same problem was encountered when iterating the process. This was caused by air trapped inside the mould once it is closed, and that naturally dwells in those areas. The presence of voids can potentially mean that there might not be resin between the layers, meaning in turn that the shear stress is not correctly transferred from one layer to the next, and the composite would fail prematurely.

A third method was then brought in to try and minimise the amount of air inside the mould. It consists in preheating the mould with the reinforcements inside for one hour, casting the resin, and using a piece of release film to displace the air bubbles to the edges of the plate. The mould is then closed with the release film still inside (Figure 4.7), which is then peeled off after the curing process. With the aid of the release film, the number of observable voids was greatly reduced, but the film tends to crimp while

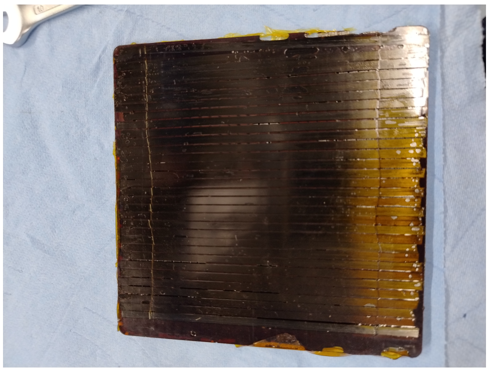

Figure 4.2: View of the bottom side of the plate made by dipping the pultrusions in resin

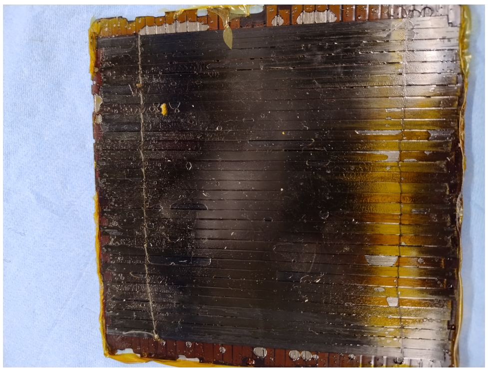

Figure 4.3: View of the top side of the plate made by dipping the pultrusions in resin

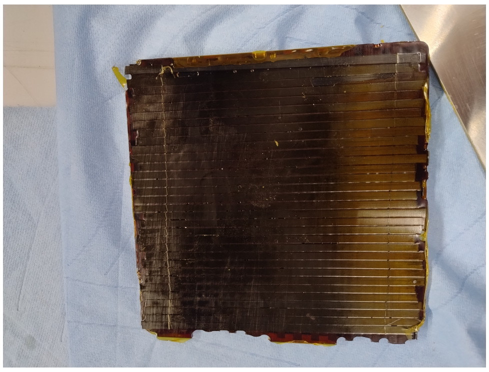

Figure 4.4: View of the top side of the cast plate

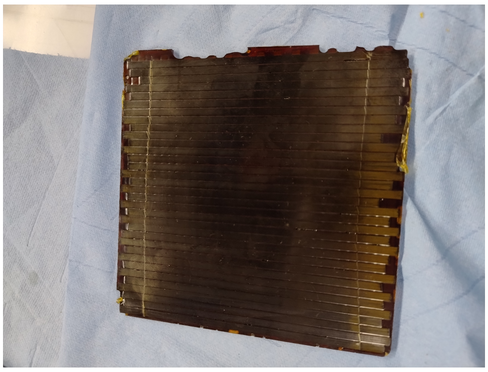

Figure 4.5: View of the bottom side of the cast plate

closing the mould, leaving an uneven texture on the topside of the plates as seen in Figure 4.8. This defect would interfere with the contact force distribution during the impact test, but the softness of the polymer would make it more forgiving than if the secondary matrix had a hard texture.

In order to establish which method was actually to be used for the final plates, it was decided to conduct a microscopy study to observe the thickness of the interlaminar resin layer, as well as to establish which defects are present in the material and if they are observed across plates with different manufacturing method. Before that, every plate had it's thickness measured with a caliper and it was noted that all exhibit a 0.1 mm difference from one side to the other. This was also observed in plates made without having the mould tightly screwed together and the thicker side did not always appear on the same edge. A slightly tilted oven tray might explain this discrepancy.

Figure 4.6: Close up to the voids in-between the pultrusions

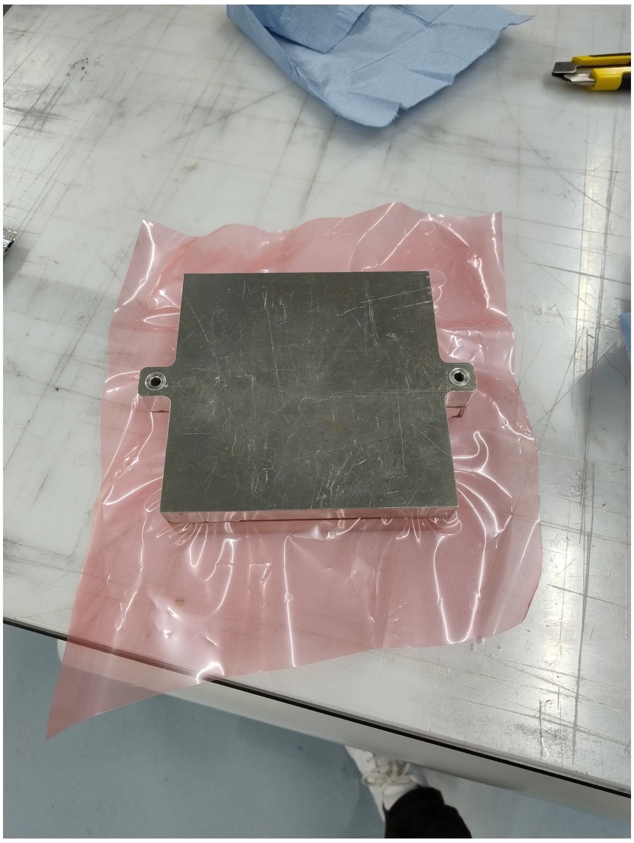

Figure 4.7: Manufacturing of a TMC in the mould with the release film in between

Figure 4.8: Example of the uneven texture left by the release film

4.3. Traditional composite manufacturing

Given that the behaviour of twin-matrix composites under impact is unknown, it was decided to manufacture samples of a traditional polymer reinforced composite to be compared under quasi-static impact to the twin-matrix plates. It was decided to cut the samples from a single plate made with vacuum infusion. This method tends to be reliable and delivers parts with high fibre volume ratios and reduces the risk of air bubbles and voids in the laminate. The process consists of laying down the dry fibres in a mould with materials to help the resin flow and fill the reinforcements. The only driving force for the liquid polymer is vacuum created by a pump, and it is maintained because the mould is sealed with a plastic foil fixed by sealant tape. After the part has been impregnated, it is left to cure in the mould and then removed. The VIP is used extensively in composite manufacturing in the aerospace, automotive and nautical sectors for its ability to deliver parts with complex geometries and dimensional accuracy, even for large laminates[37].

The reinforcement consists of SIGRATEX C U300-0/SO, a roll of unidirectional high tenacity carbon fibre provided by SGL Corporation. The matrix is an epoxy system consisting of EPIKOTE 04908 resin and EPIKURE 04908 hardener supplied by Hexion Inc., a low viscosity vacuum infusion resin with properties summarised before the curing process in table 4.1 below:

Property	Unit	Value
Viscosity at 25°C	mPa·s	130
Pot life	minutes	300
T_g(DMA)	°C	82
Mixing ratio		100:30

Table 4.1: Properties of the uncured formulation of EPIKOTE 04908 + EPIKURE 04908

Once fully cured, the resin has the following mechanical properties (table 4.2):

Property	Unit	Value
Tensile strength	MPa	74
Ultimate strain	%	9.4
Stiffness modulus	GPa	2.9
T_g (DMTA)	°C	89

Table 4.2: Mechanical properties of the cured formulation of EPIKOTE 04908 + EPIKURE 04908

The epoxy was degassed under vacuum before being used for the infusion to reduce the probability of getting air bubbles in the part.

In order to better imitate the structure of the pultrusions and the layup of the twin matrix plates, the traditional composite is made by 9 layers at $[0_3/90_3/0_3]$. As for the materials used for the infusion, on the first try their stacking order is schematised in Figures B.2 and B.3 in the appendix B. The mould was treated with Marbocoat 227CEE release agent to prevent the part to stick to it, and the dry fibres were put directly on

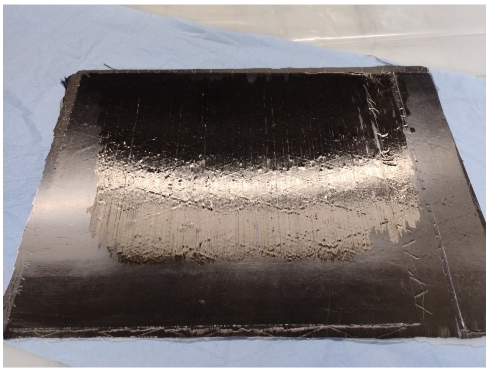

Figure 4.9: Picture of the first laminate made by VIP and its dry spot

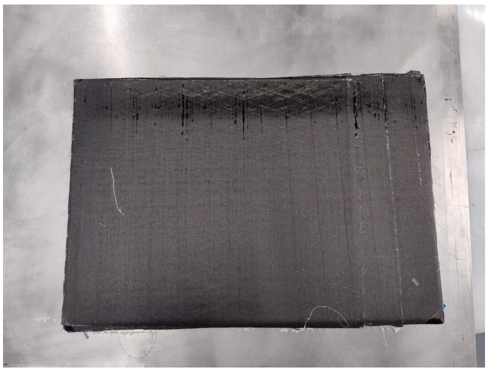

Figure 4.10: Picture of the second laminate made by VIP

top and secured with tape. To prevent the other materials to stick on the part, a peel ply separates the fibres from the rest of the materials. A sheet of perforated release film WL3700 is laid on top to help peel off the flow mesh and degass the flow front. Finally the flow mesh Greenflow 75 on top is used to speed up and guide the distribution of the resin, and wrapped around the spiral used as resin intake. The WL5400 vacuum bag is secured with LTS90B sealant tape, and the resin was guided with 100 kPa of pressure. The part was left to cure for 7 days at room temperature while the TMC plates were being manufactured, but a second attempt had to be performed after discovering during demoulding that the underside of the laminate presented large dry spot where the resin did not impregnate the fibres. This was thought to be caused by the relatively large amount of layers, which reduced the overall permeability of the laminate, and by a vacuum that was too strong.

For the second attempt, an additional layer of peel ply was put under the dry fibres given that it is more permeable than the 9 layers of UD carbon in the hope that the resin would also start to fill the part from below. The vacuum pump was set to 120 kPa and then to 500 kPa after the entire part was impregnated. This was done to slow down the flow front and let the resin fill the least permeable parts of the laminate. Additionally, reducing the vacuum means that air bubbles inside the laminate would also reduce in volume because of the higher pressure, resulting in voids that, if present, would not compromise the part performances as much. After infusing for several hours, the mould was left out to solidify at room temperature for two days and then put in an oven at 80°C for 6 hours to fully cured. This new laminate did not present dry-spots or visible defects even when cut to make the plates used for the QSI test.

5 Microscopy study

To perform the microscopy study, three plates made by casting and three plates made with the aid of the release film were cut in pieces at different sections. The samples were cut using an automatic cutting machine and stored in the freezer before being encased in Technovit 4071 embedding resin. All the samples had their dimensions measured before and after each step previously to be embedded to see if potentially they would change size due to hygrothermal effects, but this was not the case. In total, 60 samples were observed using a Keyence VHX 1000 digital microscope. Additionally, using the microscope's measuring tool, it was possible to measure the distance between the pultrusions and the resin layer thickness. It was decided to use an optical microscope instead of a SEM despite its better accuracy and resolving power because of the large volume of samples to be analysed, as well as for the fact that a SEM needs vacuum to work, meaning that the samples need to be outgassed beforehand, which is often done by heating the parts. In the case of the partially cured secondary matrix, this would have prompted the curing process to resume and result in shrinking, giving inaccurate information on the thickness of the secondary matrix between the pultrusions.

From the start it appeared that the interlaminar resin layer thickness was not as consistent as hoped, a problem that was also encountered by Moghaddam[4]. Sometimes the difference in thickness was caused by the fact that the reinforcements do not have a perfectly rectangular profile (Figure 5.1), but more often it was observed that the pultrusion in the centre layer laid on a very thick resin layer (Figure 5.2). This might be caused by an improper bind of the pultrusion layers with the thread, or improper pressure distribution. This defect was encountered in all plates, no matter which manufacturing method was used. To have a better understanding of how consistent the thickness is, it was measured for every sample and its distribution compiled. As one can see from Figures 5.3 and 5.4, the use of the release film yields a slightly more consistent result, but the thickness of the resin decreases given that the film occupies volume in the mould.

Very rarely, as seen in Figure 5.5, the pultrusions from two different layers happen to touch. Those areas are a weakpoint in shear loading, and a are probable crack initiation points.

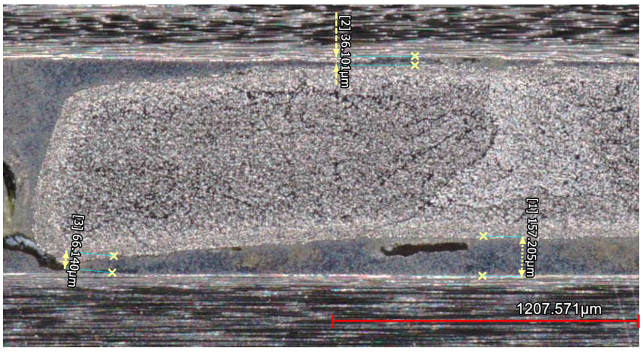

Figure 5.1: Image of an imperfect pultrusion

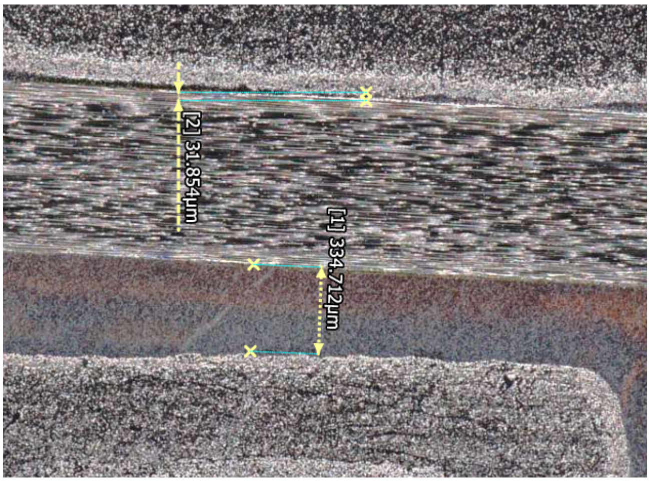

Figure 5.2: Irregular resin layers

The microscope also showed that the space between the pultrusions in the same layer is also not consistent. Once again, this problem is present in all plates regardless of what manufacturing process is used. This might be explained by uneven tensioning of the thread between the reinforcements. As done similarly to the interlaminar resin thickness, the distribution of the space between the reinforcements was compiled and shown in Figures 5.6 and 5.7, and as expected in this case there is not a significant difference between the two processes in terms of the range and average value of the distance.

A defect that was visible with the naked eye, and already mentioned in section 4.2, is the presence of voids between the reinforcements. The release film made possible to push the air bubbles, successively reducing them in the plates made with it. This was one of the most common defects, but the microscopy study revealed that, at least in shear loading, these voids are not as critical as previously thought. In fact, there is almost always a layer of resin between the middle and outer layers, meaning that the load would be transmitted, but the defect should be addressed more carefully when evaluating the behaviour in tension and compression. There was only ever one void found where the interlaminar resin layer was not present, and it was possible to see that the air bubble reached under the pultrusion, shown in Figure 5.9.

More worrisome are interlaminar voids, shown in Figures 5.10 and 5.11. These were

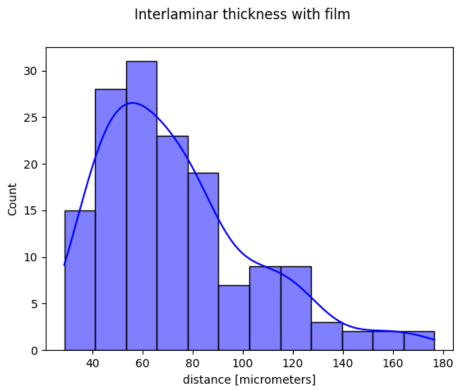

Figure 5.3: Interlaminar thickness distribution using the release film

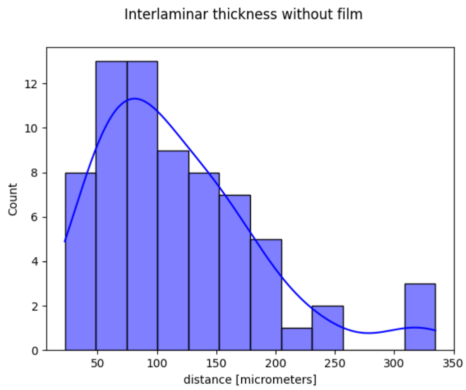

Figure 5.4: Interlaminar thickness distribution without using the release film

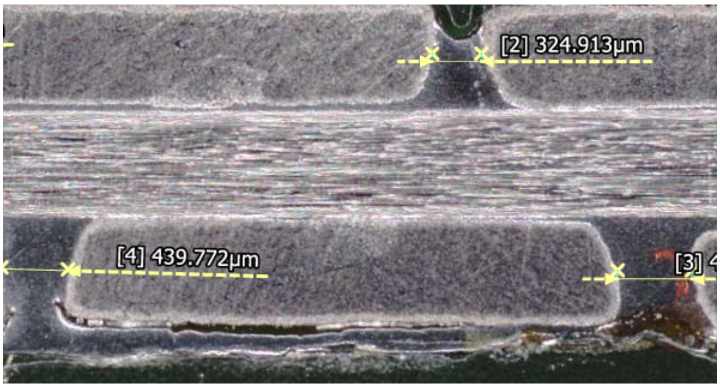

Figure 5.5: Example of pultrusions touching each other

only found once per manufacturing method, but the one found in the plate made without the release film is much bigger. This kind of defect would severely reduce the impact resistance of the composite.

Other defects that might compromise the impact resistance of the plates are microdelaminations between the pultrusions and the secondary matrix. These cracks are more often seen near and around the pultrusions in the middle layer, often jumping from a reinforcement to another like in Figure 5.12. These delaminations would grow quickly during impact loading and are relatively common, however they might be introduced in the cutting process rather than curing. This might explain why they are only observed when the rectangular profile of the pultrusions in the middle layer is visible.

At the end of the microscopy study, it was decided to not use the release film in making the plates. The main reason was that the achieved interlaminar resin layer thickness was considered too low, as the mould was not designed to account for the thickness of the release film, but knowing that interstitial voids were not as severe as previously thought also played a key role in the decision. As for the interlaminar voids, it was assumed they might constitute a problem only if laying near the impact area, given the soft nature of the secondary matrix.

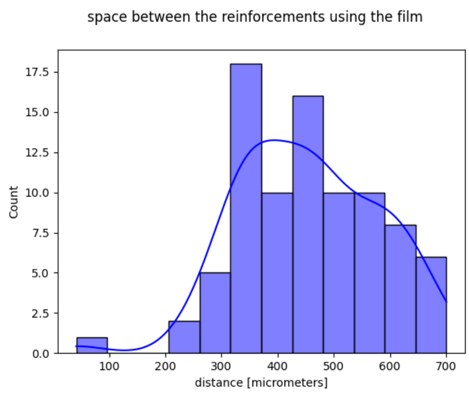

Figure 5.6: Distribution of the space between the reinforcements using the film

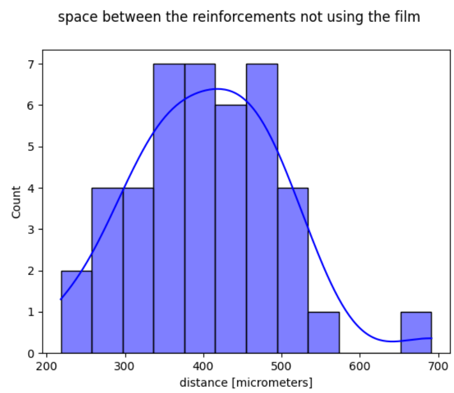

Figure 5.7: Distribution of the space between the reinforcements without using the film

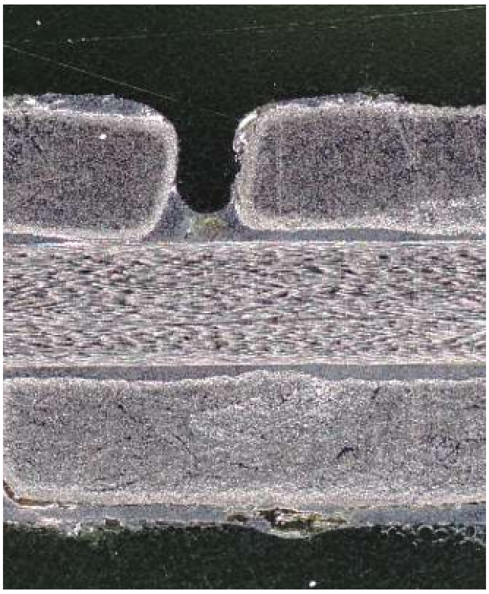

Figure 5.8: Interstitial void under the microscope

Figure 5.9: Only example found of a void where there is not resin between the middle and outer layer

Figure 5.10: Picture of the interlaminar void found in the plate made without the release film

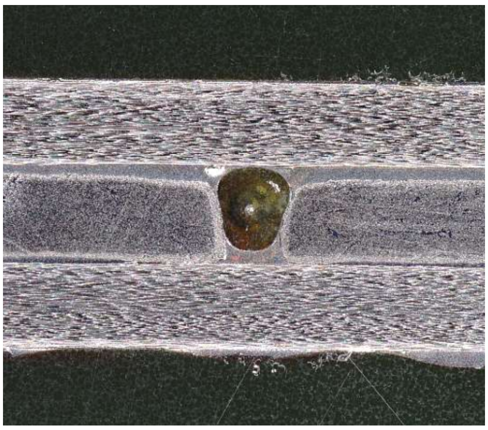

Figure 5.11: Picture of the interlaminar void found in the plate made with the release film

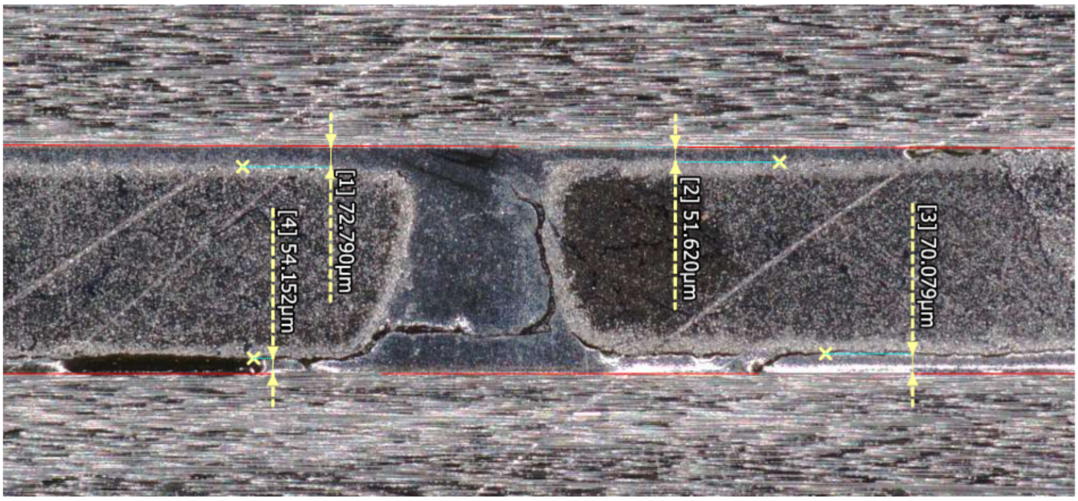

Figure 5.12: Microdelamination in the middle layer

6

Mechanical and Non-Destructive testing

In this chapter the mechanical and non-destructive test setups are discussed. Four samples of TMC plates, as well as five of the traditional composites described in section 4.3 were tested using the QSI method to simulate impacts, and then examined with ultrasonic NDT to better visualise the damage. The samples were tested for complete perforation and 10J impacts.

To prevent the secondary TMC matrix from slipping away from the clamps like it has happened while testing the resin samples, grip paper was put between the TMC and the clamps while being closed.

6.1. Mechanical test setup

The experimental setup for QSI can be seen in Figure 6.1. The machine, a Zwick-Roell BZ1-EXZW001 20kN UTM drives an indenter onto the plates, which are secured by 8 bolts to a 1 cm thick steel clamps with a circular opening. The indenter is hemispherical and has a diameter of 16mm, while the clamps' circular opening has a diameter of 8 cm. The machine measures force through the built-in loadcell and displays machine displacement. The latter measurement is influenced by the machine's arm compliance, which is corrected for as explained in section 6.2. The test is displacement controlled and the indenter is driven onto the plate at a rate of 1mm/min.

Two kind of tests are performed onto the samples. First, two plates from each type of composite are tested for fibre failure, while the remaining are tested by simulating a 10J impact. The machine determines the energy by calculating the area under the load displacement curve, and then gradually unloads the plate at a rate of 1mm/min. Naturally, the displacement is influenced by the arm's compliance, so the actual energy of the simulated impact will be lower than 10J. The reason for doing two kind of tests is to see if there is an obvious change in delamination area. For TMCs specifically, it could be possible for delamination to present itself right before the laminate fails, which would be the ideal scenario. Seeing the load-displacement curves for complete failure

Figure 6.1: Experimental setup used for the QSI tests

in section 7.1 initially prompted that this might be the case, and that the change in behaviour before break was caused by delaminations suddenly growing, but this was later proven to not be the case, and failure of the pultrusions explains the phenomenon better.

6.2. Compliance correction

When the machine exerts a force the whole system experiences at least some deformation, meaning that depending on how the displacement is measured, the machine frame's deformation might be included and consequently give an erroneous reading. For this reason, methods that measure deformation on the sample, as done in section 3.2 in the case of the extensometer, should be preferred for their ability to get more accurate measurements. The setup in section 6.1 does not use a sensor to do that, instead measuring the position of the UTM's arm. It is however possible to remove the machine's deformation by testing it against a very stiff part that is virtually undeformable, and subtract the result from the measurements[38].

For the Zwick-Roell UTM, the compliance was measured using a 3cm thick piece of aluminium. The force displacement curve measured by the machine is presented in Figure 6.2, and it is effectively the arm's deformation, as the aluminium plate's displacement is very small:

$$D = \frac{Eh^3}{12(1-\nu^2)} = 1.8 \cdot 10^8 Nmm$$

$$y_{max} = \frac{Fa^3}{16\pi D}$$

Where D is the bending stiffness of the aluminium piece, $E = 70GPa$ is the elastic modulus, h is the thickness, $\nu = 0.33$ is the Poisson's ratio, y_{max} is the displacement

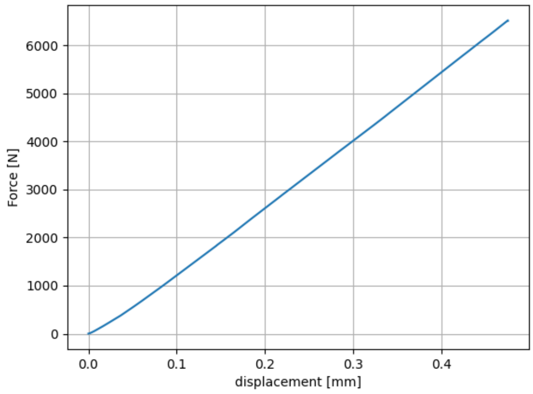

Figure 6.2: Force displacement curve of the aluminium piece used for compliance correction

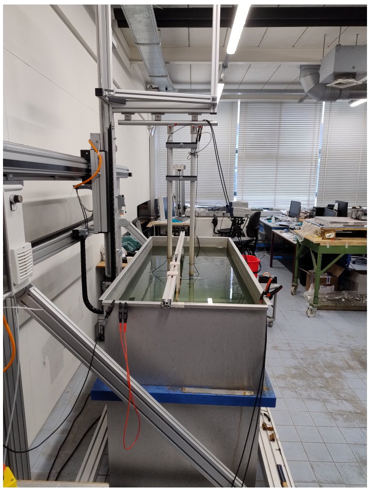

Figure 6.3: C-scan machine setup

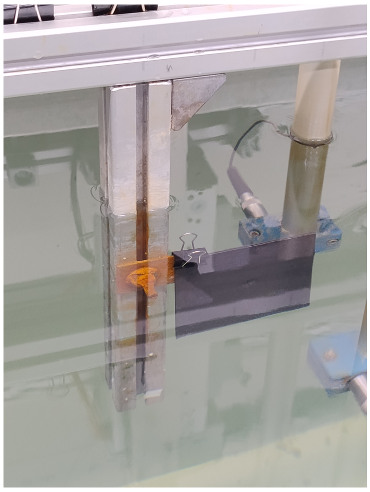

Figure 6.4: Sample being held

at the centre of a circular plate clamped at the edge, F is the force and a is the plate radius[39]. All the graphs from this point on had their displacement corrected.

6.3. NDT

The machine used for ultrasonic testing is the C-scan present at the DASML laboratory in the faculty of aerospace engineering at TU Delft. The samples are immersed in water, that acts as the coupling agent. An ultrasonic transducer and a receiver on the other side of the plate move together to scan it with a resolution of 0.5 mm. The transducer emits a beam of ultrasonic waves that travel through the bulk of the material and get dampened by defects, while the receiver measures the intensity of the waves coming through the other side of the plate. The samples are held with a clip on the corner at the top left, which shows up in the C-scan images as impermeable to the sound waves.

7
Results

In this chapter are contained some observations and the results of the QSI test and the ultrasonic NDT. All plates' thickness was measured before the indentation test with a manual caliper with a resolution of 0.05 mm.

The traditional composite plates all exhibited very similar force-displacement curves, particularly during the loading phase. This would suggest that the VIP has delivered plates with fairly consistent properties, and that the experimental setup is robust. As expected, the traditional composite is stiffer than the TMCs, and during the tests they could be heard cracking, sign that delaminations are growing. During the tests TMCs also made cracking sounds.

As for the TMCs, one sample was not considered for the test because the curing of the secondary matrix was not right, and instead of having a rubbery texture it presented a hard surface. The remaining four all had different force-displacement curves, which is to be expected considering that the curing of the secondary matrix can be subjected to variance, as well as the fact that TMCs present several inconsistencies, like when it comes to the space between the reinforcements for example.

Plate	Thickness [mm]
traditional composite 1	2.50
traditional composite 2	2.55
traditional composite 3	2.50
traditional composite 4	2.55
traditional composite 5	2.50
TMC 1	2.40
TMC 2	2.40
TMC 3	2.40
TMC 4	2.45

Table 7.1: Thickness measurement of the samples

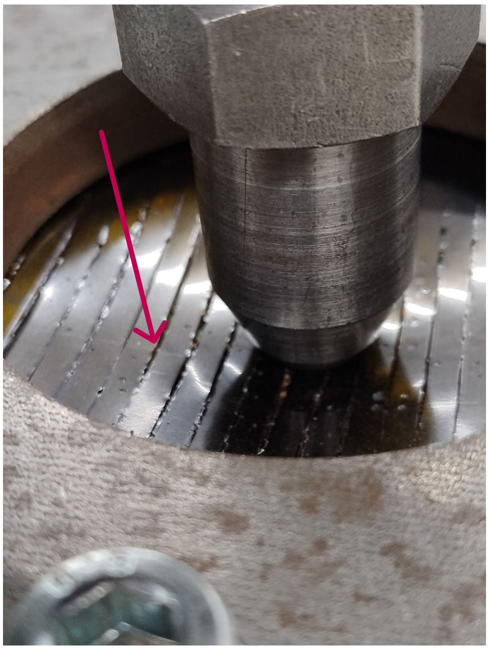

Figure 7.1: TMC being indented. The arrow points the secondary matrix failing between the pultrusions

Figure 7.2: Detail of one of the marks left by the indenter. The arrow points at the cracks formed on pultrusions

7.1. QSI test results for complete failure

All of the TMCs have lower stiffness and hardness than the traditional composites, almost wrapping around the indenter as seen in Figure 7.1. The picture also shows the secondary matrix stretching and failing between the pultrusions as they are being pulled down.

The two traditional composites brought to fibre failure do not present any damage on the side compressed by the indenter except for a small mark, but the other side has visible cracking and parts of the bottom layers have separated (Figures 7.5 and 7.6). The damage on the TMCs plates is even more visible. The indenter compressed and deformed the secondary matrix, leaving a prominent mark and the pultrsusions are cracked (Figure 7.2). On the other side, the pultrusions vertically under the indenter are also cracked, and debonded from the rest of the laminate (Figure 7.4). It was observed afterwards that the indentation mark depth decreased, likely caused by the memory effect of the secondary matrix.

Also notable is how the composites failure is presents itself on the force-displacement curves. The traditional composites' failure looks like a a series of drops in the load bear by the structure, while the TMCs gradually decreases before dropping. Interestingly, both kind of composites began to break at similar values despite the fact that the TMC have a lower fibre volume fraction, betweenn 44% and 47%. This ratio was calculated knowing the volume inside the mould, the number of pultrusions and their size as reported by Moghaddam, and by assuming that the pultrusions have a fibre volume fraction of their own of 63% as reported by the manufacturer.

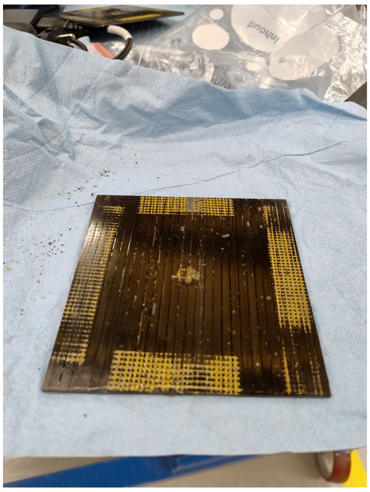

Figure 7.3: Mark left by the indenter on the topside of one of the TMCs brought to total failure.

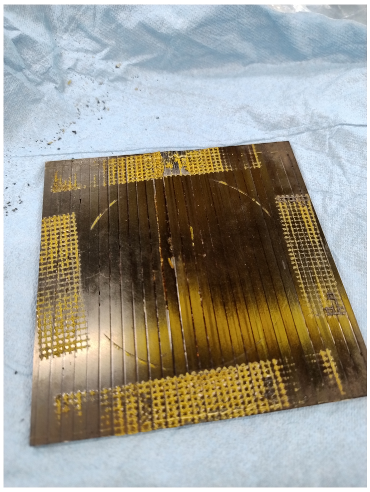

Figure 7.4: Bottom of the TMC plate in Figure 7.3

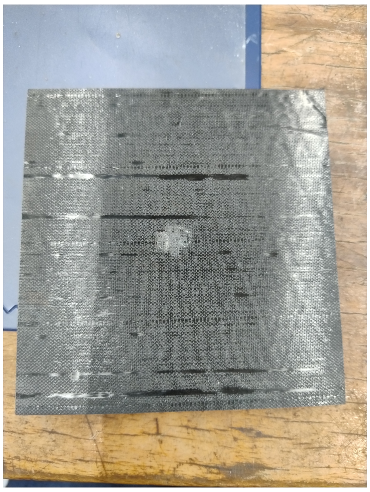

Figure 7.5: Topside of one of the traditional composite plates brought to total failure

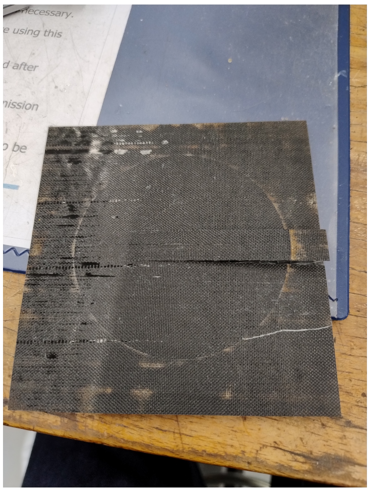

Figure 7.6: Other side of the laminate in Figure 7.5

Plate	Force at break [N]	Displacement at break [mm]	Energy at break [J]
Traditional composite 1	5900	7.02	17.9
Traditional composite 2	5000	6.13	13.6
TMC 1	4410	10.72	19.4
TMC 2	3780	10.33	15.9

Table 7.2: Data relative to the plates tested for complete failure. Their curves can be seen in Figures 7.7 and 7.8

7.2. QSI results for the 10J impacts

The traditional composites once again exhibit very similar behaviour, while the TMCs curves are inconsistent with each other. This might be explained again by the fact that the latter have several differences with the space between the pultrusions and each

layer, as well as possibly inconsistent curing of the secondary matrix.
The traditional composite samples did not present evident damage after simulating the 10J impact. The indenter left only a small mark, and the back side of the plates looks untouched (Figures 7.11 and 7.12). The TMCs on the other hand have once again a clearly visible mark where the indenter touched the plate but the backside looks undamaged (Figures 7.9 and 7.10) if not for a slight curvature that disappeared after a couple of hours, which might be explained with the secondary matrix being plastically deformed and then returning to its original shape either because of the polymer's memory effect or due to the residual elastic energy in the pultrusions.
The energy given to the plates is calculated as the area underneath the force-displacement curves during the loading phase, while the area under the curve during the unloading phase is the energy that the samples did not absorb. Subtracting the latter from the former gives the absorbed energy of every sample.

Plate	Max. force [N]	Max. displ. [mm]	Energy [J]	Absorbed energy [J]
traditional composite 3	4500	5.32	9.3	4.4
traditional composite 4	4000	5.27	9.5	5.7
traditional composite 5	4240	4.88	9.4	5.6
TMC 3	2700	9.17	9.7	6.3
TMC 4	2170	10.7	9.8	6.2

Table 7.3: Data relative to the samples tested for simulated impact. Their force-displacement curves can are the ones in Figures 7.13 and 7.14

As it can be seen from table 7.3 above, the TMCs tend to absorb more impact energy for the same strain rate. Normally this would mean that the TMCs should have a bigger delamination area, as it is proportional to the amount of absorbed energy[40]. However as seen in the C-scan images, this is not true in the examined cases. A possible explanation might be related to the plastic deformation of the vitrimeric matrix.

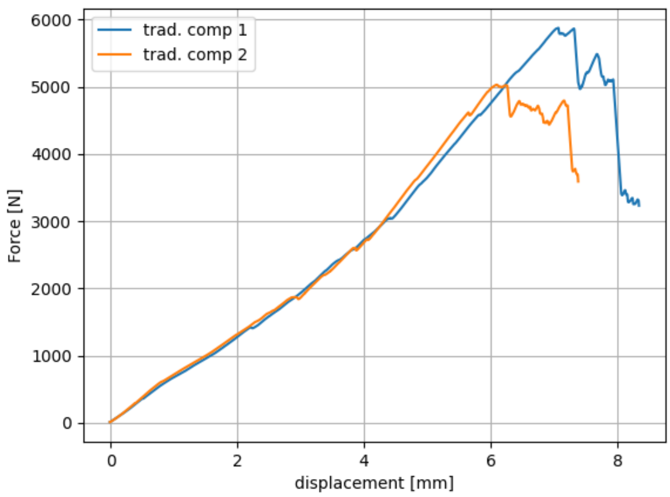

Figure 7.7: Force-displacement curve of the traditional composites tested for complete failure

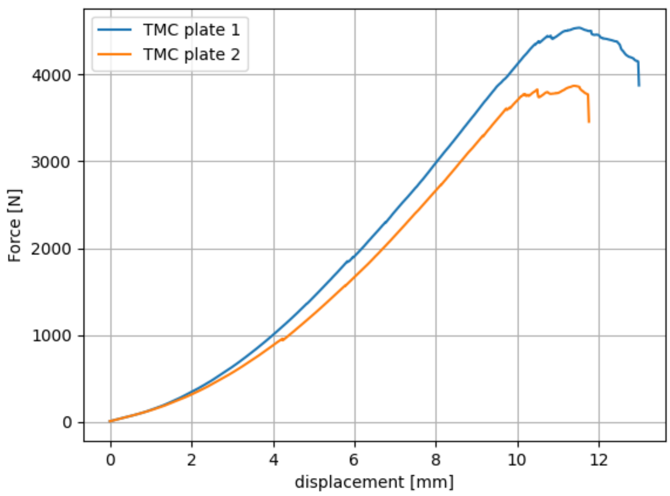

Figure 7.8: Force-displacement curve of the TMCs tested for complete failure

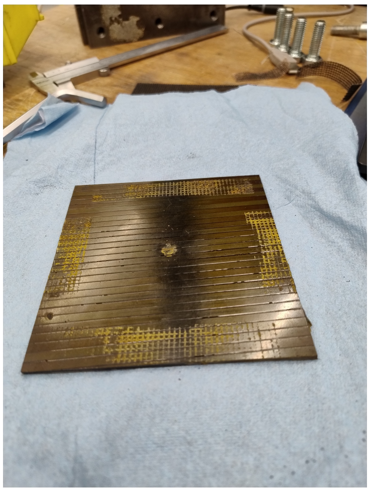

Figure 7.9: Mark left by the indenter on the topside of one of the TMCs

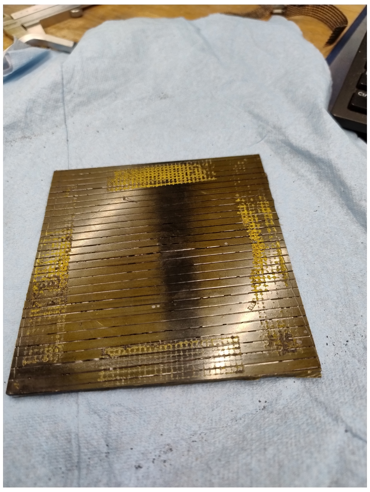

Figure 7.10: Bottom of the TMC plate in Figure 7.9

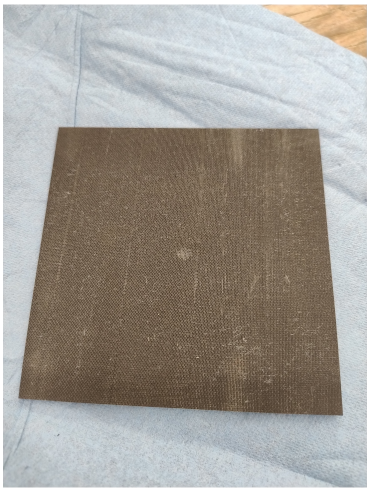

Figure 7.11: Topside of one of the traditional composite plates

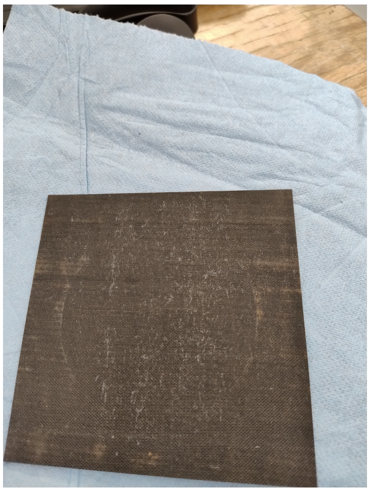

Figure 7.12: Other side of the laminate in Figure 7.11

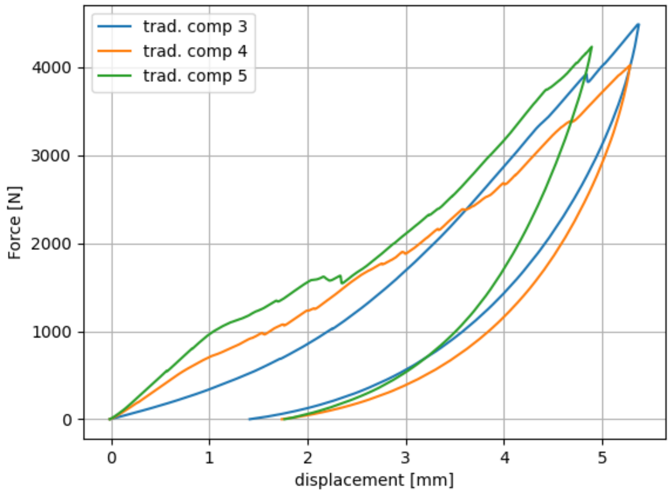

Figure 7.13: Force displacement curves of the traditional composite subjected to 10J of QSI

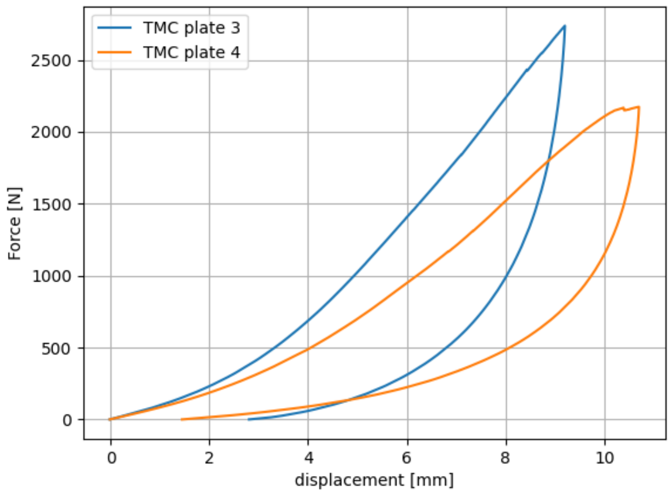

Figure 7.14: Force displacement curves of the TMCs subjected to 10J of QSI

7.3. C-scan and delamination areas

At the beginning of the project it was hypothesised that the rubbery vitrimer matrix might excessively dampen the ultrasonic waves[41], however they proved to be the easiest samples to examine with this technique. The traditional composites on the other hand proved to be harder for the waves to pass through them (Figure 7.16), and for this reason only the delamination area of three out of five traditional composite sample could be reliably determined. A possible explanation might be the surface roughness of the samples, scattering the ultrasounds entering and exiting the bulk of the composite[42][43]. The traditional composites have a rough surface caused by the imprint of the peel plies during the VIP, while the TMCs are mostly smooth, with the occasional streak of missing resin on the surface between the pultrusions and the imprints left by the grip paper on the edges, which also exhibit very strong dampening (Figure 7.15).

Because of these reasons, as well as to remove from the count the clip holding the samples on the top left corner, the delamination areas were calculated in a 8cm diameter circle in the middle of the plates using the software ImageJ.

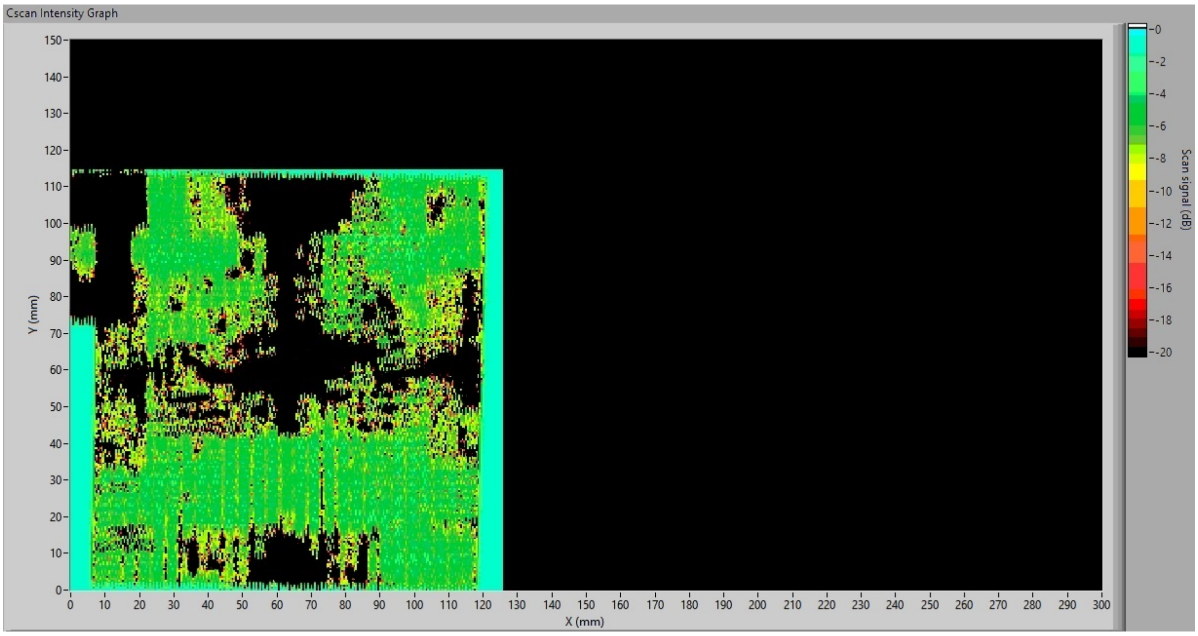

Figure 7.15: Full image of a C-scan of TMC plate with its scale, showing the actual delaminated area and the marks left by the grip paper on the edges

Delamination in the C-scans of traditional composites presents itself as round or ogival area much larger than the indenter's cross section. On the other hand, in the case of the TMCs, delamination interests mostly the pultrusions that are directly under the indenter, giving the delamination a characteristic cross shape. The areas are collected in table 7.4 below:

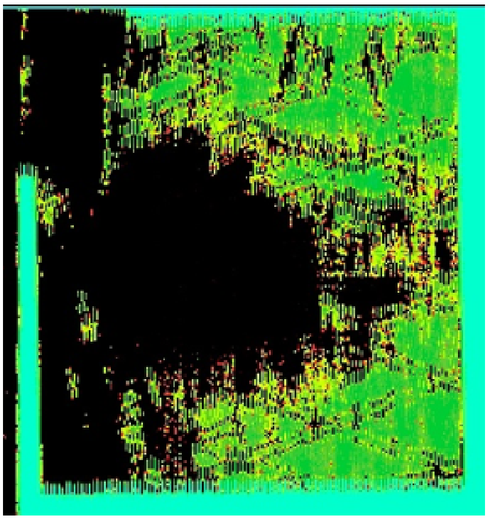

Figure 7.16: Example of a traditional composite plate where part of one edge not visible by ultrasonic testing

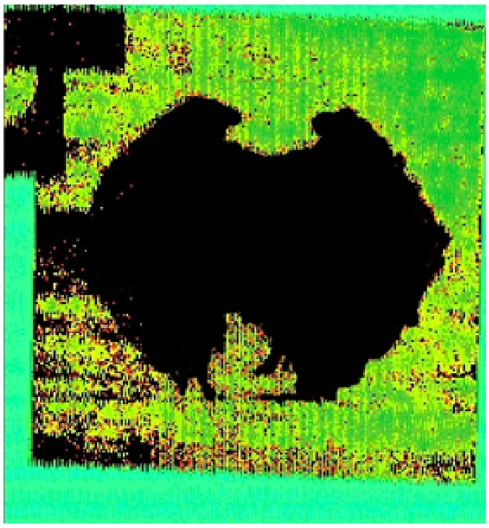

Figure 7.17: C-scan of the plate in Figures 7.5 and 7.6. In this case the ultrasonic testing delivered a satisfactory result.

Plate	projected delamination area [mm^2]
traditional composite 1	N/A
traditional composite 2	4894
traditional composite 3	4520
tradtional composite 4	N/A
traditional composite 5	3041
TMC 1	1635
TMC 2	1474
TMC 3	970
TMC 4	1741

Table 7.4: Projected delamination areas

The number of samples is clearly not sufficient to conduct a robust quantitative study, but the results clearly demonstrate that the TMCs have a smaller delamination area for the same strain rate and similar thickness.

7.4. Microscopy analysis of the fracture surface

After the mechanical and non-destructive testing, it was decided to analyse how the interlaminar layer failed by destroying two of the TMCs plates and examining the delamination surface under a microscope.

According to the theory, the of two most common ways an adhesive bond can fail are through adhesive or cohesive failure. The first happens at the boundary between the polymer and the two adherents, while the latter happens completely in the adhesive itself. Generally cohesive failure is preferred because it means that the maximum strength of the material in the joint has been reached and tends to happen at consistent stress levels, while the adhesion forces are dependant on several parameters and

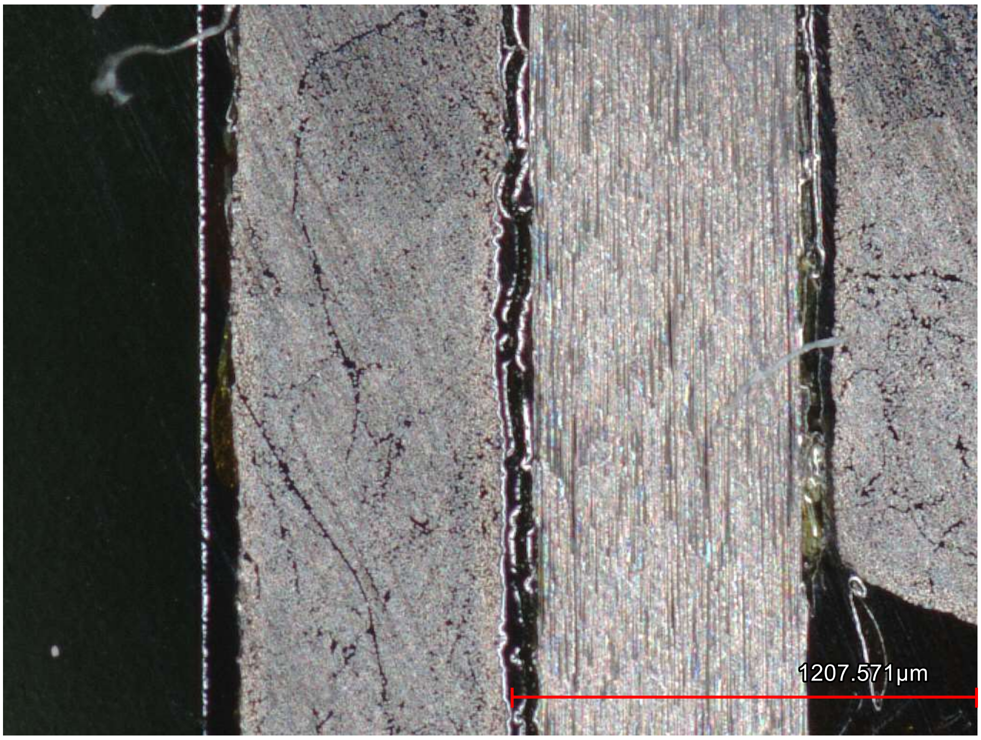

Figure 7.18: Interlaminar layers of the secondary matrix failing cohesively

mechanisms acting at different scales[44][45]. In the case of the examined samples, they each present a different kind of failure, which might also further explain the variation of the results. The two different surfaces can be seen in Figures 7.18 and 7.19

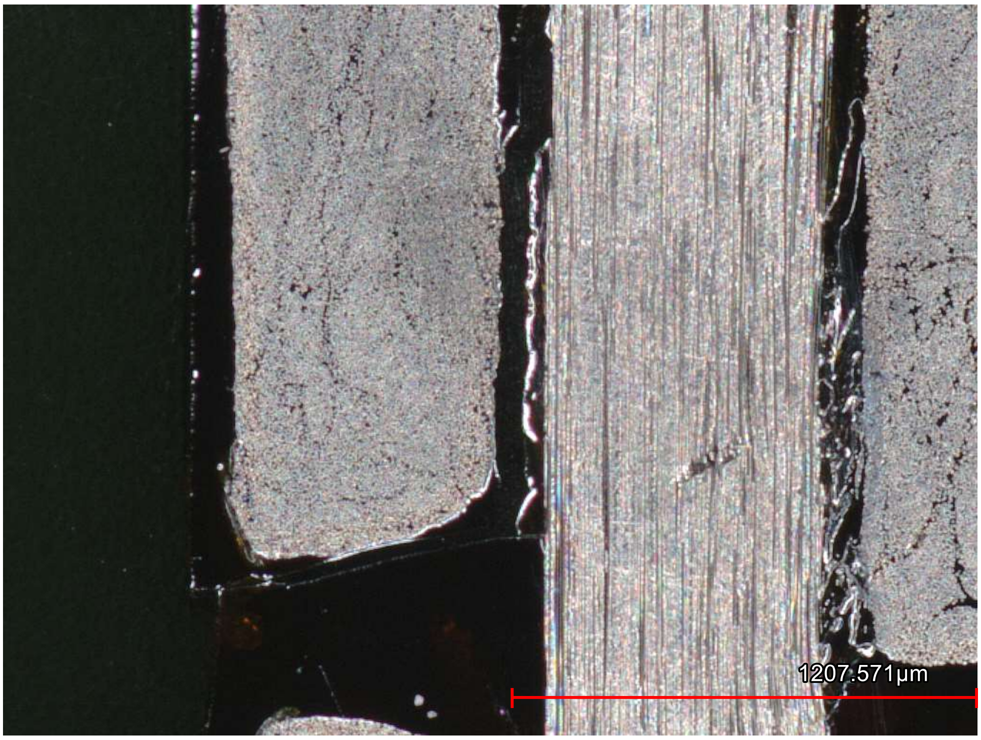

Figure 7.19: Detail showing the secondary matrix failing adhesively

8 Recommendations for future developments

In this chapter there are some considerations and possible recommendations for additional research in the impact resistance of twin-matrix composites or for future studies regarding other aspects.

8.1. Manufacturing

In this thesis an attempt has been made to achieve a better consistency of the interlaminar and interstitial secondary matrix layers' thickness, however the process is far from perfect and there ia ample margin for improvement. A more suitable thread material than cotton to bind the pultrusions would probably achieve better consistency and higher fibre volume fraction, perhaps in conjunction with a way to regulate the tension on the thread weaved between the reinforcements. Perhaps a material that can be removed as the secondary matrix is curing or after might be used for the manufacturing of bigger structures, as there can be several spacers across the length of the piece instead of just the extremities. Another improvement can be done in the selection of the secondary matrix. In this project a partially cured matrix was used, but this is of course not a viable solution for a real life application. Additionally, the matrix choice heavily influence the manufacturing method. If a more viscous thermoset would have been used, perhaps the method of dipping the reinforcements before laying them down might achieve better results. Modifying the formulation used in this study might provide some of this beneficial properties, or better elongation and possibly several other advantages. Fibre reinforced composite materials often present a significant scatter in their properties due to the fact that there are several factors in their micro, meso and macro structures that influence the overall performances. Twin-matrix composites are even more complicated, but with a consistent manufacturing techniques the study of their properties should be simpler. A faster manufacturing method would also make it possible to make more samples and perform more robust studies.

Vitrimers offer several promises as the secondary matrix for this class of composites because of their above average elongation and versatility during manufacturing. Given that the vitrimer matrix in this thesis had to be partially cured, it was not possible to attempt to join different parts of the laminate with heat, as a vitrimer could be fully cured around the single reinforcements or used to make the layers, which are then joined together in a hot press. There are several examples of fully cured vitrimers with high elongation, like the one used by Luo[27], Guerre[46] and Deng[47], with some biobased vitrimers reaching similar results as well[48][49]. At the moment of writing this thesis these formulations are often obtained with several intermediate steps to synthesise the base components.

8.2. Behaviour of TMCs

In this research, only an hemispherical indenter was used, but examining the influence of the impactor's shape might result in different failure modes and impact energies. A quasi-static impact test was used to evaluate the behaviour of the twin-matrix composite, but this test tends to underestimate the delamination area and the energy required to break the composite's fibres. A study on real impact tests will give more accurate information. Moreover with this method it was not established at which energy value the delamination initiated, which is an important parameter that would warrant their choice in an impact sensitive scenario.

Additionally, this study only focused on delamination area and energy when dealing with impacts, but another important parameter for the damage tolerance is the compressive strength after impact. A compression after impact (CAI) test study, perhaps on different layups, would give information on the ability of TMCs to retain strength.

Alternatively, if a vitrimer or another matrix capable of being healed is used, it could be possible to expand the study on the repairability of the laminates and their strength after being restored.

Several other aspects like different layup, effect of the pultrusion's shape, fracture toughness, and fatigue behaviour can also be investigated.

8.3. Other possibilities

The structure of a twin-matrix composite can also be employed to add new properties to a composite by enabling the use of a polymer that would not normally be used for structural applications. A polymer with a stronger memory effect might be used to create deployable structures by taking inspiration of previous work[7], or perhaps by using an electro active polymer that can act either as a sensor giving real time information on the level of stress in the structure, or more interesting, capable of being actuated and moving the part.

9
Conclusion

This thesis project has as its subject the manufacturing of a twin-matrix composite and examining its behaviour under impact through quasi-static indentation tests.

A TMC tries to combine the effect of a hard matrix to transfer the load across fibre reinforcements, and a matrix with high elongation to prevent cracks from initiating in the transverse direction. In this study, pultruded carbon rods made up both the fibre reinforcement and the hard matrix, while for the soft one, a vitrimer formulation was chosen, as it possess good elongation, long gel time, and low viscosity. As the resin was too stiff and not flexible enough when fully cured, it was decided to partially cure it, which resulted in an elongation at break beyond 100%.

A good TMC should have a consistent amount of secondary matrix around the pultrusions, so after some consideration it was decided to build on Moghaddam's[4] experience and make the material by casting resin in a mould. The pultrusions are separated by a thread double weaved between them. Casting was tested alongside another method, which consisted in dipping the pultrusion layers in cold resin, which is more viscous, to make a thin layer stick to them. The resin unfortunately regains its viscosity at room temperature very quickly, making the thin resin layer flow away from the layers that are dipped, as well as making dipping the remaining layers almost impossible. This method was therefore discarded in favour of casting. Even then, casting was tested alongside another variant of the process in an attempt to proactively reduce the amount of interstitial voids, believing they could be an obstacle for the correct transferring of the shear load.

A microscopy study revealed that this interstitial voids are not as a big of a deal than previously thought, as there is almost always a little bit of resin between the pultrusions. The microscope also revealed that other defects, like voids and pultrusion layers touching each other are present. It was observed that the secondary matrix around the pultrusions has a degree of consistency, but there is still ample margin of improvement. The variant of the casting process using the release film achieved a higher degree of consistency, but was ultimately disregarded in favour of the regular casting process because on average the interlaminar resin layer thickness was too low. Still, a better manufacturing method capable of giving consistent results and possibly produce in a quicker fashion is necessary if this kind of material has to see widespread application.

Five TMC plates were then manufactured for the QSI test, although one of them was then excluded because the secondary matrix cured more than desired. To get a relative comparison between performances, plates of UD carbon reinforced plastic were made by vacuum infusion. The experimental setup consisted in a 20kN UTM driving a hemispherical indenter into a clamped plate. The displacement was measured at the machine's arm, and the readings were adjusted for its compliance. The plates were then examined non-destructively using ultrasonic waves, but the method proved difficult for examining the traditional UD plates, likely because of their surface roughness scattering the sound waves.

Two plates from each batch were tested for total laminate failure. Both kind of composites began to fail around the same administered energy, but the TMCs have lower fibre volume fraction than the UD plates, and they present a lower projected delamination area. The remaining composites were tested by simulating a 10J impact. In this case, the TMCs absorbed more energy than the traditional composites, but they still presented a lower delamination area. Probably the energy went into plastically deforming the secondary matrix. Delamination in twin-matrix composites has a cross-shape and interests the pultrusions below the indenter. While the UD composites have consistent force-displacement curves, the behaviour of the TMCs is more scattered. This probably caused the conjunction of not-so-consistent space between the pultrusions and the secondary matrix not being perfectly cured the same way between plates. The fact that few samples were tested makes it impossible to express qualitative results on the TMCs, but the general trend demonstrates well their better low speed impact performance in terms of delamination area.

The two following tables summarize some of the results:

Sample ID.	normalised energy at break [J/mm]	delamination area [mm^2]
traditional composite 1	7.16	N/A
traditional composite 2	5.33	4894
TMC 1	8.08	1635
TMC 2	6.63	1474

Table 9.1: Summarisation of some results regarding the plates brought to complete failure

Sample ID.	normalised absorbed energy [J/mm]	delamination area [mm^2]
traditional composite 3	1.76	4520
traditional composite 4	2.23	N/A
traditional composite 5	2.24	3041
TMC 3	2.63	970
TMC 4	2.53	1741

Table 9.2: Summarisation of some results regarding the plates subected to the simulated impact

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A
Mould design

The mould used to make the TMCs is presented in this appendix. The mould is made by three pieces, a female, a male, and a plate to be put in between. The female has two holes on the bottom where a tool can be inserted and eject the part when it is time to demould. These holes are covered in teflon tape during manufacturing to prevent the resin from flowing out. The plate sits on top to get a smooth finish on the TMC, as well as to protect it from the tool used for ejecting it. The middle plate and the male are made to leave a space of 2.4 mm inside the mould where the reinforcements and the resin will be located, creating laminates with a fairly consistent thickness. The female and the male have two flanges where two bolts can be used to tighten the mould pieces together and ensure they fit as intended. The male additionally has two grooves so that a tool can be inserted to make a lever and force the mould open if necessary. The female's cavity is slightly tilted to aid the ejection of the middle plate and the TMC. All the pieces were made by machining aluminium blocks.

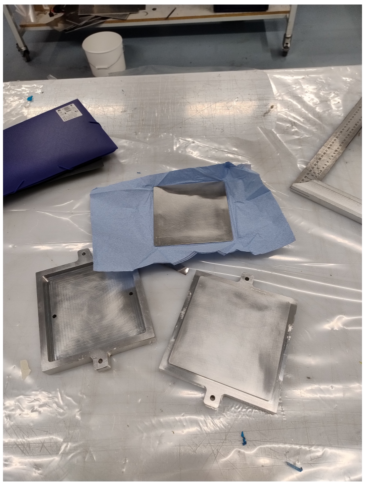

Figure A.1: Picture of all the mould pieces

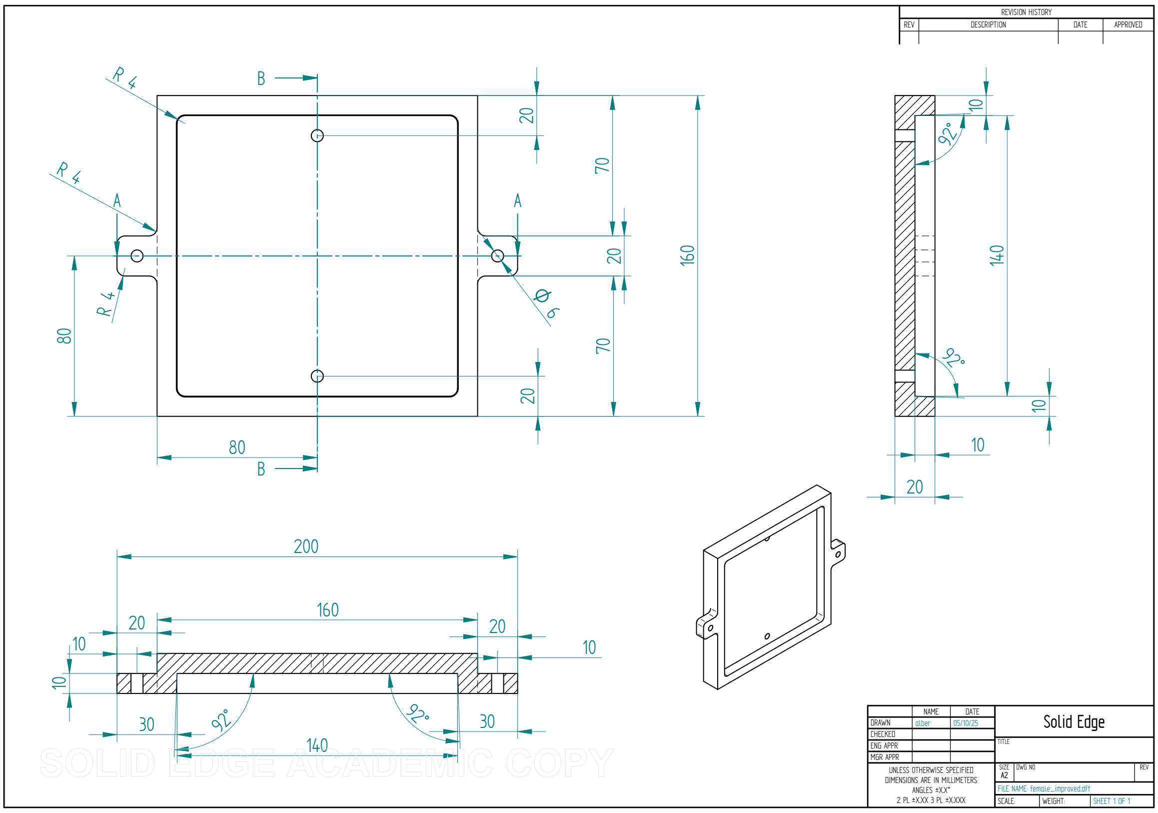

Figure A.2: Technical drawing of the mould's female part

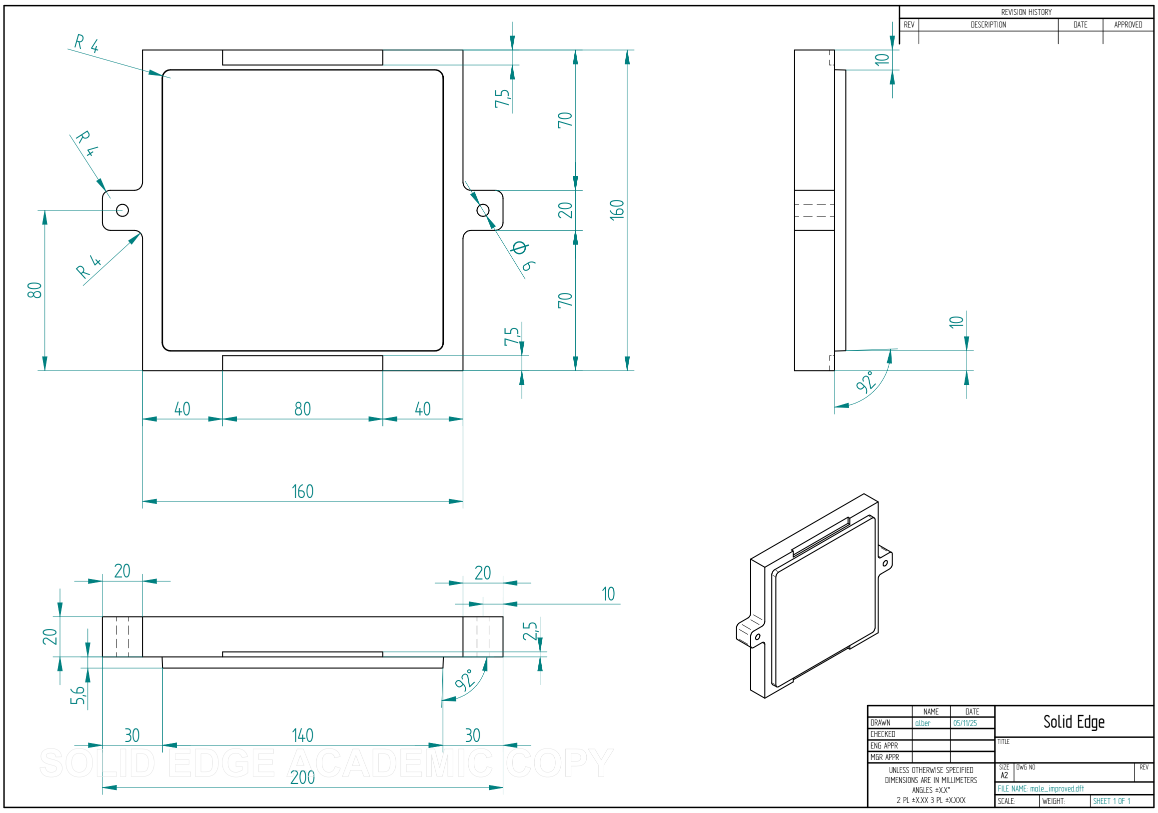

Figure A.3: Technical drawing of the mould's male part

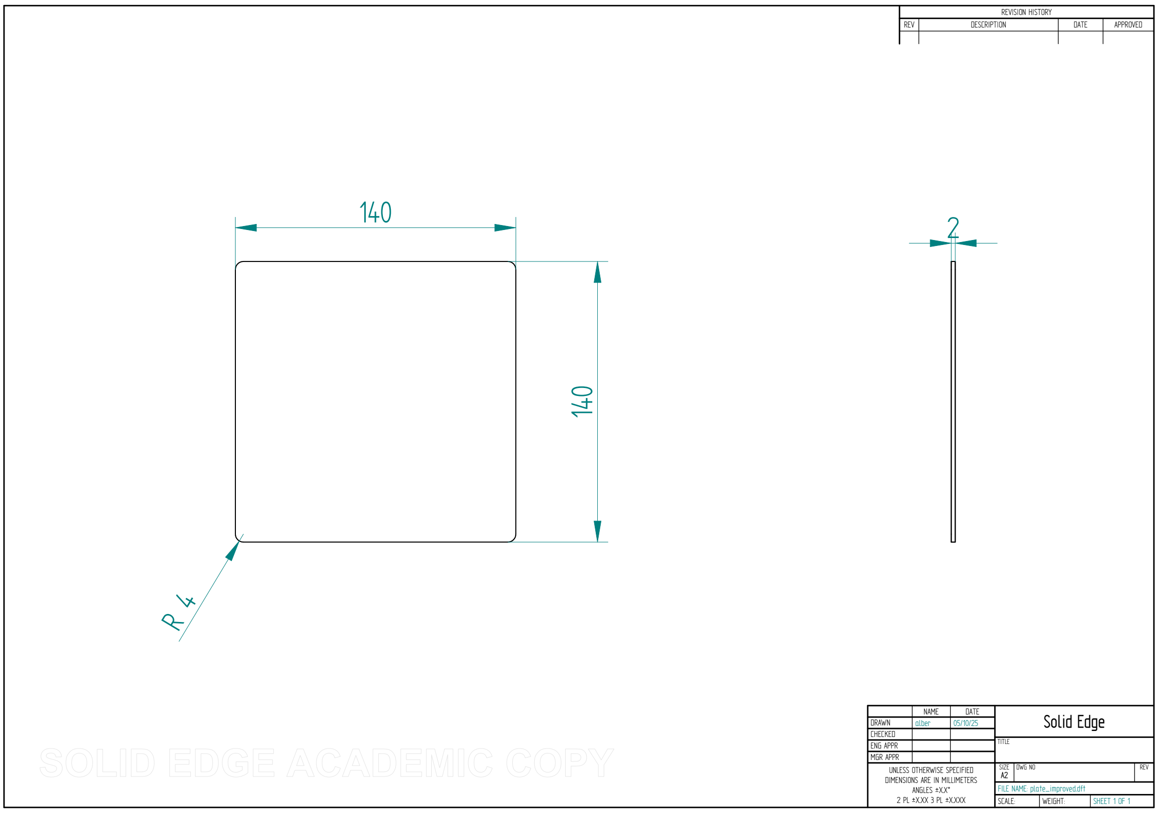

Figure A.4: Technical drawing of the mould's middle plate

B
Vacuum infusion layup

The materials used are indicated in the table below, as well as the colour used to represent them in the schematic views:

Material	Colour	Maximum service temperature [°C]
peel ply	red	232
Fibres	dark grey	2000
WL 3700 perforated release film	blue/light blue	121
Mould	grey	660
WL 3700 vacuum bag	light grey	121
Greenflow 75 flowmesh	green	150
LTS90B seal tape	black	150
Marbocoat 227CEE	not indicated	400

Table B.1: Legend for the materials

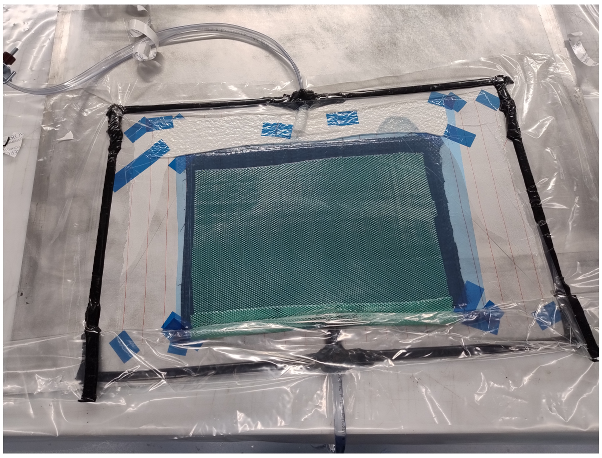

Figure B.1: Infusion of the first plate

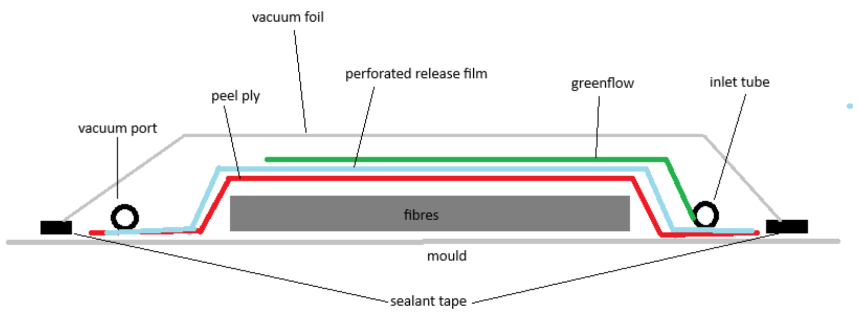

Figure B.2: Scheme of the stacking order of the VIP materials used for the first plate

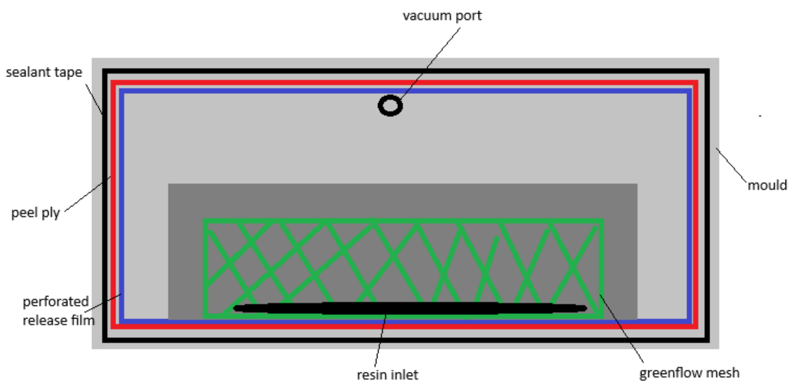

Figure B.3: Stacking material seen from the top

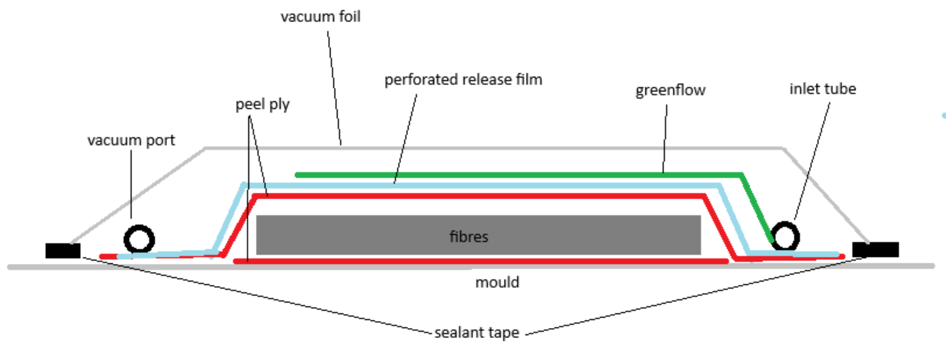

Figure B.4: Scheme of the stacking order of the VIP materials used for the second plate

C
Additional microscopy images

In this appendix are the some more pictures taken by the optical microscope of the twin matrix composites. The measurements taken with the microscope did not show any relevant pattern depending on the location where the samples were cut from the plates. In total, around 120 pictures were taken to make the distribution curves in section 5.

Figure C.1: One of the interstitial voids in a TMC made without the release film

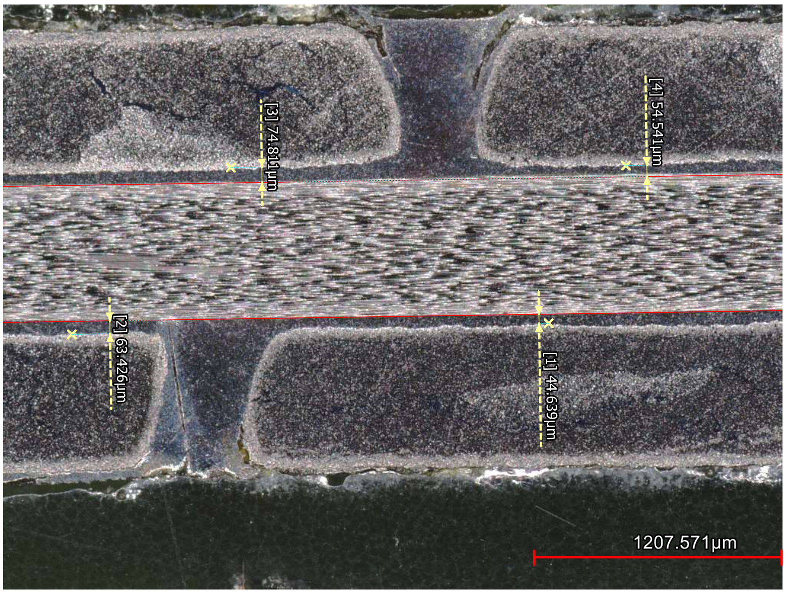

Figure C.2: Section of a TMC made with release film

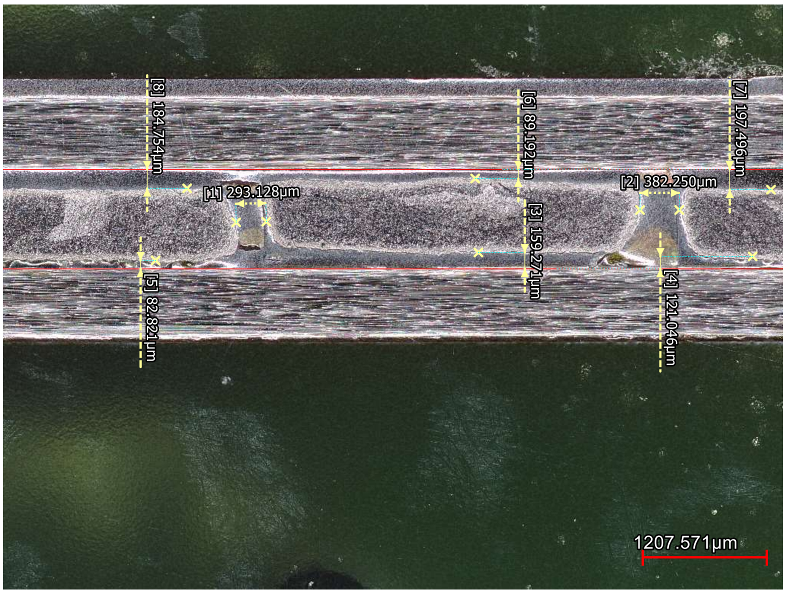

Figure C.3: Section of a TMC

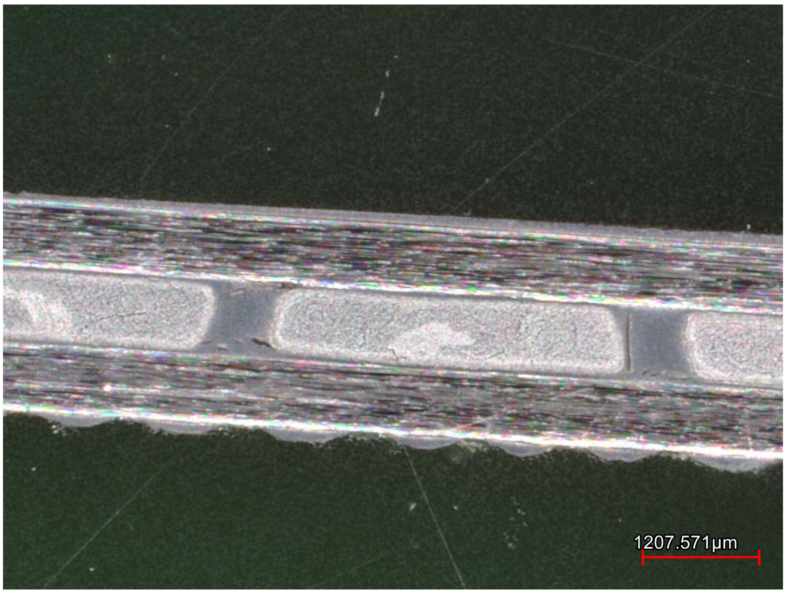

Figure C.4: Image of a TMC made with release film

Figure C.5: Specular side of the interlaminar void in Figure 5.10

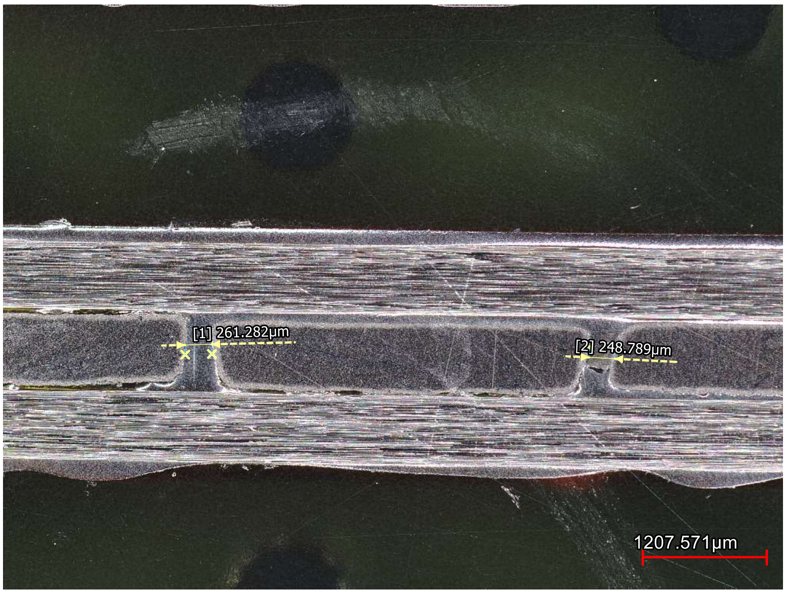

Figure C.6: Microdelamination in a TMC made with the release film

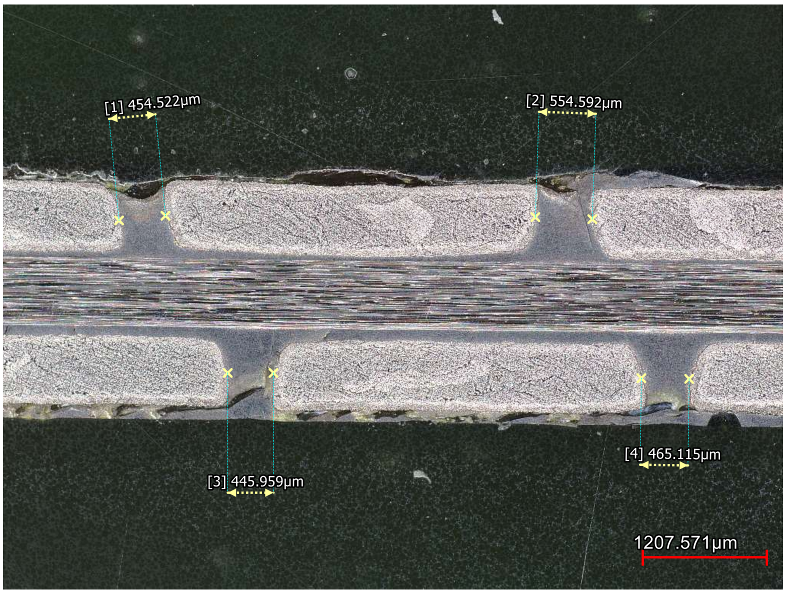

Figure C.7: Interstitial space between the pultrusions of a TMC

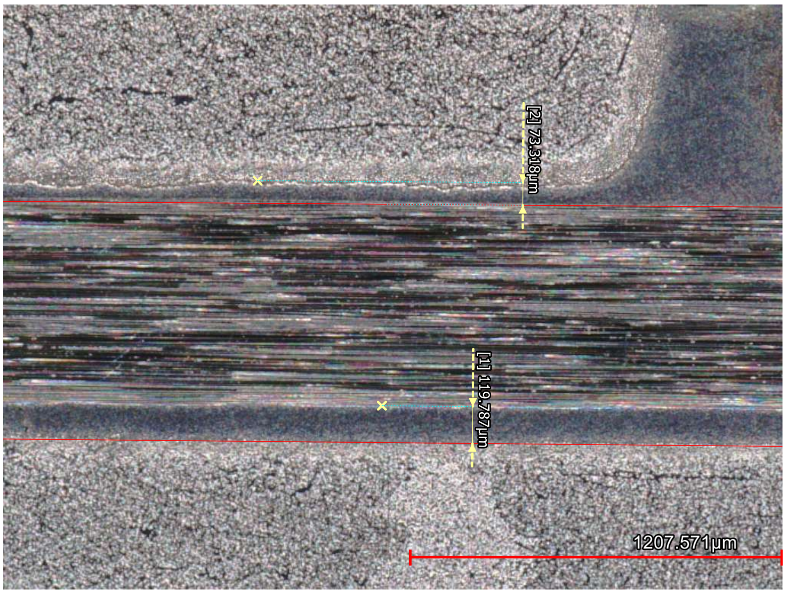

Figure C.8: Detail of the interlaminar resin layer in a TMC

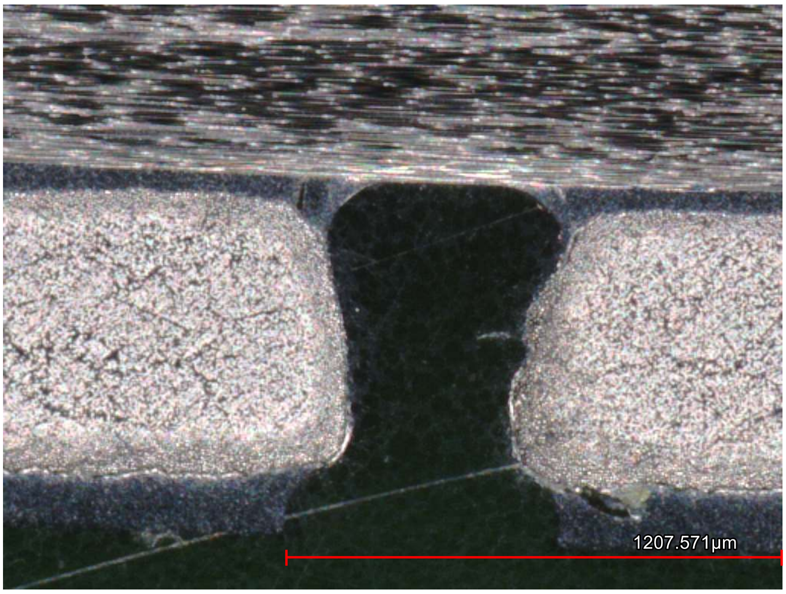

Figure C.9: Detail of a interstitial void

D
C-scan images

In this appendix are all the 9 C-scan images of the examined samples. Area calculations were not performed on the traditional plates identified as "1" and "4" because the delamination area overlaps with the parts of the samples that the ultrasonic waves cannot penetrate.

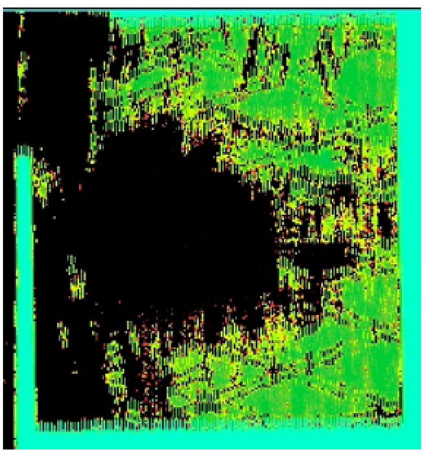

Figure D.1: C-scan image of traditional composite 1

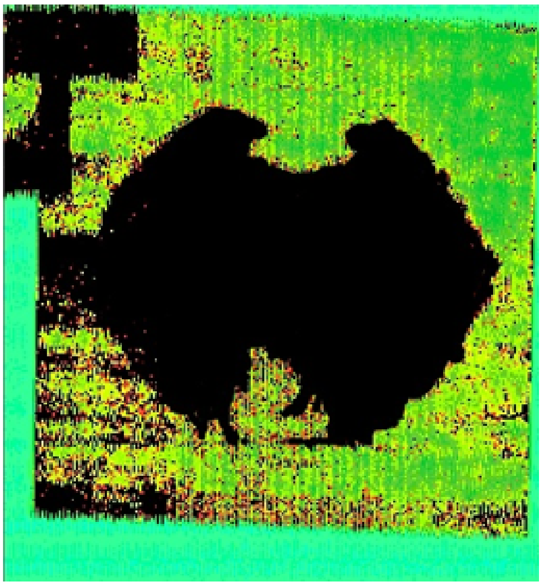

Figure D.2: C-scan image of traditional composite 2

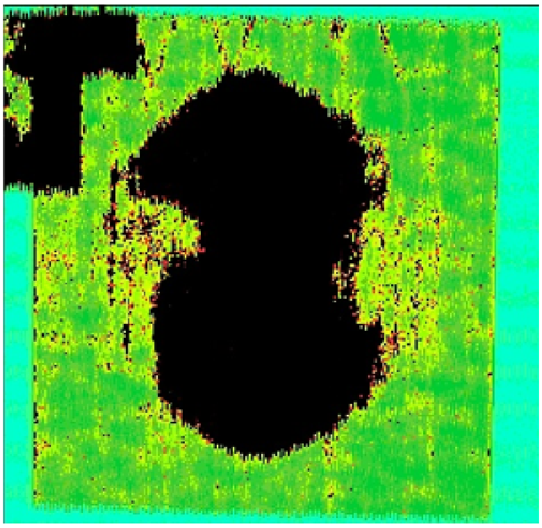

Figure D.3: C-scan image of traditional composite 3

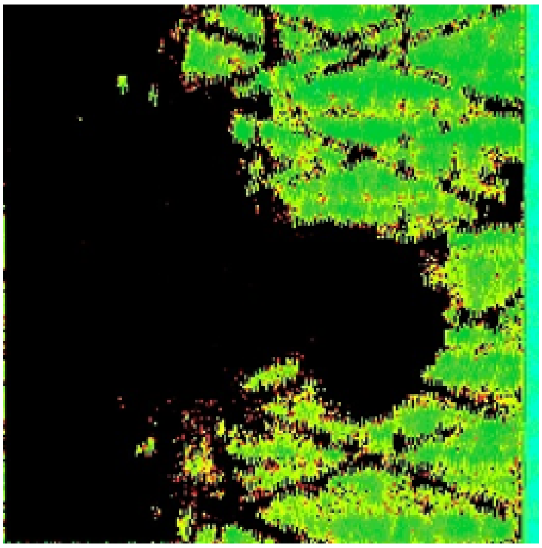

Figure D.4: C-scan image of traditional composite 4

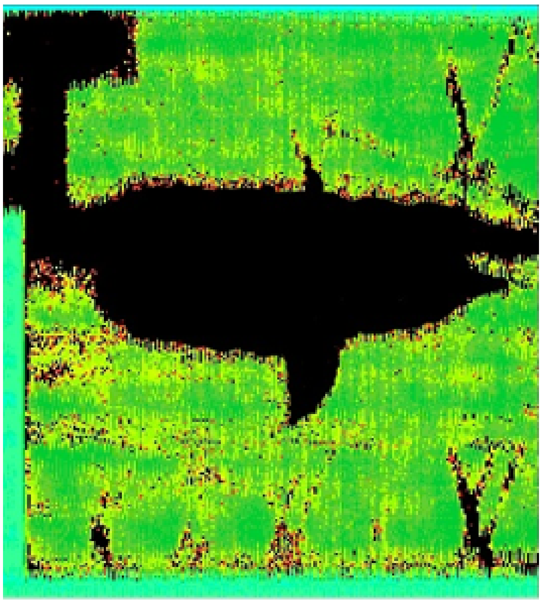

Figure D.5: C-scan image of traditional composite 5

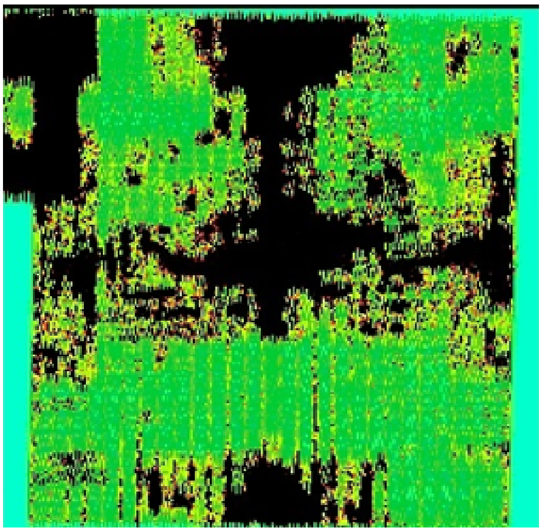

Figure D.6: C-scan image of TMC 1

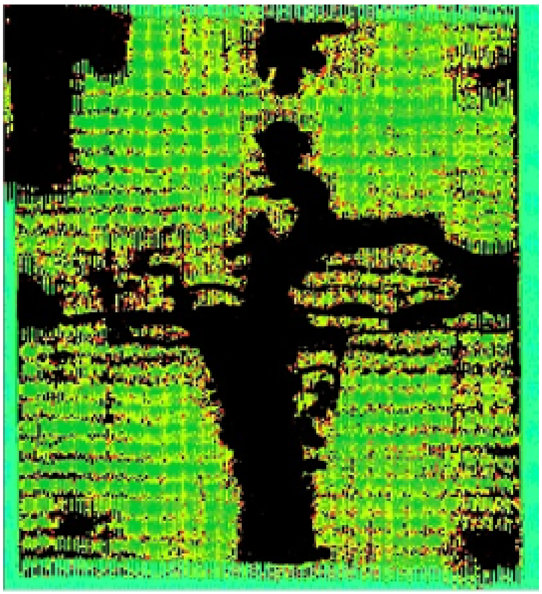

Figure D.7: C-scan image of TMC 2

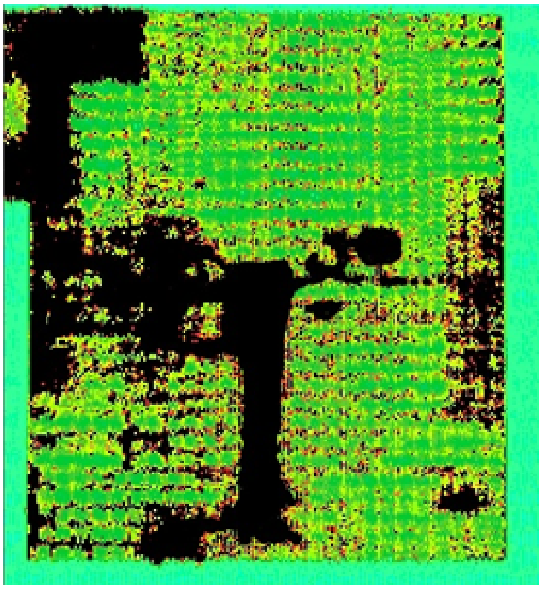

Figure D.8: C-scan image of TMC 3

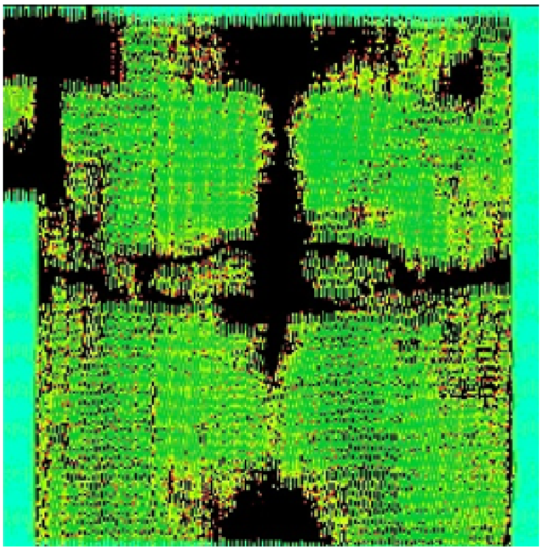

Figure D.9: C-scan image of TMC 4