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Influence of polar solvents on the functionalisation of carbon fibres with microfibrillated cellulose and its effects on the mechanical properties of the final composite laminate

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Completion of course work presented to the São Carlos School of Engineering of the University of São Paulo, to obtain the Bachelor's Degree in Aeronautical Engineering

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A mi mayor ejemplo: la ama,
quien me lo ha dado todo y más.

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Resumo

ABECIA HERNANZ, S. C. **Influência de solventes polares na funcionalização de fibras de carbono com microfibrila de celulose e seus efeitos nas propriedades mecânicas do laminado compósito final.** 2019. Trabalho de conclusão de curso – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2019.

O presente trabalho empregou celulose microfibrilada (MFC) como subestrutura hierárquica de laminados compósitos bicamadas, como agente de interfaceamento entre a matriz polimérica e as fibras de reforço, vislumbrando potenciais aplicações aeronáuticas. O objetivo foi desenvolver uma metodologia para a aplicação de MFC, recebida na forma de pasta aquosa, por intermédio de diluição direta em água e em solventes orgânicos polares como acetona e álcool isopropilico. O tratamento viabilizou a deposição da MFC sobre as fibras de reforço, via dip-coating assistido por banho ultrassônico de baixa frequência, anteriormente ao processo de manufatura do compósito por infusão de resina líquida assistida à vácuo (RIFT). A determinação das morfologias de deposição, por microscopia eletrônica de varredura (SEM) das fibras na forma de tecido bidirecional, mostrou uma distribuição diferenciada entre os três solventes empregados. O efeito da funcionalização das fibras com MFC nas propriedades mecânicas do laminado compósito foi estudado através de ensaios de flexão em 3 pontos. Dentre 3 diferentes concentrações de MFC em agua, a que resultou em melhores propriedades mecânicas do laminado final foi a de 0,4% m/m. Para essa mesma concentração, os solventes acetona e álcool isopropílico não se mostraram apropriados em vista da aparente desidratação da fase fibrilada e baixa interação com as fibras de carbono.

Palavras-chave: Materiais Compositos. Polímeros Reforçados com Fibra de Carbono. Microfibrila de celulose.

Abstract

ABECIA HERNANZ, S. C. **Influence of polar solvents on the functionalisation of carbon fibres with microfibrillated cellulose and its effects on the mechanical properties of the final composite laminate.** 2019. Completion of course work – São Carlos School of Engineering, University of São Paulo, São Carlos, 2019.

In the present work microfibrillated cellulose (MFC) was used as a hierarchical substructure in bilayer composite laminates, acting as an as an interfacial agent between the polymeric matrix and the reinforcement fibres, aiming at potential aeronautical applications. The objective was to develop a methodology for the application of MFC, which was provided in the form of aqueous paste, by means of direct dilution in water and in polar organic solvents like acetone and isopropyl alcohol. The treatment enabled the MFC deposition on the reinforcement fibres, via dip-coating assisted by low-frequency ultrasonic bath, previous to the vacuum-assisted liquid resin infusion (RIFT) manufacturing process. The determination of the deposition morphology, by scanning electron microscopy (SEM) of the bidirectional woven fibers, showed differentiated distributions among the three solvents employed. The effect of the functionalisation of the fibres with MFC on the mechanical properties of composite laminate was studied through 3-point flexural testing. Among 3 different MFC concentrations in water, the 0.4% w/w one resulted in better mechanical properties of the final laminate. For the same concentration, acetone and isopropyl alcohol solvents were not shown to be suitable in view of the apparent dehydration of the fibrillated phase and low interaction with carbon fibers.

Keywords: Composite Materials. Carbon Fibre Reinforced Plastic. Microfibrillated Cellulose.

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Chapter 1

Introduction

Since advanced composite materials were introduced into aviation, being the first major application the fiberglass rotor technology of the 1960s (ROESELER *et al.*, 2007), until today when aircraft structures are commonly made up of 50 to 70% by weight composite material with average empty weight savings of 20%, such as in the Boeing 787 Dreamliner (QUILTER, 2018), it has come a long way in their technological development. They provide structural strength comparable to metallic alloys but at a lighter weight, which leads to improved fuel efficiency and performance from aircraft (VIKTOR POCAJT, 2004). In addition to aerospace, numerous other engineering sectors take advantage of these materials such as the automobile, naval and wind industries.

Among these materials carbon fiber reinforced plastics (CFRP) are of great importance due to their high strength to weight ratio. However, further enhancing of these resistance values is of great interest and a way to achieve this that recently began to be developed due to its potential, is to improve the interface between the matrix and

the fiber since being an area of utmost importance to load transference and distribution, it is also the most critical. One of the challenges that appear in this attempt is to make manufacturing possible through processes that imply efficiency in terms of time and costs and therefore the hierarchical structures at the interface are being studied as an option that in addition to its positive contribution to the functional and mechanical properties, can also meet this requirement.

For this purpose, different types of hierarchical reinforcements such as monolayer graphene and carbon nanotubes have been investigated, but also more accessible options derived from cellulose such as microbrilillated cellulose (MFC). This research proposes the study of the last one added to the dry carbon fibers using the dip coating technique in ultrasonic bath, being this a much more cost-effective method than incorporating the MFC to the polymeric resin which would hinder vacuum-assisted liquid resin infusion manufacturing techniques where good flow, permeability and wettability properties are of critical importance (KEPLINGER *et al.*, 2019).

The question that arises immediately afterwards is to know which would be the best method to create said cellulose substructures in a way that optimizes the dispersion of microfibrils and thus maximizes the increase in properties that can be achieved with them. With this objective in mind, this work is an approach to a possible method of manufacturing carbon fiber / epoxy resin laminates with a hierarchical substructure of cellulose microfibrils, taking into account that the application in the industry of a manufacturing process based on it

could later be feasible. A series of variations of the methodology will be tested in two of the variables of the elaboration process to study their effects. Specifically in this work the variables chosen are the solvent in which the MFC are applied and their concentration, as will be detailed later. Once the various test specimens have been crafted, the characterization is carried out by means of spectroscopic techniques in order to have a notion of the morphology of the interface, as well as mechanical testing to determine the ultimate properties of the different materials.

In respect to the structure of this monograph it is as follows: after defining in the second chapter the motivation for this work as well as the specific objectives that it intends to pursue, in the third chapter the theoretical framework is addressed, giving an overview of the results of previous research and theories that are considered valid. In this way, a greater understanding of the questions that remain to be answered in the field of composite material interfaces is sought. Next in chapter four, the technical specifications regarding the materials, the methodology and also the laboratory equipment that has been used are collected. In chapter five the results obtained in the different laboratory tests are presented in order to evaluate the effects of the different manufacturing processes on the laminates, to finally reach the conclusions of the research.

1.1 Justification

Among the various applications of the material on which this project is focused– the CFRP with optimized MFC interface– the use of non-structural aeronautical components is sought. The importance of the use of composite materials, and the main reason why they are progressively replacing metals in the manufacture of aircraft parts, relies on the weight reduction of the aircraft that this entails and the consequent cutback in fuel consumption, as this is a crucial factor that motivates the industry to investigate the improvement of their properties.

Aiming at progressing in this direction, the implementation of cellulose materials as reinforcing elements into polymeric composites has become a topic of interest, justified by the appealing mechanical properties as well as the wide availability of these materials.

In recent works of GECoM – Group of Engineered Composite Materials –, where this project was developed, great results were obtained with 0.3% w/w MFC aqueous suspension-application directly on bidirectional woven fibres via dip coating (URIBE et al., 2016, 2017a, 2017b, 2017c, 2018). Additional to that, MFC was incorporated to the epoxy resin, after the treatment of the aqueous MFC with solvent exchange using acetone and isopropilic alcohol, successfully for 0.5, 0.7 and 1% w/w (SILVA; TARPANI, 2019). These promising results motivated further studies of the use of MFC dispersed in other solvents such as acetone and isopropyl alcohol in

various concentrations, with the goal of discovering the best solvent for this application, as well as aiming to optimise the manufacturing process reducing the execution time.

The studies in this area now focused in the understanding of the MFC/CF interactions and the development of possible chemical treatments of MFC that improve the final performance of the composites.

This way, the successful addition of this MFC substructures into CFRP could mean the reduction of the resin and carbon fibre amounts (both derived from non-fossil sources, in contrast to the cellulose derivatives) used in the manufacture of the composite laminate, with respect to a traditional laminate of the same properties. Therefore, the residues generated after the service life of the composite materials, which present great difficulties when it comes to recycling, could be reduced.

1.2 Objectives

1.2.1 General objective

The main purpose of this work is to conform the initial stages of a research that strives for the development of an effective, low-cost MFC application method into carbon reinforcement fibres by using the dip coating technique in ultrasonic bath, in order to create hierarchical cellulose-substructures.

In doing so, the MFC interphase is intended to enhance the mechanical properties of the CFRP laminates, thus expanding their field of application, especially in the industrial aeronautics area.

1.2.2 Specific Objectives

- Testing of three polar organic solvents, so as to guide future works into using the most appropriate one for the effective chemical treatment of MFC;
- Analysis of the stability of different MFC suspensions with various solvents and concentrations, and how that relates to the morphology of the MFC dispersion on carbon fibres, through microscopy imaging techniques;
- Determine the tendency of the mechanical properties of bilayer carbon fibre/epoxy resin composite laminates, when varying the MFC-concentration of suspensions applied to the fibres;
- Maintaining the cost of the MFC-treatment method to the lowest possible by considering the execution times and the availability and price of the raw materials and the equipment;

Chapter 2

Literature review

Being aerospace one of the most demanding technological fields in terms of materials having to bear the foreseen high-stresses, high-impact and cyclic loads, over time a need for new materials was developed. It is within this context that the well-known composite materials were introduced to the industry, which have the capacity to convene the characteristics of several materials in one. Now comes a new stage in the issue of composite materials, continuous fibre reinforced polymers in particular, where the improvement in interfacial strength between the polymer matrix and reinforcing fiber system is leading to the enhancement of their overall mechanical performance (URIBE *et al.*, 2017a).

Among the first steps made towards such aim, investigations revealed that the shear strength of a fibrous polymer composite is closely related to the shear strength of the fiber surrounding polymer matrix domain. It was also noted that the latter property strongly depends upon the mechanical performance of the interphase, which

constitutes an intermediate, different phase when compared to the reinforcing fiber and the bulk resin (KIM; MAI, 1991). Based upon these findings, many efforts were then devoted to build stronger fiber/ matrix interphases by controlling physicochemical interactions and frictional forces acting on this particular region of composite systems (KARGER-KOCSIS *et al.*, 2015).

MFC has been employed to that end in several ocasions, it having the advantage of being the cheapest cellulose nanoderivative, to coat reinforcing glass fibers in epoxy-matrix composite laminates, thus obtaining very promising results with regard to overall mechanical performance improvement (CARVALHO, 2014). Before the more facile method of incorporating MFC directly to the fibres that is used in this work was presented, MFC had been incorporated to fiber reinforced polymer matrix composites only by addition to the polymer at its liquid phase, which complicated the resin infusion process as it affected flow properties, thus preventing its use in cost-effective vacuum-assisted liquid resin infusion manufacturing techniques (GABR *et al.*, 2010). The addition of MFC directly onto the unsized CF performs before the RIFT process represented a innovative form to obtain significant gains in stiffness, ultimate strength and tenacity under tensile, flexural and shear strength testing. Atomic force microscopy provided characterisation of the cellulose-rich interphase which was attributed as the responsible for the enhanced mechanical performance (URIBE *et al.*, 2017b). Once the effectiveness of this easier manufacturing method to produce highly cost-effective CFRP laminates with hierarchical MFC

substructures was validated, the favourable results allowed to further develop the MFC suspension dipping process for optimisation. This research work is thereby its logical sequel.

Chapter 3

Materials and methods

The flow chart in figure 3.1 sumarizes the processes followed at each stage of this work.

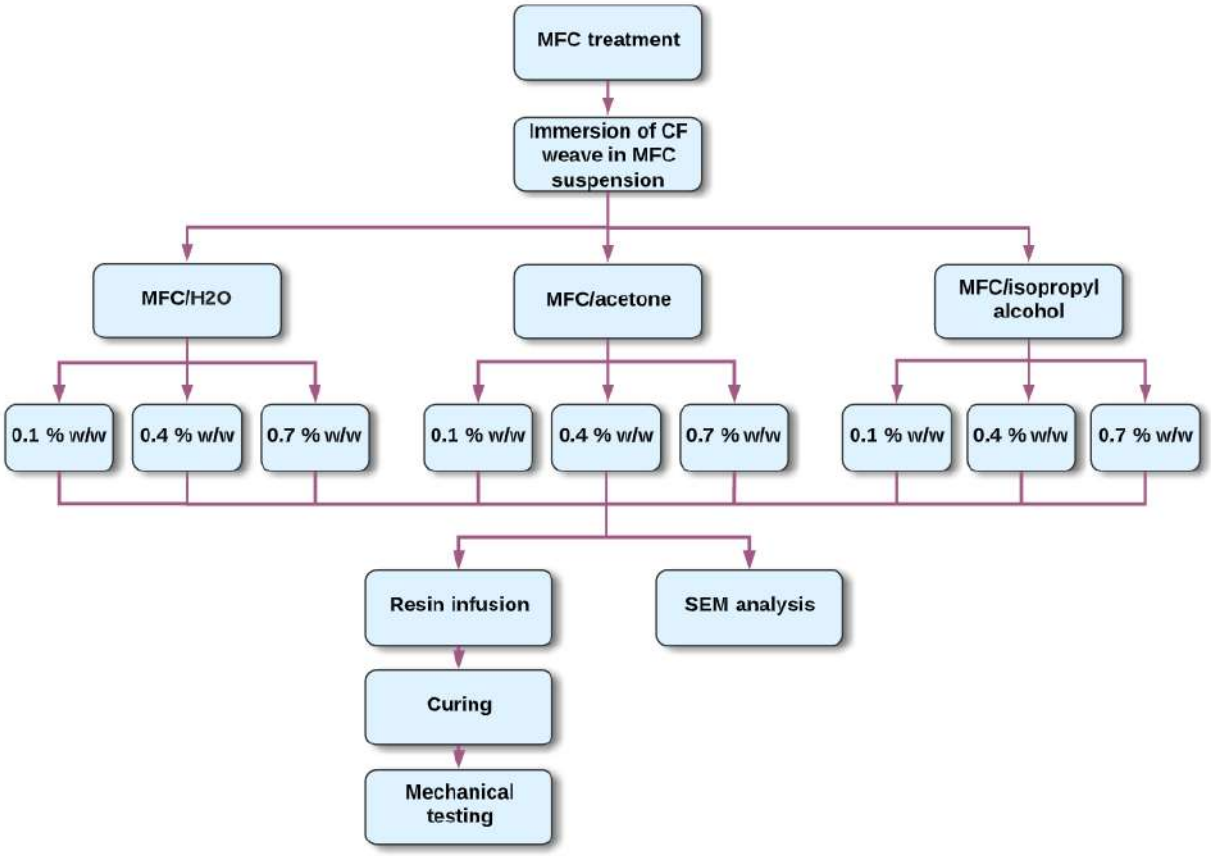


Figure 3.1 – Analytic process to which the composite laminates were subjected.

Source: The Author (2019)

3.1 Materials

Microfibrillated cellulose

The MFC of hardwood of the genus *Pinus* was donated in aqueous pulp form with a concentration of 10% w/w by Borregaard^{TM}.

Solvents

- Deionised water
- Acetone, P.A.: 99.5% minimum purity spec. purchased from Synth^{TM} (LABSYNTH, 2019)
- Isopropyl alcohol, P.A.: 99.5% minimum purity spec. purchased from Neon^{TM} (NEONCOMERCIAL, 2019)

Reinforcement fibre

Unsized T300-type (both standard and intermediate modulus fibres with high strength values used in aerospace applications) carbon fibers (CF) were used in the form of bidirectional 2x2 twill weave, displaying an areal weight of 200 g/m^2 with 5 bundles/cm in both the warp and weft directions, provided by Fibertex® (FIBERTEX, 2019).

Polymeric matrix

A two-phase (monomer and hardener) liquid epoxy resin was utilized: EPIKOTE MGS RIMR 035C epoxy resin based on bisphenol A diglycidyl ether (DGEBA) monomer, cured with EPIKURE MGS

RIMH 037 hardener based on poly(oxypropylene) diamine (POPDA), both donated from Hexion Inc. According to the supplier, the high degree of hydrophobicity of this resin system is remarkable (ASHCROFT, 1993).

3.2 Preparation of the MFC suspensions

MFC/H_2O

For the preparation of 1000g of a 0.1% w/w suspension, 10g of the aqueous MFC described in 3.1 were weighted on an analytical balance. Subsequently, 990g of deionised water were added. The mixture was then processed in an Ultra Turrax^{TM} homogenizer at 10,000 rpm for 4 minutes.

The same procedure was repeated for the 0.4 and 0.7% w/w suspensions.

MFC/acetone

For the preparation of 1000g of a 0.1% w/w suspension, 7.84g of the aqueous MFC described in 3.1 were weighted on an analytical balance. Subsequently, 776.16g of acetone were added. The mixture was then processed in an Ultra Turrax^{TM} homogenizer at 10,000 rpm for 4 minutes.

The same procedure was repeated for the 0.4 and 0.7% w/w suspensions.

MFC/isopropyl alcohol

For the preparation of 1000g of a 0.1% w/w suspension, 7.86g of the aqueous MFC described in 3.1 were weighted on an analytical balance. Subsequently, 778.14g of isopropyl alcohol were added. The mixture was then processed in an Ultra Turrax^{TM} homogenizer at 10,000 rpm for 4 minutes.

The same procedure was repeated for the 0.4 and 0.7% w/w suspensions.

The compositions of the obtained suspensions can be found in table 3.1.

Table 3.1 – Concentration of the MFC suspensions

Solvent	**MFC % w/w**		
H_2O	0.7	0.4	0.1
Acetone	0.7	0.4	0.1
Isopropyl alcohol	0.7	0.4	0.1

3.3 Manufacturing of the test specimens

3.3.1 Cutting and preparation of the reinforcement fibres

Previous to the cut, the CF weave was heated in an oven at 100ºC for an hour with the purpose of removing moisture, as the ingress of moisture in CFRP significantly weakens the materials mechanical properties (RYAN *et al.*, 2009). CF weave samples were then cut to 10x16 cm. To mark the measurements on the fabric as well as to lessen

fraying at the edges crepe tape was used. In this phase measurements do not need to be exact, it being sufficient that each layer is big enough to fit the rectangular mould to which the CF fabric layer was sewn so as to provide stiffness and facilitate the handling of the fabric when wet. The parts were assembled employing an aramid fibre so that it would not react with the rest of the components in the following stage. An example of a weave layer that had been sewn to the mould is shown in figure 3.2 as well as the measurements.

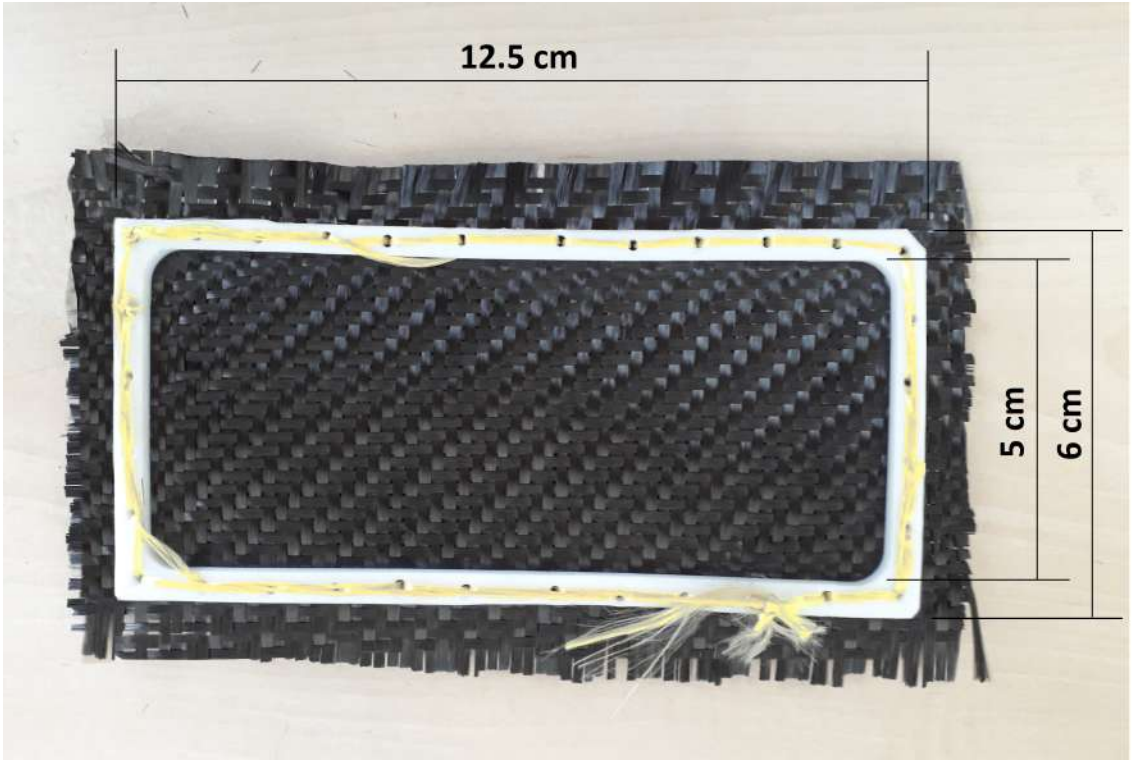


Figure 3.2 – CF weave attached to the mould.
Source: The Author (2019)

To ensure the minimum moisture as well as to diminish the possibility of deposition of airborne dust and particles onto the CFs, which could alter the results, the fabric pieces that had been previously cut were stored in a vacuum desiccator with silica gel.

3.3.2 Immersion in MFC suspension

Each of the nine different suspensions was applied individually to 6 of the dry CF weave layers employing the dip coating ultrasonic bath technique. With the aid of a 250 ml beaker 75 ml of each suspensions was measured and poured into a glass vessel containing a single fabric layer. The vessel was then placed into the ultrasonic bath for 15 minutes. After that time, the piece was removed from the suspension and introduced to the oven at 100^{o}C for 15 minutes. Once dry, it was positioned under a fume hood and left to cool until ambient temperature. Last step to this stage is removing the aramide stitching and the mould from the layer.

After a small sample was extracted from each dry MFC-coated bidirectional layer in order to perform SEM analysis, the specimens were stored in small sealed bags to prevent moisture or other pollutants.

3.3.3 Resin preparation

According to the area within the bagging tape measured and the indications of the supplier, the calculated amount of resin that would be used was calculated to be a total of 250g for each stack approximately. Then 70% of the total weight was measured for the epoxy resin and put into a magnetic mixer with a hot plate to maintain it at a temperature of 40^{o}C. The remaining 30% is then measured for the hardener and stirred into the epoxy. Last step was degassing the

resin has it has been proven to delay the onset of defects and reduce residual porosity, therefore improving RTM manufacturing processes (PUPIN *et al.*, 2017).
This was accomplished introducing the mixture into a desiccator connected to a vacuum pump until no more air voids were observed in the surface.

3.3.4 Resin infusion

Vacuum-assisted liquid Resin Infusion under Flexible Tooling (RIFT) was carried out on the MFC coated pieces. Three stacks of bagging materials were configured, one for each of the solvents used. The arrangement of the reinforcement pieces was made as shown in figure 3.3 (leaving sufficient space between them to ensure that they do not overlap or touch during the infusion), thereby obtaining two test specimens of each nature to enable the verification of the repeatability of the manufacturing process by comparison of the two.

Using a glass counter top as the mould surface, reinforcement pieces were laid into a layer of vacuum bagging film to ensure that the parts will release from the mould. Bagging tape was then applied around the edges, leaving some additional flange area to place the resin feed and vacuum connectors, infusion mesh and resin flow channels. The first layer over the reinforcement is the peel ply which is the one to be peeled off from the finished part. Subsequently, infusion mesh was added to ensure that the resin can flow freely through the laminate, from the resin feed spiral tube positioned lengthwise on the feed side

and directly above the mesh, to the opposite spiral tube positioned in parallel on the suction side. The spiral on the resin feed side was connected to the resin feed pot via a PVC hose and the opposite spiral to the vacuum pump (avoiding direct contact between the spiral tubes and the bagging tape with the help of crepe tape). The stack was then enclosed with bagging film applying it tightly to prevent wrinkles as much as possible.

For good functioning of the vacuum bag, it was ensured that all the layers that compose the stack, except the topmost bagging film, were contained within the bagging tape perimeter without touching it to prevent air voids, while fully covering the reinforcement parts. Also, after the stack was assembled and before the resin feed, the intake was clamped with a pipe clump and the vacuum pump switched on to evacuate the air from the bag and test the vacuum. 10 minutes after the pump was switched off, if no air leak was observed (otherwise adjusting the bag) the pump was activated again and the resin hose unclamped. Slowly, the liquid resin that had been previously prepared as explained in section 3.3.3 was infused into the reinforcement and once it had fully infused through all the specimens, the supply was cut off.

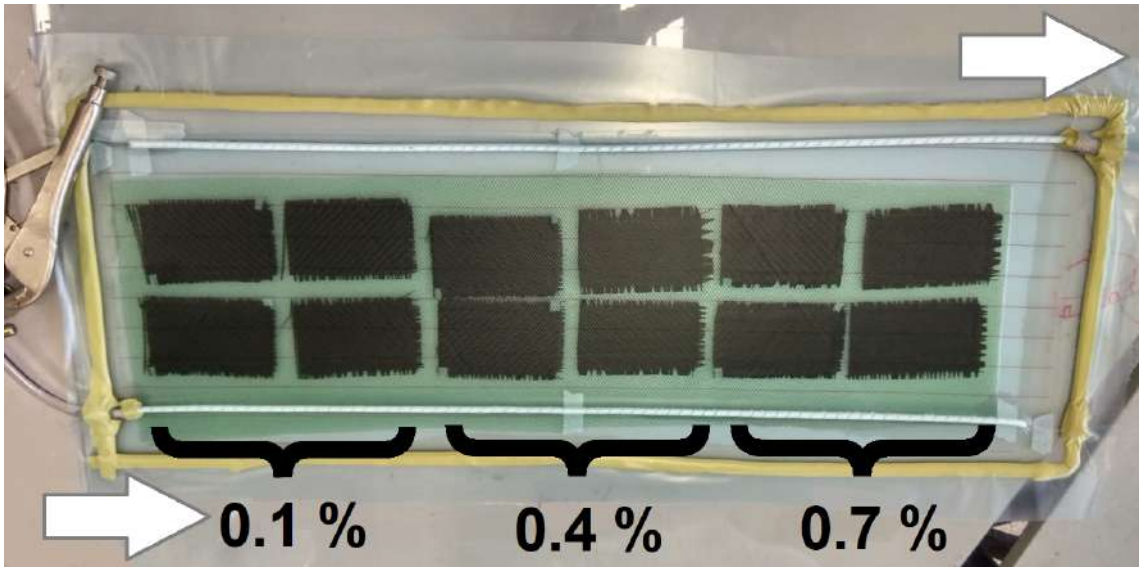


Figure 3.3 – Vacuum bag for each solvent type (arrows indicate resin flow direction; under the brackets, MFC concentrations in weight of the applied suspensions).

Source: The Author (2019)

3.3.5 Curing

The thermoset curing process before demoulding is generally carried out until a full conversion is reached, i.e., all possible reactions have occurred, or until vitrification has taken place. However, for economical reasons (time and expensive moulding equipment), the preferred methodology at the laboratory of GECoM is to demould at earlier stages when the part possesses enough strength not to deform upon demoulding and that the remaining cure will not induce dimensional changes of the part, and complete the curing with a post-cure at higher temperatures (FAN; WECLAWSKI, 2016). Therefore, after the resin supply was cut off, the laminates were allowed to cure at ambient temperature for 48h and were then demoulded. After that they were post-cured in an oven via controlled

ramp heating in the following sequence, as recommended by the manufacturer: 1h at 30ºC, 1h at 50ºC and 5h at 70ºC.

3.4 Testing

3.4.1 Scanning electron microscopy (SEM)

The MFC-coated CF weave samples were taken to the Electron Microscopy Laboratory at the Institute of Physics of São Carlos IFSC — USP, where analysis was carried out in a Sigma-Gemni ZEISS equipment with an InLens detector, at a voltage of 7.00 kV and a work distance of 7.8 mm.

3.4.2 Mechanical testing

A microprocessor-based electromechanical universal testing machine EMIC model DL 10000 was utilized in the mechanical tests performed at ambient temperature of 25°C, with the speed of testing set at a rate of crosshead movement of 1.0 mm/min and a support span of 40 mm. Flexural stress tests were carried out according to the D7264/D7264M15 standard as regulated by ASTM International (ASTM, 2016).

Two test coupons with in plane nominal dimensions of 60x15 mm^2 were used for each class of CFRP composite laminate tested.

Chapter 4

Results and discussion

4.1 MFC dispersion on CF

4.1.1 SEM images

The objective of the test is to optically define the MFC-coated preforms as compared to the pure CF preforms, by means of imaging techniques that can provide sufficient resolution, such as scanning electron microscopy (SEM), which is a type of electron microscope that scans the surface of the sample with a focused beam of electrons that interact with the atoms in the sample producing various signals that contain information about the surface topography and composition, and can achieve resolution better than 1 nanometer. Although the resolution of SEM is not as good as transmission electron microscopy (TEM), the first avoids the difficulties of preparing thin samples (ZANICH, 2012). In addition, a fundamental requirement of SEM is the need to observe the specimens in vacuum conditions and therefore,

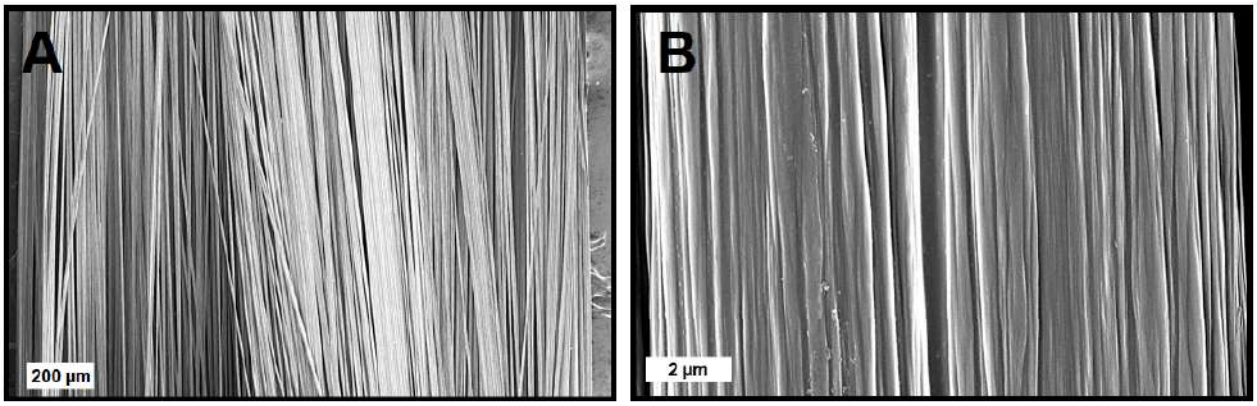
they must be vacuum-friendly, as is the case of our CF preforms.

In order to analyse the morphological features of the dispersion, unsized CF-weave surfaces were observed, as shown in figure 4.1, as well as MFC-coated CF surfaces for samples impregnated with suspensions of every MFC concentration/solvent combination, as shown in figures 4.2, 4.3 and 4.4. The images correspond to regions displaying linkage of the fibrils to the main reinforcement.

4.1.2 Unsized CF

Untreated reinforcement fibres are shown in figure 4.1 for different magnifications in their unsized form, for reasons of comparison with the MFC-covered fibres.

Figure 4.1 – SEM images of pure unsized CF weave.



Source: The Author (2019)

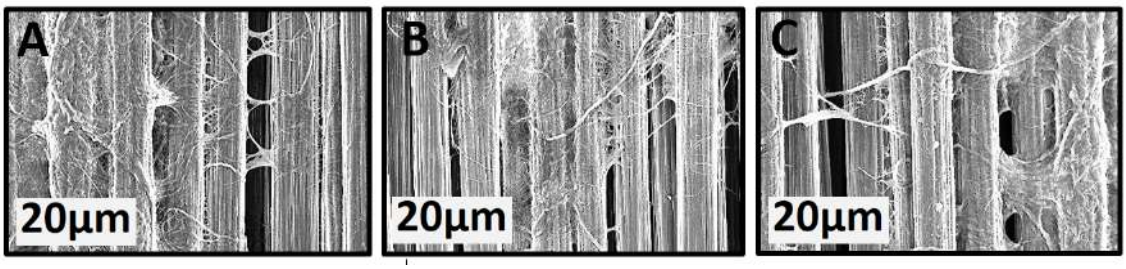
While in figure 4.1A part of a bundle of fibres is displayed, in figure 4.1B the surface of two individual fibres can be appreciated, clearly showing the texture created by the carbon crystals that are more or less aligned parallel to the long axis of the fiber.

The reason for using unsized fibres instead of sized ones is not to interfere with one of the main purposes of the research, which is to develop a cost-efficient method, since the price of the later is approximately tenfold that of the first one (URIBE *et al.*, 2017a). Also, some studies report that (COMPOSITE WORLD, 2016) despite improving the handling of the fibres, sizing can create a weak interphase between the fibre and the resin (and thus affect mechanical properties) in the case of epoxy matrix systems, as the bounding interactions depend on sizing/resin compatibility.

MFC/H_2O

Figures 4.2A, 4.2B and 4.2C show the typical web-like aspect of the cellulose fibrils over the CFs, evidencing their high specific surface area which is characteristic of MFC. This web creates some kind of bridges from one CF to the adjacent, thus binding them together.

Figure 4.2 – SEM images of CF immersed in deionised water suspension: (A) 0.1% w/w MFC, (B) 0.4% w/w MFC and (C) 0.7% w/w MFC.



Source: The Author (2019)

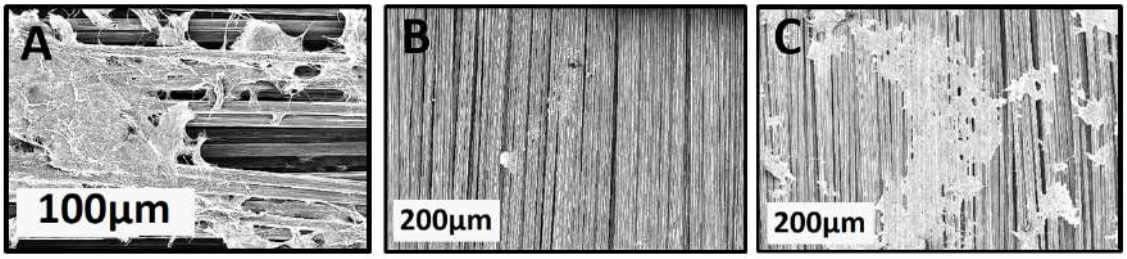
With increasing MFC concentration in the suspension a tendency of the fibrils to coalesce was perceived, resulting in less homogeneity of the dispersion. This is made clear in the specimen that had been immersed in the 0.7% MFC suspension as it reveals more

agglomeration of the fibrils (bottom left of figure 4.2C), opposite to the 0.1% and 0.4% ones that exhibit a more even layer of MFC with a thinner appearance.

MFC/acetone

In figures 4.3A, 4.3B and 4.3C it can be appreciated that MFC did not effectively permeate the CFs when compared to the case of water. The dispersion is not as homogeneous and MFC appears to create a superficial layer of its own with little interlocking with the fibres.

Figure 4.3 – SEM images of CF immersed in acetone suspension: (A) 0.1% w/w MFC, (B) 0.4% w/w MFC and (C) 0.7% w/w MFC.



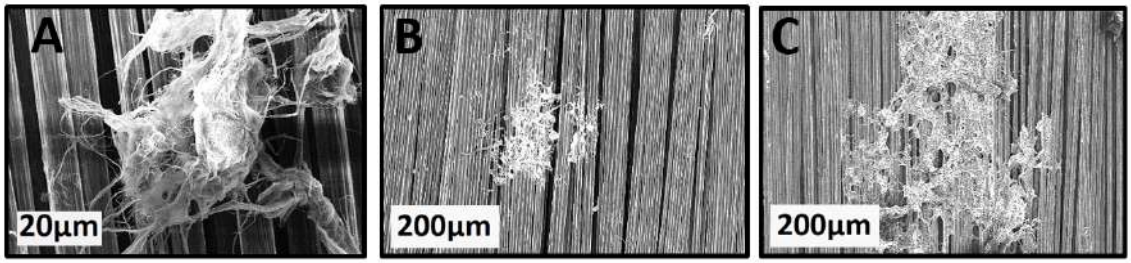
Source: The Author (2019)

It can be observed that large regions of the reinforcement remain uncoated. Although an increase in the covered area is attained with a higher percentage of MFC in the suspension, this goes hand in hand with a rise in the MFC clusters, which can be clearly observed when looking at figures 4.3B and 4.3C.

MFC/isopropyl alcohol

Figures 4.4A, 4.4B and 4.4C display an entirely different pattern to the previous one, as the MFC clearly forms agglomerates that sit on top of the CFs instead of interlocking with them. From the images with a lower degree of magnification (4.4B and 4.4C) two facts become apparent: there was less nanostructure deposition from the suspension into the CFs, and this deposition was highly heterogeneous, leading to a patched appearance where big regions of the carbon weave were not impregnated with MFC.

Figure 4.4 – SEM images of CF immersed in isopropyl alcohol suspension: (A) 0.1% w/w MFC, (B) 0.4% w/w MFC and (C) 0.7% w/w MFC.



Source: The Author (2019)

The increase in MFC concentration of the applied suspension does not seem to have neither a positive or negative overall effect on the morphology of the surfaces, besides perhaps the larger size of the clusters of cellulose fibrils.

4.1.3 Discusion

Microscopy images reveal shape and size differences within the cellulose network that lies on the CFs, showing a variety of fibril

diameters. This can be easily seen in figure 4.5 (close-up view of the CF coated with 0.7% MFC/H_2O) where the arrow indicates a fibril with a micrometric-size diameter and the circle indicates a group of nanofibriles. This is because in spite of nano-structures being their main component, MFC materials may be composed of fibrillar fines, fibre fragments and fibres in addition to the nanofibrils (CHINGA-CARRASCO, 2011).

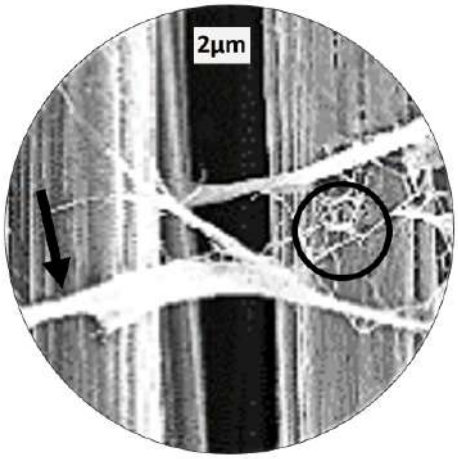


Figure 4.5 – MFC structure on CF.
Source: The Author (2019)

This hierarquical array has been shown to enhance the load transference and distribution in CFRP and GFRP (URIBE *et al.*, 2016), resulting in cooperative dynamics of the thinner nanofibrils acting as an energy dissipater for the thicker ones (URIBE *et al.*, 2018). The main interaction between MFC and CF is by mechanical anchoring mechanism which can be appreciated in the images, although there is also evidence of electrostatic attraction between the two phases via Van der Waals dipole-dipole forces that contribute with the adhesion. In this last sense, functional groups of type –OH

or >C=O, which come from oxygen on the carbon fiber surface, are important to provide interactions with the hydroxyl groups (OH–) present in MFC (URIBE *et al.*, 2017c).

Two more solvents other than deionised water were tested in an attempt to prevent the problems associated with water during the resin infusion: the hydroxyl groups react affecting the linkage of the polymeric system in a process known as plasticization. The selection of the alternative solvents was based on the similarity of their electrochemical properties and their higher evaporation rate, as well as previous research that proved the value of acetone for this purpose (ANSARI *et al.*, 2014). Also acetone is an inherent component of the resin hardener, which makes it easily compatible with the epoxy system.

However, it was already visible to the naked eye that after the immersions not much MFC adhered to the CF surface when using the acetone or alcohol, in comparison to using water as the solvent. SEM images also supported the observation that the dispersion was undermined when using the non-aqueous suspensions. The fact that these two solvents create less stable MFC suspensions was also suspected due to the settling of the MFC to the bottom of the bottles containing the suspensions, and the agitation of the particles in ultrasonic bath was tried in order to overcome this problem.

Once determined that deionised water gave the best results, we come to discuss the other variable of the work: MFC suspension concentration. With less concentration, more nanofibril-links between

the CFs were observed such as in figure 4.2A, while higher concentration exhibited more coalescence in some concentrated regions.

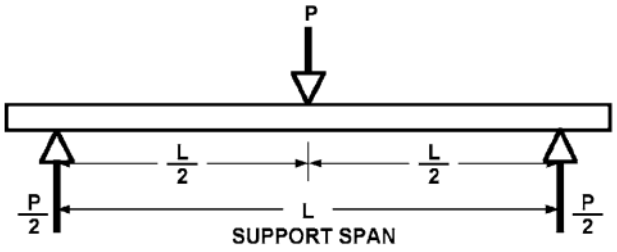
4.2 Mechanical properties

Bending tests at room temperature were realized to the finished laminates, following the D7264/D7264M–15 standard as regulated by ASTM International (ASTM, 2016). These tests can be advantageous in cases where the tensile stress test cannot be easily carried out, to prevent the damaging of the ends of the specimen with the jaws of the test machines. The fracture will begin at the opposite point to where the central force is applied.

Since the preceding research on this topic carried out in the GECoM provided the basis for this work, and with the objective in mind of creating a consistent and bigger collection of data obtained under similar conditions, the three-point loading system was used in the equipment at the laboratory. This loading system is referred to as *Procedure A* in the standard, and its load/supports configuration is shown in figure 4.6.

Foreseeing from the results of the imaging techniques that laminates impregnated with acetone and alcohol suspensions would have worse performance than the water-impregnated ones, the decision was made to test the laminates impregnated with all the three concentrations (0.1%, 0.4% and 0.7%) for the water solvent, and only the 0.4%

Figure 4.6 – Three-point flexural test



Source: ASTM D7264/D7264M–15

ones for the rest. For each solvent/concentration combination, two specimens were tested because even though the standard indicates that at least five specimens should be tested for statistically signicant data, the purpose of the present work is not to rigorously determine the properties of the materials, but to identify the behavioural trend that the different kinds of laminates follow for comparison reasons (see section 1.2).

In table 4.1 the tested specimens are listed along with the measurements of their cross-sections. The naming guideline adopted to identify each specimen is as follows: the number after the letter A represents the concentration, the next letter represents the solvent (H for water, A for acetone and I for isopropanol) and the last number indicates the number of the specimen, as there are two of each kind. Thickness is represented as h and width as b.

In table 4.1 a subtle difference among the thickness of the specimens was noticed, which may be associated to the amount of MFC that adhered to the reinforcement surface, since for the highest concentrations the specimens were thicker. Additionally, the disparity of the thicknesses of samples A4I1 and A4I2 might support the

Table 4.1 – Measurements of the test specimens

Laminate	h (mm)	b (mm)
A7H1	0.70	14.60
A7H2	0.67	14.83
A4H1	0.68	15.30
A4H2	0.66	15.01
A1H1	0.63	15.13
A1H2	0.60	15.80
A4A1	0.58	15.20
A4A2	0.55	15.07
A4I1	0.62	15.50
A4I2	0.53	15.14

observation in the microscopy that the MFC dispersion was uneven (see figure 4.4), as heterogeneity of the dispersion would produce heterogeneity in thickness, as well.

4.2.1 Flexural stress-strain curves

In order to translate the mid-span deflection, δ (mm), and load, P (N), values provided by the equipment into the *Maximum Strain*, ϵ (mm/mm), and *Maximum Flexural Stress*, σ (MPa), both of which occur at the mid-span of the outer surface, the following relationships (ASTM, 2016) were used respectively:

$$\epsilon = \frac{6\delta h}{L^2} \tag{4.1}$$

$$\sigma = \frac{3PL}{2bh^2} \tag{4.2}$$

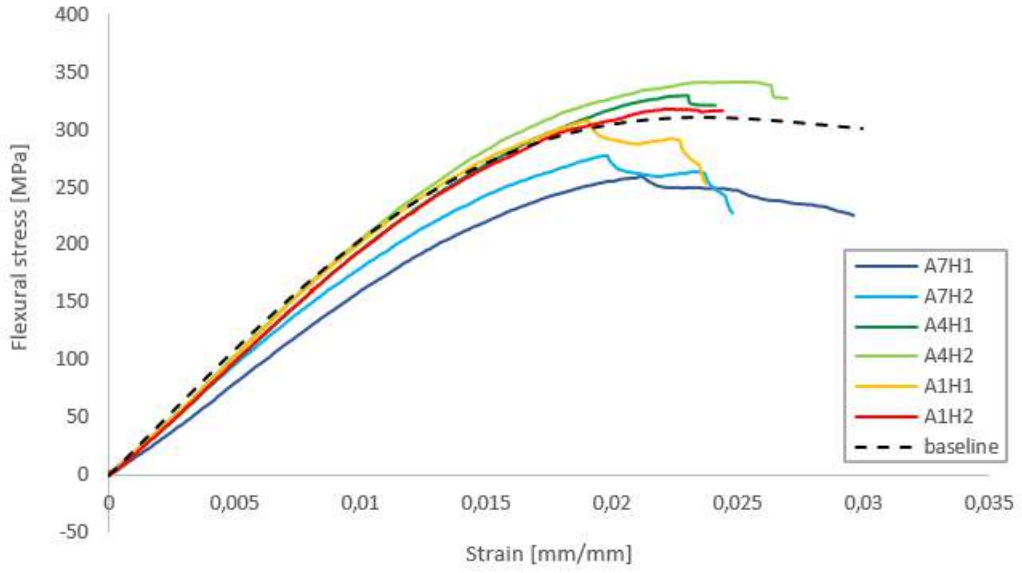
Equation 4.2 applies strictly to materials for which the stress is linearly proportional to strain up to the point of rupture and for which the strains are small (less than 2%). Since this is not the case for the

laminates, which also present a plastic region, a slight error will be introduced in the use of this equation. The equation will however, be valid for comparison data, as specified in the standard. Similarly for equation 4.1, the calculated ϵ does not correspond with its associated σ value, so elongation values should only be considered for comparison and not in the strict sense.

For the next graphs, averaged data from five reference specimens is presented as a baseline for traditionally manufactured laminates, without MFC addition.

Figure 4.7 shows the flexural stress-strain curves of the specimens that used water as the solvent. It can be appreciated that 0.1% MFC is very close to the baseline. However, highest strengths were obtained with 0.4% MFC and from then on, the increase of MFC negatively affected the behaviour.

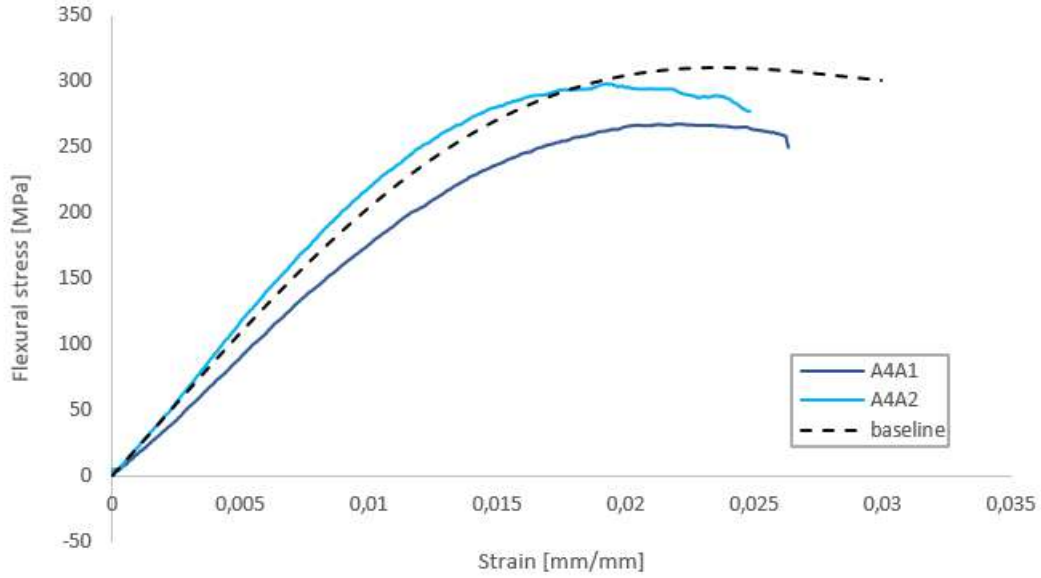
Figure 4.7 – Flexural stress-strain curves of CFRP composite laminates prepared with MFC/deionised water suspensions.



Source: The Author (2019)

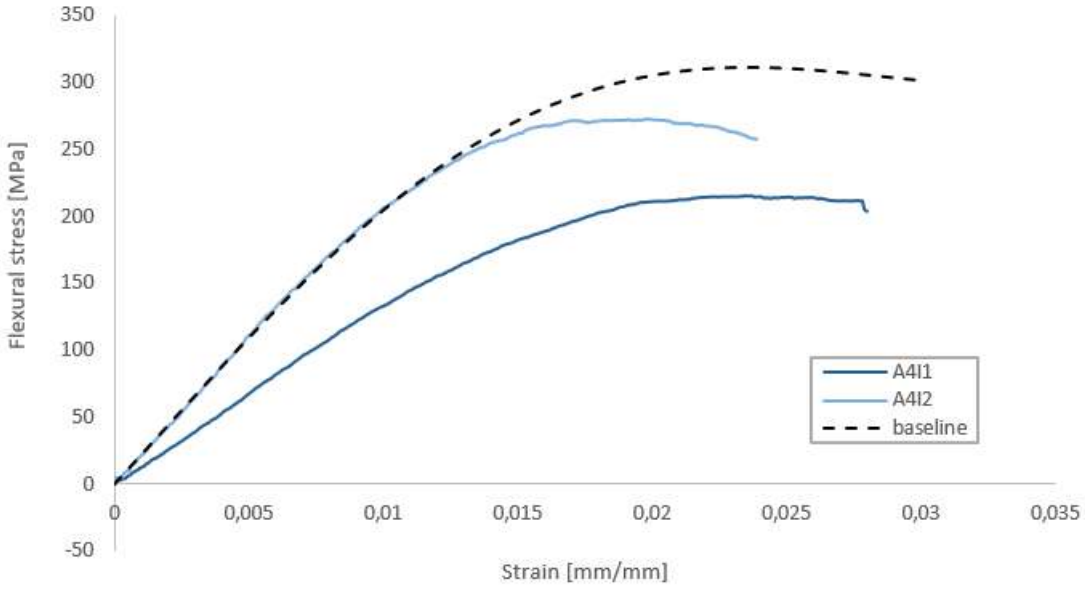
The case of the specimens in which acetone and isopropyl alcohol was used is shown in figures 4.8 and 4.9 respectively.

Figure 4.8 – Flexural stress-strain curves of CFRP composite laminates prepared with MFC/acetone suspensions.



Source: The Author (2019)

Figure 4.9 – Flexural stress-strain curves of CFRP composite laminates prepared with MFC/isopropyl alcohol suspensions.



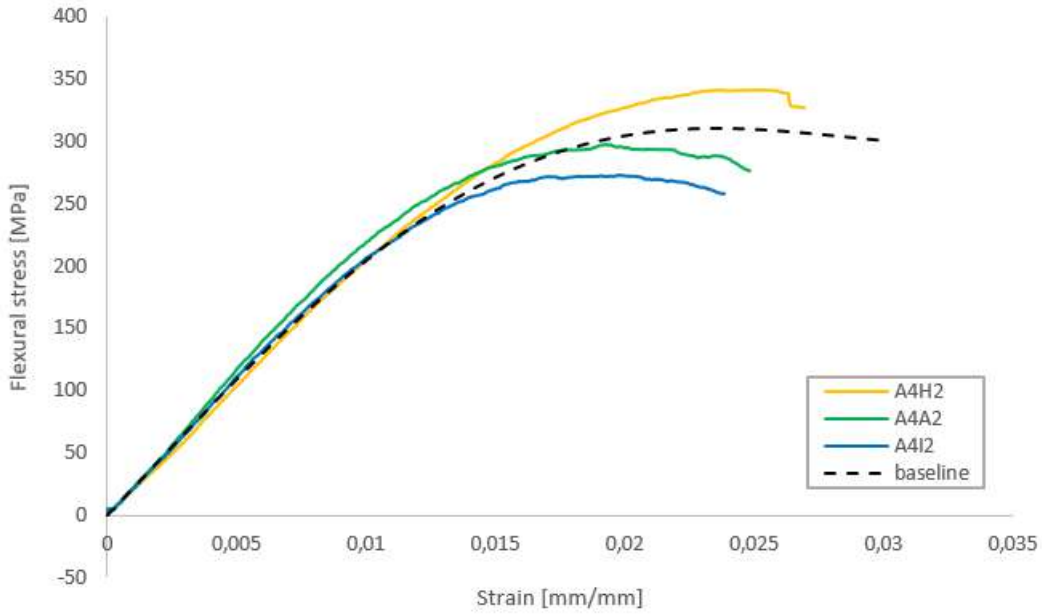
Source: The Author (2019)

For both solvents, acetone and isopropyl alcohol, the curves of

samples nº1 and nº2 are considerably more distant one from the other than in the case of aqueous suspension. This suggests that even though the two samples were cut from the exact same laminate, the heterogeneity in the dispersion and therefore in the composition throughout the laminate (as seen in figures 4.3 and 4.4), also leads to more heterogeneous behaviour. When compared to the baseline, a decrease in the flexural strength is observed for both solvents.

For a better comparison of the effects of the different solvents, the best-performing samples were chosen and overlayed in figure 4.10.

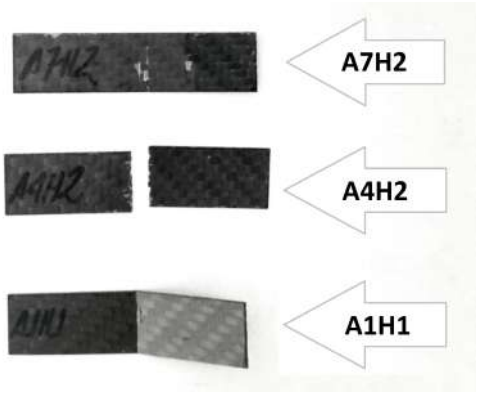
Figure 4.10 – Flexural stress-strain curves with different solvents.



Source: The Author (2019)

Greater flexural strength, tenacity (as determined by the area under the stress-strain curve) as well as elongation was achieved with the MFC/water immersed laminate, while a higher rigidity is observed for the MFC/acetone and MFC/isopropyl alcohol.

Figure 4.11 – Composite laminates after flexural fracture.



Source: The Author (2019)

As can be observed in figure 4.11, failure occurred from propagation of cracks at the centre of span (in A7H2 and A1H1 the middle region presents damage in form of catastrophic cracking, though there was no split), as expected from the fact that it is the load application point.

For futher comprehension of the failing modes of the MFC-added laminates, conducting SEM imaging to the fracture surfaces would be interesting and is proposed for future works.

4.2.2 Flexural strength and modulus

The *Flexural Strength*, σ_f (MPa), is defined as the maximum stress at the outer surface corresponding to the peak applied force prior to failure and the *Flexural Chord Modulus of Elasticity*, E_f^{chord} (MPa), is commendably calculated for a strain range of 0.002 with a start point of 0.001 and an end point 0.003. Their values for the laminates are compiled in table 4.2 which were once again calculated according to the D7264/D7264M15 standard (ASTM, 2016), as follows:

$$\sigma_f = (\sigma)_{max} \tag{4.3}$$

$$E_f^{chord} = \frac{\Delta\sigma}{\Delta\epsilon} \tag{4.4}$$

where,

- $\Delta\sigma$ is the difference in flexural stress between the two selected strain points (MPa)
- $\Delta\epsilon$ is the difference between the two selected strain points, nominally 0.002 (mm/mm)

Once again, it should be taken into account that strength values are not accurate as they occur out from the elastic region, and should be considered for comparison purposes only. On the other hand, modulus of elasticity could be considered as a valid if more tests had been carried out for more specimens, as it was calculated in a range where strains are small.

Table 4.2 – Flexural Strength and Flexural Chord Modulus of Elasticity of the composite laminates.

Laminate	σ_f (MPa)	E_f^{chord} (GPa)
A7H1	260.77	16.91
A7H2	280.23	21.19
A4H1	332.48	21.46
A4H2	344.25	21.76
A1H1	310.66	20.20
A1H2	319.42	21.40
A4A1	269.67	19.70
A4A2	298.03	26.50
A4I1	217.81	13.54
A4I2	276.55	21.37
baseline	296.95	23.37

It can be appreciated that, as it could already be seen in the strain-stress curves, the laminate with the highest flexural strength

values were A4H1 and A4H2. Once again, the heterogeneity of the MFC dispersion is present in the results, as the samples with the most uneven morphology (A4A1/A4A2 and A4I1/A4I2) are the ones that show the greatest disparity between their strength and modulus values. In contrast, samples that showed the better interaction between the MFC and the CFs (see figures 4.2A and 4.2B) demonstrate more similarity between the results.

When compared to the baseline, the only specimens that have superior strength values are the ones that used the 0.1 and 0.4 % aqueous suspensions. In contrast, when using acetone and isopropyl alcohol this property was not improved for most cases and moreover, it was deteriorated.

4.2.3 Discussion

As mentioned before, two of each kind of specimen were tested, which despite lacking statistical validity for materials specification, was useful to determine a trend in the mechanical behaviour of the different laminates for the sake of simplicity.

From the comparison between the best-performing MCF/water-immersed specimens (A7H2, A4H2 and A1H2), the CF impregnated with the 0.4% suspension showed an increment in flexural strength of 7.8% when compared to the 0.1% suspension-impregnated one and an increment of 22.8% when compared to the 0.7% suspension-impregnated one.

From the comparison between the best-performing MCF/water, MFC/acetone and MFC/isporopyl alcohol-immersed specimens (A4H2, A4A2 and A4I2), the CF impregnated with the water suspension showed an increment in flexural strength of 15.5% when compared to the acetone suspension-impregnated one and an increment of 24.5% when compared to the alcohol suspension-impregnated one.

As for the flexural modulus, the variable showed a moderate decrease (differences of less than 2.7%) when compared to the baseline, except for the A4A2 sample which revealed a 13.0% higher modulus than the traditionally manufactured one. More specimens would need to be tested to verify if this higher modulus for acetone is statistically significant and not a mere exception. Were it indeed higher, it would mean that this MFC-application method would be indicated for parts subjected to limited bending deformations such as the wings, which support buckling loads.

Therefore, it could be observed that the use of acetone and isopropyl as solvents did not have the same positive effects on mechanical properties as when using water. This can be explained with the SEM images of the impregnated CFs, as well as with the disparities on the results for these two solvents, which confirmed that the dispersion of the MFC was poor and highly heterogeneous.

From the use of the various MCF concentrations with water as the solvent, it was deduced that even though a moderately higher concentration has positive effects in the flexural strength

of the material, this property was drastically deteriorated with higher concentrations. This could be due to the increased MFC agglomeration that occurs for higher MFC contents in the suspension, as above mentioned (see figure 4.2C) since this leads to a less efficient MFC/CF load transfer (ANSARI *et al.*, 2014) as well as introducing stress concentration points, which favour the crack formation and growth in the material.

Chapter 5

Conclusions

In the water suspension-immersed specimens, an increase in the coalescence of the MFC was noticed above a certain MFC percentage. It is subtracted from this observation that when using water as the solvent, an optimum MFC concentration that maximizes the mechanical properties of the composite material exists. When the manufacturing procedure followed is parallel to the one presented in this work, this occurs for a MFC concentration between 0.1% and 0.7%. For a content of 0.4% of MFC in the suspension, there was an increase of 7.8% in flexural strength over the 0.1% MFC-content one.

In addition, even though the use of acetone and isopropyl alcohol as solvents for the manufacture of CFRP with MFC interphase would have been advantageous over the use of water (in order to minimize the risk of plasticization), their suitability for the application of MFC to the CFs using the dip coating technique was contradicted, as they promote more heterogeneous dispersion of the nanofibrils. The mechanical performance when using these two solvents was

consequently lower in terms of flexural strength and tenacity.

This work conforms the initial stages of a research that strives for the development of an effective, low-cost MFC application method in order to achieve superior properties in CFRP composites.

Chapter 6

Suggestions for future work

From the here presented findings, some issues that would benefit from further research are the following:

- The utilization of MFC concentrations around 0.4% in order to determine the value that optimises mechanical performance, beyond which the properties begin to decline;
- Other mechanical testing in order to study the behaviour of the laminates under different load cases, such as tensile test, ballistic impact tests or drop tower impact tests;
- Now that the effectiveness of MFC/water concentrations of around 0.4% was demonstrated even with short drying times, the search for a compromise solution between improved mechanical behaviour and longer drying times;
- Adopting a parallel manufacturing process to the one followed for the 0.4% MFC/water suspension, trying laminates with more layers and with different orientations.

- Compare the achieved MFC penetration in between the CFs with unidirectional layers, in contrast with bidirectional layers.
- Analyse the fracture surfaces after the flexural test to determine the failure mode and for a deeper understanding of the interactions among the phases.

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