

**UNIVERSITÀ DI BOLOGNA**

**MASTER IN INDUSTRIAL ENGINEERING**

**MASTER THESIS**

**EXPERIMENTAL INVESTIGATION ON THE ENHANCEMENT OF  
MODE I FRACTURE TOUGHNESS OF ADHESIVE BONDED JOINTS  
BY ELECTROSPUN NANOFIBERS**

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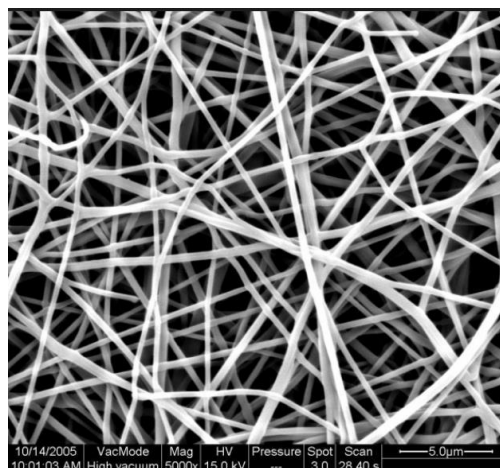
## Resumen

Hoy en día, el constante desarrollo tecnológico está haciendo que los métodos tradicionales ocupen un segundo lugar en las nuevas técnicas de unión. La necesidad de unir diferentes sustratos, formas estructurales complejas o nuevos materiales que a menudo no son adecuados para unirse; así como la necesidad de reducir el peso de la estructura, los costes y el tiempo, ha desarrollado un mayor interés en el uso de adhesivos.

El uso de uniones adhesivas ofrece muchas ventajas con respecto a otros métodos de unión como la soldadura, remachado o atornillado; pero presentan, a su vez, una serie de desventajas, entre las cuales se encuentra la baja tenacidad a fractura frente a las uniones mecánicas. Este estudio se centrará en mejorar dicha tenacidad a fractura, por medio del uso de nanofibras obtenidas mediante la técnica del electrospinning.

### Nanopartículas y nanofibras

Las nanopartículas y nanofibras, son elementos cuyo tamaño se encuentra en la nano-escala con una capa interfacial circundante, que son de gran interés en la ciencia, ya que son un puente entre los materiales en bruto y las estructuras moleculares. Las propiedades físicas de los materiales en bruto deben mantenerse constantes independientemente de su tamaño, pero a escala nanométrica se observan algunas propiedades diferentes. Por lo tanto, las propiedades del material cambian a medida que se aproximan al tamaño de nano-escala cuando la relación de la superficie con el volumen de un material se vuelve significativa. Esta variación de las propiedades puede generar diferentes efectos sobre los adhesivos, como: incrementar el módulo elástico y la fuerza de la adhesión.



En este estudio se muestran a su vez diversas investigaciones donde se observan los efectos de las nanofibras y nanopartículas en las uniones adhesivas.

### **Diferentes procedimientos para producir nanofibras**

Para producir las nanofibras, existen multitud de procedimientos, siendo los más comunes: dibujado, la síntesis de plantilla, el autoensamblaje, la separación de fases y el electrospinning. Este último procedimiento es el más empleado en la actualidad y será el que se utilice en el estudio.

Para obtener un incremento de la tenacidad a fractura del adhesivo es necesario tener en cuenta diferentes parámetros: El tipo de partículas que se introducirán en el adhesivo, el pretratamiento de las superficies a unir, y el tipo de adhesivo a utilizar.

Una vez seleccionadas las nanofibras, el pretratamiento y el adhesivo, las probetas se unen, se curan y posteriormente se ensayan con una prueba DCB a tracción para comprobar la fuerza de la unión.

### **Elección de la resina**

En esta investigación el primer paso a realizar es la elección de la resina, proporcionada por la compañía Elantas, entre tres diferentes tipos: EC152TIX, AS46, AS53. Estas resinas se impregnan en láminas de nanofibras de Nylon 6,6, se introducen en una bolsa de vacío y se curan. Una vez curadas se rompen y se observan las superficies de rotura con microscopio óptico y SEM. La elección de la resina depende de la cantidad de burbujas formadas y de la homogeneidad de la impregnación en las nanofibras.

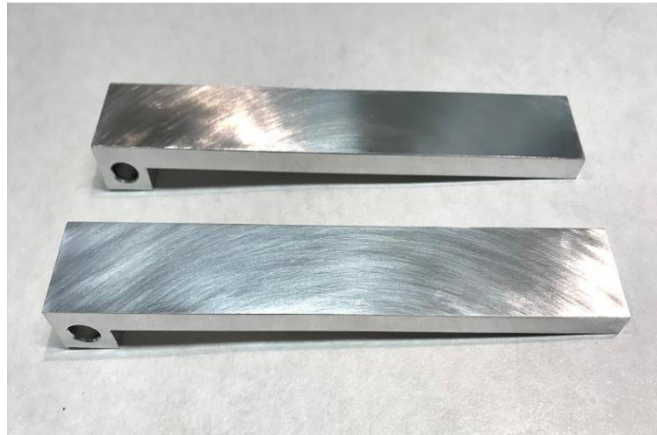


### **Elección del aluminio y el pretratamiento**

Posteriormente se selecciona la aleación de aluminio a emplear y el pretratamiento. Al7075, Al2000 y Al2024-T3 serán tratados con una solución de soda caustica y posteriormente con P2etching, solución a base de ácido sulfúrico y sulfato férrico. Las piezas tratadas serán observadas con un microscopio SEM para comprobar el efecto del pretratamiento sobre su superficie, comparándolas con piezas vírgenes de las mismas aleaciones.

### **Fabricación de los especímenes**

Tras haber seleccionado el aluminio se procede a la fabricación de los especímenes que serán unidos posteriormente. Se realizan 3 tipos diferentes de diseños, todos ellos siguiendo el estándar ASTM 3433 pero empleando una escala reducida, para una mayor facilidad de trabajo en el laboratorio. Los 3 diseños tienen en común la presencia de una superficie lisa, la superficie de unión, sobre la que irá extendida la resina y las nanofibras. Las probetas son fabricadas mediante fresado, con un acabado pulido en la cara de unión.



Además de los especímenes es necesaria la fabricación de sujeciones para colocar las probetas una vez estén unidas con la resina. Se crean dos diseños diferentes de sujeción, siendo más eficaz el segundo ya que impide el deslizamiento de la lámina de nanofibras y de otros elementos colocados entre las piezas a unir.

### **Pretratamiento de los especímenes**

Para la obtención de la solución de soda caustica al 1%, se mezclan soda caustica con la cantidad necesaria de agua destilada a temperatura ambiente, y se mezcla hasta obtener una solución homogénea y se vierte en un recipiente de plástico. Las piezas, con la cara de unión pulida, se introducen en la solución durante 10 minutos. Posteriormente, se extraen de la solución de soda cáustica y se introducen en otro recipiente de plástico con agua destilada durante otros 10 minutos. Pasados los 10 minutos en el agua destilada, las piezas se introducen en la solución de P2etching.

Para obtener el P2etching al 34% de ácido sulfúrico, se mezcla ácido sulfúrico al 64% con agua destilada, se añade el sulfato férrico, se vierte la mezcla en un recipiente de vidrio y se incrementa la temperatura hasta los 60°C. Cuando se alcanza la temperatura deseada, se introducen las piezas y se deja actuar durante 12 minutos. Pasado este tiempo, las piezas se extraen, se limpian ligeramente con agua destilada para eliminar las impurezas y posteriormente se introducen en un recipiente lleno de agua destilada durante 10 minutos más. El resultado es una superficie mate, eliminando todo el brillo que poseía anteriormente el aluminio.



### **Producción de las nanofibras**

Para la producción de las nanofibras, se ha empleado el polímero Nylon 6.6 disuelto en una solución de TFA/acido fórmico/cloroformo. Esta solución se inserta en unas jeringuillas con unas agujas en su parte delantera. La solución es eyectada a través de la punta de las agujas cuando se aplica un voltaje suficientemente alto. La solución viaja desde la punta de las agujas, evaporándose el disolvente, hasta el colector, donde las nanofibras son recogidas formando láminas de aproximadamente 200 micrómetros. Este proceso descrito es conocido como electrospinning, y es una de las técnicas más empleadas en la actualidad para la fabricación de este tipo de nanopartículas. Para que el proceso de electrospinning sea óptimo y que las nanofibras se formen correctamente, diferentes parámetros deberán ser establecidos: el flujo de solución a través de las agujas, el voltaje aplicado, la distancia aguja-colector, la temperatura y la humedad presente en el ambiente.

### **Proceso de pegado**

A la hora de unir las piezas para luego testarlas, es necesario hacer lotes de dos probetas (4 piezas unidas dos a dos), una de las probetas estará unida únicamente por resina (probeta virgen) y la otra irá unida con la lámina de nanofibras impregnada con el adhesivo (probeta nanoreforzada).

El proceso de pegado para ambos casos es diferente:

- Probeta virgen: se colocan dos láminas de cobre en los extremos de una de las piezas a unir, dicha lámina servirá para alcanzar el espesor de la resina deseado (que deberá ser aproximadamente igual al espesor de las nanofibras). Se recorta una lámina de teflón con las dimensiones necesarias y se coloca al inicio de la pieza (la parte que irá unida a la máquina); esta lámina de teflón se emplea para generar la pre-grieta en el adhesivo. Una vez colocado el teflón, se extiende la resina sobre la superficie y se coloca la otra pieza de aluminio encima, presionando y eliminando el exceso de resina.
- Probeta nanoreforzada: existen dos procedimientos para la unión de las probetas nanoreforzadas dependiendo de si la lámina de teflón va unida o separada de las nanofibras. Si ambas láminas van separadas, el proceso que se sigue es el siguiente: en una de las piezas se coloca el teflón, mientras la lámina de nanofibras se impregna con la resina. Se elimina el exceso de adhesivo de las nanofibras y posteriormente se coloca sobre la superficie a unir seguida de la otra pieza de aluminio para crear la probeta. En el caso de la lámina de nanofibras unida al teflón, las nanofibras deben de abrirse a la mitad en uno de sus extremos para poder introducir el teflón en su interior. Posteriormente se impregna todo el conjunto con la resina, eliminando el exceso, se coloca sobre una de las superficies de contacto y se une con la otra pieza.

### **Proceso de cura**

Una vez que se han creado las dos probetas del lote, estas se colocan en la sujeción. El conjunto de sujeción y probetas se introduce en una bolsa de vacío y todo ello se lleva al horno para el proceso de cura de la resina. Se emplean diferentes procesos de cura para cada lote, para así poder comprobar el efecto de este procedimiento en el incremento de la tenacidad a fractura del adhesivo.



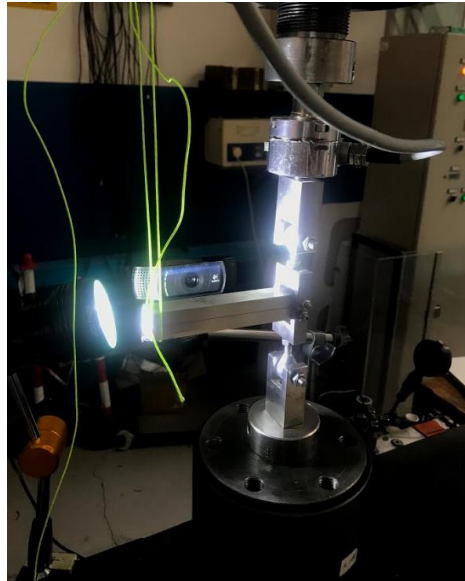
Además de las probetas, en el horno también se introducirá la resina sobrante del proceso de pegado, vertida en recipientes de plástico, para así verificar si la resina se ha curado completamente. La primera vez que se realizan los ensayos de estas probetas, la resina ya curada es testada con un proceso de flexión a tres puntos, para comprobar si su rigidez es óptima para el estudio.

### **Test DCB**

Cuando el curado de la resina se ha completado, se procede al ensayo de las probetas. Para realizar dicho ensayo, se seguirá el estándar para obtener la fractura del adhesivo en modo I. EL proceso a realizar en dicha prueba es el siguiente: se une la probeta a la máquina y se comienza a ejercer una tensión axial de tracción que se incrementa de una forma controlada con el tiempo. Durante este proceso de carga, se inicia la creación de la grieta y las dos piezas que conforman la probeta comienzan a separarse, siguiéndose la propagación de la grieta. Se continúa aumentando la tensión hasta que se alcanza el colapso de la probeta. En este punto, los datos obtenidos en el ensayo son recogidos y se muestran gráficamente mediante una curva tensión-deformación y una curva tenacidad-propagación de la grieta.

Con los datos recogidos, las gráficas y observando las superficies de fractura de las probetas, se pudo determinar el efecto final de las nanofibras sobre el adhesivo, así como los posibles problemas que puedan aparecer durante todo el proceso, obteniendo unas conclusiones del estudio.





### **Resultados**

En los ensayos se ha podido observar el incremento de la tenacidad a fractura de la resina gracias a las nanofibras; sin embargo, algunas de las pruebas realizadas han fallado debido a la fractura adhesiva (rotura interfacial entre el aluminio y la resina) obtenida, en lugar de la rotura cohesiva (por el interior del adhesivo), que era necesaria para que las nanofibras desarrollasen todo su potencial.



### **Conclusiones**

La efectividad de la mejora de la tenacidad a la fractura utilizando nanofibras se demostró a pesar de que no funcionó para todas las muestras. Se observó que, en algunos casos, la grieta no progresó a través de las nanofibras, sino que se produjo una fractura interfacial entre la superficie y el adhesivo.

En estudios posteriores, el potencial del nano-refuerzo puede desarrollarse con un control más cuidadoso en el modo de fractura ya que, con una fractura cohesiva, la tenacidad del adhesivo puede duplicar el valor de la resina virgen. Además, el pretratamiento debe estudiarse a fondo, para comprobar si el desengrasado es necesario y si modifica las propiedades mecánicas de las superficies tratadas.

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## Summary

1. Objectives .....	14
2. Background and State of the art .....	16
2.1. Mechanisms of adhesion .....	16
2.2. Advantages and disadvantages of adhesive bonding .....	17
2.3. Methods to increase the joint toughness.....	18
2.3.1. Nanoparticles.....	18
2.3.2. Nanofibers .....	21
2.3.3. Other type of nanostructures on adhesive toughening .....	22
2.4. Production of nanofibers .....	22
2.5. Electrospinning process.....	25
2.5.1. Parts of the electrospinning apparatus.....	25
2.5.2. Electrospinning process .....	25
2.5.3. Electrospinning parameters .....	26
2.6. Pre-treatments.....	28
2.7. Relationship between the thickness of the adhesive layer and the strength of the adhesion.....	31
2.8. Double cantilever beam test .....	32
3. Methodology.....	35
3.1. Selection of the pre-treatment and the aluminium alloy .....	35
3.2. Fabrication of the specimens .....	35
3.3. Pre-treatment of the specimens and bonding process .....	35
3.4. Production of the nanofibers .....	36
3.5. Resin cure process .....	36
3.6. Double Cantilever Beam (DCB) test.....	36

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4. Production.....	37
4.1. Selection of the epoxy resin .....	37
4.2. Selection of the Pre-treatment and aluminium alloy .....	39
4.2.1. Preparation of the solutions.....	39
4.2.2. Pre-treatment Test .....	40
4.2.3. SEM microscope observations .....	41
4.3. Fabrication of the specimens .....	43
4.3.1. Support fabrication.....	45
4.4. Pre-treatment of the specimens .....	46
4.4.1. Caustic soda solution.....	47
4.4.2. P2 etching solution .....	48
4.5. nanofiber mat production .....	50
4.5.1. Preparation of the solution .....	51
4.5.2. Electrospinning process .....	51
4.6. Bonding process .....	52
4.6.1. Mixture of the resin and the hardener .....	52
4.6.2. Bonding of the substrates .....	52
4.6.3. Curing.....	55
4.6.4. Thickness measure .....	57
4.7. Resin curing.....	61
4.8. DCB test .....	62
5. Results and discussion.....	65
5.1. Specimen type 1 – DCB test.....	65
5.2. Specimen type 2 -DCB test .....	67

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5.3. Specimen type 3 - DCB test .....	69
5.3.1. Batch 0 .....	69
5.3.2. Batch 1 .....	71
5.3.3. Batch 2 .....	74
5.3.4. Batch 3 .....	76
5.3.5. Batch 4 .....	78
5.3.6. Batch 5 .....	80
5.3.7. Batch 6 .....	82
5.4. Overall results.....	84
6. Conclusions .....	86
7. Bibliography.....	87

# 1. Objectives

The main objective of this work is to increase the toughness of adhesive bonded joints in mode I fracture, by the use of electrospun nanofibers in an epoxy matrix. To make that, different parameters will be studied and analysed, in order to obtain a more resistant adhesion between two aluminium specimens. Those parameters are:

The nanofibers → The introduction of nanofibers in the polymer to reinforce the adhesion between the adhesive and the adherent, is a technique that has been developed over the recent years, since they provide the polymer a large surface area to volume ratio, flexibility, and better mechanical performance.

By a state of the art study, different types of nanoparticles, and more concretely nanofibers, will be analysed to have a larger knowledge of the different characteristics and properties that they have when in contact with the adhesive, and also the advantages they provide to the adhesion.

The pre-treatment → The main requirements for a high bond strength and lasting durability reside at the interface between the substrate and the adhesive. Preparing the surface chemically helps the adhesion. So, one of the objectives is to find, experimentally, the pre-treatment that produces the best chemical preparation of the surface, in order to obtain a bigger penetration of the adhesive on it.

Type of resin → The adhesive used to perform the adhesion is an epoxy resin provided by the company Elantas. The resin must be chosen from their catalogue according to the needed viscosity and ductility to increase the bonding strength.

Thickness of the adhesive → Different thicknesses from the bond line will be studied in order to find a relationship between them and the fracture toughness of the adhesive joint. A research in other investigations will be done in order to have a base and understand the effect of this parameter in the adhesion.

Those last three points, as is already said in some of them, will be experimentally studied by: producing the aluminium specimens, treating them with the pre-treatment, bond and then test them with a mode I fracture test known as DCB (Double Cantilever Beam) in which, by applying a tension force perpendicular to both of the bonded substrates, the crack

of the joint will be obtained, and the fracture toughness will be measured. Then, the surfaces of the aluminium specimens will be observed with a SEM microscope in order to study the aspect of the fracture surface and provide some conclusions to the studies carried out.

## 2. Background and State of the art

Adhesive bonding methods to join metals, are becoming increasingly used in the recent years by aerospace and automotive industries, due to its advantages over the traditional technologies such as welding, soldering or fastener applications.

On this chapter, different points will be considered in order to understand better the steps carried out in this study:

- The different theories about how the bonding between two materials is formed.
- The pros and cons of adhesive bonding will be shown, followed by how the toughening can be improved with the use of nanoparticles and nanofibers.
- Obtention of nanofibers, and how do they affect adhesive properties.
- A deep research of how pre-treatments of the surface affect bonding, and also the relationship between the thickness of the adhesive layer and the strength of the adhesion.
- An explanation of the test used to verify the toughness of the bonded specimens.

### 2.1. MECHANISMS OF ADHESION

There are several theories of adhesion to explain how the adhesive bond between two materials is formed. In [1] Silvia G. Prolongo et al. explain the different mechanisms of adhesion that can be considered:

- Mechanical interlocking: this theory suggests that the adhesion is directly related to the toughness of the substrate.
- Diffusion theory: this theory considers that two polymers, or a polymer and a solvent, are miscible when they have similar solubility parameters.
- Electronic theory: When the surfaces to bond are metals, the different nature of the materials, the metal and the polymer, facilitates the transfer of electrons from the metal to the polymer, forming an electric double layer at the interface.



- Adsorption theory: Proposes that, the materials will adhere because of the forces between atoms and molecules in the surface of the adhesive and substrate. This means that the adhesive has to spread over the surface.

## **2.2. ADVANTAGES AND DISADVANTAGES OF ADHESIVE BONDING**

Nowadays, the constant technological development is making traditional methods take a second place to the new joining techniques. The necessity to join dissimilar substrates, complex structure forms, or new materials that are most often unsuitable for joining; as well as the necessity to reduce the structure weight, costs and time, has developed a higher interest in adhesives.

As it is described in [1], adhesive joints offer many advantages, with regard to other joining methods, such as welding, brazing, riveting or bolting:

- Adhesives distribute stress across the bond line while mechanical fasteners create stress concentration points which lead to premature failure.
- Minimize or eliminate secondary operations such as punching holes required with many fastener applications, reducing the costs and time needed to those subsequent processes.
- Allow to join dissimilar materials without structural changes of the joined substrates.
- Adhesives are composed by lightweight polymers, while welding and most mechanical fasteners contain metals.
- They also have a greater aesthetic than fasteners, since adhesives are hidden between substrates providing a beautiful exterior.

They also have some drawbacks:

- In order to attain a long service-life in hostile environments, surfaces of the adherends must be carefully prepared.
- Limitation on upper service temperature.
- Disassembly cannot be carried out without generating some damage to the joint.

- Heat and pressure may be required for assembly.
- Jigs and fixtures may be required for assembly.
- The joint strength is relatively low compared to mechanical joints.

### **2.3. METHODS TO INCREASE THE JOINT TOUGHNESS**

This study is based on solving the last drawback mentioned on the previous point, the low strength of adhesive joints compared to mechanical joints.

To increase the toughness of the adhesion, three main processes can be followed:

- Use of nanoparticles
- Use of nanofibers
- Chemical modification of resin toughening

This investigation is related to the increase of the toughening by developing the two first points. The third point is developed by the company which supplies the resin, Elantas. Chemical modification of resin consists on the addition of liquid modifiers which react with the resin to increase the toughness.

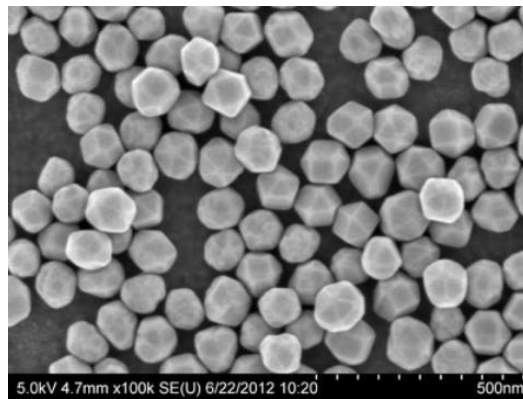
In the recent years, the addition of nanofibers and nanoparticles in the adhesive matrix has received considerable interest as a promising option to improve the fracture toughness of adhesives, among others.

#### **2.3.1. Nanoparticles**

Nanoparticles are particles with 1 to 100 nano-meter size with a surrounding interfacial layer, which are of great interest in science as they are a bridge between bulk materials and molecular structures.

As it is explained in [2] physical properties of bulk materials should keep constant regardless of their size, but in nano-scale some different properties are often observed. Therefore, material properties change as they approach the nanoscale size when the ratio of the surface in relation with the volume of a material becomes significant. These size-dependent properties have the following results in the adhesive:

- Increase the elastic modulus and adhesion strength, the interaction between nanoparticles and the polymer matrix can generate microstructures, improving the mechanical properties and prevent the rapid crack propagation.
- Enhance their interaction with the matrix through chemical bonds.
- The increase of the surface-volume ratio provides a bigger interface area without increasing the dimensions or weight of the components; and also reduces the probability to find imperfections, increasing the adhesion.



Picture 2-1 Standard gold nanoparticles

Different types of nanoparticles are used to increase the toughness of the adhesive.

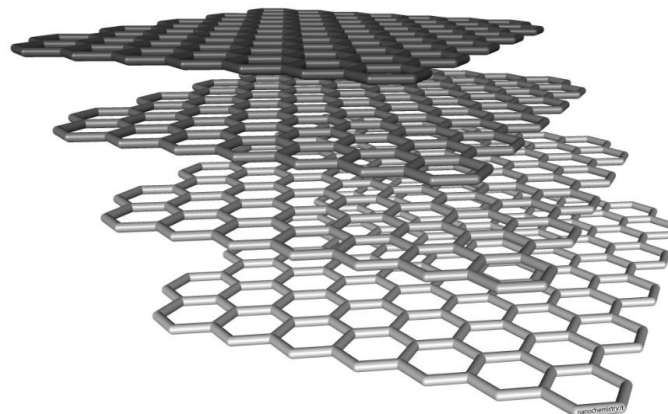
Rubber, for example, has an extended use on the reinforcing of epoxy resins. There are two conventional methods for the modification of epoxies using rubber [3]: use reactive oligomers (liquid rubber) or use pre-formed elastomeric particles. These particles, when used in place of liquid rubbers, provide better thermo-mechanical properties.

Core Shell rubber nanoparticles have been studied by Dong Quan et al. [4]. This type of nanoparticles changed the fracture of the adhesive from unstable to stable. Also, different percentages in volume of CSR were added to the epoxy to study the effect on the bonding of two mild steel plates, and it was observed that the addition of 30%vol of nanoparticles increased the toughening of the adhesive compared to the neat epoxy.

Other type of nanoparticles widely used are silica nanoparticles. These nanoparticles can produce comparable or even greater improvement in fracture toughness but without losing stiffness and strength at elevated temperatures compared to rubber particles, as Qingshi Meng et al. mentions on [5]. On this article, DCB tests with aluminium as adherend and epoxy resin as adhesive (using two different hardeners), were performed obtaining an increase on the toughness as the nanoparticle volume increase, with respect to neat epoxy.

Another research by Soran Hassanifard et al. [6] carried out applying uniaxial test procedures and single-lap joints to measure the bonding strength on carbon fibre-reinforced plastic (CFRP)-epoxy bonded specimens, obtained an increase of the bonding strength by 22% with 2wt% of silica nanoparticles.

A different kind of nanoparticles studied on recent years is the nanoplatelets, concretely graphene nanoparticles. These nanoparticles are comprised of short stacks of platelet-shaped graphene sheets that are identical to those found in the walls of nanotubes, but in a planar form.



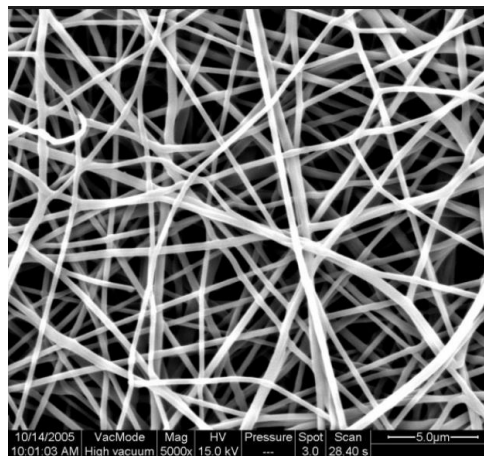
Picture 2-2 Nanoplatelets morphology

This type of nanoparticle was used by H. Khoramishad to study its effect on the fracture behaviour of adhesively bonded joints [7]. On this investigation, a DCB test was used to obtain the fracture energy on the debonding of aluminium-epoxy samples with different percentages of nanoparticles added to the resin. The result was an increase on the fracture energy in comparison with the neat epoxy (0.2997 kJ/m<sup>2</sup>), obtaining the maximum value for the 0.3 wt% of GOPs (0.4749 kJ/m<sup>2</sup>).

### 2.3.2. Nanofibers

Nanofibers are fibers with a diameter in the nanometre range. These fibers can be obtained from different type of materials such as natural polymers, synthetic polymers or nano-materials based on carbon.

Nanofibers produced with electrospinning technique provide epoxy the same properties as nanoparticles, but in this case, since the fibers are larger, the length-diameter ratio is more extreme respect to nanoparticles. This factor avoids stress concentration and allows superposition of fibers, increasing the stiffness.



Picture 2-3 SEM image of nanofibers

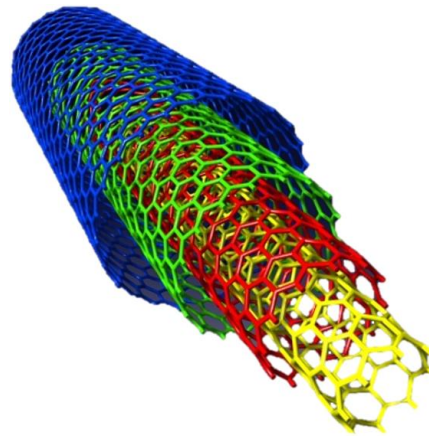
As there exist a huge variety of nanofibers used to enhance the toughness of epoxy, this state of the art is focused on some of those, which are used on different articles, to increase the strength of the adhesion between aluminium samples and epoxy, since it's what will be studied on this investigation.

- M. Ekrem et al. [8] used polyvinyl alcohol nanofibers (PVA) to increase the strength and fracture toughness of epoxy adhesive joints. On this study, PVA nanofibers were obtained by electrospinning, and they were added to the epoxy used to bond two aluminum samples. The results obtained using DCB and SLJ tests were a cohesive failure of the epoxy with the PVA nanofiber, and an increase on the fracture toughness and strength adding 10w/w% of PVA to thee resin, with reference to the neat epoxy (from 0,252 kJ/m<sup>2</sup> to 0,497 kJ/m<sup>2</sup>).

Another type of nanofiber is PAN, and their effect on the fracture of the epoxy was studied by S.M.J. Razavi et al. [9] The nanofibers were obtained by electrospinning directly on the adherend surface. Using a DCB test, they obtained an increase of the final toughness of the 127% using 2g/m<sup>2</sup> of nanofibers with respect to the neat epoxy resin.

### 2.3.3. Other type of nanostructures on adhesive toughening

Multi-walled carbon nanotubes (MWCNTs) are elongated cylindrical nanoobjects made of sp<sup>2</sup> carbon. Their diameter is 3–30 nm and they can grow several cm long, thus their aspect ratio can vary between 10 and ten million.



Picture 2-4 Nanotube morphology

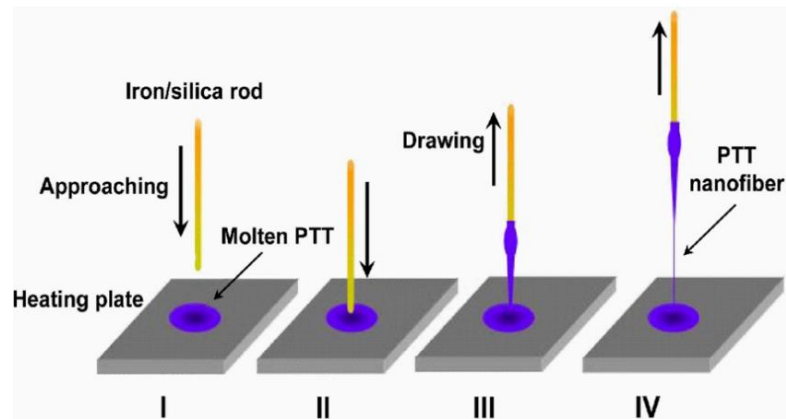
These nanotubes were also used by H. Khoramishad on another study, in this case, to investigate their effect on the fracture toughening of Aluminum-epoxy samples [10]. Using different weight percentages of nanotubes to reinforce the resin, and debonding the specimens with a DCB test, it was observed that the maximum improvement in the adhesive fracture energy was obtained for 0.3wt% of MWCNTs with respect to the neat epoxy.

Using a SEM microscope, it was observed that MWCNTs agglomerations generate high local stress concentrations in the epoxy adhesive and caused the fracture energy to decrease in the adhesives reinforced with higher quantity of nanotubes.

## 2.4. PRODUCTION OF NANOFIBERS

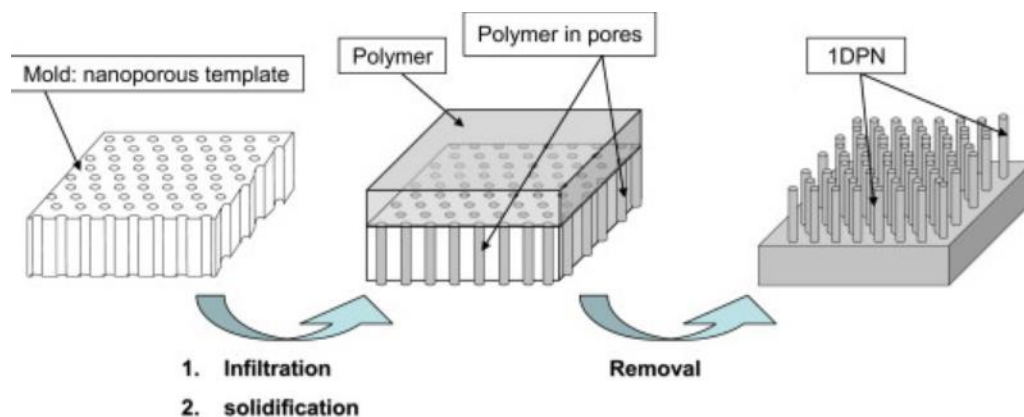
Nowadays, there are several processes to obtain nanofibers [11], the most important are:

Drawing → A micropipette and micromanipulator are used to stretch nanofibers from a solution deposition. It is a discontinuous process and the dimensions of the fibers can't be controlled.



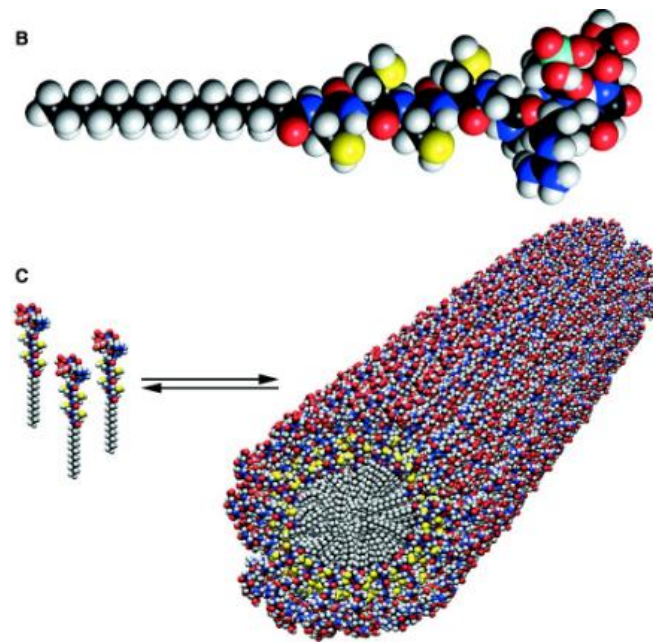
Picture 2-5 Nanofibers drawing process

Template synthesis → Templates or membranes are used to obtain the nanofiber materials. The solution is extruded through the nanometric-size holes in the membrane, allowing to control the diameter of the nanofibers by choosing the diameters of these holes.



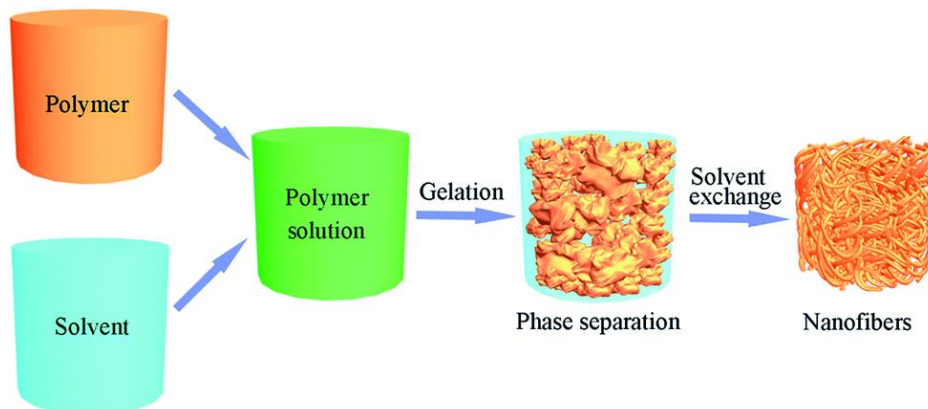
Picture 2-6 Template synthesis of nanofibers

Self-assembly → A structured filament is created by the addition of chemical reactants to the solution, producing an automatic disposition of molecules along to a predefined direction.



Picture 2-7 Formation of nanofibers by self-assembly

Phase separation → A gelation process happens when a polymer is mixed with solvents. This gelation generates the separation of phases, due to the incompatibility of the component's phases in the solution. The nanofibers are extracted once the gelation is finished.



Picture 2-8 Phase separation of nanofibers

Electrospinning → The nanofibers are obtained by stretching the solution through a needle supplied by a syringe above a collector, using electric forces. This technique is nowadays the most interesting process to obtain nanofibers.



## 2.5. ELECTROSPINNING PROCESS

As it was mentioned before, the electrospinning technique is the most used processes to generate nanofibers and the one that will be used in this study, hence it must be explained in detail.

Is a technique that consists on the application of a high electric fields, from 10 to 30 kV, applied to polymer solutions or melts, in order to produce fibers with a diameter in the range of nano and micrometres.

### 2.5.1. Parts of the electrospinning apparatus

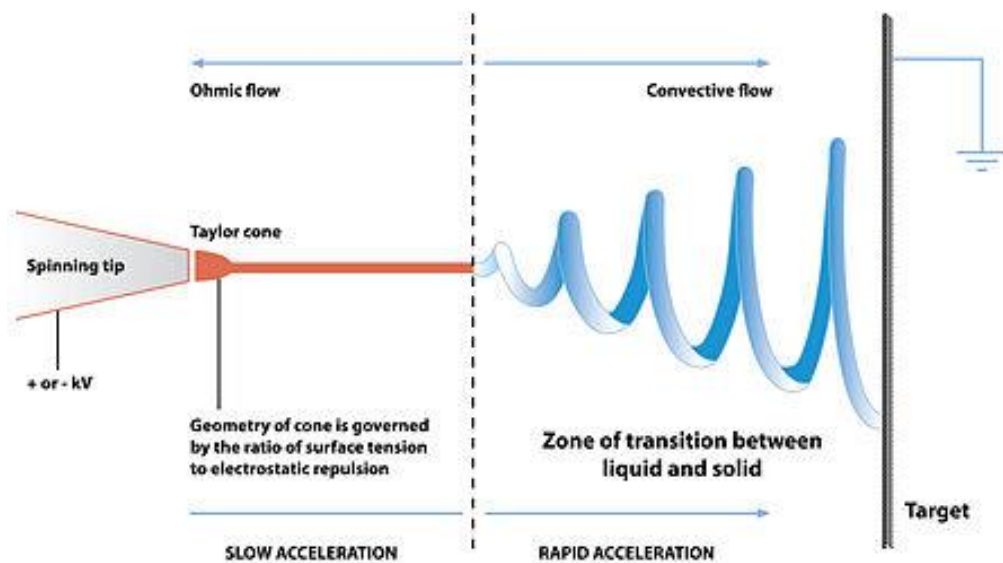
The main components of the machine are:

- High voltage generator → connected with the solution's ejection system.
- Pumping system → composed of one or more pumps acting on the syringes filled with the solution. These syringes are in turn connected to needles with calibrating dimensions.
- Collector → the electrospun nanofibers are collected in a surface, which is usually grounded and acts also as counter-electrode.

### 2.5.2. Electrospinning process

As it is explained in [12], [13] and [14], the electrospinning process is based on the application of a high electric field between the needle and the collector.

The solution inside the syringe is pushed through the needle thanks to a pump. As the intensity of the electric field increases, the solution drop at the tip of the needle elongates and forms a conical shape known as Taylor cone. At this point, the electric field reaches a critical voltage level where the electric forces overcome the surface tension of the drop, and the solution is ejected through the needle. During the flight, the solvent evaporates and the charged polymer fiber is deposited in the collector, located perpendicularly to the needles, forming a non-woven mat of nanofibers.



Picture 2-9 Fiber formation with electrospinning

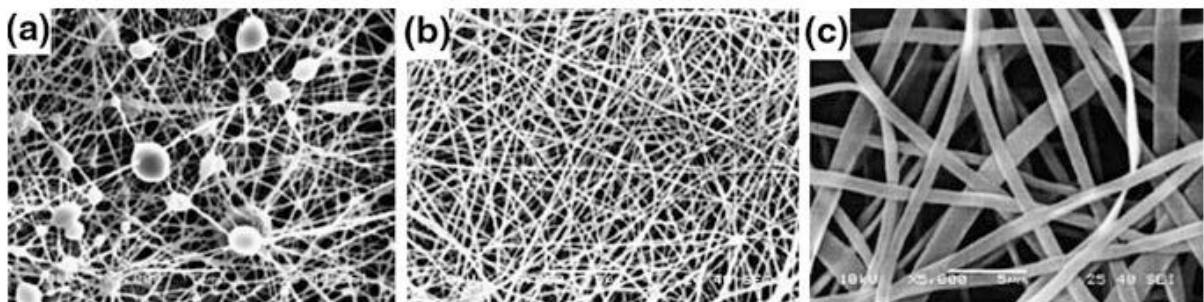
### 2.5.3. Electrospinning parameters

The morphology and diameter of the electrospun nanofibers can be controlled by modifying several parameters. Some of these parameters are related to the polymer solution, and others are related to the process. Details can be found below, based on [15], [16]:

#### Parameters related to the solution

- Concentration → The concentration of polymer in the solution plays an important role, since the final nano material obtained will have different aspect and properties depending on that concentration. Exist four critical concentrations, reported from low to high:
  1. With a very low polymer concentration, nano particles will be obtained by electrospray and not electrospinning process, due to the low viscosity and high surface tension of the solution.
  2. Little higher concentration generates a mixture of beads and fibers.
  3. With a consistent concentration, smooth nanofibers can be obtained.
  4. If the concentration is very high, instead of nanofibers, helix-shaped micro-ribbons will be generated.

- Molecular weight → The molecular weight of the polymer has also an effect on the final particles morphology. With the concentration fixed, a low molecular weight generates beads rather than smooth fibers, which will be obtained increasing that parameter. If the molecular weight is too high, micro-ribbons will be obtained.



Picture 2-10 SEM images showing different structures of electrospun nanofibers with different molecular weights

- Viscosity → Is the critical key in determining the fiber morphology. Low viscosity will not enable the smooth nanofibers to be achieved, and high viscosity supposes a hard ejection of the solution through the needles. It is necessary to find a suitable viscosity for the electrospinning process, and it depends closely on the polymer concentration and the molecular weight.
- Surface tension → Fixing the concentration, a reduction on the surface tension of the solution can transform beaded fibers into smooth fibers. The reduction of this parameter can be obtained using a surfactant or a solvent/solvent mixture with a lower surface tension.
- Conductivity/Surface charge density → On the polymer type, solvent sort and salt, depends the conductivity. Usually, with natural polymers, poor fibers are obtained, due to the high tension under the electric field generated by the increase on the charge carrying ability of the polymer jet. These poor fibers can be enhanced with the aid of ionic salts, which reduce the diameter of the fibers. Also, a high conductivity can be achieved with the use of organic acid.

### **Parameters related to the process**

- Voltage → An applied voltage higher than the threshold voltage is needed to charge the solution ejected from the Taylor cone. The threshold voltage is the limit below which no electrospun process will occur.
- Flow rate → Another important parameter is the flow rate with which the solution ejects from the needles to the collector. Lower flow rates allow for a better polarization of the solution. Very high flow rates will provide bead fibers instead of the desired smooth fibers with a small diameter.
- Distance needle tip/collector → This distance also affects the electrospinning process. With too short distance, the fiber will arrive to the collector without a complete solidification. With too long distance, bead fibers will be obtained.
- Ambient parameters → Humidity and temperature can also influence the process. With a higher temperature the diameter obtained will be smaller. Related to humidity, low humidity may dry the solvent completely and increase the evaporation velocity of the solvent. High humidity will generate a thicker diameter of the fiber.

## 2.6. PRE-TREATMENTS

As said before, to obtain a high bond strength in the adhesion, a good interface between the aluminium layers and the epoxy is needed. To obtain this optimum boundary, different pre-treatments of the metal specimens can be carried out. Also, depending on the type of aluminium alloy the treatments can have a better or worse reaction, relying upon the concentration percentage of the metals that it contains.

The pre-treatments give the surfaces an increase of the initial adhesive bond strength of the aluminium joints. These processes involve the elimination of contaminants in the interlayer, which can make it weaker, by cleaning the surface. With aluminium specimens, these treatments can be segregated into three groups, depending on the final results that are wanted to reach: simple cleaning and abrading, chemical etching, and primers and conversion coatings. [17]

### Simple cleaning and abrading

The simple cleaning and abrading involves the elimination of the contaminants and the oxide, exposing the bare aluminium. This treatment is useful for low-moderate strength aluminium joints, when permanence is a primary consideration, like they improve bondability and maintain protection. They are also used as a previous step to chemical etching. There are three main procedures on this category:

- Degreasing → is normally performed using solvents to remove heavy soils without having an impact on the chemical structure surface. One of the most effective procedures is vapor degreasing, which uses solvents in a vapour form to clean efficiently the aluminium surface.
- Alkaline cleaning → Uses an immersion of the workpiece into an alkaline solution. This method is used to remove gross contamination, especially organic materials such as protecting oils and machining lubricants by solubilizing these contaminates.
- Abrasives → The intention of the abrasive treatment is to remove oils and friable materials, in addition to increase the surface area. Sandblasting is an example of this kind of cleaning, which uses sandpaper to remove the oxide layer of the aluminium surface.

### **Chemical etching**

With the chemical etching, the aluminium specimens could be protected also from the effects of environment, especially water and corrosion, thanks to the formation of an artificial oxide layer in the surface. This process has been considered the most effective way to obtain good and durable adhesion between aluminium layers.

A large number of fine pores occur in the oxide layer during the treatment, generating an increase on the surface area and in consequence, a higher bonding strength.

In this category, different procedures can be highlighted. The sulfuric acid-dichromate (FDL etch) and the Chromic acid anodize are the most recognized chemical pre-treatments for bonding aluminium joints.

- Sulfuric acid-dichromate (FDL etch) → This process is the most recognized etching pre-treatment of aluminium surfaces in structural adhesive bonding. Is a solution of a dichromate salt in sulfuric acid, preceded by an alkaline detergent bath and a rinse bath. The different parameters that can modify the treatment are the temperature, the etching time, the type of rinse water, the dichromate salt and the level of contaminants in the bath [18].
- Chromic acid anodize (CAA) → Is an electrolytic passivation process used to generate an increase on the natural oxide layer thickness in the aluminium surface. The specimen that will be treated forms the anode electrode of the electrical circuit and the electrolyte where is immersed should consist of 50-100 g/L chromic acid with a temperature of 95-105F [19].

These two pre-treatments described above are known to be harmful to health because of the content of chrome which is carcinogenic, so FDL etch and CAA are being phased out and other more environmentally friendly alternatives are being developed, such as:

- Sulfuric boric acid anodizing (BSAA) → Is a chrome-free alternative to the chromic acid anodize that results in a thin oxide layer with optimal adhesion properties and good a corrosion resistance [20]. This treatment has been introduced as an alternative to the CAA treatment. The oxide film from the boric-sulfuric electrolyte has an adhesion that is equal, or superior, to the one formed on chromic acid [21].
- Sol-gel process → Consists in stablishing an aluminium-oxide based coating using inorganic ceramics. This process is a good alternative due to the environmentally friendly production and non-toxicity.
- P2 etch → Is a chemical pre-treatment which uses a solution of sulfuric acid and ferric sulphate. This kind of treatment provides similar results on the surface to chromic acid etch, but with no toxic chromates, which makes it more environmentally friendly and safe.

### **Primers and conversion coatings**

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Both procedures are coatings applied on the surface of the aluminium specimen in order to protect the surface from environmental effects. In the case of the conversion coating, it is produced by a chemical or electrochemical process.

## **2.7. RELATIONSHIP BETWEEN THE THICKNESS OF THE ADHESIVE LAYER AND THE STRENGTH OF THE ADHESION**

There are two types of adhesion failure: adhesive failure, when the crack appears on the interface adhesive-adherend; and the cohesive failure. This second one occurs on the bulk adhesive, the crack appears inside the resin, generating a higher fracture strength than the adhesive failure. Hence, to get a higher fracture toughness, it's necessary to have a cohesive failure of the joint, rather than adhesive debonding. These two types of failure of the adhesion are quite related with the thickness of the adhesive layer (among other factors).

There are several researches about the relationship between the thickness of the adhesive layer, and the strength of the adhesion. The main idea that can be obtained from all of them is: there is a limit value of layer thickness that, if exceeds, the fracture toughness decreases.

However, the interpretation of the variation on material properties can be complex, as there are various factors that can modify the behaviour of joints when their thickness is increased, as it is explained in [22]:

- The dimensions and the nature of defects may vary with adhesive thickness.
- Differences in the curing conditions of the resin may change the adhesive structure as thickness increases.
- Internal stresses developed at the interface will modify the adhesive-substrate interface properties as thickness increases.
- The variation on the distance between the substrates will modify the energy dissipating mechanisms as plasticity and damage development.
- The change in specimen geometry may cause a change in the stress state when increasing bond line thickness, so the tests performed on specimens with different thicknesses are not measuring the same properties.

In [23], Ramazan Kahraman et al. observed that, using a single lap joint test to measure the shear strength of the adhesion between aluminium and Fusor 309 epoxy if the thickness was increased from 0.03mm to 1.3mm resulted a decrease of about 35-40% in adhesive joint shear strength. However, the effect was not significant for adhesive thickness up to 0.7 mm.

Kawashita et al. [24] used an arm peel test, to observe the effect of 3 different thicknesses (0.1, 0.25, 0.4 mm) of the bond line below the optimal thickness, between aluminium substrates and two different types of epoxy resin. The toughness increased with thickness.

## 2.8. DOUBLE CANTILEVER BEAM TEST

The double cantilever beam (DCB) test is a standard method to obtain the mode I fracture energy of adhesive bonds, in other words, it measures the fracture toughness in presence of flaws [25]. This test is carried out by creating an initial crack on the bond line between the metallic substrates, by inserting a wedge. The specimens are then loaded with a tensile axial load, which increases in time, and generates the separation of the beams enhancing their deflection. At a certain critical load, the crack begins to propagate rapidly. At this point, the load is stopped, and the crack growth curve is followed on the chart. When the load has achieved an approximate constant value, the crack has stopped growing and the following values must be determined and recorded:

- Load when the crack starts.
- Load when the crack stops.
- Distance from loading end of the specimen to the stationary crack tip.

The ASTM method calculates the value of the fracture toughness on the basis of elastic stress analysis and hold for a sharp-crack condition under severe tensile restrictions. It is assumed that the plastic region of the crack-tip is small if compared with the size of the crack.

The fracture toughness is computed for the initiation of the crack, where the load is maximum, and for the moment when the crack propagation stops (arrest load):

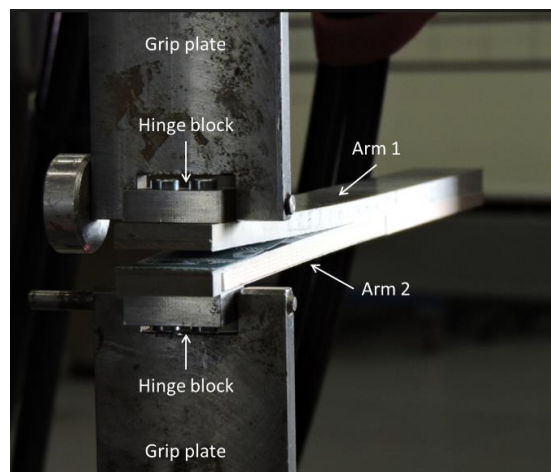
$$G_{Ic} = \frac{[4L^2(\max)][3a^2 + h^2]}{EB^2h^3} [J/m^2]$$



$$G_{Ia} = \frac{[4L^2(\min)][3a^2 + h^2]}{EB^2h^3} [J/m^2]$$

Where:

- $G_{Ic}$  → Fracture toughness from load to start crack
- $G_{Ia}$  → Fracture toughness from arrest load
- $L(\max)$  → Load to start crack (N)
- $L(\min)$  → Load at which load stops growing (N)
- $a$  → crack length (mm)
- $h$  → thickness of adherends (mm)
- $B$  → Specimen width (mm)
- $E$  → Tensile modulus of adherend (MPa)



Picture 2-11 Double Cantilever Beam for mode I fracture

In [26] the energy release rate of the DCB is expressed directly in terms of the moment  $Pa$  and the bending stiffness of the cantilever beams  $EI$ . The formula is expressed as follows:

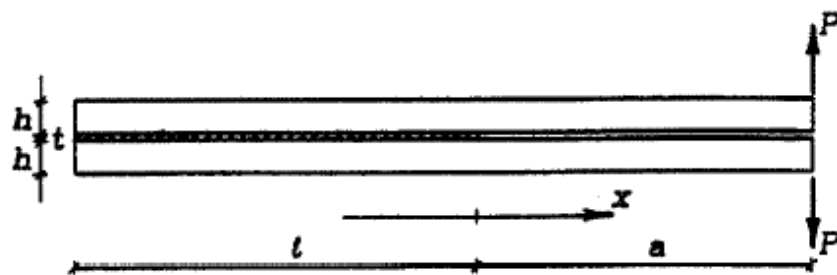
$$G_I = \frac{(Pa)^2}{bEI} \left(1 + \frac{1}{\lambda_0 a}\right)^2$$

Where:

$$\lambda_0 = \sqrt[4]{\frac{k}{4EI}} = \sqrt[4]{\frac{6 E'_a}{h^3 t E}}$$

- $h$  → thickness of adherends (mm)

- $a \rightarrow$  crack length (mm)
- $E \rightarrow$  Tensile modulus of adherend (MPa)
- $k \rightarrow$  Spring stiffness (N/mm)
- $t \rightarrow$  Adhesive layer thickness (mm)
- $EI \rightarrow$  Bending stiffness of an individual beam (N/mm)
- $E'_a \rightarrow$  Plain strain value of the adhesive elastic modulus  $E'_a = E_a / (1 - \nu_a^2)$



Picture 2-12 Parameters for DCB test in Mode I

### 3. Methodology

The methodology followed is described in this chapter, in order to have a first view of the process carried out on the study.

#### 3.1. SELECTION OF THE PRE-TREATMENT AND THE ALUMINIUM ALLOY

In this study, different types of pre-treatments have been carried out in different types of aluminium specimens to check in which of them have the best reaction, to obtain the roughest surface as possible, and to produce the DCB specimens in the best aluminium alloy. First, some of the sample's surfaces are abraded with sandpaper and others are milled with a milling machine; then an immersion in a caustic soda and distilled water solution is made to remove the grease and oils that could be embedded on the surface. Finally, a chemical etching, P2etch, is completed to obtain the final surface of the aluminium.

These treatments are tested in small pieces of different types of aluminium alloys to check in which of them the process responds better. The whole process is developed and explained in point 4.

#### 3.2. FABRICATION OF THE SPECIMENS

Once the aluminium is selected, the next step in the study is to fabricate the specimens which are going to be bonded. Those pieces must follow some requirements collected in the ASTM (American Society for Testing and Materials) standards, concretely in ASTM B209 for the aluminium and aluminium-alloy sheet and plate, and D3433 about standard test method for fracture strength in cleavage of adhesives in bonded metal joints.

Following these norms, eight specimens have been produced in order to treat, bond and test them to see the behaviour.

#### 3.3. PRE-TREATMENT OF THE SPECIMENS AND BONDING PROCESS

The specimens are treated with the caustic soda solution and the P2etch, and then they are bonded using the epoxy provided by Elantas, in particular, AS53 with AW09 as hardener in a ratio 100/50 wt%.

The specimens are bonded in pairs, in order to test at least one batch with virgin resin and one batch with nano-reinforced resin and compare the results obtained in both cases.

Then, they are placed on the support, which is introduced in the vacuum bag, and everything is introduced on the oven for the curing process of the resin.

### **3.4. PRODUCTION OF THE NANOFIBERS**

The nano-mat will be produced using the electrospinning process with Nylon as nanofiber polymer. The parameters of the electrospinning machine will be set in order to have an efficient process and to obtain the desired thickness of nanofibrous mat.

### **3.5. RESIN CURE PROCESS**

At the same time that the vacuum bag with the specimens inside is introduced in the oven, the extra resin which is left over from the bonding process, is placed in a vessel and it is also introduced in the oven, to verify its complete cure.

A three-point test is performed to the cured resin, to verify its rigidity.

### **3.6. DOUBLE CANTILEVER BEAM (DCB) TEST**

Once the specimens are bonded and the resin is completely cured, the next step in the study is to test the batches and then compare the results to arrive to certain conclusions.

As there are several ways to test the fracture toughness, in this case it was decided to use a DCB test. As it was already explained in chapter 2, the DCB test consists on the application of a tensional axial force on the end of the batch, where the Teflon laminate is placed. The axial force initiates the crack, and while the tension increases, the crack propagates generating an adhesive or cohesive failure of the joint, until the collapse of the batch. The values of the axial force, fracture toughness, time and crack propagation are collected by a computer, and then exported to an excel file where a force-displacement graph shows the failure behaviour.

## 4. Production

### 4.1. SELECTION OF THE EPOXY RESIN

The choice of the resin was done by testing different types of epoxies with different viscosities and uses, provided by the company:

- EC152TIX: used for the impregnation for the production of composite materials. It is free of halogens and solvents. Has good mechanical characteristics, adhesion to aluminium laminates and thermal resistance. It has a low viscosity (5000-15000 mPas).
- AS46: It's an adhesive for materials with different natures. It has an excellent resistance to peeling, solvent-free, and provides resilient bonding. Its viscosity is high (38000-50000mPas).
- AS53: It's an adhesive for semi-rigid structural bonding. Solvent-free. Depending on the use, the resin-hardener ratio varies. It has a medium viscosity (12000-18000 mPas for 100/50% wt).

The test was performed impregnating with the different resins, nanofiber mats of Nylon with a thickness of 150um and introducing them on a vacuum bag for 20 minutes.

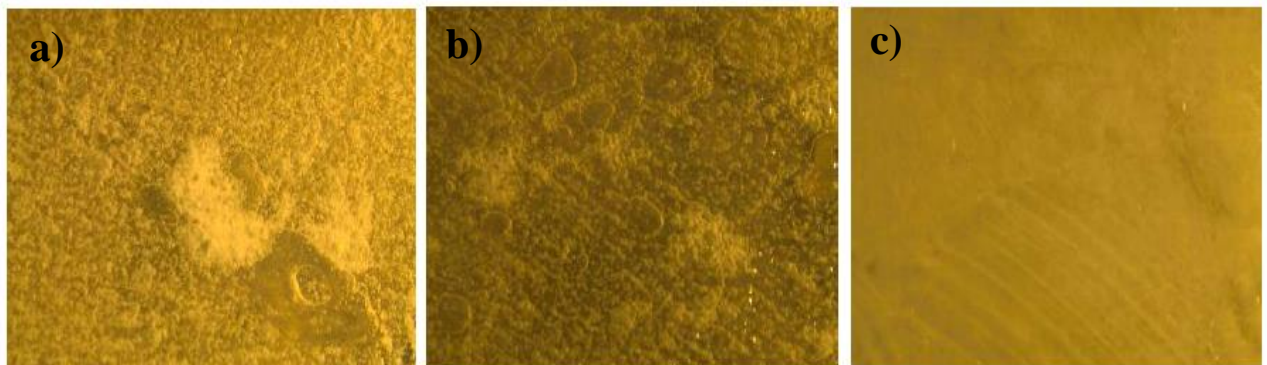
The resin and the hardener are mixed in a glass becker in the quantities suggested by the supplier. The nanofibers are impregnated with this mixture, pouring it on a large bowl and immersing the nanofibers on it in order to fully wet.

Once the nano-mats are completely wet, checking the transparency of the mat when picked up and exposed to light, they are introduced in a vacuum bag (Picture 4-1) and then fully cured, following the indications of the supplier.

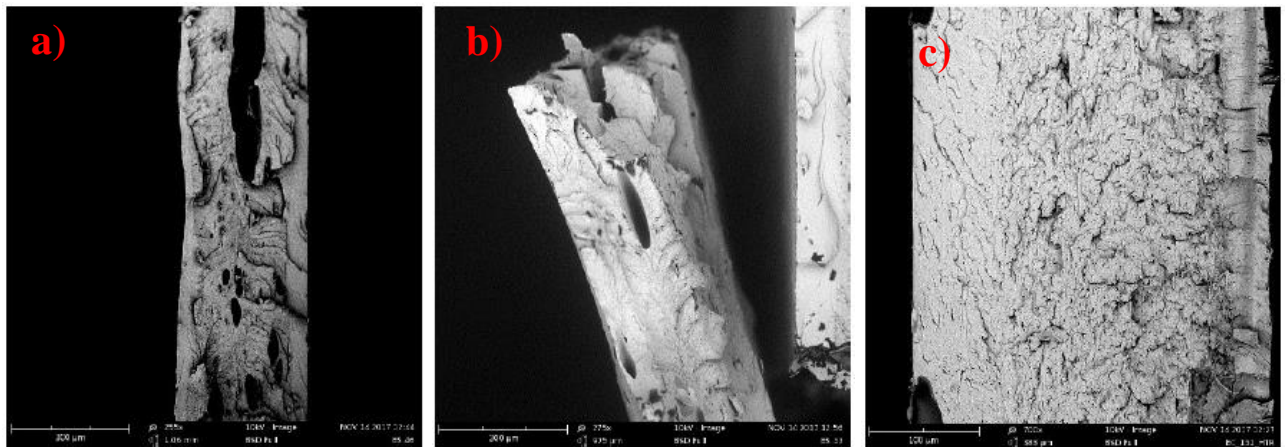


Picture 4-1 Vacuum bag with the impregnated nano-mats

After curing, the nano-mats are observed with an optical microscope to check the presence of air bubbles, then they are broken manually and examined with SEM. The results are shown in Picture 4-2 and Picture 4-3.



Picture 4-2 Optical images of the different resins. a) AS46/AW46. b) AS53/AW09. c) EC152TIX/AW192



Picture 4-3SEM images of the different resins. a) AS46/AW46. b) AS53/AW09. c) EC152TIX/AW192

Optical images show that resin EC152TIX Picture 4-2c) presents the minimum quantity of bubbles. However, since this adhesive is between an epoxy resin for wet layup and a structural adhesive, it was preferred to choose the medium viscosity resin AS53 although the images show a higher number of bubbles Picture 4-2b).

The following processes will be carried out using resin AS53 with hardener AW09.

## 4.2. SELECTION OF THE PRE-TREATMENT AND ALUMINIUM ALLOY

How it is already said in point 3, the pre-treatment was tested in small samples of different types of aluminium to verify that it has the expected results, and to check in which specimen has the best effect. Once the aluminium is selected, the DCB test samples will be fabricated.

### 4.2.1. Preparation of the solutions

#### P2 etch

The P2 etch preparation process is based on ASTM D256I standard guide for the preparation of metal surfaces for adhesive bonding.

Two different solutions of P2 etching are used in the test of the pre-treatment. The first one is a solution with a sulfuric acid concentration of 36%, and the other one has a percentage of acid of the 30%.

To obtain a litre of solution, 370g of H<sub>2</sub>SO<sub>4</sub> must be mixed with 150g of ferric sulphate and the sufficient distilled water.

In the process, the sulfuric acid must be added to the distilled water, and not the other way, paying attention to the increase in the temperature as it is an exothermic reaction.

When the addition of the acid is finished, the ferric sulphate is incorporated and the whole solution is mixed at room temperature until it is homogeneous.

### **Caustic soda**

The caustic soda solution is prepared mixing caustic soda with distilled water at room temperature. This solution is needed to remove the greases and oils that could be in the surface of the aluminium and achieve better results when the P2 etch process is applied.

#### **4.2.2. Pre-treatment Test**

##### **Test with AL2000 and Al 7075**

In a first test, 2 types of metal were used: Al2000 and Al7075. Two pieces of Al7075 and three of Al2000 were treated with sandpaper in one of their surfaces, and the other stayed virgin.

These specimens were immersed in the caustic soda solution for 5 minutes, and then introduced in distilled water for 5 more minutes.

When this process was finished, the P2 etch was developed. One piece of each aluminium alloy was introduced for 10 minutes in a solution of sulfuric acid + ferric sulphate. The resting sample of Al2000 was just treated with the caustic soda to see the effect of this treatment.

The final step was to put the samples in distilled water for other 10 minutes and then dry them with pressured air.

##### **Test with Al2024-T3**

This second test was done with another type of aluminium alloy, specifically AL2024-T3. Two pieces were done; one stayed virgin and the other one was milled.



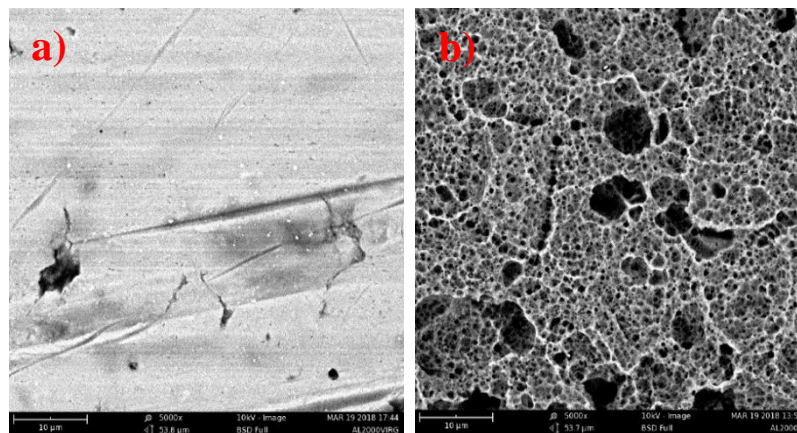
The process was the same as in the previous case, first the specimens were treated with caustic soda, then each piece was immersed in a different solution of P2 etch, to be finally dried with the pressured air.

#### 4.2.3. SEM microscope observations

When the tests were done, the SEM microscope was used to observe the outcomes in the surfaces. Different pictures were taken at diverse distances to check the results.

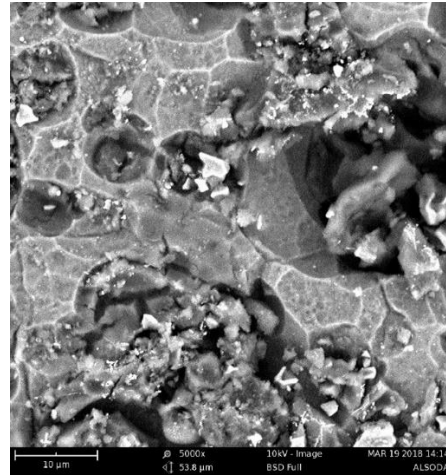
##### Al2000 observations

As it can be seen in the pictures, the specimens have responded correctly to the treatment. In image a) from Picture 4-4 virgin sample can be seen; it's surface is smooth with some imperfections. If it is compared with the picture of the treated specimen's image b) from Picture 4-4, it can be seen that the surface from the treated one, is rougher and full of holes, increasing the surface area, and so, increasing the posterior adhesive bond strength.



Picture 4-4 10 µm SEM images from the Al2000 specimens, a) virgin surface; b) surface treated with caustic soda and P2 etch.

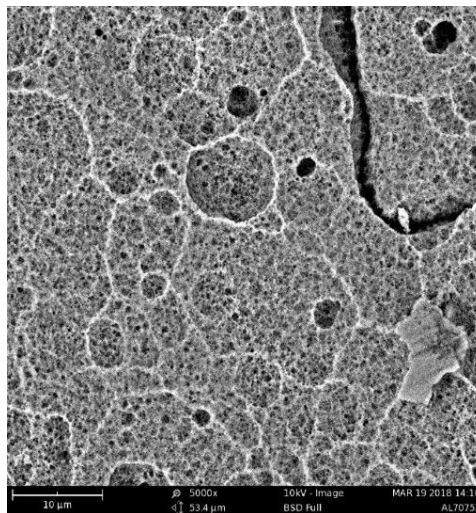
In Picture 4-5 the image from the Al 2000 treated just with caustic soda is seen. It can be observed that there are some holes and imperfections, but the surface is not enough rough; so, the effect of applying only the caustic soda treatment is not useful.



Picture 4-5 10 μm SEM image from Al2000 specimen treated with caustic soda

### **Al 7075 observations**

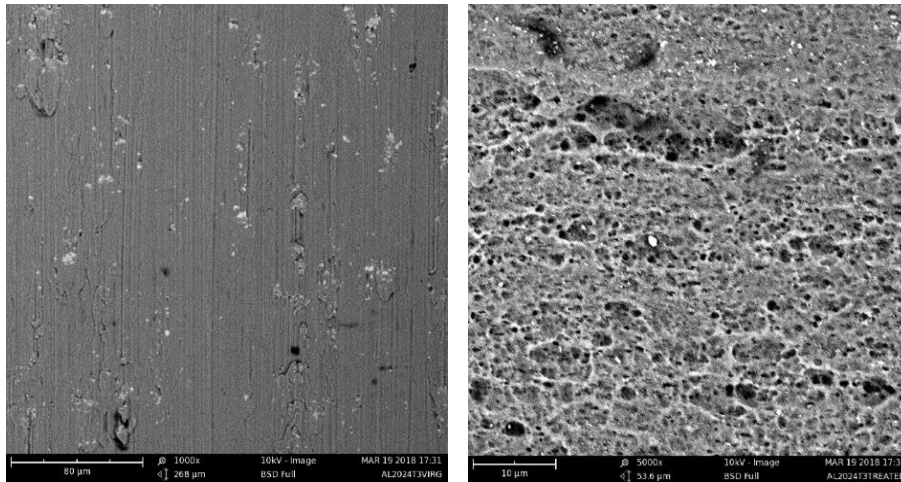
The Al7075 has also responded correctly to the treatment, but in this case the effect is not as intense as in the Al2000. Picture 4-6 shows the result mentioned before, but the etching hasn't attacked deeply inside the surface. Some holes can be seen but they are superficial.



Picture 4-6 10 μm SEM image of the Al7075

### **Al 2024-T3 observations**

In the last tested pieces of aluminium, the SEM images Picture 4-7 display the virgin surface, where is able to see the milling lines and some imperfections of the metal, and the one treated with a wrinkled substrate. In this occasion, as in the AL2000 test, the etching attacked the surface deeply, achieving the required roughness.



Picture 4-7 a) 80 µm SEM image of Al2024-T3 milled; b) 10µm SEM image of Al2024-T3 treated with caustic soda + P2 etch

Finally, with the results seen in the microscope, it was decided to choose the Al2024-T3. The next step is to produce the DCB specimens with that aluminium and treat them with the solutions.

### 4.3. FABRICATION OF THE SPECIMENS

After choosing the aluminium, the specimens were produced.

Three different types of specimens, with three different geometries were fabricated. All of them have been designed following the ASTM standards, but with different dimensions.

ASTM 3433 standard proposes, for flat specimens, dimensions of:  $356 \pm 2.5$  mm long, and  $25.4 \pm 0.3$  mm width. Specimens with these dimensions are difficult to manage in laboratory; also, the necessary products for the pre-treatment and the bonding will increase and so the costs. But there are several investigations in which it is verified that the use of smaller specimens provides the same results in strength and fracture toughness as the bigger ones.

Thus, 3 types of specimens have been fabricated on a reduced scale.

- Specimen type 1 → It is composed of a flat surface where will be located the adherent and therefore, the joining area of the sample; and a thicker part with

a hole on it, in which will be located the mechanism that is going to join the specimen with the machine. The bonding surface has an area of 120mm x 10mm



Picture 4-8 Specimen type 1

- Specimen type 2 → It has bigger dimensions compared to the first type (120mm x 20mm bonding surface area), but in this second case, the whole sample is continuous (14 mm thickness).

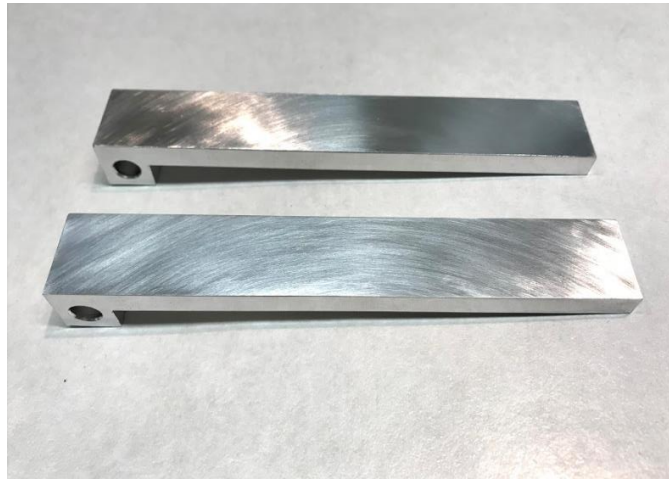


Picture 4-9 Specimen type 2

- Specimen type 3 → The geometry of this last specimen type is the same as in the first case, but with bigger dimensions. The bonding surface area is 120mm x 20 mm with a thickness of 6mm on the thin part.

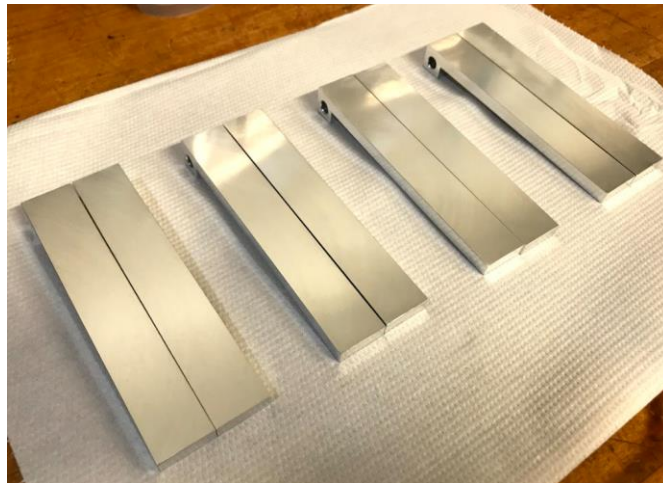
Once the specimens are performed, the bonding surface of each one is polished to obtain a smooth surface.

Picture 4-10 shows two of the eight third type specimens with the polished bonding surface.



Picture 4-10 Specimens with polished bonding Surface (sandpaper grit 800).

Picture 4-11 shows the bonding surface of the eight samples, separated in four pairs, according to have a similar bonding part thickness.



Picture 4-11 DCB specimens separated in four pairs

#### 4.3.1. Support fabrication

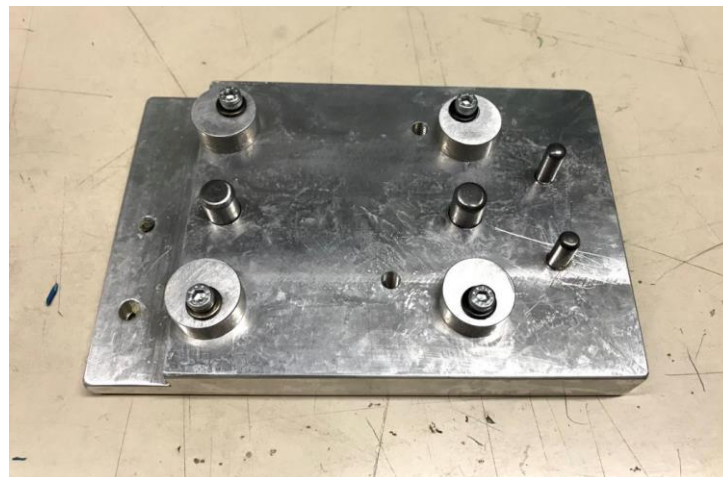
A holder is needed in order to place the specimens once they are bonded, to avoid the displacement between them during the curing process.

This support is fabricated in aluminium with enough space to place two pairs of samples bonded, one with the nanofiber and the other one virgin.

The final result is shown in the following pictures. There are two different types of supports. In Picture 4-12 is shown the one used for the first tests, which wasn't very effective because it allowed the nanofiber mat and the copper laminates between the two specimens to move from their initial position (the specimens were placed together and, they pushed each other). So, in order to solve this problem, a second support was designed and fabricated (Picture 4-13), where the specimens are separated by metallic dowels.



Picture 4-12 First specimen support



Picture 4-13 Second specimen support

#### 4.4. PRE-TREATMENT OF THE SPECIMENS

The next step on the study is to treat the specimens with the caustic soda and P2 etching solutions.

In this case, the process is the same as the one mentioned in point 4.1 but producing a higher quantity of both solutions, as the specimens that are going to be treated now, have bigger dimensions.

#### 4.4.1. Caustic soda solution

The 1% soda solution is obtained by mixing caustic soda with the necessary distilled water, at room temperature. When the transition component and the solvent are homogeneously mixed, the solution is poured in a plastic vessel, and then the specimens are submerged inside for 10 minutes. Once the time is over, they are removed from the solution and introduced in another plastic vessel full of distilled water, for 10 more minutes (Picture 4-14).



Picture 4-14 Caustic soda solution process

In Picture 4-16 is shown the aspect of the samples once they are taken out the soda solution and submerged in the distilled water. As it can be seen, their colour has changed becoming darker.



Picture 4-15 Initial aspect of specimens inside soda solution



Picture 4-16 Specimens after soda treatment

#### 4.4.2. P2 etching solution

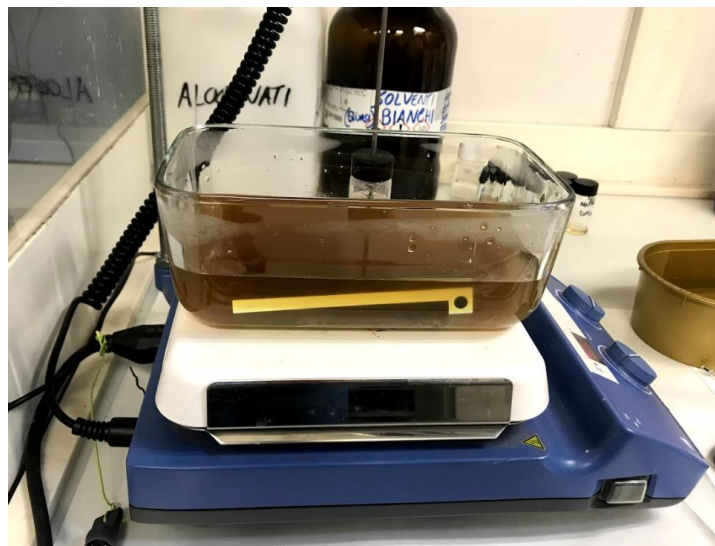
After the treatment with the caustic soda, the next step is to treat them with the P2 etch.

The P2 etch is a process in which 370g of sulfuric acid are mixed with 150g of 75% ferric sulphate and distilled water, to obtain 1 litre of solution.



To obtain a solution with 34% of H<sub>2</sub>SO<sub>4</sub>, we need to add 250g of 62% H<sub>2</sub>SO<sub>4</sub> to 186 g of distilled water and mix them at room temperature. When the solution is mixed, 77g of 75% ferric sulphate and blended until the solution is homogeneous.

When the solution is finished, its temperature must be increased to 60°C and the specimens, previously treated with caustic soda, are submerged in the solution as shown in Picture 4-17.

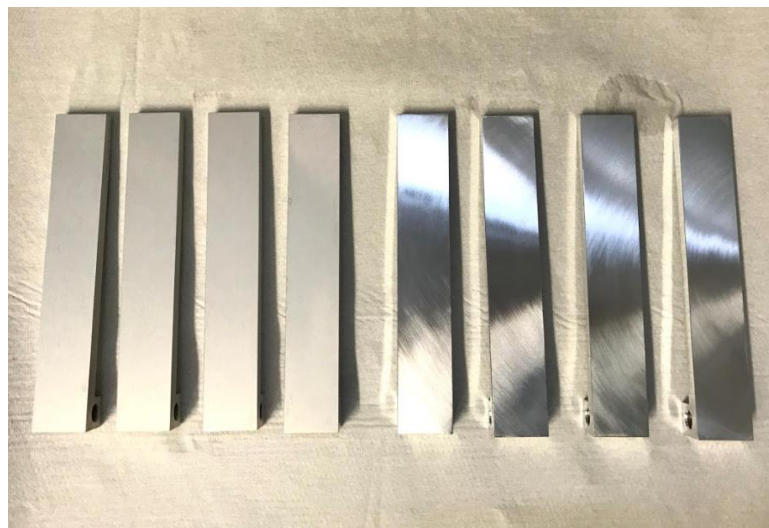


Picture 4-17 Specimens submerged in P2 etch

The specimens are introduced in the P2 etch for 12 minutes, and then putted in water for 10 more minutes. In Picture 4-18 and Picture 4-19 are shown the changes in the samples surface. Its colour has become lighter, and the brightness, given by the milling and the polish processes has disappeared obtaining a matte surface.



Picture 4-18 Specimens treated with Caustic soda and P2 etch

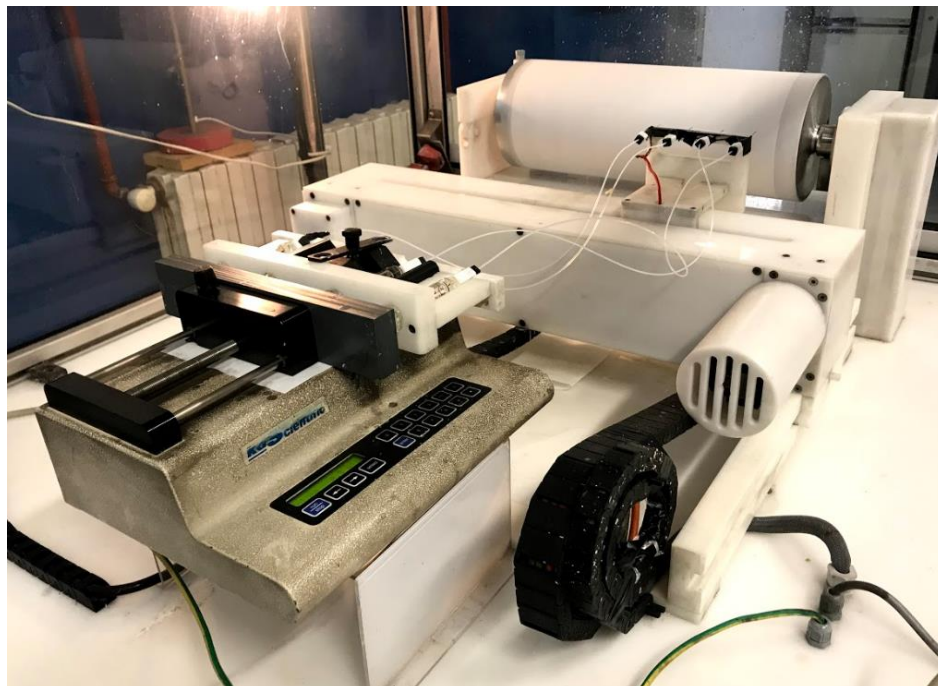


Picture 4-19 Different surface aspect between treated and non-treated specimens

#### 4.5. NANOFIBER MAT PRODUCTION

The nanofibers that are going to be used on this study are based on nylon 6.6. This polymer has been already used on the laboratory for other investigations and it is known to have good properties, and it is suitable for its use with the electrospinning machine.

The electrospinning machine used to fabricate the nanofibers is a Spinbow®, equipped with a rotating drum collector on which the nanofibers will be jetted with the help of four needles connected to the syringes with the solution Picture 4-20.



Picture 4-20 Electrospinning machine

#### 4.5.1. Preparation of the solution

The solution is composed by 13% wt of Nylon 6.6 and 87% wt of Trifluoroacetic acid (TFA)/formic acid/chloroform on 10:60:30 vol.

18g of solution will be produced to fill the syringes. 1.2ml of TFA are added to 7.1ml of formic acid, and the solution is agitated for 5 min. Once the temperature is stabilised, 2.35g of nylon are added and the solution is heated to 45°C till the nylon is completely dissolved. When the solution is homogeneous, and the temperature returns to room temperature, the chloroform is added, and the solution is mixed for 30 min.

#### 4.5.2. Electrospinning process

The syringes are filled with the solution, all of them with approximately the same quantity and as few bubbles as possible.

The electrospinning process must be as fast as possible in order to obtain the desired nano-mat thickness in the shortest time. It is also necessary to avoid the formation of agglomerations of the solution in form of gobs on the collector's surface, which spoils the nanofiber sheet. To do that, the parameters must be modified to reach the best combination.

The electrospinning parameters are set as it is shown in Table 4-1:

Table 4-1 Electrospinning parameters

<b>Parameter</b>	
<b>Flow rate per nozzle</b>	0.9 ml/h
<b>Applied voltage</b>	25 kV
<b>Distance needle-collector</b>	5.5 cm
<b>Relative humidity</b>	33 %
<b>Temperature</b>	24 °C

With this process, it will be obtained a nanofiber sheet with a 400um thickness, which will be impregnated with the resin to bond the specimens.

#### **4.6. BONDING PROCESS**

Once the pre-treatment is done, is time to bond the specimens. Two pairs of samples are joined; one with the nanofiber met impregnated with resin and the other one with the virgin epoxy. Then, when the resin has been cured, the thickness is measured with an optical microscope.

##### **4.6.1. Mixture of the resin and the hardener**

The first step is to mix the resin and the hardener. In this case, the resin used is an Elan-tech epoxy AS53 which is a medium rigidity resin with the hardener AW09. 30g of these two components are mixed in 100:50 ratio, enhancing epoxy ductility to 12000 -18000 mPas.

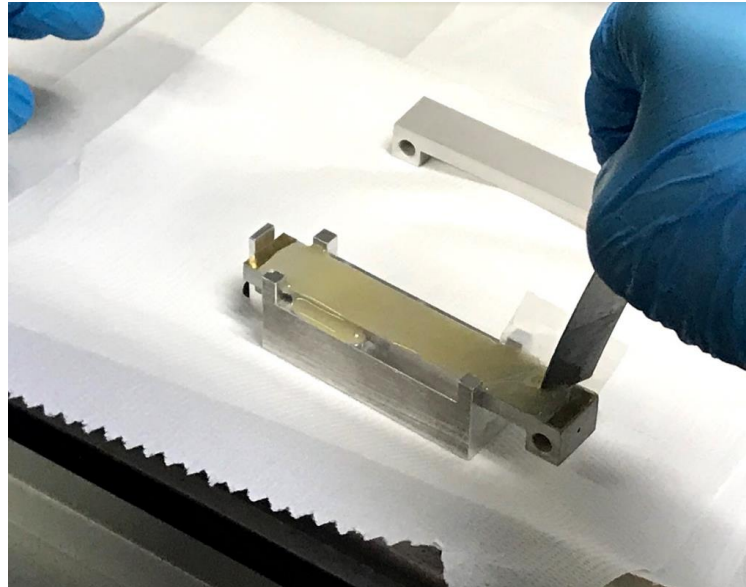
##### **4.6.2. Bonding of the substrates**

Once the epoxy and the hardener are homogeneously mixed, ensuring that the bubbles made are the fewest as possible, the surfaces of the specimens are bonded. To join them, the nanofiber and Teflon laminates must be cut first.

There are two different processes to join the specimens:

### Virgin batches

- For the virgin specimens copper laminates are put in the surface ends, with the purpose of giving the resin the needed thickness, and also the Teflon laminate is placed. Then, the resin is spread on one of the surfaces and bonded with the other.

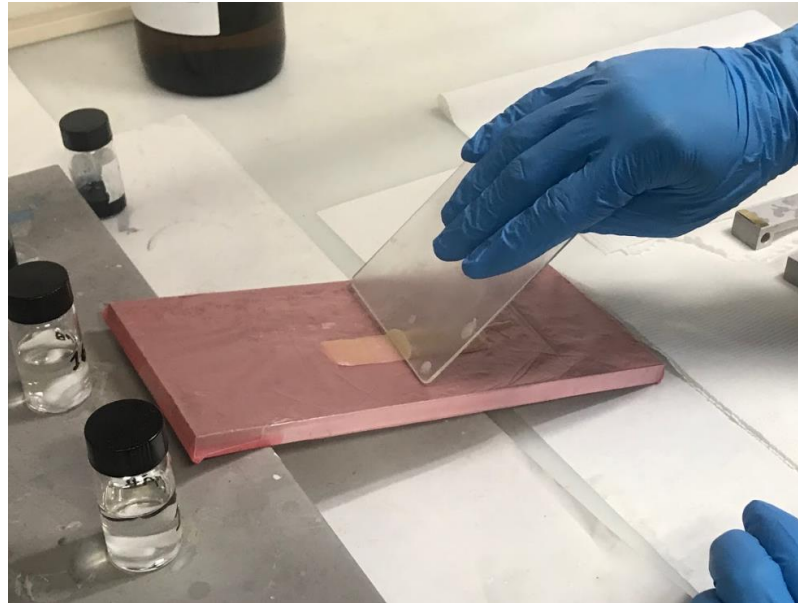


Picture 4-21 Spread of the resin on the virgin specimens

### Nanofiber batches

Two different procedures were considered to bond the specimens with the nanofiber mat inside:

- Teflon and nano-mat separated → The nanofibers are cut with the dimensions of the bonding surface. The total surface is 120x20mm for type 2 and type 3 specimens and 120x10mm for type 1, so the nanofibers are cut with 85x20mm and 85x10mm dimensions respectively, in order to let part of the surface without resin. This resting part of 35x20mm (or 30x10mm) will be covered with a Teflon laminate and is the area where the crack will be initiated. The Teflon laminate is placed. The nanofiber sheet is impregnated with the resin, removing the excess of adhesive, and then placed in the surface to bond both specimens. In this case the copper laminates are not necessary since the nanofibers already have the expected thickness.



Picture 4-22 Remove the excess of resin from the nanofiber mat



Picture 4-23 Bonding of the specimens

- Teflon inside nano-mat → On this second procedure, the nanofiber mat is cut with the dimensions of the hole surface, that is 120x20 mm, and is separated in half in order to place the Teflon inside the nano-mat, as is shown in Picture 4-24. Then the nanofibers are impregnated with the resin, removing the excess, and placed between the two specimens to bond them.

This second procedure is used to try to obtain a crack propagation inside the nanofibers and the resin, in other words, to have a cohesive failure instead of adhesive.



Picture 4-24 Teflon placed inside the nanofiber mat

#### 4.6.3. Curing

Once the specimens are bonded, they must be placed in the support, previously wrapping them with Teflon as is shown in Picture 4-25 and Picture 4-26, to avoid the spread of the resin in the holder and between the samples.



Picture 4-25 First support with bonded specimens



Picture 4-26 Second support with bonded specimens

The holder with the specimens is placed in a vacuum bag and then introduced in the oven (Picture 4-27). Different curing processes have been carried out to see the effect on the fracture toughness.

The following table shows the different curing processes depending on the batches.

SPECIMEN	CURING PROCESS
<b>TYPE 1</b>	24h at 20°C, 20min at 80°C
<b>TYPE 2</b>	24h at 20°C with vacuum pump, 36h at 80°C without vacuum.
<b>TYPE 3 – BATCH 0</b>	80°C for at least 24h
<b>TYPE 3 – BATCH 1</b>	80°C for at least 24h
<b>TYPE 3 – BATCH 2</b>	80°C for at least 24h
<b>TYPE 3 – BATCH 3</b>	Increase of 15°C each 10 min until reach 80°C, 15 hours at 80°C + 3h at 115°C
<b>TYPE 3 – BATCH 4</b>	Increase of 15°C each 10 min until reach 80°C, 15 hours at 80°C + 3h at 115°C
<b>TYPE 3 – BATCH 5</b>	Increase of 10°C each 10 min until reach 80°C, 16 hours at 80°C + 4.5h at 115°C
<b>TYPE 3 – BATCH 6</b>	Increase of 10°C each 10 min until reach 80°C, 72 hours at 80°C + 5h at 115°C

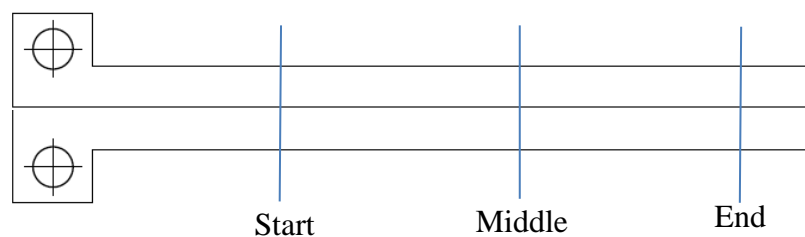




Picture 4-27 Second support inside the vacuum bag

#### 4.6.4. Thickness measure

Once the resin is cured, the thickness is measured with an optical microscope. The measurements are taken in three different points of the bonded specimens: start, middle and end of the bond line as is shown in Picture 4-28. These measurements are useful to observe if the thickness is in the range of expected values.



Picture 4-28 Points where the thickness is measured

The measures are collected in tables, differentiating between virgin or with nanofiber and the sides of the specimens, which are already indicated in the pieces to differentiate left from right. Also, the mean and the standard deviation are obtained.

For the different performed tests, the thickness measured values are shown on the following tables.

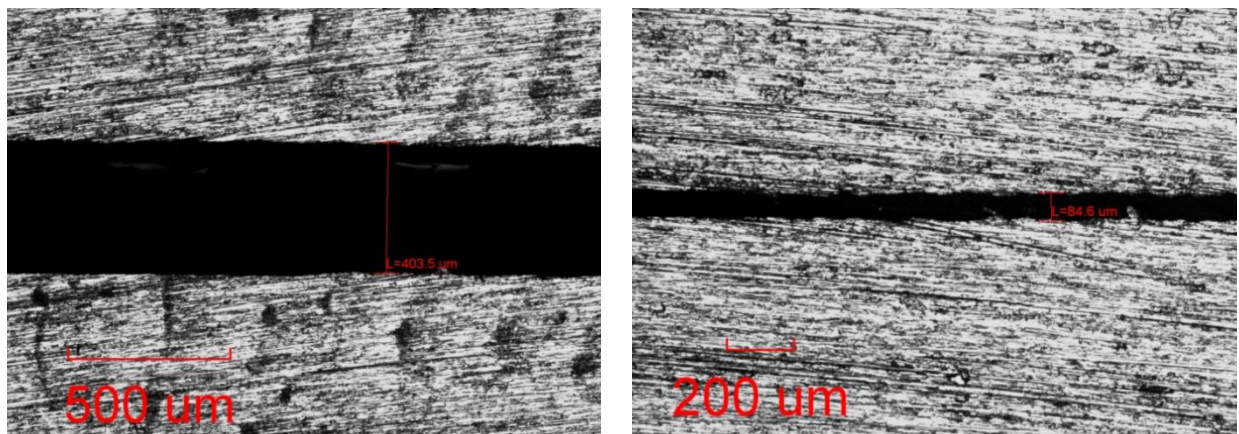
**Specimen type 1**

In this case, the measure has been done only on one side.

	Virgin	Nanofiber	
Start	124,4	333	um
Middle	84,6	403,5	um
End	194,7	378,1	um
Mean	127,01	370,37	um
St. Deviation	55,75	35,71	um

The bond line thickness measures are taken in um.

As it can be seen, there is an important difference between the specimen with the virgin resin and with the nanofiber. The measure must be almost the same but in the case of the virgin batch, the mean value is half the mean value with nanofiber, this may be due to the movement of the copper laminates from their initial position. In addition, looking at the measures on the different points of a specimen and the standard deviation, it is observed that the thickness along the bond line of each specimen is not the same, which means that the resin hasn't been spread in a homogeneous way all over the surface.

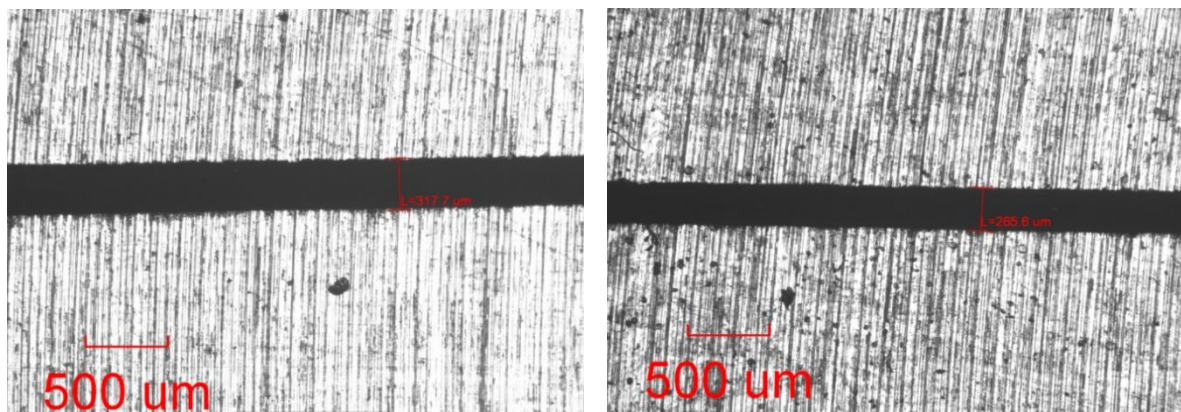


Picture 4-29 Microscope images of the bond line thickness of specimen type 1. Left, with nanofibers. Right, virgin resin.

**Specimen type 2**

	Virgin		Nanofiber		
	Left	Right	Left	Right	
Start	305	328	300	365	um
Middle	266	296	318	338	um
End	265	291	338	390	um
Mean	278	305	318	364	um
St. Deviation	23	20	19	26	um

In this second type of specimen, with bigger dimensions, the mean values in the virgin case and with nanofibers are more similar than for type 1. The desired thickness must be similar to the nanofiber thickness, in this case 300um, so the measures are considered to be correct. The standard deviation in this case is quite small, which means that the impregnation of the resin on the nanofibers, and its spread on the substrate's surfaces is homogeneous.



Picture 4-30 Microscope images of the bond line thickness of the specimen type 2. Left, with nanofibers. Right, virgin resin

**Specimen type 3**

For this last geometry, there were fabricated 6 different batch. In this point, the thickness measure of the four first batches produced is shown.

## Batch 0

	Virgin		Nanofibers		
	Left	Right	Left	Right	
Start	337	234	348	331	um
Middle	360	258	375	343	um
End	437	339	424	452	um
Mean	376	273	381	372	um
St. Deviation	52	55	38	67	um

## Batch 1

	Nanofibers		Virgin		
	Left	Right	Left	Right	
Start	414	309	478	486	um
middle	462	345	482	535	um
end	434	362	431	476	um
mean	436	338	463	498	um
St.deviation	24	27	28	32	um

## Batch 2

	Nanofibers		Virgin		
	Left	Right	Left	Right	
Start	467	419	408	404	um
middle	472	458	366	372	um
end	433	437	294	306	um
mean	457	437	353	358	um
St.deviation	21	20	57	50	um

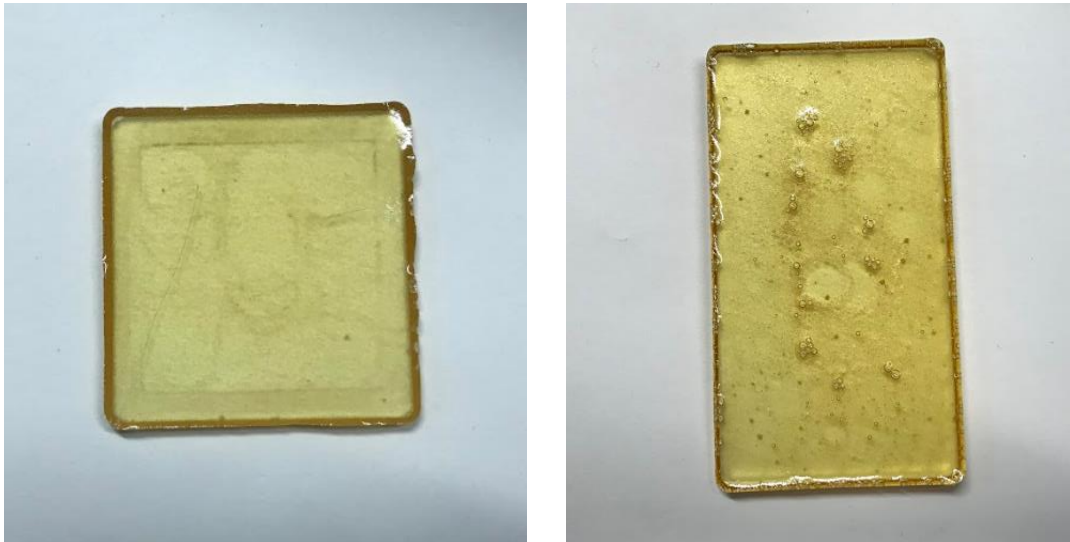
## Batch 3

	Virgin		Nanofibers		
	left	right	left	right	
Start	184	238	487	294	um
middle	165	244	403	176	um
end	223	245	385	181	um
mean	189	242	423	211	um
St. deviation	30	4	54	67	um

#### 4.7. RESIN CURING

It is necessary to verify that the curing of the resin has been carried on completely. To do that, the extra resin left from the bonding process is placed in a vessel and introduced in the oven with the specimens, for the same time. Once the time is up, the cured resin is taken out from the vessel and it is verified if the curing process has been completed, and also it is observed if there is presence of air bubbles or not.

Picture 4-31 shows an example of cured resin. In the picture from the left, it can be seen the absence of bubbles, while in the right picture air bubbles can be seen in the centre of the specimen.

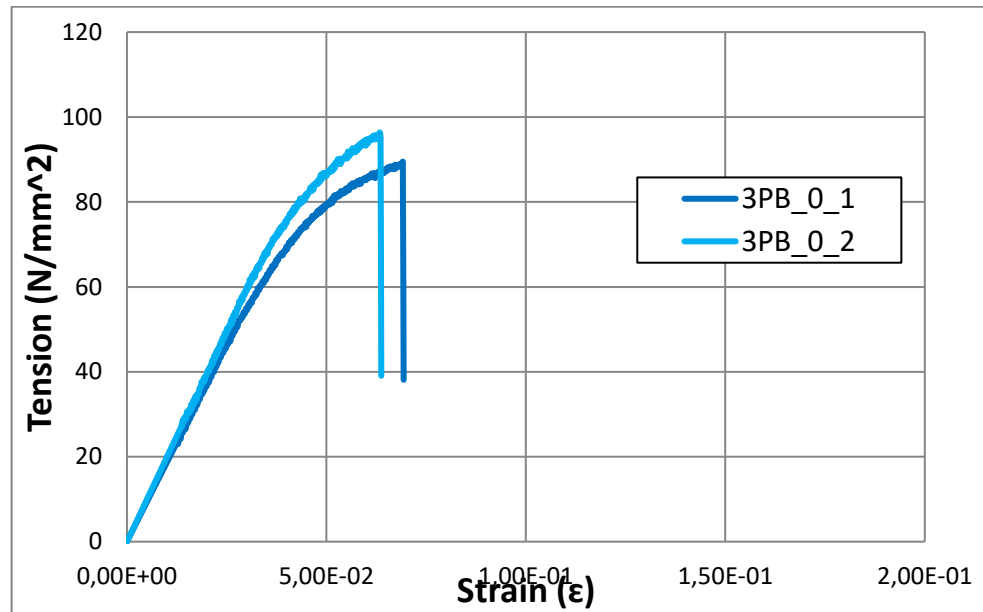


Picture 4-31 Examples of cured resin

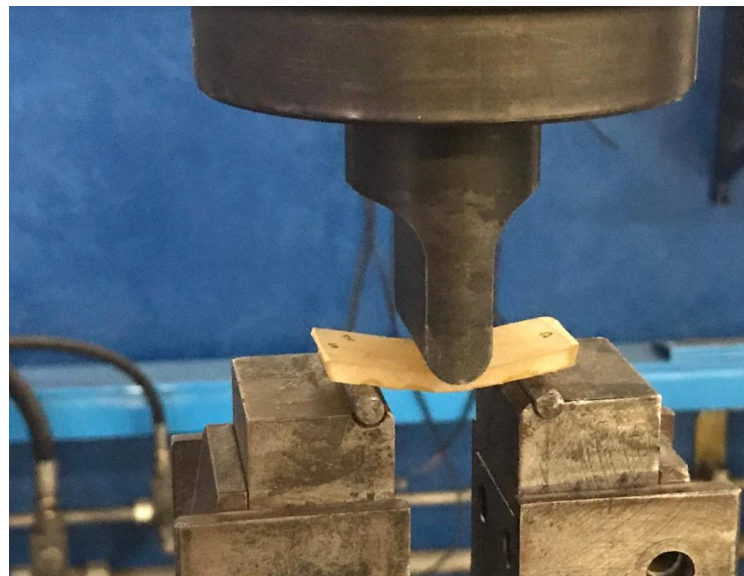
A three-point test (Picture 4-32) has been carried on for the first time this type of resin was used in order to obtain the elastic modulus of the resin.

The tested resin has been curing 24 hours at room temperature, then it was introduced in the oven for 15 hours at 80°C and 3 extra hours at 100°C. Once it was cured, the 3-point test was performed.

Graph 4-1 shows the stress-strain curve for two different tests of the resin, where it can be observed that the elastic modulus (tangent of the curve) obtained for both tests is almost the same.



Graph 4-1 Stress-strain curves for 3-point test of the resin



Picture 4-32 3-point test to verify resins rigidity

#### 4.8. DCB TEST

As it was already explained on chapter 2, DCB test is used to obtain the fracture toughness of the adhesive, by the application of a tension on the end of the tested specimen and following the crack growth with time.

Before placing the specimen on the machine, a millimetric scale is placed on one side of the batch, in order to follow the crack propagation during the test (Picture 4-33).



Picture 4-33 Specimen with millimetric scale

The specimens are attached to the machine with the aid of pins passing through the holes drilled on the specimens, which join the batches to the machine.

The load is applied until the collapse of the beam, increasing it till the initiation of the crack propagation, when the peak value of the load is reached, and then letting it decrease. The data is recorded by a specific software, and the results are represented in two different curves:

- A force-displacement curve
- A  $G_I$ -crack length curve

The debonded specimen is now removed from the machine, and the failure surface is observed to check if the fracture was cohesive or adhesive.

The following image shows the machine used on the laboratory with one specimen already placed on it.



Picture 4-34 DCB test machine with specimen

The different results obtained are collected on the following chapter.

The DCB test was performed for each geometry (specimen's type 1, 2 and 3). In the case of type 3 specimens, six different batch were produced, so for this last geometry there will be six different results.



## 5. Results and discussion

On this chapter, the results of the tests will be presented.

A first summary of how the specimens were obtained (geometry, nanofibers type, bonding type and curing time) is shown for each test.

Eight different DCB tests were performed in which the final fracture toughness, the maximum applied load, and the crack length are obtained for both, the virgin resin specimens and the one with the nanofibers.

Force-displacement and fracture toughness-crack length curves are obtained with the recorded data for both, the virgin and the nanofibrous specimens and they are compared to understand the effect of the nanofibers on the bonding.

Also, pictures of the different fracture surfaces are shown on this chapter for each test.

### 5.1. SPECIMEN TYPE 1 – DCB TEST

#### PROCESS

Aluminium specimens production	Al2024-T3 specimens designed with type 1 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/acetone 65:35wt 87%wt. Thickness: 200 $\mu\text{m}$
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	24h at 20°C, 20min at 80°C

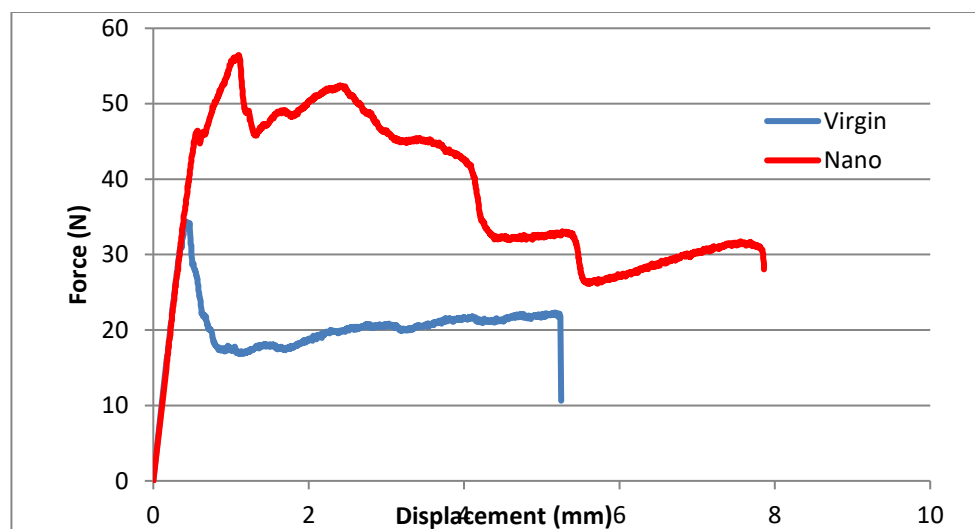
This type of specimens was the one used for the firsts tests. They had smaller dimensions, especially the width and the thickness.

After the bonding and the curing of the resin, the bonding line seemed plenty of bubbles, especially in the virgin batch. Also, the resin thickness wasn't homogeneous, thinner in the middle part and thicker on the endings, as it could be seen in the thickness measures shown in the preceding chapter.

These preliminary observations were reflected on the subsequent tests.

For the nano-reinforced batch, the peak load of 57 N was reached when the displacement of the crack arrived at approximately 1 mm. After this point, the load had a decrease, arriving at values of almost half of the first peak load. When the collapse occurred, the crack displacement had a value of almost 8 mm. This behaviour was due to the bending of the specimens. They weren't rigid enough and the axial tension applied, generated a bending moment over the specimens.

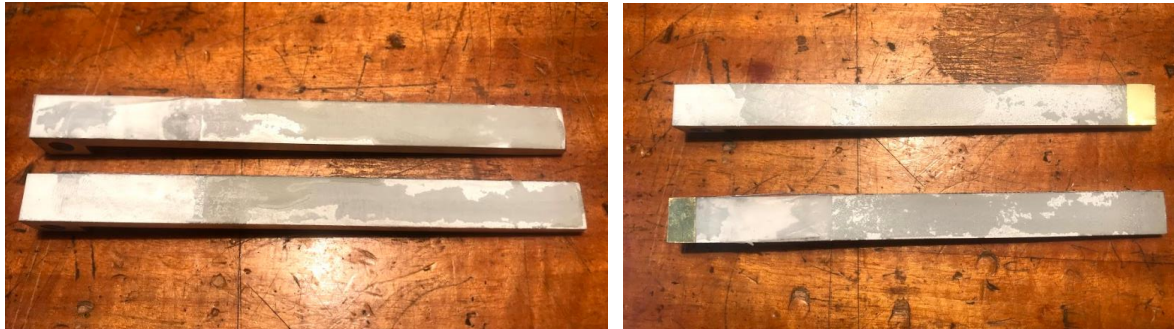
Something similar happened to the virgin batch. In this case, the peak load value reached was 35N, the crack was initiated and then the load dropped to a value that remained rather constant. The crack propagation in this case, was shorter than for the nanofibrous batch, but also long, arriving to a value higher than 5 mm.



Graph 5-1 Force-displacement curve for type 1 specimens

Looking now at the fracture surfaces of both specimens:

For the reinforced one, it can be seen that the fracture was produced in a mixed way, cohesive failure in the central part, while on both longitudinal sides the fracture was adhesive. For the virgin specimen, the fracture was almost adhesive over the whole surface.



Picture 5-1 Fracture surface type 1 specimen. Left, reinforced. Right, virgin.

## 5.2. SPECIMEN TYPE 2 -DCB TEST

### PROCESS

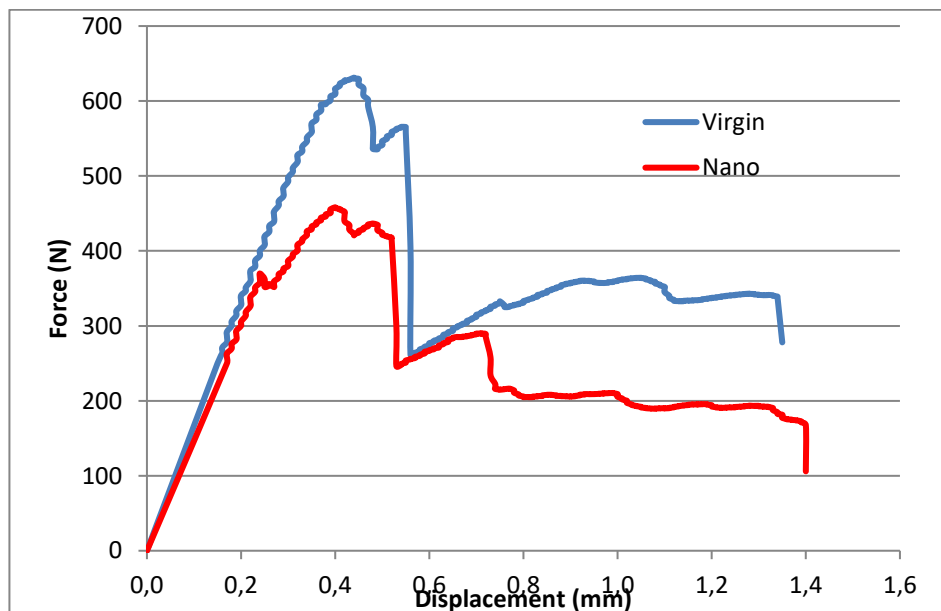
Aluminium specimens production	Al2024-T3 specimens designed with type 2 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu$ m
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	24h at 20°C with vacuum pump, 36h at 80°C without vacuum.

This second type of specimen, as it was already mentioned in chapter 4, is continuous, without a different thickness on the ending part.

In this case, once the resin was cured, it didn't seem to be as many bubbles as in the first case, and also the resin thickness was quite homogeneous. The problem was seen when the tests were performed for each sample.

For the virgin batch, the initiation of the crack propagation occurred at 1.3 mm with a peak load which reached values over 600N. Then the load was stabilised at a range between 300 and 400N. The collapse of the specimens happened when the crack displacement arrived to 2.2mm.

After performing the test for the reinforced specimen, it was noticed that the peak load reached for this second batch was lower than for the virgin one: for this second specimen the highest value was 450N, approximately 200N less than in the case of the unreinforced one. This behaviour doesn't make sense, since the nanofibers should increase the needed load applied to generate the crack. This could have been caused due to: the use of an old nanofiber mat which didn't absorbed properly the resin or, during the impregnation of the nanofibers with the resin, it was removed in excess.



Graph 5-2 Force-displacement curve for type 2 specimens

Looking at the fracture surfaces, it could be seen that the failure was cohesive in the case of the virgin specimen and adhesive for the reinforced one.



Picture 5-2 Fracture surface of type 2 specimens. Left, virgin. Right, reinforced.

### 5.3. SPECIMEN TYPE 3 - DCB TEST

#### 5.3.1. Batch 0

##### PROCESS

Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu$ m
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	80°C for at least 24h

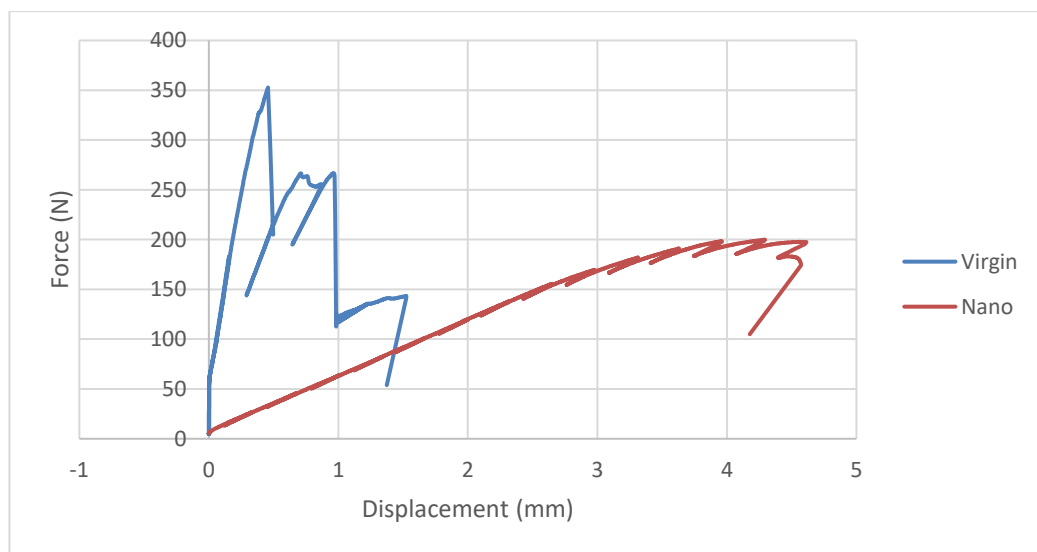
For type 3 specimens, a fatigue load process was used to initiate the crack.

There was a problem with the software of the machine. The fatigue load for the fatigue pre-cracking was supposed to have a value of approximately 90N, sufficient to generate the

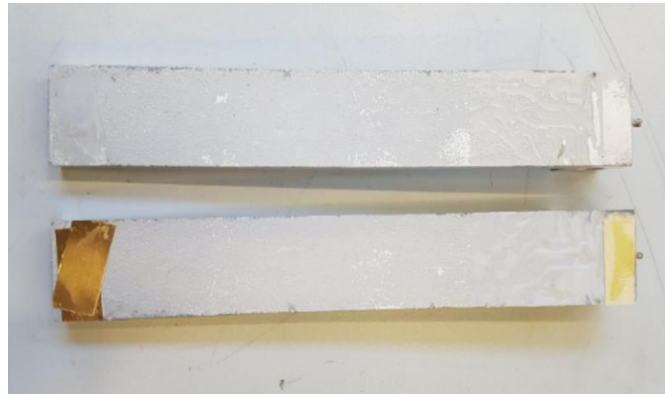
crack but not its propagation. The problem arrived when the machine applied an excessive force which supposed the premature collapse of the virgin specimen. That's why the virgin specimen has a crack displacement of less than 2 mm.

The peak value of the load for the virgin batch is so much higher than the needed to generate the crack in the case of the specimens with the nanofiber mat. This lower resistance for the reinforced specimen can be due to the non-homogeneous spread of the resin on the nanofiber mat, or an excess of epoxy which generates a non-homogeneous adhesion between the surfaces, generating an adhesive fracture.

The following graph represents the force-displacement curve for the virgin and the nano-reinforced batches.



Graph 5-3 Force-displacement curve for Batch 0, type 3 specimens



Picture 5-3 Cohesive fracture surface of virgin specimen of batch 0

### 5.3.2. Batch 1

#### PROCESS

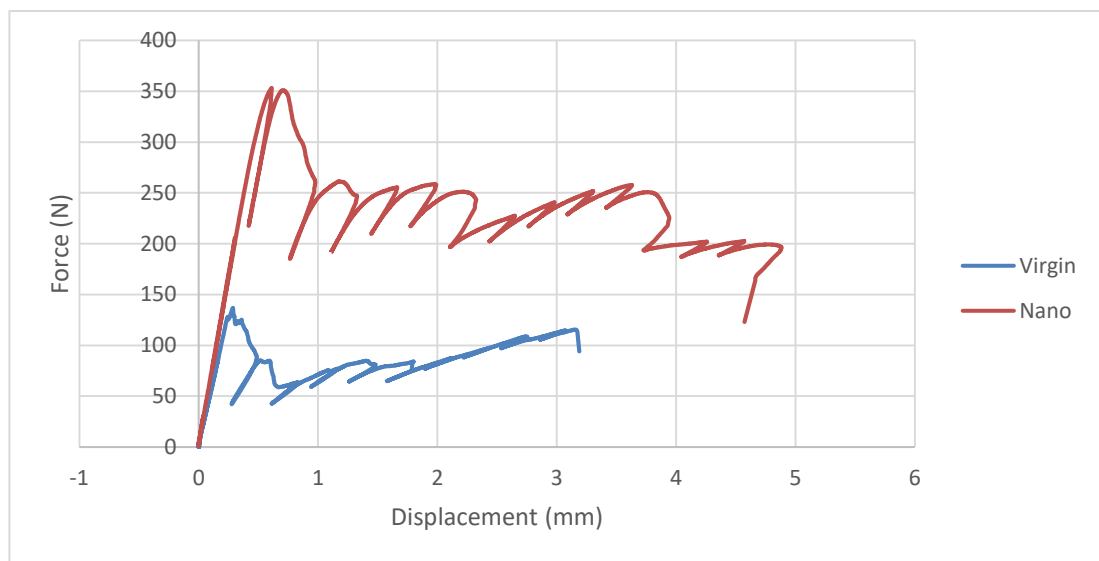
Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish+Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu\text{m}$
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	80°C at least 24h

Before the test, it was observed that the virgin specimen was affected by defects along the interface: in different points of the bond line the adhesive wasn't present, specially denoted on the central part, probably due to an irregular spread of the resin during the bonding process.

These defects are reflected on the force-displacement curve, where the initial resistance of the virgin specimen (140 N) is lower than for the virgin specimen of batch 0 (350 N).

On the other hand, the nano-reinforced specimen has developed a better behaviour. The first peak of the load is obtained at 350N, followed by a rather constant pattern, with peak values around 250N.

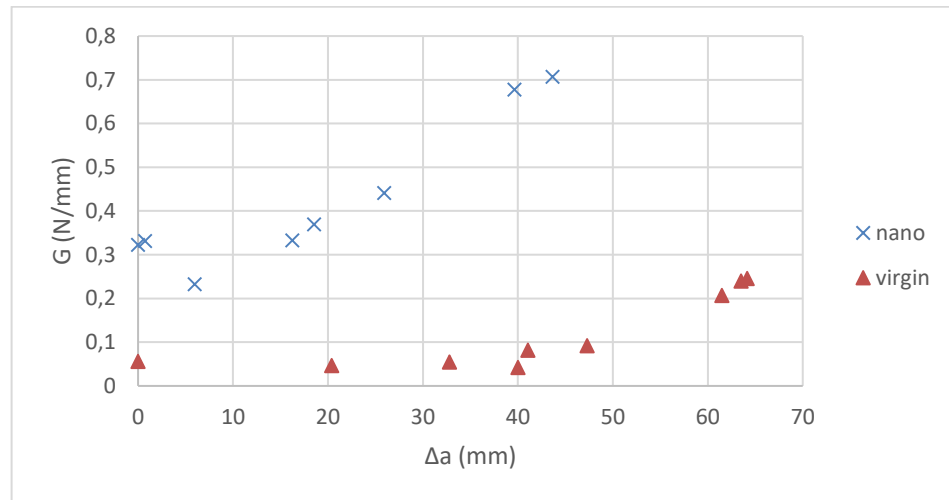
The crack displacement for the virgin specimen, is higher than for the case of batch 0, arriving to a value over 3mm before the collapse. In the case of the reinforced specimen, the crack displacement was very similar to batch 1, with a displacement value close to 5mm.



Graph 5-4 Force-displacement curve for batch1, type 3 specimens

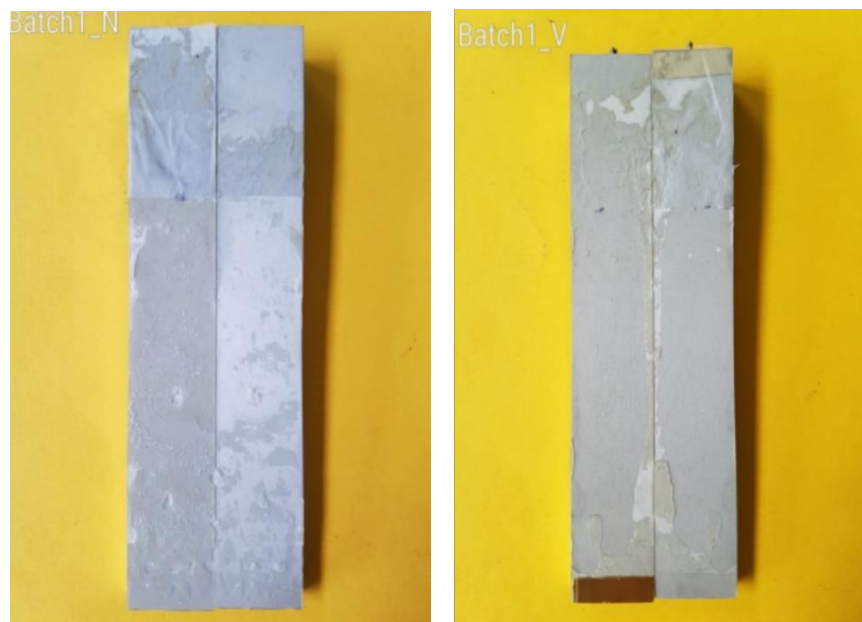
The fracture toughness on the first curve section has values quite similar to those obtained for batch 0 virgin, but it can be observed a progressive increase trend of  $G$  which, when the crack arrives to a consistent length (about 39 mm with respect the initial length), acquires values approximately 2 times the initial one.





Graph 5-5 Fracture toughness - crack length curve for batch 1, type 3 specimen

Picture 5-4 shows the fracture surface. The virgin specimen shows an almost non-existing quantity of adhesive, which is probably the reason why the force and the fracture toughness have very low values. For the nanofibrous specimen instead, the fracture is practically adhesive, with some points of cohesive failure starting on the central part, which may be the reason of the increase of the fracture energy with the propagation of the crack.



Picture 5-4 Fracture surfaces of batch 1. Left, nano-reinforced with adhesive fracture. Right, virgin with cohesive fracture.

## 5.3.3. Batch 2

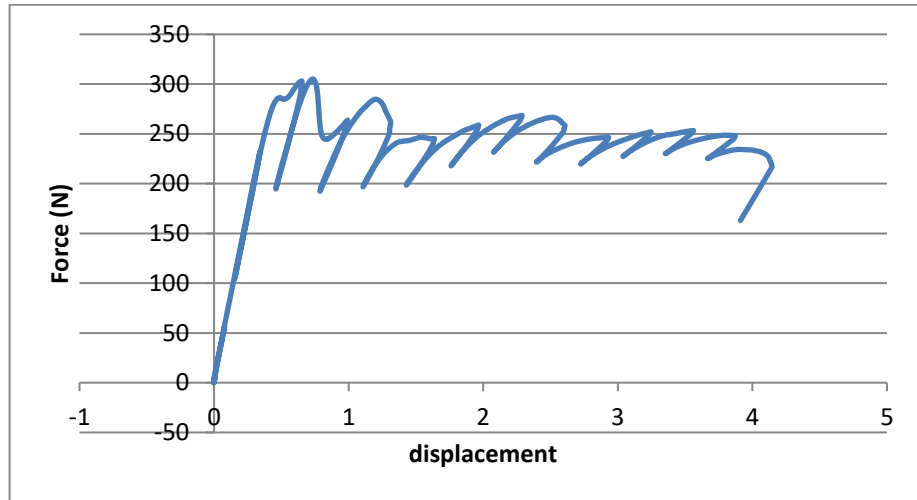
**PROCESS**

Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu\text{m}$
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	24 hours at 80°C

During the process to apply fatigue loads, the virgin specimen failed before starting the pre-crack, at 90 N. This specimen presented the same problem as batch 1; there were defects along the interface, so the failure would be due to an excessive lack of adhesive at that point where the fracture overcame.

Since the virgin sample has failed before starting the test, the force-displacement and the toughness-crack length curves are obtained for the nano-reinforced one.

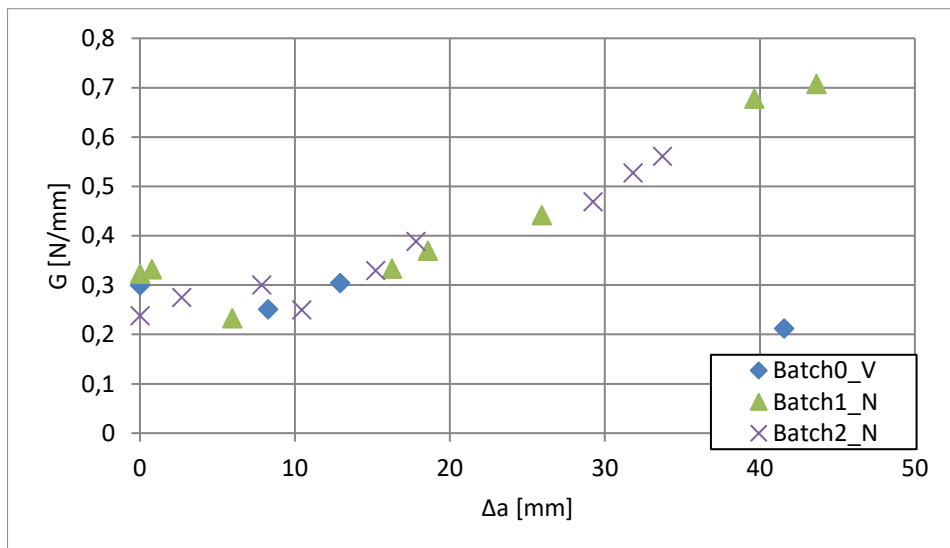
Looking at the force-displacement curve, it can be noticed that has a similar behavior to batch 1, but with smaller values of crack displacement and first peak load (300N).



Graph 5-6 Force-displacement curve for reinforced batch 2, type 3 specimens

The toughness- crack length curve, has also a similar behavior to batch 1, but in this case, it starts with similar  $G$  values to batch 0, and when the crack arrives to a certain threshold, the value of the toughness increases, and it approaches values reached by batch 1.

To understand better what is explained in the previous paragraph, Graph 5-7 shows the  $G$ -crack length curve for batch 0 virgin, batch 1 nano-reinforced, and batch 2 nano-reinforced:



Graph 5-7 Comparison between fracture toughness-crack length curves, for batch 0 virgin, batch 1 reinforced and batch 2 reinforced

The fracture surface is shown in the following picture (Picture 5-5). For this nano-reinforced specimen, it can be seen the prevalence of adhesive failure compared to cohesive failure which is present in smaller amount.



Picture 5-5 Fracture surface of batch 2 nano-reinforced

#### 5.3.4. Batch 3

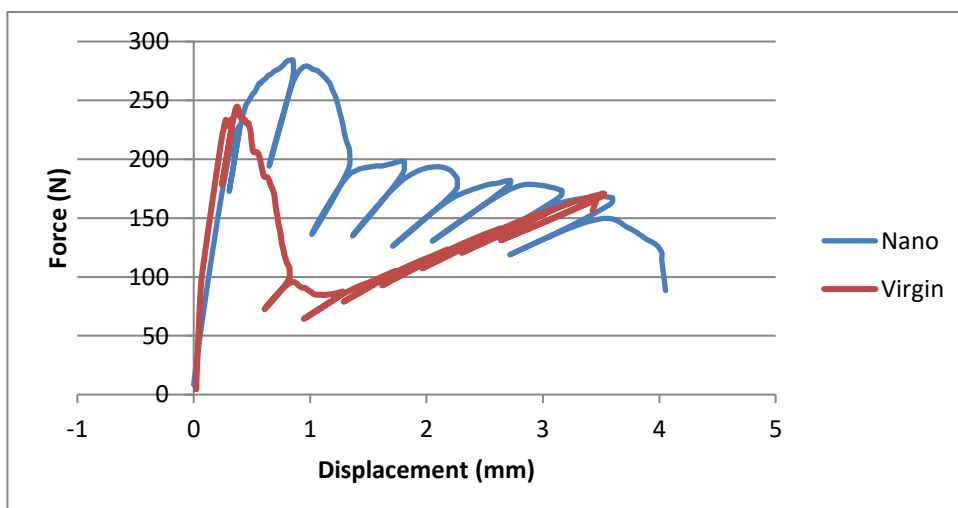
From batch 3 to batch 6, the production process is the same for all of them, with a difference on the curing process. During the curing, the temperature and the time have been modified for each batch of specimens and the effect on the fracture energy has been studied.

At this point, for the batches already mentioned, the production process will be exhibited on their respective tables, with the different curing processes; and also, the force-displacement curves, comparing nano-reinforced and virgin specimens, will be shown for each test.

**PROCESS**

Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu$ m
Bonding	Resin: AS5309W (100:50). Teflon separated from the nanofibers.
Curing process	Increase of 15°C each 10 min until reach 80°C, 15 hours at 80°C + 3h at 115°C

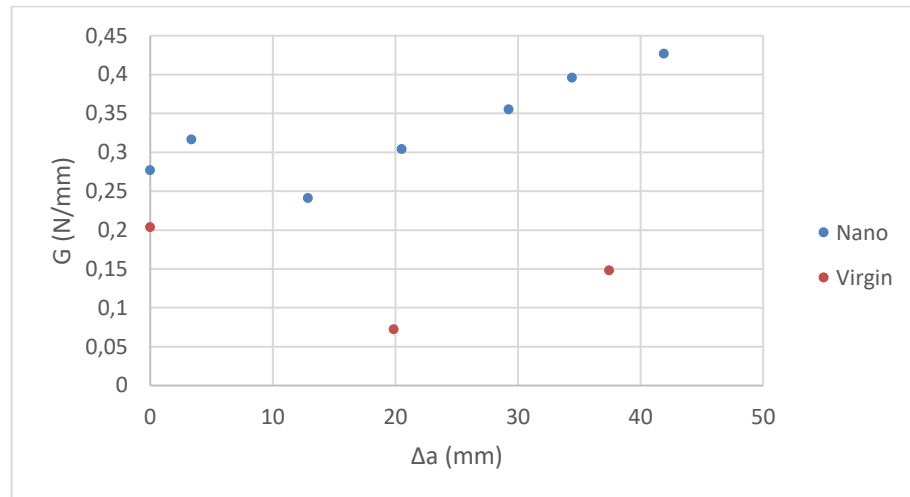
The following graph (Graph 5-8) represents the force-displacement curve for the comparison between reinforced and virgin specimens. As it can be seen, the reinforced sample has a higher peak load than the virgin one, but the difference between them is very low (a difference of less than 50N).



Graph 5-8 Force-displacement curve for the comparison between nano and virgin batch 3, type 3 specimens

On Graph 5-9 it can be seen that the fracture toughness of the reinforced specimen is higher than for the virgin one, starting from similar values, with a reduction when the crack

length had values between 10 and 20 mm, probably due to adhesive fracture or adhesive lack; and then an increase of the energy, with values over 0.4 N/mm for the reinforced specimen, which almost triplicate the values of the virgin one.



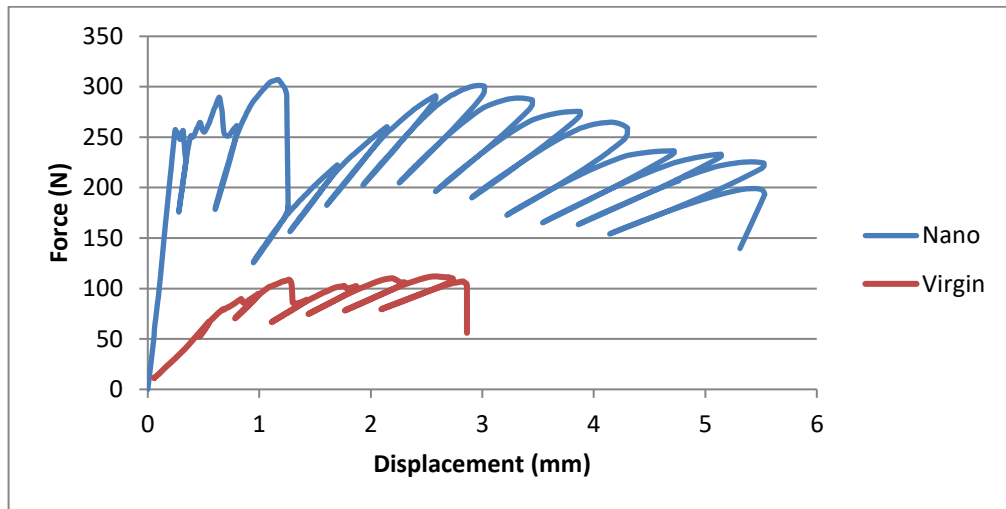
Graph 5-9 Fracture toughness-crack length curve for batch 3, type 3 specimens.

### 5.3.5. Batch 4

#### PROCESS

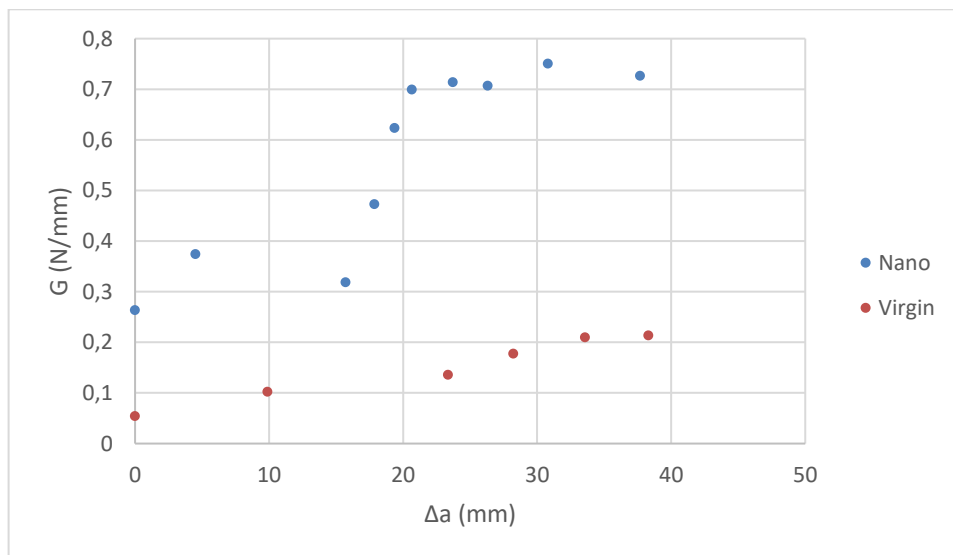
Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 160 $\mu\text{m}$
Bonding	Resin: AS5309W (100:50). Teflon inside the nanofiber mat.
Curing process	Increase of 15°C each 10 min until reach 80°C, 15 hours at 80°C + 3h at 115°C

In the Graph 5-10 a low force for the virgin specimen can be seen compared to the peak load of the reinforced one, which reaches values over 300N. The low force in the case of the virgin specimen can be due to the adhesive lack which can be observed in Picture 5-6.



Graph 5-10 Force-displacement curves for Batch 4, type 3 specimen

Graph 5-11 shows the effect of the reinforcement on the fracture toughness. The initial values of the toughness around 0.3 N/mm increase, when the crack length exceeds 20mm, to 0.7 N/mm. At that point, as it can be seen in Picture 5-6, the crack propagation becomes cohesive and the nanofibers develop their real potential.



Graph 5-11 Fracture toughness-crack length for batch 4, type 3 specimens



Picture 5-6 Fracture surfaces of batch 4. Left, reinforced specimen. Right, virgin specimen

### 5.3.6. Batch 5

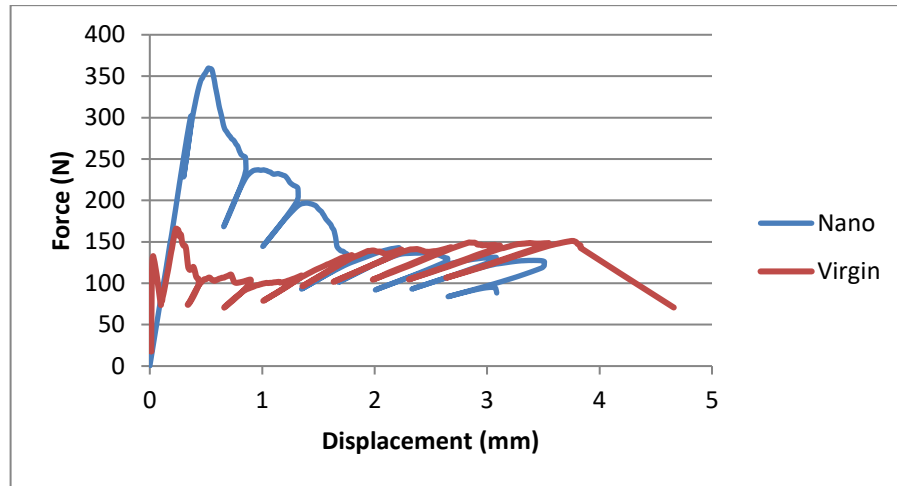
#### PROCESS

Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu$ m
Bonding	Resin: AS5309W (100:50). Teflon inside the nanofiber mat.
Curing process	Increase of 10°C each 10 min until reach 80°C, 16 hours at 80°C + 4.5h at 115°C

Similarly to batch 4, batch 5 reaches a higher load value for the reinforced specimen than for the virgin one at the moment when the crack propagation is initiated; but in this case,



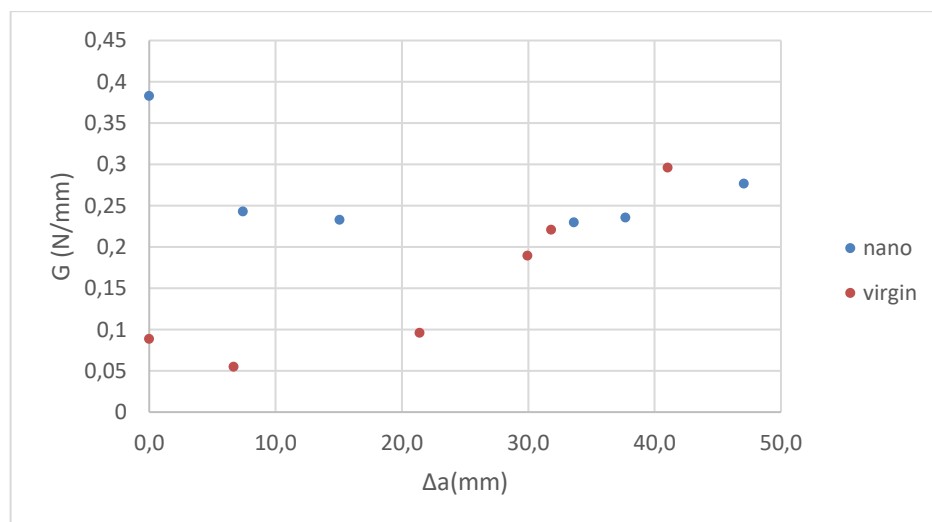
when the crack displacement acquires a value close to 2mm, the axial load for both, nano and virgin specimens, is almost the same.



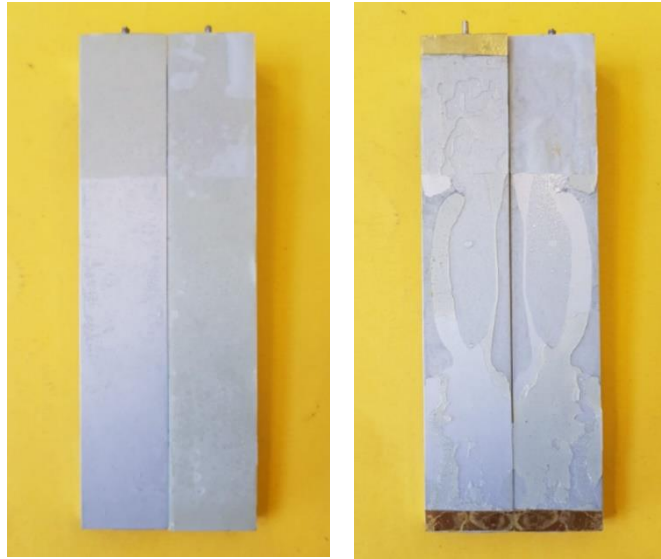
Graph 5-12 Force-displacement curve for Batch 5, type 3 specimens

Graph 5-13 shows initial values of fracture toughness for the virgin and the reinforced specimens distant one from the other, but which get closer while the crack propagation increases, becoming very similar over a value of the crack length around 30 mm.

This behaviour can be related to the fracture surface. In Picture 5-7, for the nano-reinforced specimen, it is clear that the crack doesn't propagate into the nano-mat, but it probably ran close to the interface.



Graph 5-13 Fracture toughness-crack length curve for batch 5, type 3 specimens



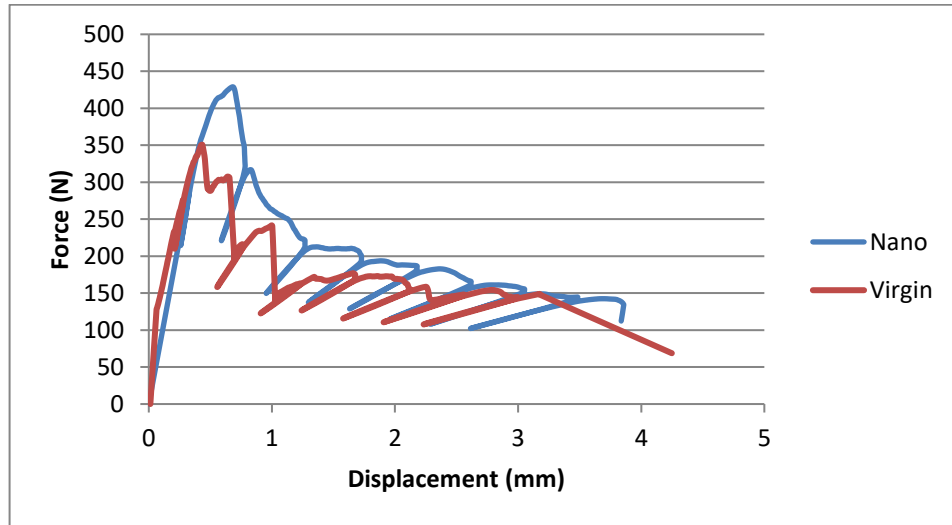
Picture 5-7 Fracture surfaces of batch 5. Left, reinforced specimen. Right, virgin specimen

### 5.3.7. Batch 6

#### PROCESS

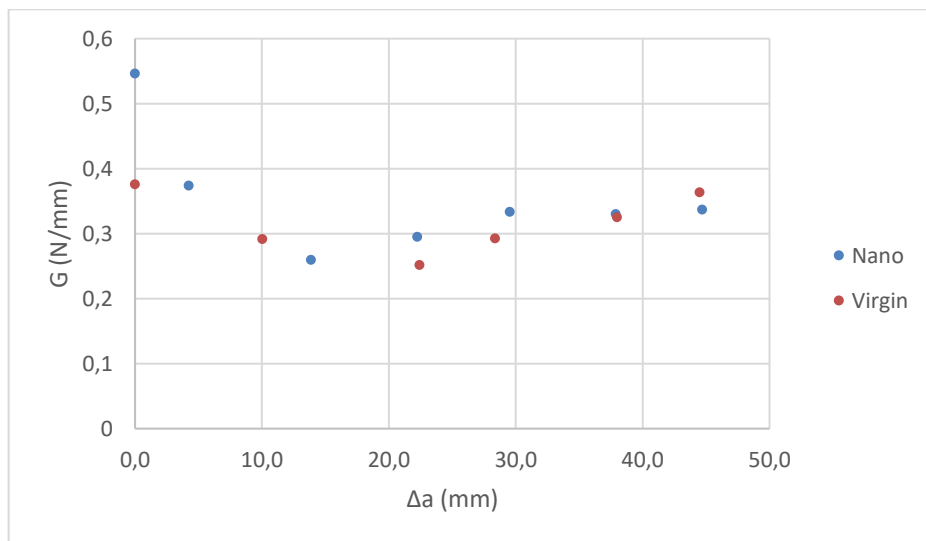
Aluminium specimens production	Al2024-T3 specimens designed with type 3 geometry
Pre-treatment	Polish + Caustic soda + P2 etching
Nanofibers	Nylon 13%wt + TFA/formic acid/chloroform 10:60:30 vol 87%wt. Thickness: 200 $\mu\text{m}$
Bonding	Resin: AS5309W (100:50). Teflon inside the nanofiber mat.
Curing process	Increase of 10°C each 10 min until reach 80°C, 72 hours at 80°C + 5h at 115°C

For this last case, the peak load for the nano-reinforced specimen is higher than the virgin one, but the difference between them is small so the potential of the nanofibers on this case is not completely developed.

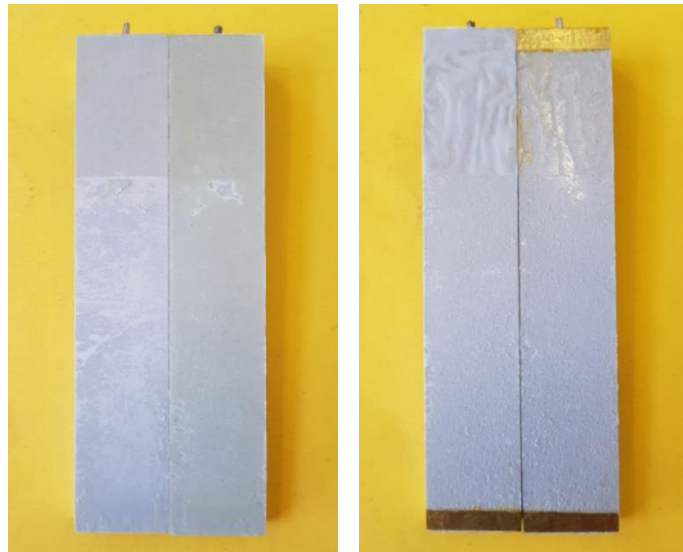


Graph 5-14 Force-displacement curve for Batch 6, type 3 specimens.

Looking at Graph 5-14 and observing the fracture surfaces in Picture 5-8, it can be deduced that the similar curves for the reinforced and the virgin specimens are due, probably, to the cohesive failure on the virgin specimen, which increases the fracture toughness, and the adhesive failure on the reinforced specimen, which decreases the energy.



Graph 5-15 Fracture toughness- crack length curves for Batch 6, type 3 specimens

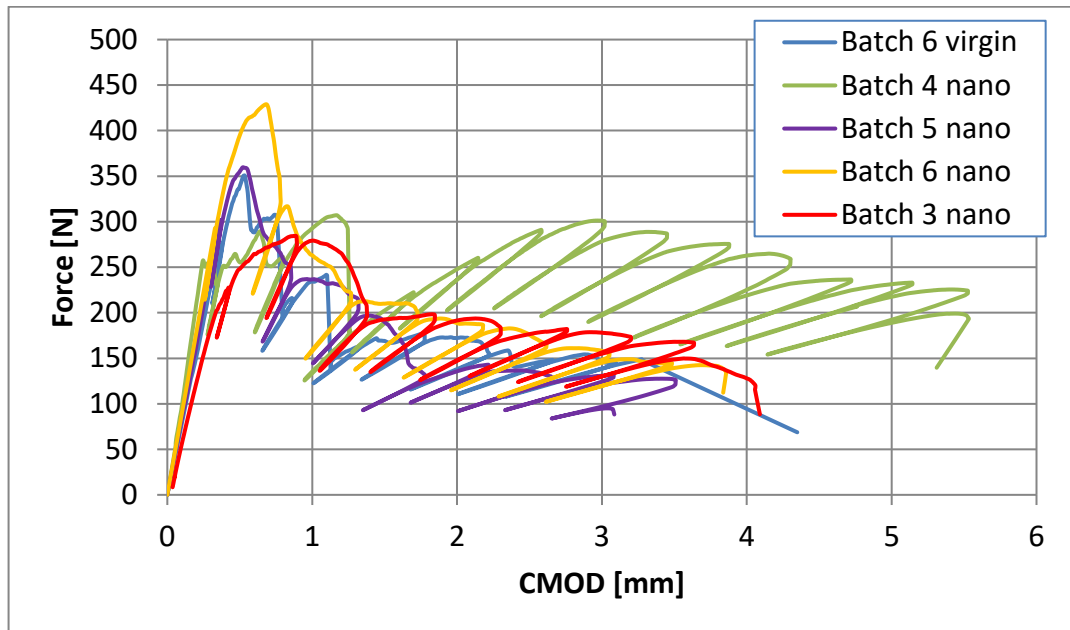


Picture 5-8 Fracture surface of batch 6. Left, reinforced specimen. Right, virgin specimen.

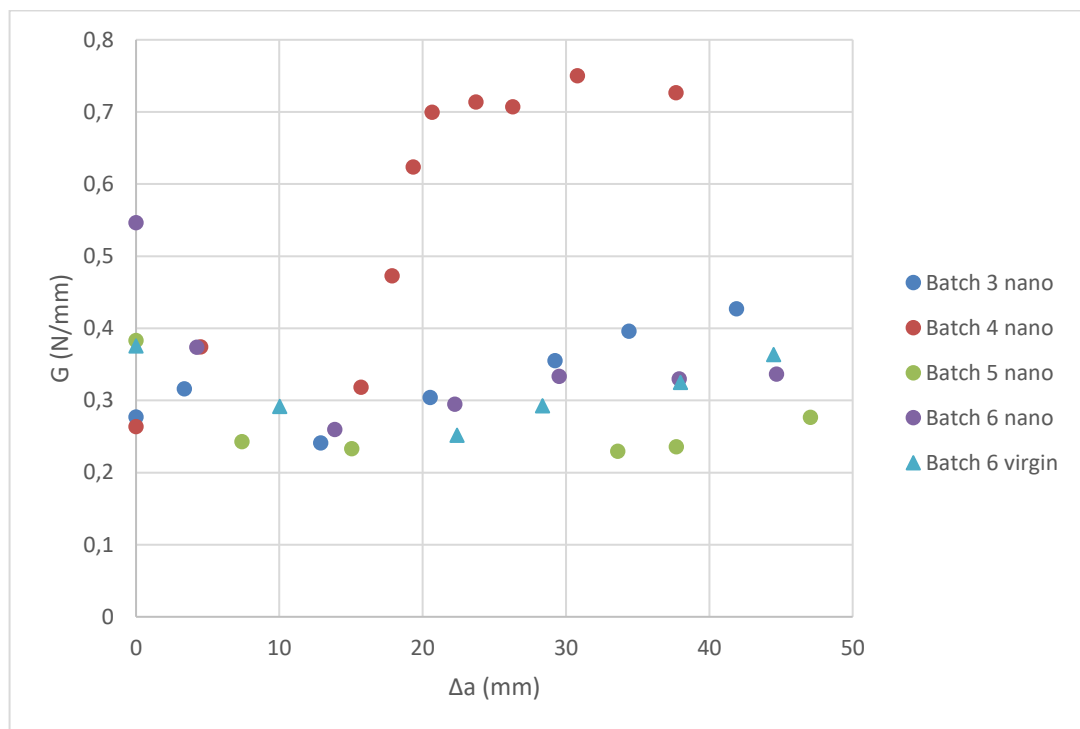
#### 5.4. OVERALL RESULTS

In Graph 5-16 and Graph 5-17 are shown the force-displacement and fracture toughness-crack propagation curves, respectively, for nano-reinforced batches 3 to 6. These graphs are performed in order to have an overall view of the different effects that the nanofibers have on each batch.

In Graph 5-16 it can be observed the similar behaviour of the curves, except for batch 4. Every curve has an initial peak load with values between 300N and 350 N (except batch 6 nano that has a higher peak value, over 400 N), and then all of them stabilise in a range between 100N and 200N, except batch 4, which has a higher stabilized load. This behaviour is also reflected in Graph 5-17 where the fracture toughness value of batch 4 doubles the neat epoxy value and the  $G_I$  of the other batches, which have similar behaviours.



Graph 5-16 Force-displacement curves for batches 3-6 [31]



Graph 5-17 Fracture toughness- crack propagation curves for batches 3-6 [31]

## 6. Conclusions

In that project, the production of aluminium specimens bonded with nano-reinforced epoxy adhesive was developed to study the enhance of the fracture toughness. The nanofibers were obtained with electrospinning process.

Three different geometries were used to produce 9 batches composed of two specimens. These specimens were bonded, one with neat epoxy and the other with the nano-mat impregnated with the resin, for each batch. After the bonding, they were cured, following different curing processes and then tested with a Double Cantilever Beam technique, generating a Mode I fracture, to check the effect of the nano-reinforcement compared to the neat epoxy. It was observed an improvement of the fracture toughness that, in the cases where the fracture was developed inside the nano-mat, it doubled the value obtained for the non-reinforced resin.

The effectiveness of fracture toughness enhancement using nanofibers was proved even though it didn't work for all of the specimens. It was observed that for some cases, the crack didn't progress through the nano-mat, rather it was produced an interfacial fracture between the surface and the adhesive.

In subsequent studies the potential of the nano-reinforcement can be developed with a more careful control on the failure mode since, with a cohesive fracture, the toughness of the adhesive can double the neat epoxy value. Also, the pre-treatment should be studied deeply, in order to prove if the degreasing is necessary and if it modifies mechanical properties of the treated surfaces.

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