

FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO



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UNIVERSIDADE DO PORTO

Department of Mechanical Engineering

**Development and Mechanical Characterization of a Novel
Flexible Adhesive**

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Master Degree in Mechanical Engineering
Specialization in Aeronautic and Vehicle Structures

July 16, 2023

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"O sentido para a vida é a curiosidade pelo futuro"

me auctore

À minha avó

Abstract

Adhesive technology has gained popularity in various industrial sectors, particularly in the automotive and aerospace industries. In comparison to traditional mechanical joining methods, fastening or riveting, adhesive bonding offers numerous advantages over other conventional joints. It enables seamless joining of different materials and produces stronger joints with a more uniform stress distribution. One key factor in adhesive development is related to the material foot-print due to environmental effects. Thus, while seeking the development of cost-effective and reliable bonded products it is still crucial to ensure minimal environmental impact. To understand the material behaviour, a series of experimental procedures was used to help determine the adhesive properties. Furthermore, with the assistance of novel numerical tools, it is also possible to accurately model the behaviour of the material providing a suitable way to predict its behaviour under a determined loading condition and adjust its geometry. This is a crucial step in the development of cost-effective products.

The aim of the presented work is to, for the first time, mechanically characterize a novel two-component polyurethane adhesive which adds benefits of silyl groups in its composition under quasi-static conditions. Silylated polyurethane resins (SPUR) are a versatile and highly functional materials that have gained attention in various industries, serving as a sealant and as potential candidates for structural adhesive. Some developments of SPU formulations have focused on incorporating renewable and bio-based materials as alternatives to fossil fuel-based components.

Four different tests were performed for the mechanical characterization of the adhesive. Bulk specimens allowed the prediction of the tensile properties whereas the thick adherend shear test helped in determining the properties under shear conditions. Hereafter, double cantilever beam specimens were manufactured to conduct fracture energy tests in pure opening (mode I) and under mixed-mode conditions to further extrapolation of the critical energy release rate for in-plane shear (mode II). For both fracture characterization tests, the compliance based beam method (CBBM) was used to extrapolate the fracture toughness values. Lastly, single lap joints (SLJ) with aluminium and CFRP substrates were manufactured with two overlap lengths and tested in order to analyse the adhesion quality as well as the lap shear strength value. A scanning electron microscopy (SEM) examination was performed in the fracture area of bulk specimens to explore the surface morphology and chemical composition (EDS). The influence of resin modifier additives was also carried out showing a decrease in both tensile and shear properties. To finalise, three different molecular weight SPU samples were studied and were found to possess different fracture toughness values in mode I: the intermediate SPU viscosity reached the highest value.

The achieved results were employed to validate a numerical model of the adhesive itself, using a cohesive zone model (CZM) implemented in a finite element (FE) software. This involved the tuning of parameters of the numerical approach as well as defining a proper CZM shape law. Thus, a validation for all experiments was performed, following a discussion summarizing the CZM specifications.

Resumo

Os adesivos têm ganho popularidade em diversos setores industriais, especialmente na indústria automóvel e aeronáutica. Em comparação com os métodos tradicionais de ligação, como a fixação por rebites e parafusos, a ligação adesiva oferece inúmeras vantagens: permite uma conexão sólida de diferentes materiais e produz juntas fortes com uma distribuição uniforme de tensões. Consequentemente o uso de juntas adesivas em estruturas não proporciona apenas uma solução mais leve, mas também mais eficiente em termos energéticos. De facto, nos dias que correm é fundamental relacionar o impacto ambiental com o desenvolvimento de adesivos.

A fim de perceber o comportamento de adesivos, é necessário recorrer a uma série de procedimentos experimentais de modo a determinar as propriedades mecânicas que estes exibem sob diferentes tipos de solicitações. Por conseguinte, estes valores serão introduzidos em ferramentas numéricas de simulação, sendo assim possível modelar com precisão o comportamento do material prevendo o seu comportamento sob um determinado tipo de solicitação. Este processo permite uma optimização da geometria sem a necessidade de ensaios dispendiosos, o que torna os métodos numéricos bastante apelativos nas primeiras fases pré-produção.

O objetivo deste trabalho é caracterizar mecanicamente, em condições quasi-estáticas, um novo adesivo flexível à base de poliuretano com silício. As resinas de poliuretano com silício (no inglês SPUR) são versáteis e altamente funcionais tendo recebido uma atenção significativa em várias indústrias de selantes e adesivos estruturais. Alguns desenvolvimentos de formulações de poliuretano com silício incorporam também materiais renováveis, baseados em bioplásticos, como alternativas aos componentes à base de combustíveis fósseis.

Foram realizados diferentes testes para a caracterização mecânica do material. Para isso provetes de ensaios de tração e de corte foram manufaturados e posteriormente testados, de modo a se prever as propriedades do material sob solicitações puras de tração e de corte. Para tal, um software de correlação de imagem digital foi utilizado de modo a determinar o campo de deformações em ambos os testes. Posteriormente, foram fabricados provetes DCB para realizar testes de fratura em modo I puro e sob condições de modo misto. Para ambos os testes de caracterização das propriedades de fratura, o *compliance based beam method* (CBBM) foi usado para extrapolar o valor da tenacidade à fratura. Por fim, foram fabricadas juntas de sobreposição simples (no inglês SLJ) com substratos de alumínio e fibra de carbono reforçada com polímero (do inglês CFRP) com dois comprimentos de sobreposição. Seguiu-se uma análise de microscopia eletrónica efetuada ao adesivo com e sem a resina epoxy, permitindo entender o tipo de superfície de fratura e os constituintes químicos das duas soluções.

As propriedades obtidas nestes testes foram implementadas num software de simulação de elementos finitos de modo a criar uma lei coesiva adequada para reproduzir o comportamento real do material. Assim, foram contruídos modelos numéricos para os ensaios efetuados, permitindo determinar as curvas de força deslocamento e compara-las com os resultados obtidos experimentalmente, o que permitiu validar o modelo coesivo adotado.

Acknowledgements

I wish to commence by conveying my utmost appreciation to Professor Lucas da Silva for the opportunity of developing the thesis aim. I also would like to express gratitude to my esteemed supervisor Eduardo Marques which showed the opportunity to engage in this research under a constant astute guidance. Furthermore, I am profoundly grateful to my co-supervisor Alireza Akhavan-Safar for affording me the experimental component assistance during experimental tests.

A special expression of gratitude is also extended to the researcher Ricardo Carbas, whose diligent experimental groundwork formed the bedrock upon the results outcome. I must emphasize the significant contribution of the AJPU group members for helping when needed during the laboratory experimental work. A huge appreciating for the other master students Vasco Pires, Mafalda Couto and Élio Fernandes for being a group of four students of the the same vehicle and aeronautical structures master branch for sharing the same engagement role in the adhesives area. A special recognition to Maria Ribas for her friendship during the endured long hours at the laboratory. I also truly appreciate the help of the doctoral and postdoctoral researches, which provided knowledge and intellectual support during the development of my work: special appreciation to Farin and Shahin that helped me to performed my first step and to Beatriz, Catarina, Fernando and Daniel which have provided background academic knowledge and good discussions at break times. All in all, a warm thanks and to all of the AJPU members.

To Momentive Performance Materials, Inc.[®], I would like to congratulate the experience provided as well as the feedback towards the mechanical characterization and chemical background. Thank you Anne Dusseau and Michael Youngberg for endorsing in the experimental work performed.

In conclusion, I wish to extend my deep gratitude to my family and friends who have provided unwavering support throughout this journey and have been a constant source of encouragement and motivation, spurring me on to successfully complete this and later works.

Vasco Couto M. B. Rodrigues

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Abbreviations

1k	One-part component
2k	Two-part component
ADCB	Asymmetric double cantilever beam
AF	Adhesion failure
AHEW	Amine hydrogen equivalent weight
ATDCB	Asymmetric tapered double cantilever beam
CBBM	Compliance-based beam method
CBT	Corrected beam theory
CCM	Compliance calibration method
CERR	Critical energy release rate
CF	Cohesive failure
CFRP	Carbon fibre reinforced polymer
CLS	Cracked lap shear
CNC	Computer numeric control
CZM	Cohesive zone model
DCB	Double-cantilever beam
DIC	Digital image correlation
EEW	Epoxy equivalent weight
ENF	End-notched flexure
FEM	Finite element method
FPZ	Fracture process zone
LC	Liquid chromatographic column
LEFM	Linear elastic fracture mechanics
LVDT	Linear variable differential transformer
MMB	Mixed mode bending
NDT	Non-destructive technique
PSA	Pressure sensitive adhesive
SEM	Scanning electron microscope
SLB	Single-leg bending
SLJ	Single lap joint
SPUR	Silylated polyurethane resin
RT	Room temperature
RTV	Room temperature vulcanizing
TAST	Thick adherent shear test
TDCB	Tapered double cantilever beam
UV	Ultra violet

Symbols

a	Crack length
a_0	Initial crack length
a_{eq}	Equivalent length of the crack
a_{eqI}	Equivalent crack length for mode I in the mixed-mode test
a_{eqII}	Equivalent crack length for mode II in the mixed-mode test
a_{FPZ}	Length of the crack FPZ
B	Width of the DCB substrate
c	Half of the thickness of DCB substrate
C	Experimental compliance in the CBBM
C_0	Initial compliance
δ	Displacement for the DCB
Δ	Crack length correction in the CBBM
$\delta_{o,i}$	Displacement for highest traction in CZM law
$\delta_{om,i}$	Displacement for highest traction value in the mixed-mode CZM law
$\delta_{u,i}$	Maximum displacement for the CZM law
$\delta_{um,i}$	Maximum displacement for the mixed-mode CZM law
d_n	Damage variable for tensile
d_s	Damage variable for shear
E	Young's modulus
E_f	Corrected flexural modulus
E_x	Longitudinal normal modulus of DCB substrate
E_y	Transverse normal modulus of DCB substrate
Φ	Mixed-mode phase angle
G	Shear modulus
G_c	Critical energy release rate
G_{Ic}	Critical energy release rate in mode I
G_{IIc}	Critical energy release rate in mode II
G_{xy}	Shear modulus of DCB substrate
I	DCB substrate second moment of area
J_c	Critical energy release rate following the J-Intergal formulation
k	DCB specimen deflection correction factor
K	Stress intensity factor
$\mathbf{K}$	Stiffness matrix
K_c	Critical stress intensity factor

M_f	DCB substrate bending moment
P	Load for the DCB
σ_f	Tensile strength
σ_R	Remote stress applied
σ_u	Traction in CZM law
$\sigma_{u,n}$	Maximum traction value for tensile
$\sigma_{u,s}$	Maximum traction value for shear
$\sigma_{um,i}$	Maximum traction value for mixed-mode CZM law
t	DCB substrate thickness
t_{TAST}	Adhesive thickness in TAST specimens
T_g	Glass transition temperature
ν	Poisson's ratio
T	Traction vector perpendicular to the applied contour in the J-Integral formulation
τ_f	Shear strength
u	Displacement vector in the J-Integral formulation
U	Material internal elastic deformation energy
V	Transverse load in each DCB adherend
w	Elastic deformation energy in the J-Integral formulation
W	Work done by the external loads
Y	Geometrical parameter in fracture mechanics
z	distance in the normal axis for DCB specimens

Chapter 1

Introduction

1.1 Background and motivation

The usage of adhesives within the industrial domain has witnessed a notable surge, particularly in automotive and aerospace applications [1]. In contrast to conventional mechanical joining techniques, such as fastening or riveting, adhesive bonding technology offers distinct advantages: it facilitates the combination of distinct materials and provides enhanced design flexibility, leading to highly robust joints, exhibiting more uniform stress distribution [2]. Consequently, this translates into lightweight structures which will provide a lower carbon emission and reduced environmental footprint. Silylated polyurethane resins (SPUR) represent a multifaceted and exceptionally functional material that has garnered considerable interest across diverse industries, acting primarily as a sealant and having the potential to serve the base as structural or semi-structural adhesives. Noteworthy advancements in silylated polyurethane formulations have centered around the integration of renewable and bio-based substances, serving as viable alternatives to conventional fossil fuel-derived constituents [3–6].

The development of cost-effective and dependable products necessitates a comprehensive knowledge of the employed materials, with special attention on how they behave under different loading conditions [2, 7]. Thus, standard and non-standard test methodologies were developed to further mechanically characterize the novel adhesive. To commence, the adhesive may be characterized under simple quasi-static conditions where the tensile and shear properties are determined following the tensile bulk [8] and thick adherend shear test (TAST) [9] standard experiments. Digital image correlation (DIC) provides the convenience of outputting the full strain field for the tested specimens, independently of the material behaviour. Regarding the fracture toughness of the material, researchers have consistently employed the Double Cantilever Beam (DCB) test to determine the critical energy release rate in mode I, G_{Ic} (pure opening), whereas the End Notched Flexure (ENF) test has been the predominant choice for assessing the critical energy release rate in mode II, G_{IIc} (in-plane shear) [2, 10]. In more elastic adhesives, the fracture toughness in mode II may be estimated with the assistance of a fracture envelope extrapolation, a characteristic of the adhesive. This can be determined by condition to mixed-mode fracture tests using multiple

apparatus [11–13]. The usage of the compliance based beam method (CBBM) provides accuracy when estimating the fracture toughness values for mode I tests [14], mode II [15] and mixed-mode [13]. Single lap joints (SLJs) using aluminium and carbon fibre reinforced polymer adherends (CFRP) were manufactured to analyse the joint failure mode and understand the adhesive bonding capability using different material substrates.

The characterization of such material properties allows for the estimation of the cohesive law implemented in the numerical model [16]. Furthermore, the cohesive zone mode (CZM) shape can be determined and introduced in a finite element (FE) element. This allows for the simulation of the material under different quasi-static loading conditions for a wide range of geometries.

This work was developed in cooperation with Momentive Performance Materials Inc.[®] (NY, USA), which provided the necessary materials and financial support for its completion.

1.2 Objectives

The work reported in this document has three main purposes. The first one is to mechanically characterize the novel flexible two-component (2k) SPUR adhesive, employing tensile, shear, fracture and SLJs tests. The second aim is to establish a numerical CZM law that predicts the adhesive behaviour under quasi-static conditions. This will be performed by numerically modelling the experimental procedure and the comparing this response to experimental results. In addition, procedures are carried out to understand the behaviour of the adhesive when different resin modifier additives are included in the formulation, as well as considering different SPUR molecular weights.

1.3 Research methodology

The present work proceeded following the listed tasks

- A comprehensive literature review of flexible adhesives and SPUR was undertaken with the primary objective of acquiring in-depth knowledge regarding the current state of the art;
- A review of the mechanically characterization techniques was performed in order to determine the experimental procedure to adopt, as well as the most suitable CZM law shapes;
- Experimental testing of the first adhesive batch to determine the fracture toughness properties;
- Development and validation of suitable numerical models;
- Analysis of the effect of the inclusion on 3 different resin modifier additives on the tensile and shear properties of the adhesive;

- Study of the variation of the first mode fracture toughness as a function of different SPUR molecular weights (viscosities).

1.4 Thesis outline

The thesis is structured into eight distinct sections, each serving a specific purpose to address the main research problem. The initial chapter offers a concise introduction, providing an overview of the problem at hand, the background context, the underlying motivations driving the research, and the set goals. The second chapter delves into a comprehensive state of the art review that encompasses a thorough examination of adhesive joints with a mode detail part in SPUR, accompanied by an exploration of the most suitable approaches for failure load prediction, especially for fracture characterization tests.

The third chapter describes with detail the experimental procedures followed. Hence, the specimens were tested and the results reported as a summary in the fourth chapter. The detailed results are displayed in paper A appended to this thesis [A](#). The fifth chapter contains all the numerical analysis from the choice of the cohesive shape law to the validation of the experimental results, more in deeply described in the paper B also appended in this document [B](#).

The last two chapters, seven and eight, summarize the main conclusions of the work and suggest themes worthy of further investigation, respectively.

By structuring the thesis in this manner, the reader is guided through a logical progression of topics, ensuring a comprehensive understanding of the problem, the relevant literature, and the methodologies employed in characterizing and modelling of the novel 2k flexible adhesive.

Chapter 2

State of the Art

2.1 Adhesive bonding

Adhesive bonding is often seen as novel and highly developed process, hinged on modern chemistry. In fact, it has been ubiquitous in nature for a long time in earth's history. From plant resin, to starch or animal glue, adhesive bonding plays an important role in nature, even in adverse environmental conditions such as those found by marine mussels under water [17]. The gecko is a well-known example of adhesive application in the animal kingdom. This species uses the concept of dry adhesion to be able of climbing steep slopes [18]. Despite the early existence of such technology, its application in the engineering field only became active over the last century. For instance, in earlier aircraft manufacture, traditional joining methods like welding, riveting and bolting were mainly used, nevertheless with adhesive joints, structures can be made lighter through the combination of dissimilar materials in a single joint [1]. The ability to synthesize polymers ultimately led to growth of synthetic adhesives, which are nowadays highly used in the industry as highly specialized materials [2].

As referred, adhesive joints are seen as an alternative to mechanical fastening. In fact, the joint itself takes less volume and weight, providing a more normalized stress distribution. The bond quality depends on the two surface bonding quality, since the interface is key for a decent adhesive joint. The design of a good performing adhesive joint must take into account three main factors [2]:

- The adhesive must be in a solid state to be easily applied to the substrates surfaces;
- The material must be hardened by the so-called curing stage;
- The dimension of the joint geometry must take into account loading condition and the working environment of which will be subjected.

Pressure sensitive adhesives (PSA) are an exception to one of these factors, since there is no curing stage needed. Nonetheless the adhesion properties must still be studied over time, during active load conditions [2, 19].

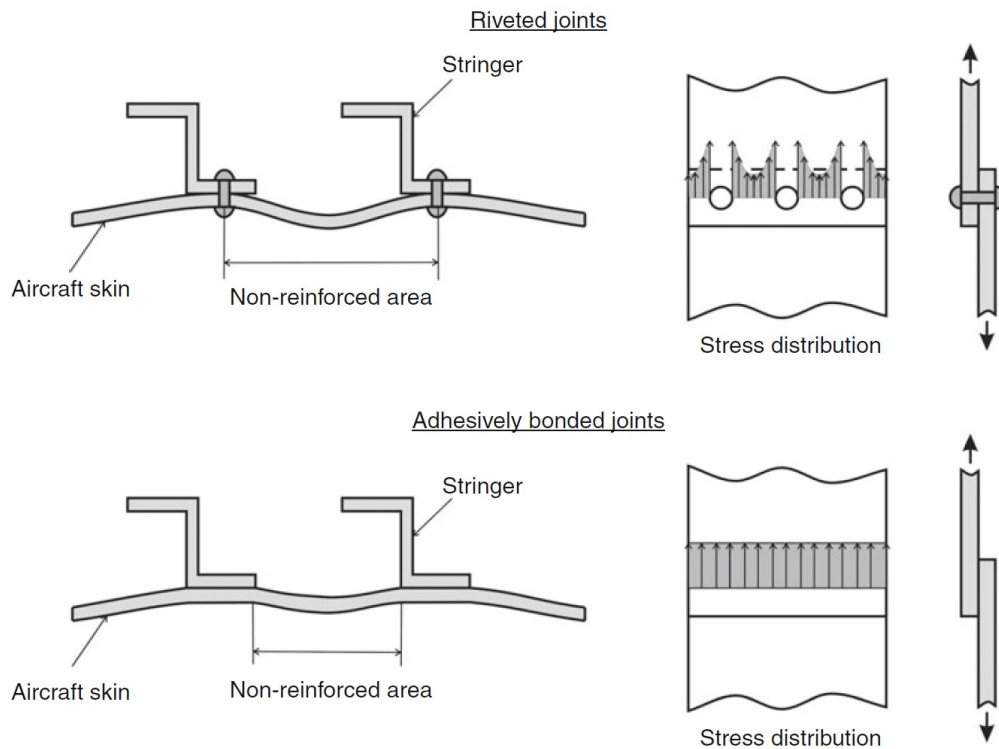


Figure 2.1: Riveted and adhesive joint configuration (*left*) and stress distribution (*right*). Adapted from [2]

Adhesive joints have dissimilar definitions between peers [2], notwithstanding they can always be interpreted as being a connection between two solid substrates, joined together with adhesive. In other words, it can also be described as a means to obtain adhesion between the two adherends in the adhesive overlap area. This will induce and create interfacial forces when the substrates are subjected to dissimilar external force. In the engineering field, this represents a valuable alternative to mechanical joints, which provides benefits in terms of load and stress distribution [2]. The loads acting on conventional joints, such as those fastened or riveted, originate uneven stress distributions with peak values in localized points. Adhesives provide a more even stress distribution field throughout the bonded area, since the load is spread over a relatively large overlap. Figure 2.1 displays two types of joints used for the assembly of a stringer and an aircraft skin: this connection can be performed with standard riveting, adhesive bonding, or an hybrid solution combining both philosophies. The stress distribution varies along the stringer connection length, whereas the adhesively bonded alternative provides the same stress amplitude along the bonded overlap length. This allows for a higher stiffness and greater transmitted load, together with cost and weight reductions, as the adhesive is lighter and the sheet thickness can be safely reduced since the stress concentrations are lower [2].

Adhesives bring important advantages to the mechanical joining processes [1, 2]. Ductile adhesives have high vibration damping or shock absorption, which allows for a relatively high

fatigue strength. The bonding capabilities are excellent for thin plates and dissimilar materials, providing a greater design flexibility that leads to designs such as the sandwich structures. Importantly, although adhesives have a much lower strength than metals, the distributed area (length vs overlap) provides enough strength to make adhesives competitive within the structural joint field. Furthermore, the separation between the materials also brings an increased corrosion resistance [2]. Notwithstanding, adhesives can still perform poorly when joints are subjected to loads which induce stress concentrations, like peel and cleavage. Since the aim of adhesive joint is to homogenise the stress along the overlap bonded area, it is important to ensure that the adhesive layer is correctly designed for a given loading condition.

Since it relies on adhesion, a bonding process requires a good surface preparation, ensuring compatibility between the adhesive and the adherend. Furthermore, adhesives require some time to harden (at a certain temperature) and jigs or moulds to keep the component in position during manufacture. Although the great vibration damping capabilities of some elastomers, the polymer nature restricts the environment working capability of adhesive joints in terms of temperature or even humidity [2]. One of the most important disadvantages of adhesives is the lack of suitable inspection techniques. Non destructive techniques (NDT) are usually employed to detect voids, porosities, unbound areas and cracks. However, the detection of weak adhesion phenomena is very hard to achieve, since it is not yet possible to detect such defect without compromising the structural bond quality. This is one of the main reasons why aircraft manufactures and regulators not to allow adhesive bonding as the sole method of joining in primary structural aircraft components [20–22].

2.2 Types of adhesives

Adhesives and sealants are polymer based materials which can be natural or synthetic [23]. A polymer can be classified as a plastic, elastomer or a fibre, depending on the intermolecular bond strength and its molecular structure [2]. Elastomers are noncrystalline polymers which have weak intermolecular forces and a lower glass transition temperature T_g , whereas plastics possess greater intermolecular connection but lower than hydrogen bond polymers, which can be turned into fibres provided their high crystallinity.

There are a few different methodologies used for adhesive classification [2]:

- polymer base;
- type of the polymer "backbone";
- chemical components;
- functional type.

In what concerns the polymer base, natural polymers have an organic origin from natural rubber, animal glue or even tree resin. This leads to a novel trend of adhesive family, the so-called

bio-adhesives [24, 25]. On the other hand, inorganic polymers are organized in numerous families, such as epoxies, phenolics, aromatics, acrylics and silicones, among many others.

The main backbones of engineering polymers are thermosets, thermoplastics and elastomers (rubbers). Engineering thermosets such as polyurethanes and epoxies are cured and hardened with a curing cycle, a chemical process which changes the adhesive state. These cycles can be performed at room temperature (RT) or higher temperatures for a determined period of time. Polyurethane adhesives are industrially offered as a one-part component (1k), which normally cures at a higher temperature and has a short shelf-life, or as a two-part (2k) or multiple component system, which cures at lower temperatures (RT for instance) but possess a greater shelf-life. Usually these adhesives are not intended for structural use due to the carbon dioxide (CO_2) release during the curing cycle at room temperature which is a cause for the formation of porosities along the bond surface. Besides, two-component formulations provide larger elongation at failure and lower tensile, shear modulus together with a reduced lap shear strength when compared to one-part PUR [2]. Nevertheless, a two-component urethane with a cross-linked network can be considered as a semi-structural adhesive to bond composite structures in the automotive industry. Such definition will be further detailed in section 2.4.

2.3 Silylated polyurethanes

Polyurethane-based adhesives are characterized for being soluble polymers, heavily dependent on the crystallinity degree. This adhesive family is well-known for being capable of forming a wide variety of mechanical properties suitable for numerous applications. It is possible to create flexible and tough polyurethanes or rather stiff and strong formulations, competing with epoxy based adhesives [26]. Since in the thermoset polymer field two-component urethane adhesives can be used as semi-structural adhesives for plastic and metal bonding, joining another inorganic thermoset like epoxy could provide a higher strength and shear capability. As previously referred, polyurethanes usually come in one or as a two-part component, quoted commonly as 1k and 2k PUR respectively. One-part polyurethane adhesives are usually more stiff, provide greater strength at lower temperatures and possess the capability to bond substrates with lower surface energy, which augments the material range of their applications [4]. Normally, 1k components cure at room temperature (due to moisture) for longer periods of time. These are usually employed for structural and semi-structural purposes. On the other hand, two-part components have a higher elongation at breakage point and provide adequate resistance to peel and shear loads. A semi-structural classification can be a subjective definition, balancing the drop in strength with a higher capability for damping [3, 4, 6, 27]. The curing process is faster than 1k formulations, and can be cured at RT or at temperatures slightly above it. The mechanical properties of polyurethane formulations diminish with the increase of the temperature, nevertheless this family possesses excellent damping properties, being for instance suitable for bonding car windscreens (for 1k PUR component) or to bond car panels, in the case of 2k formulations. This last applications can

be seen in the BMW i3, where CFRP panels of the bodywork are bonded with a 2k PUR [28, 29]. This solution of bonding composite panels with a flexible and vibration damping adhesive is very attractive since, due to the external dynamic loading, the delamination of the panels can be avoided: if a stiffer adhesive like epoxy would be used instead of a structural polyurethane, the overlap tip stresses would be higher, function of the lower flexibility of epoxies, which would lead to a stress concentration in the overlap edges, causing a high stress peak in the composite substrates [2]. These adhesives also provide benefits to the overall performance of the structure, since it absorbs more energy during a crash with an even stress distribution along the bonded area: the structure is compliant and can remain unbroken even after the impact [26].

Silylated polyurethane resin adhesives are a group of the polyurethane family. Silane reacts with moisture present in the air, which initiates the cure state of SPUR. These adhesives allow for a wide range of material substrates, ranging from plastics and composites to metals, provide outstanding adhesion and flexibility, which translates in a decent vibration damping capability. In terms of chemistry, silane terminated polyurethanes show resistance to environmental factors like solvents, UV exposure but above all moisture. These are also low in volatile organic compounds. The synthesizing process of SPUR were first patented in the 1970's by the 3M company [4]. SPUR can be prepared in different ways, as described by several authors [3, 27, 30, 31]. For instance, the silane end-capper can be synthesized recurring to aminosilane and acrylate addition or even the addition of a diisocyanate compound, in order to form free isocyanate groups in the polyurethane backbone: this would reduce the adhesive toxicity levels [3]. To be noted, the "end-capper" refers to a specific type of functional group which is added to the stationary phase of a liquid chromatographic column (LC) [30]. Usually these SPUR are rather viscous pastes, hence a study of the molecular weight reduction by acetone application in the polyurethane black carbon part was conducted [31]. Furthermore, the addition of distilled water to remove the acetone embedded into the mixture by distillation means was also performed [27]. The production of SPUR takes a vast knowledge in the chemistry field, which goes beyond the scope of this thesis.

Despite the advantages of SPUR, common silicones and polyurethanes possess a certain level of toxicity which can be diminished [4]. In other words, having already reached a decent mechanical cost solution, the environmental costs will play a role during the manufacture life and the global adhesive life span as well as the end of life of the product. Thus, silane terminated polymers showed to be a hybrid material which contains lower toxicity levels, similar to 1k polyurethane adhesives.

The adhesive studied is a SPUR base 2k adhesive, inserted in the silyl terminated polyurethanes group. The hybrid chemistry of silane terminated prepolymers plays already a role in the industry supplying it from sealants, coatings and adhesives [4]. In fact, during the silane adhesive hybridisation, polyurethane-based adhesives had relatively better mechanical properties in terms of tensile strength, shear strength and elongation [5]. Silylated PU with special capping agents, which reduce the cross-linking density of the solution, were said to provide higher mechanical properties [5]. In simple one component polyurethane adhesives, there is a compromise within the organic backbone of the polyurethane link and alkoxysilyl groups formation at the chain edges.

The modified silane based polyurethanes create a free isocyanete group solution, which withdraws the toxicity hazard of the product [32].

Epoxies are known for their good adhesion to a large variety of materials, for being a low shrinkage resin and their effective reaction with numerous catalysts. Hence, hybrid formations are easily constituted, such as elastomers.

2.4 Semi-structural adhesives

An adhesive is considered structural when it allows to support structural loading and bearing components [33]. Structural adhesives possess high strength and are generally significantly more stiff and brittle than polyurethanes. A subset of these is known as crash stable adhesives, able to increase the impact resistance of the overall structure, achieved with the hybridization of the adhesive. For instance, due to the high stiff and brittleness, the elastic regime of the epoxy adhesive family is limited, making these adhesives unsuitable for composite bonding. Large structural loads would induce stress concentration points in the overlap edges, increasing the event of composite delamination. Epoxies, acrylics, phenolics and cyanoacrylates are examples of structural adhesives.

Unlike structural adhesives, semi-structural adhesives are much more less explored in the literature. Nevertheless, this sub-category can be defined to a material which combines both structural and elastic bonding [34], being capable of at least support its own weight and able to bear light external loading cases [35] and capable of bonding a wide range of materials [34, 35]. Usually, semi-structural adhesives come in a two-part form (2k) and are cured at relatively low temperatures, when compared to structural ones [36]. Hence, semi-structural adhesives will possess more elasticity (elastomeric deformation), allowing them to bond composite panels, with less strength and stiffness but increased vibration damping capabilities.

Despite the few studies available on the determination of the mechanical properties of this sub-family, table 2.1 agglomerates some typical property values to distinguish between structural and semi-structural adhesives. The tensile strength of structural adhesives is usually very high [33] as is the case for the tensile modulus. Due to the increased flexibility in the elastic regime, semi-structural adhesives possess a lower Young's modulus. Interestingly, the shear properties were not found to vary much from each group. In what concerns fracture mechanics properties, the critical energy release rate in mode I, G_{Ic} , is much lower in structural adhesives, this is, the structural family requires less energy to propagate an already existing crack. The fracture toughness in mode II can be around five to ten times higher than the mode I critical fracture energy in epoxy adhesives [37], and around three times higher in polyurethane adhesives.

2.5 Adhesive joint

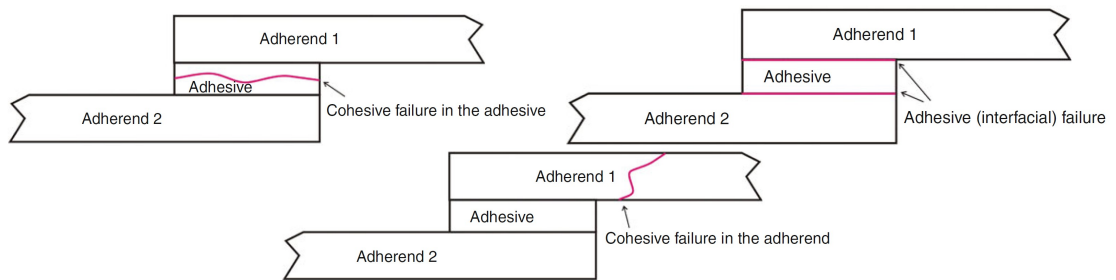
Table 2.1: Structural and semi-structural mechanical properties range

	Structural	Semi-structural
Tensile strength, σ_f	10 to 40 [MPa]	5 to 15 [MPa]
Youngs's modulus, E	1 to 10 [GPa]	20 to 500 [MPa]
Shear strength, τ_f	15 to 30 [MPa]	5 to 15 [MPa]
CERR mode I, G_{Ic}	below 0.5 [N/mm]	0.5 to 4 [N/mm]

Adhesive joints come in different configurations and possess different failure modes.

2.5.1 Types of failure modes

Adhesive joints possess a few modes of failure. For instance, a SLJ may fail on the substrate which translates to a high load bearing capacity over the bonding overlap area rather than the substrate cross section [2]. The other two loci of failure belong to the adhesive and can be cohesive and adhesive or interfacial. Cohesive failure happens when the adhesive itself is the point of fracture, remaining the substrates bonding area covered with adhesive. This means that the overlapped adhesive layer is weaker than the bond between the adhesive and the substrate. On the other hand, interfacial failure represents a lack of adhesion, where the adhesion between the adhesive and the substrate was the weakest part of the joint [2]. This phenomena can occur due to voids, inadequate surface treatment or cleaning and excess of thermal stresses. The interfacial failure is undesirable since the aim of the adhesion is to ensure there is an excellent couple between the two surfaces [1, 2, 33]. Figure 2.2 illustrates the three types of failure in adhesives joints. Furthermore, mixed failure which combines adhesive and cohesive failure can also occur.

**Figure 2.2:** Types of failure for adhesive bonded joints. Adapted from [2]

A particular review analysis can be performed more in-depth on the double-cantilever beam (DCB), a test performed in this work. For the crack propagation in DCB specimens tested in pure opening condition, four types of sub-failure modes can be defined, where further techniques of post fracture analysis can be carried out. For instance, the mixed-failure between the debonding path and adhesive failure can occur. For that, four types of failure can be defined, as fully cohesive,

interfacial, oscillatory and alternating [2]. On the cohesive case, the crack propagates fully in the adhesive layer close to the middle cohesive plane, whereas in the interfacial face, the crack travels away from the middle plane to the substrate adhesion surface. An oscillatory failure is a particular case of cohesive failure [2, 38], where the propagation oscillates in-between the middle cohesive plane (throughout the adhesive thickness) and it may reach the adherends for small overlap lengths. Similarly, the crack propagation constantly changes the path for an alternating failure type between the two substrates surfaces. Image 2.3 illustrates the four failure modes in DCB specimens under pure opening tests, as described.

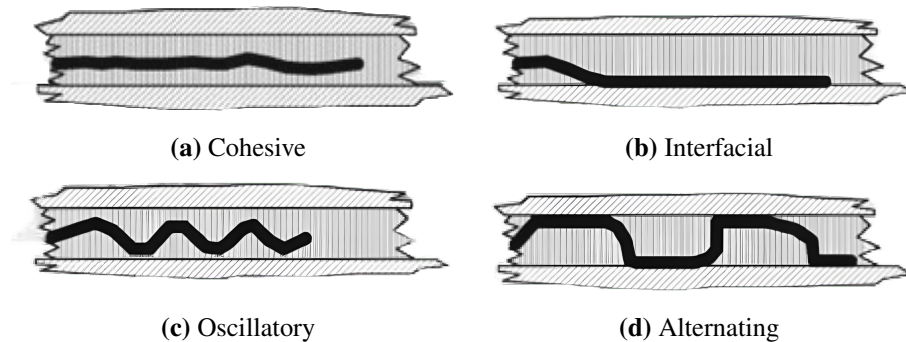


Figure 2.3: Crack trajectories in four different failure modes for DCB specimens. Adapted from [2, 38]

Adhesive bonded joints have multiple types of loading conditions in practical applications. Essentially, joining the eventual thermal internal stresses, five main loading types can be differentiated from each other, taking into consideration the fact that some of this loading scenarios will certainly be crosslinked in physical applications [2]. Image 2.4 illustrates the five most common types of loading: compression, tension, shear, cleavage and peel.

Lap joints are the most common design where the adhesive is mostly submitted to shear stresses (also referred to lap shear stresses) and can be branched to several other geometries. The simplest one is the classical SLJ, which is convenient to manufacture and provides adequate mechanical performance. Double lap joints provide increased performance, since they have twice the adhesive bonded area, thus providing a higher lap shear strength than the SLJ or even the better aligned joggle lap joints. Nonetheless the manufacturing processes is significantly more complex. Curved joints have been shown to perform better under tension [40, 41] by increasing the failure load and maximum extension to failure. Two highly effective concepts are the wavy and reversed bent lap joints [2, 41]. Figure 2.5 identifies these five lap joints geometries.

2.5.2 Joint design

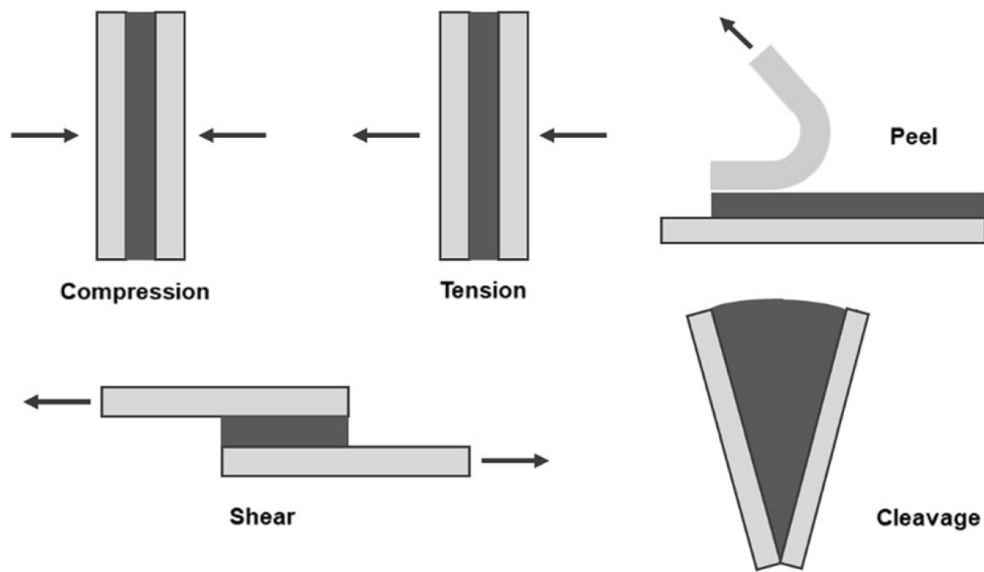


Figure 2.4: Types of adhesive loading condition. Adapted from [39]

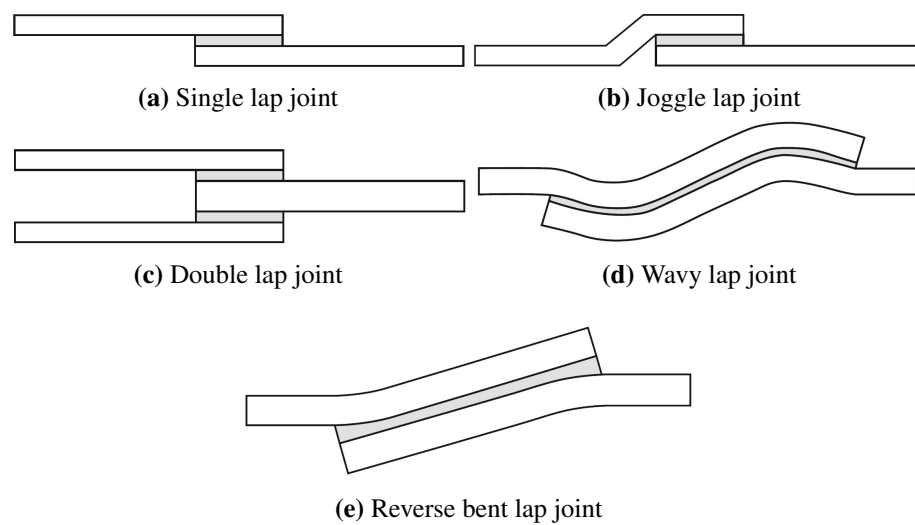


Figure 2.5: Types of lap joint design. Adapted from [2]

In terms of design, adhesive joints can possess various geometries. Figure 2.6 illustrates other joint designs rather than the SLJ variations. The choice of adhesive for a bonded joint must consider the joint design for two primary reasons:

- It is essential to account for the load transmission characteristics within the adhesive joint. For instance, whether the joint is subjected to significant cleavage or peel loading scenarios, a toughened adhesive system, capable of withstanding such loads would be required. Conversely, high shear or tension loads are better managed with a more rigid adhesive system [2];

- The assembly requirements of the joint are also important to consider in the geometrical design. In the case of larger joints, the adhesive should have a sufficiently long working life prior to the curing process to allow ample time for proper adhesive application [2, 7].

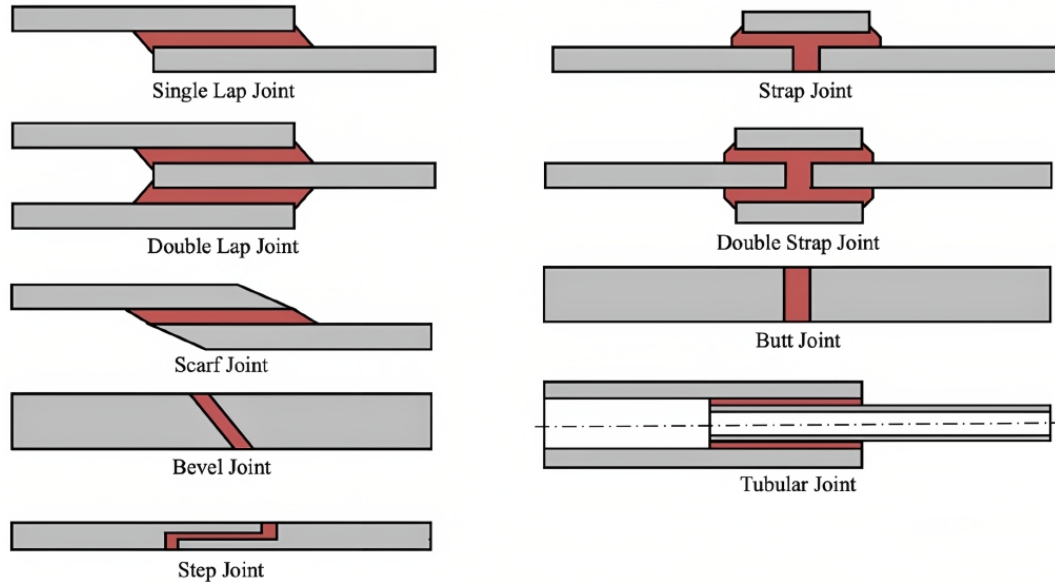


Figure 2.6: Examples of configurations for adhesive joints. Adapted from [33]

2.6 Failure prediction approaches

Given the wide range of possible loads acting on adhesive joints, there is a need to understand the behaviour of adhesives under those conditions. In fact, peel and shear stresses are commonly the most significant for the strength capability of adhesive joints [2]. For instance, in SLJs, due to the misalignment between substrates and the short overlap length, there will be a non-uniform distribution of the peel and shear stresses along the overlap length and along the joint width, considering a non-infinite three dimensional joint. In general, there are three approaches for analysis of adhesive joints, which assess their strength capability [7, 42]:

- Continuum mechanics;
- Fracture mechanics;
- Damage mechanics.

being the last one enumerated a combination between the previous two.

2.6.1 Continuum mechanics analysis

The continuum mechanics methodology has been used for various researchers to predict the failure in adhesive bonded joints. It is based on the strength of materials and the main thesis of such formulation is based on a perfect adhesive-adherend interface, thus not taking into consideration the adhesion properties in-between materials. The principles of continuum mechanics revolves around understanding the stress distribution and the resulting distortions in bonded joints [2]. It also involves determining the highest amount of external forces which can be exerted on the joint under various loading conditions, including tension, shear, peeling and cleavage, as previously described. This criteria is also known for its susceptibility to the presence of singularities, mainly on the edge or overlap limits of adhesive-adherend interface, illustrated in figure 2.7 [42]. This is mathematically inconvenient since the stress at those points depends on the mesh in finite element simulations as the stress value on those points tends to infinity: this leads to non-convergent solutions, even as the mesh becomes more deeply refined [43]. This represents a roadblock in the estimation of an accurate lap shear strength, therefore the failure load ought to be expected according to linear elastic analysis. An often proposed solution is to use a filleted adhesive layer, but the literature shows that the singularity points still appear and are dependent on the fillet radius [42]. The solution for this issue are applicable only to continuum structures, not taking account for material defects.

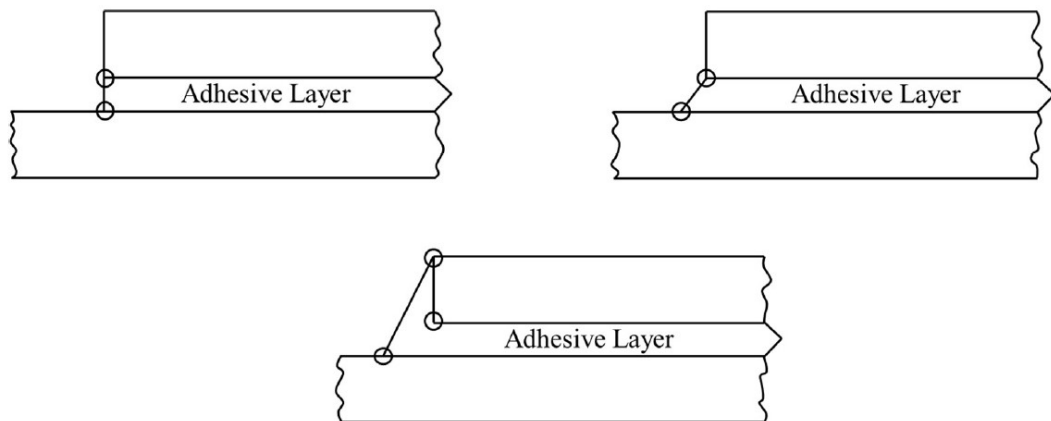


Figure 2.7: Localization of the point singularities following a continuous mechanics approach. Adapted from [42]

2.6.2 Fracture mechanics formulations

The fracture mechanics approach is based on the previous methodology and has the same hypothesis of not inducing defects on the materials, assuming a perfect continuous behavior [42]. Notwithstanding, this philosophy allows for the existence of defects due to manufacturing issues

or previous flaws which will determine and predict the failure of the structure as well as how will the material fail. This differs from the previously described formulation [42], following the well-known Griffith-Irwin theory [44]. This methodology evaluates whether the dimension of the defects are critical and whether they can lead to structural failure. Examples of such imperfections may be delamination, the presence of cracks or debonding.

In order to investigate the crack propagation within materials, fracture mechanics relies on two simple criteria. The first one is referred to as the stress intensity factor criterion (K) which is a dimensionless parameter that scales the stress state field in the vicinity of the crack. The second, so-called the energetic criteria, establishes a relation between the strain energy release rate, G , as a function of the load applied [42, 45, 46]. The critical energy release rate, G_c , corresponds to the maximum energy the material can absorb right before the crack commences to propagate. Provided this, it is crucial to estimate the G_c value, which is an intrinsic material property.

The literature generally agrees that the estimation of the stress intensity factor is hard to acquire, and following an energetic approach is mathematically a more concise option. Hence several methodologies have been developed in order to extract the critical fracture energy of bonded joints [14].

Energy release rate approaches consider effects on materials in which, at a given point, provide the material loading and will induce stress intensification points, nucleating cracks. For instance, whether the focus is on a particular defect, its propagation will occur when the energy at the edge becomes equal or greater than the energy necessary to propagate a crack in the specific material. Having known the value for the critical energy release rate for each material, the first fracture mechanics formulation describes that it is possible to estimate and prevent crack propagation [47]. Thus, a crack is propagated when the condition $G \geq G_c$ is verified. Considering now the material elasticity, there is a greater mechanic energy dissipation like plastic deformation on the verge of the crack tip. The so-called fracture process zone (FPZ), taken into account in linear elastic fracture mechanics (LEFM), is a small region ahead of the crack tip in which the material suffers an inelastic behaviour due to the crack existence [45]. LEFM considers this zone is relatively small when compared to the crack length. Nevertheless, in elastomers, the FPZ can in reality be larger than the crack length, introducing a constrain on the usage of linear fracture mechanics formulation as an energetic accurate approach for materials with such behaviour [2, 26]. Generally, the energy release rate corresponds to the variation of the elastic energy provided the crack propagation increment. The G value can be written by

$$G = \left(\frac{dW}{da} - \frac{dU}{da} \right) \quad (2.1)$$

where a corresponds to the crack length, W is the work done by the external loads and U the material internal elastic deformation energy [42, 45].

The scalar stress intensity factor in the neighborhood of the crack is a function of the crack tip

(a), remote stress applied (σ_R) and a geometrical parameter (Y) and can be given by [45, 46]:

$$K = Y \sigma_R \sqrt{\pi a} \quad (2.2)$$

The stress intensity factor can be related with the energy release rate, the energetic approach. The parameter K_c corresponds to the critical stress intensity factor value for which the crack will commence its propagation: $K = K_c$. The relation between the material critical stress intensity factor and the critical energy release rate is given by [45]:

$$G_c = \frac{K_c^2}{E} \quad (2.3)$$

in a plane stress state, whereas in a plane strain scenario the following is valid:

$$G_c = \frac{K_c^2(1 - \nu^2)}{E} \quad (2.4)$$

It is important to highlight that the considerations showed above are also valid in a non critical state.

After briefly explaining how a crack can propagate, there are three different loading scenarios for such occurrence, referred as mode I, II and III in the literature [45, 46].

- Mode I $\Rightarrow$ Opening;
- Mode II $\Rightarrow$ In-plane shear;
- Mode III $\Rightarrow$ Out-of-plane shear.

Figure 2.8 illustrates the three different modes for crack propagation each of them in its pure state.

Any material defect can be nucleated and propagated under pure mode I, II or III independently or as a mixed condition, combining opening, shear and/or in-plane shear loading.

Adhesive joints are non-homogeneous materials, thus energetic fracture approaches are preferable over stress intensity factors estimations. Hence, when the materials do not obey to the hypothesis supposed by LEFM, alternative methodologies must be compelled. One remarkable method used in adhesive bonding to measure fracture properties is the J-integral [26, 45]. This approach allows for the neutral equilibrium condition at the crack tip edge [44, 48] and is extendable to not only brittle but also elastic materials, providing a wider range of application. Sun et. al. [49] found that for brittle adhesives, like epoxy based for instance, the G_c and J_c are very close, nonetheless for more ductile adhesives, like polyurethane, the value of G_c provided by LEFM analysis would be 15% greater than J_c . This is due to the larger FPZ in elastomeric materials when compared to brittle and stiff adhesives. A contour integral is established around the specimen geometry considering a bi-dimensional model without out-of-plane changes. The formulation follows:

$$J = \int_{\Gamma} \left(w dy - T \frac{\partial u}{\partial x} ds \right) \quad (2.5)$$

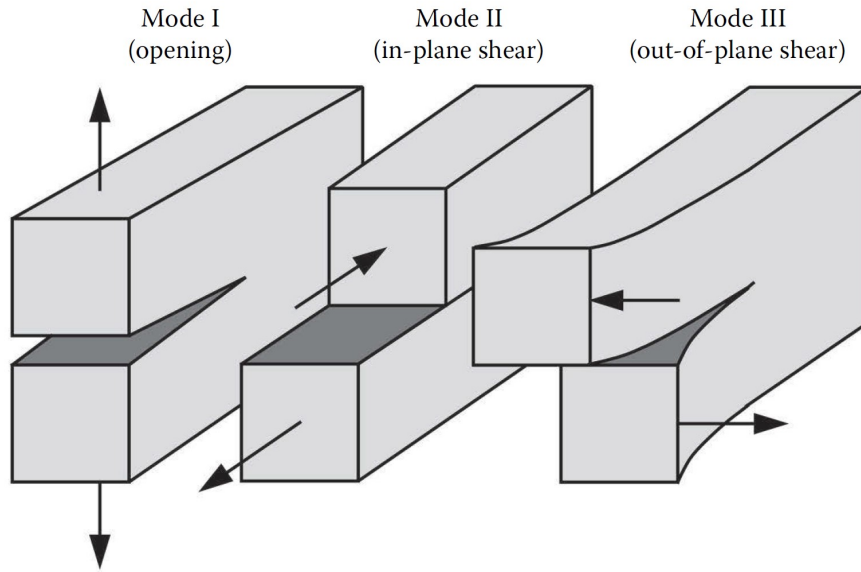


Figure 2.8: Fracture modes. Adapted from [45]

which is given by the contour integral where w corresponds to the elastic deformation energy, u is the displacement vector and T the traction vector perpendicular to the applied contour [45]. By recurring to a deformation theory of plasticity the J-Integral is valid for elastic-plastic materials such as ductile adhesives [48].

The aim for the energetic methodologies is to extract the critical energy release rate value, a material property, in order to mechanically characterize the adhesive behaviour under pure opening and pure in-plane shear conditions. The material fracture toughness property will depend on the three different types of loading presented in figure 2.8. The two tests most commonly employed for adhesive characterization in the literature to measure the fracture toughness under mode I and mode II conditions are the DCB and the end-notched flexure (ENF) tests, respectively [1, 2, 26].

Several formulations were developed in order to capture and withdrawn the critical energy release rate value from these two mode tests, being the J-integral one of them. The inconvenience of this approach remains on an experimental constraint, which demands constant monitoring of the specimen using other physical components during the test. Provided the fact J-integral formulation has two physical inputs being the rotation of the substrates as well as the crack length, it is crucial to withdraw those values during the test. To be noted that the load as well as the displacement can be directly provided by the testing machine data process unit. In order to keep track of the rotation, inclinometers can be used [50] whereas for the instantaneous crack length digital image correlation (DIC) can be helpful [49], although there is a need for photographs or recordings of the the tests. Such approach demands a special attention on the specimen preparation (coated with white mate paint and speckled with black mate pain) and illumination, since the image quality has an important role in the accuracy of the results. For polyurethane adhesives, the J-integral is a attractive approach since it correlates with the large FPZ in a satisfactory way [49]. Other methodologies

like the compliance calibration method (CCM) and the corrected beam theory (CBT) need instantaneous input values of the crack length [14]. Moura et. al. [14] arrived at a novel sophisticated formulation which competes with the J-integral and allows to more easily perform experimental tests and extract data. The so-called compliance-based beam method (CBBM) does not require a measurement of the crack length throughout the tests, which facilitates the testing methodology, especially under various temperatures, where a thermal chamber is used to fulfill the needs of the study. This methodology makes use of an equivalent crack length concept which estimates the crack size along the tests by taking into consideration the loading, displacement, experimental compliance and as a consequence, the FPZ [14, 51]. This has the advantage of eliminating the need to record crack progression, avoiding errors stemming from the processing of this data.

2.6.3 The compliance-based beam method

The CBBM is based on previous establishes relations like the Irwin-Kies theory which serves as based for the CCM [52], in which the critical energy release rate in mode I is given by:

$$G_{Ic} = \frac{P^2}{2B} \frac{dC}{da} \quad (2.6)$$

where P is the load measure by the testing machine loading cell, B is the width of the DCB substrate, a is the crack length and C corresponds to the experimental compliance [14, 51], which is a function of the testing machine displacement δ and the load, being written as:

$$C = \frac{\delta}{P} \quad (2.7)$$

As evident, the compliance is indirectly a function of the crack length, where its partial derivative can be calculated recurring to the displacement and the measured load. Following Moura et. al. [14], the flexibility of the adherend can be approximated to a cubic polynomial as a function of the crack length.

$$C = f(a) = C_3 a^3 + C_2 a^2 + C_1 a + C_0 \quad (2.8)$$

By derivation the expression above,

$$\frac{dC}{da} = 3C_3 a^2 + 2C_2 a + C_1 \quad (2.9)$$

So the G_{Ic} value can be rewritten as

$$G_{Ic} = \frac{P^2}{2B} (3C_3 a^2 + 2C_2 a + C_1) \quad (2.10)$$

The G_{I_c} value can be withdrawn following the CBT since both load and displacement are known [14, 47, 51]

$$G_{I_c} = \frac{3P\delta}{2B(a + |\Delta|)} \quad (2.11)$$

where the Δ corresponds to the crack length correction value for the crack tip deflection and rotation. This value can be determined following Wang and Williams [53]

$$\Delta = t \sqrt{\frac{1}{13k} \left(\frac{E_x}{G_{xy}} \right) \left(3 - 2 \left(\frac{\Gamma}{1 + \Gamma} \right)^2 \right)} \quad (2.12)$$

where t , E_x and G_{xy} are substrates parameters, being t the DCB substrate thickness, E_x the longitudinal normal modulus and the G_{xy} the shear modulus and k the shear stress constant distribution as a scalar value for the deflection correction due to the induced shear loads which takes the value of 0.85 for DCB specimens [51]. Lastly Γ is given by

$$\Gamma = \frac{1}{k} \frac{\sqrt{E_x E_y}}{G_{xy}} \quad (2.13)$$

where E_y is the transverse Young's modulus of the DCB substrate.

Recurring to the beam theory, it is possible to established a relation between the experimental compliance and the crack length as being:

$$C = \frac{8(a + |\Delta|)^3}{E_x B h^3} \quad (2.14)$$

In order to estimate the crack correction factor it is also possible to extrapolate a linear regression of the compliance, C , to the power of $1/3$ as a function of the crack length, a , being

$$C^{1/3} = \frac{2}{h(E_x B)^{1/3}} (a + |\Delta|) \quad (2.15)$$

The strain energy of the specimen can be given by the following equation

$$U = 2 \left[\int_0^a \frac{M_f^2}{2E_x I} dx + \int_0^a \int_{-h/2}^{h/2} \frac{\Gamma^2}{2G_{13}} B dy dx \right] \quad (2.16)$$

where M_f corresponds to the substrate bending moment and I to the second moment of area for each independent substrate. The parameter τ is equal to

$$\tau = \frac{3V}{2Bh} \left(1 - \frac{z^2}{c^2} \right) \quad (2.17)$$

where V is the transverse load in each adherend for $0 \leq x \leq a$, z is the distance in the normal axis and c half of the thickness of each DCB substrate. The displacement δ can be withdrawn following Castigliano's methodology by considering an approach based on beam's theory, where

it is obtained as a partial derivative of the strain energy to failure, U , in order of the load P .

$$\delta = \frac{\partial U}{\partial P} = \frac{8Pa^3}{E_x Bh^3} + \frac{12Pa}{5BhG_{13}} \quad (2.18)$$

Provided this approach, it is therefore possible to define the compliance, $C = \delta P$, of the specimen among the $P - \delta$ curve obtainable by the testing machine acquisition data system. Nevertheless, the classical beam theory does not take all the phenomena that happens in a crack opening occurrence, like the stress concentration in the crack tip during the initial part of the pure mode I test [14]. Such event will influence the $P - \delta$ curve which are not predicted by the methodology. In order to account for those effects, a novel parameter is introduced named the corrected flexural modulus (E_f) which will substitute the value of E_1 . Hence, the novel altered flexural modulus of the specimen can be written as follows

$$E_f = \left(C_0 - \frac{12(a_0 + |\Delta|)}{5BhG_{13}} \right)^{-1} \frac{8(a_0 + |\Delta|)^3}{Bh^3} \quad (2.19)$$

where C_0 is the initial compliance, a_0 the initial crack length and Δ a correction for the root rotation for the crack length size (a_0). Henceforward, the thesis of the CBBM can be achieved as the so-called crack equivalent concept. This crack length estimation can be determined recurring to

$$a_{eq} = \frac{A}{6\alpha} - 2\frac{\beta}{A} \quad (2.20)$$

where the α and β coefficients can be written as

$$\alpha = \frac{8}{Bh^3 E_f} \beta = \frac{12}{5BhG_{13}} \quad (2.21)$$

and A given as

$$A = \left(\left(1 - 108\gamma + 12\sqrt{\frac{3}{a}(4\beta^3 + 27\gamma^2\alpha)} \right) \alpha^2 \right)^{1/3} \quad (2.22)$$

where the last parameter γ corresponds to the negative value of the compliance.

$$\gamma = -C \quad (2.23)$$

Lastly, the failure energy following the CBBM criterion comes

$$G_{I_c} = \frac{6P^2}{B^2h} \left(\frac{2a_e^2}{h^2 E_f} + \frac{1}{5G_{13}} \right) \quad (2.24)$$

It is important to note that this methodology is based on an equivalent crack length, where it estimates the crack size per each point of the obtained $P - \delta$ curve and is also a characteristic of each specimens compliance for each test performed. This equivalent concept take into account the FPZ phenomena which agglomerates micro-cracking as well as plasticization (inelastic behaviour) ahead of the crack tip. The a_{eq} corresponds to the length of the crack together with half of the

fracture process zone [14, 51]. Figure 2.9 illustrates the influence of the FPZ together with the equivalent crack length estimation.

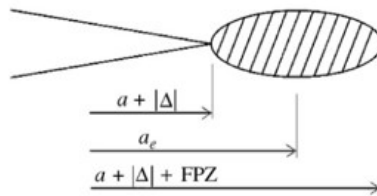


Figure 2.9: Equivalent crack length concept and fracture process zone illustration [14]

$$a_{eq} = a + \Delta + \Delta a_{FPZ} \quad (2.25)$$

2.6.4 Fracture characterization under mixed-mode condition

The end-notch flexure (ENF) tests or three point bending allows for the fracture characterization of an adhesive under pure in-plane shear conditions. These tests are suitable for mostly brittle adhesives and some ductile materials. Notwithstanding, ductile adhesives with an elastomeric behaviour like some one or two-component polyurethane as well as elastomer sealants possess an extended plasticization ahead of the crack tip, much larger than the fracture process zone of brittle adhesives [54]. Chai [54] reported the behaviour between a brittle and a ductile epoxy adhesive under multiple adhesive layer thicknesses $P - \delta$ curves for the ENF test and revealed that, for the brittle adhesive, there was a loss of load bearing capability due to crack propagation in mode II, whereas in the ductile trial, the load always increased until the test was stopped. When computing the R-curves, it was noticed that, for the ductile adhesive, the FPZ ahead of the initial crack tip did not occupy the bondline thickness uniformly. No stable plateau for the G_{IIc} value was found since the plot G_{IIc} versus adhesive thickness always increases, as contrary to the brittle adhesive, where there was a clear plateau. This indicates that, due to the large FPZ in ductile adhesives [55], it might not be possible to test these materials under pure mode II conditions, since a bigger displacement will be needed to propagate the initial crack, with the downside of the existence of plasticization on both ENF substrates, as will be reported in the third chapter of this document. The FPZ is a function of the specimen length, and if this parameter is shortened so is the fracture process zone [55]. Nonetheless it is significantly bigger and can intercept the middle of the specimen length. The ENF test may show that the crack propagates as the substrates plasticize, leading to erroneous values.

What could be preformed to overcome this issue is to test the material under a mixed-mode condition for further extrapolation of the adhesive fracture envelope. A mixed-mode test loads the material under a combination of mode I and mode II, being the relative weight of these loading types variable [56]. Thus, it is possible to establish a relation between the two fracture modes

induced weights. Xiau et. al. [11] used Kanninen's elastic beam formulation for an Asymmetric Double Cantilever Beam (ADBC). Park and Dillard [57] tested an acrylic adhesive under mode I condition using tapered double cantilever beam (TDCB) specimens and under mixed-mode a Asymmetric Tapered Double Cantilever Beam (ATDCB). Other solutions like the Single-leg Bending (SLB), Cracked Lap Shear (CLS) were found in the literature [56] to reproduce decent energy fracture envelopes for adhesives. Despite the vast apparatus and methodologies for the fracture envelope extrapolations, the majority of those concepts oblige to use dissimilar adherends, distinct both in size and shapes, in order to induce peel and shear loads in the adhesive layer, accordingly to the mixed desired.

Other recent philosophy is to used equal size adherends, provided that is simpler to manufacture. Notwithstanding, the peel and shear stresses will not be applied due to the joint geometry, but by varying its assemblage in an apparatus which allows different loading configurations employed to the specimen. Both Arcan and Modified Arcan fixture tests use equal geometry adherends, in which the apparatus itself (that supports the Arcan specimens) can vary its assembly [56, 58, 59]. Arcan fixtures results are usually compared to other apparatus like the Mixed-Mode bending (MMB), a normalized ASTM standard test [59]. Other concepts like the Fernlund and Spelt Jig [12] were recorded to estimated the G_{IIc} using their own developed apparatus, which like in the MMB test used single-equal adherends accordingly sized from the standard DCB specimens in order to extrapolate the adhesive fracture envelope.

The apparatus used for mixed-mode testing in the present work was developed by Costa et al [56] and allows for the usage of standard DCB adherends. It is much more compact than the Spelt Jig concept and enables the usage of metal substrates, an inconvenience for the MMB. In order to define the weight of opening and in-plane shear loading quantities an angle Φ , so-called the mixed-mode phase angle, establishes a ratio between the fracture toughness in mode I and mode II [56].

$$\Phi = \arctan \left(\sqrt{\frac{G_{II}}{G_I}} \right) \begin{cases} \Phi = 0^\circ & \Rightarrow \text{pure mode I} \\ 0^\circ < \Phi < 90^\circ & \Rightarrow \text{mixed - mode} \\ \Phi = 90^\circ & \Rightarrow \text{pure mode II} \end{cases} \quad (2.26)$$

The versatility of the structure permits testing under pure mode I until close to pure mode II, combining multiple mixed-mode phase angles. One advantage of this concept is the avoidance of the usage of DIC to measure the instantaneous crack length along the test, but incorporate a mixed CBBM formulation that takes into account the FPZ and the phase angle of the tests. It is possible to extrapolate two P - δ curves (from mode I and mode II) to withdrawn the fracture toughness independent values: G_{Ic} and G_{IIc} . Thus, the indirect methodology does not require filming equipment which facilitates laboratory testing, especially under controlled temperature (high or low) where the apparatus is inside a thermal chamber. This is a significant advantage when compared to other recent apparatus like the Spelt Jig [12], which is more bulky and requires constant crack length measurement.

Two linear variable differential transformers are needed to measure the displacement of both

adherends throughout the tests. Image 2.10 illustrates the apparatus itself with the two LVDT's assembled. It is possible to rearrange the length of the beams by reassemble the structure in different ways, in depth described by Costa et al [56], in order to test the specimens under various phase angles values. The marked s_1 , s_2 , s_3 and s_4 correspond to the pin repositioning to modify the apparatus configuration and re-balance the forces applied to the DCB specimen. The L values correspond to the distance between the loading point and the upper pre-load bar, L_1 , and the lower metal bar, $2L$. The pin holes are 20 [mm] equally distanced from each other. Figure 2.11 displayed the force diagram induced by the apparatus to the DCB specimen, which are constantly balanced depending on the structure configuration: the forces applied to the upper adherend are represented as F_1 whereas for the lower adherend as F_2 . The figure also shows the dimensions for the point supports of the specimen on the apparatus itself.

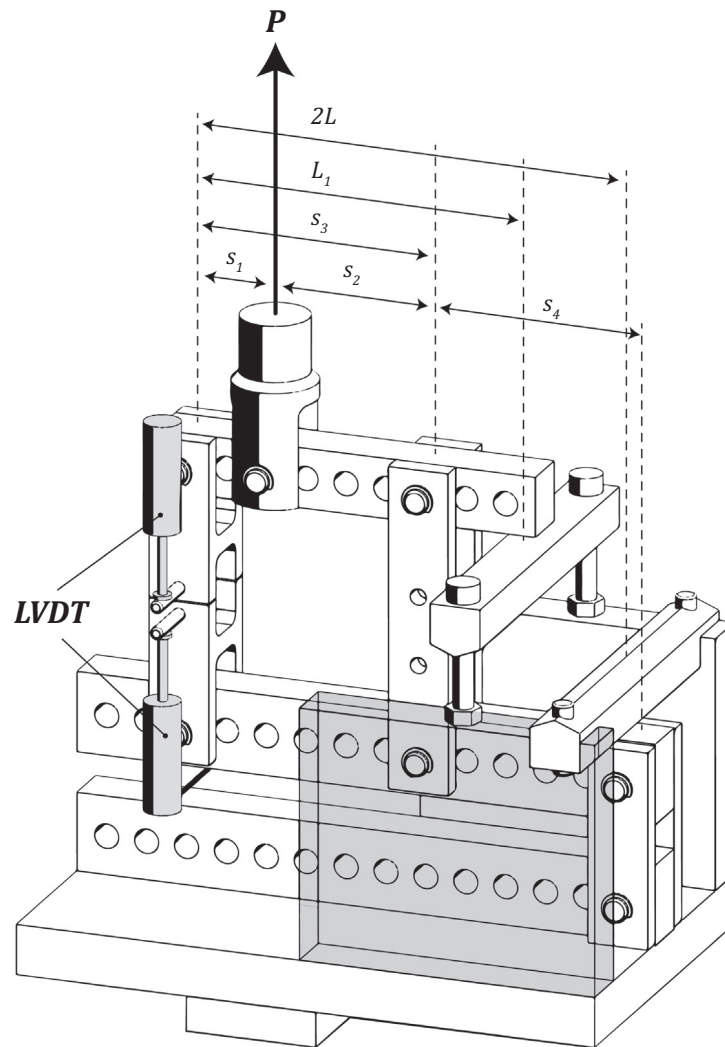


Figure 2.10: Mixed-mode apparatus developed by Costa et al. Adapted from [14]

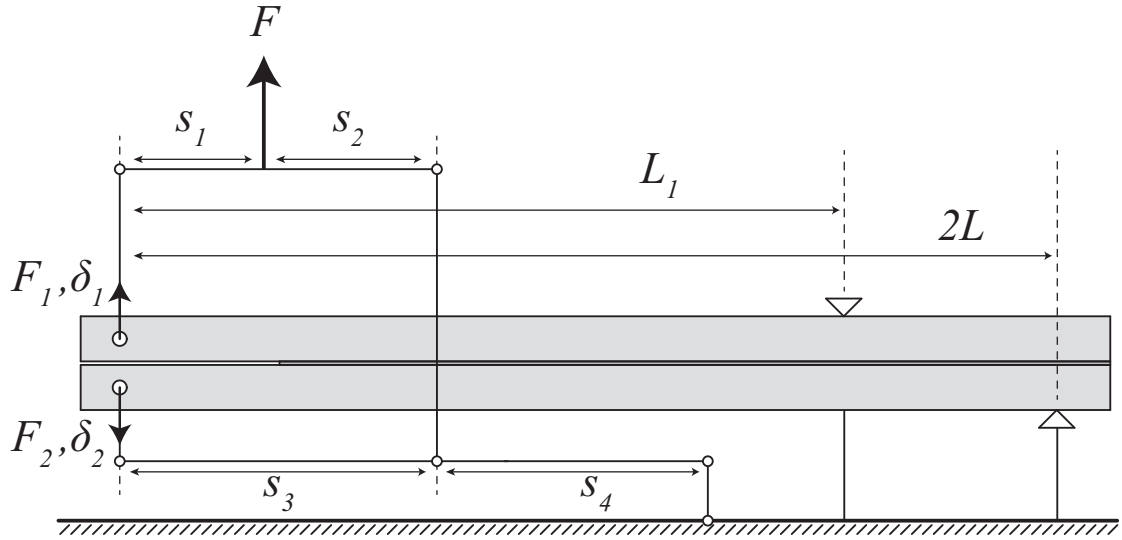


Figure 2.11: Support points and dimension of the DCB specimen. Adapted from [14]

A static equilibrium can be performed in each adherend, establishing the following relations:

$$F_1 = F \frac{s_1}{s_3} \quad F_2 = F \frac{s_1 s_4}{s_3(s_3 + s_4)} \quad (2.27)$$

The displacements measured by the two LVDT's are represented as δ_1 for the upper adherend and δ_2 for the lower one. Hence, the displacement in each particular mode can be written as:

$$\delta_I = \delta_1 - \delta_2 \quad \delta_{II} = \frac{1}{2}(\delta_1 + \delta_2) \quad (2.28)$$

The theoretical phase angle of the apparatus can be geometrically determined by

$$\Phi_{apparatus} = \arctan \left(\frac{\sqrt{3} \left(\frac{F_1}{F_2} + 1 \right)}{2 \left(\frac{F_1}{F_2} - 1 \right)} \right) \quad (2.29)$$

Figure 2.12 displayed different value examples for the mixed-mode phase angle.

The CBBM formulation agglomerates both formulation for mode I [14] and mode II [15] combining them into a mixed-mode CBBM approach [13], based on Timoshenko's beam theory to estimate an equivalent crack based on the specimens current compliance along the test. Figure 2.13 displays a force diagram decomposition for the mixed-mode loaded specimen.

What varies in this methodology is that for the Spelt Jig apparatus [12], the displacements δ_1 and δ_2 were estimated using Castigliano's theorem, as in the CBBM formulation for pure mode I. Chaves et al [13] calculated the $\delta = \frac{\partial U}{\partial P}$ for both upper and lower substrates provided the strain energy expression determined by Timoshenko beam theory. In this apparatus [56] uses two LVDTs to measure both δ_1 and δ_2 and the already described steps are not needed. Thus, the compliance's

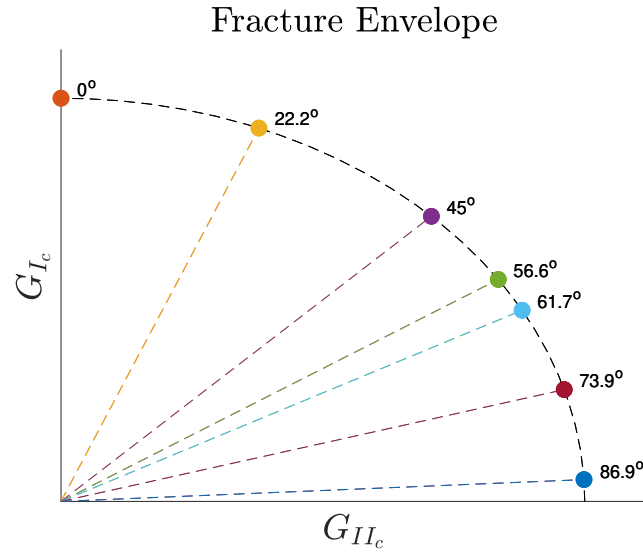


Figure 2.12: Examples of support points and dimension of the DCB specimen [14]

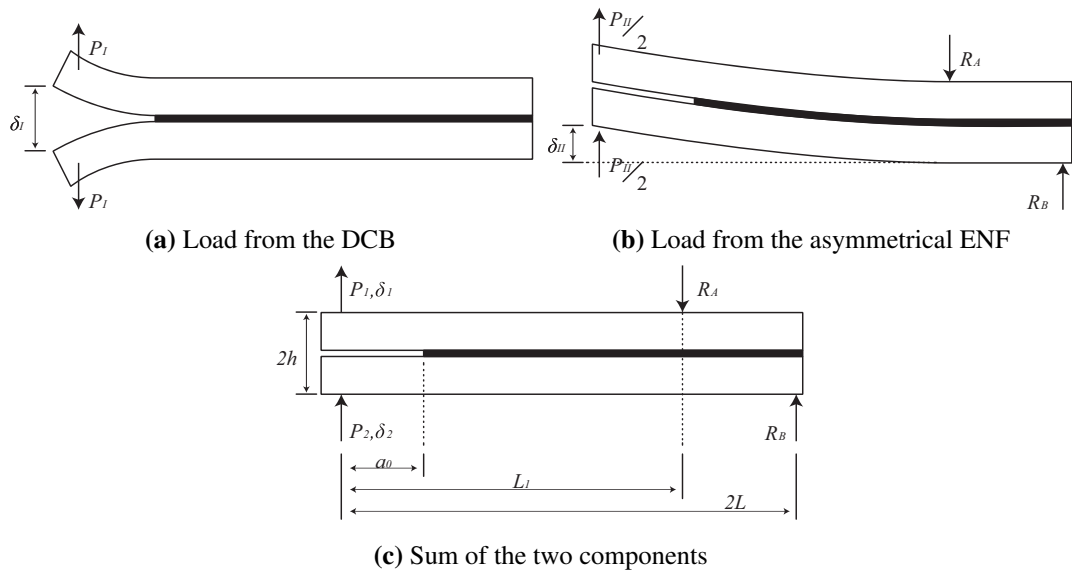


Figure 2.13: Decomposition of the DCB and asymmetrical ENF loading in the mixed-mode apparatus. Adapted from [56]

can be determined for pure mode I

$$C_I = \frac{8a^3}{EBh^3} + \frac{12a}{5BhG_{13}} \quad (2.30)$$

and for mode II

$$C_{II} = \frac{3a^3 + 2LL_1^2}{2EBh^3} + \frac{6LL_1}{5BhG_{13}(2L - L_1)} \quad (2.31)$$

The equivalent crack sizes should be determined for both mode I (a_{eqI}) and mode II (a_{eqII}). As in the CBBM formulation, the equivalent crack concept can be determined from a third degree polynomial equation which follows

$$\alpha a_{eqI}^3 + \beta a_{eqI} + \gamma = 0 \quad (2.32)$$

where the parameters α , β and γ are given as

$$\alpha = \frac{8}{Bh^3E_f} \quad \beta = \frac{12}{5BhG_{13}} \quad \gamma = -C_I \quad (2.33)$$

Computing the equation the only zero for the mode I equivalent crack length is

$$a_{eqI} = \frac{A}{6\alpha} - \frac{2\beta}{A} \quad (2.34)$$

where

$$A = \left(\left(-108\gamma + 12\sqrt{\frac{3}{\alpha}(4\beta^3 + 27\gamma^2\alpha)} \right) \alpha^2 \right)^{1/3} \quad (2.35)$$

For mode II, the equivalent crack size is given by

$$a_{eqII} = \left[\frac{2}{3} \left(\left(C_{II} - \frac{6LL_1}{5BhG_{13}(2L - L_1)} \right) Bh^3E - 2LL_1^2 \right) \right]^{1/3} \quad (2.36)$$

The fracture toughness values comes from the Irwin-Kies, as referred in the previous chapter. The critical energy release rate for mode I is obtain as

$$G_I = \frac{6P_I^2}{B^2h} \left(\frac{2a_{eqI}^2}{h^2E} + \frac{1}{5G} \right) \quad (2.37)$$

and for mode II

$$G_{II} = \frac{9P_{II}^2 a_{eqII}^2}{4B^2h^3E} \quad (2.38)$$

2.6.5 Damage mechanics analysis

Damage mechanics can be seen as a much further step of fracture mechanics. In fact, this methodology only takes into consideration the propagation of a crack in a single plane, not its nucleation or initiation [14, 42]. Taking this example, what happens in reality is more complex: a crack has to nucleate before propagation. Thus a damage approach ought to be consider to estimate when and where will the material degrade and lastly fail, commencing the initiation of a crack [45, 46]. In addition, damage mechanics seek to solve degradation problems which enables modelling of a degraded specimen over a load/displacement input, or over a period of time.

Cohesive and continuum damage models aim to address the limitations found in continuum and fracture mechanics [2, 16, 42]. When a stress criterion is met at an integration point, a relaxation process occurs guided by a fracture energy criterion. This gradual material degradation reduces stress at the integration point, leading to redistribution of nearby stresses and avoiding numerical stress peaks. Cohesive Zone Models (CZM) employ interface elements that attach two-dimensional plane or three-dimensional solid elements [60]. Cohesive elements have no thickness and rely on traction separation laws to estimate damage occurrence and damage evolution. For instance, not only it is possible to simulate the propagation of a crack but also to numerically compute its nucleation without the need to input an initial crack [42]. Notwithstanding, it is important to note that there has to be some kind of expected outcome in order to input cohesive layers accordingly to what happens in reality, this is, it is not suitable to build a full model of cohesive elements with the insertion of them only on the adhesive layer: to study the possibility of decohesion phenomena or delamination it is essential to establish a cohesive layer on the interface components or composite adherends to catch such effects [2, 16]. This has become one of the most adequate methodologies to study composite delamination and adhesive joint debonding or degradation since in the numerical models, both adhesive and composite minute layers are removed from the global general equilibrium and substituted by interface traction forces (or separation laws) which act in-between substrates. CZM depends on the loading history, displacement and dynamic effects being an excellent candidate to reproduce the behaviour for both impact, fatigue and creep loading scenarios [2, 16]. Cohesive zone modeling relies on a cohesive law that characterizes the initial elastic response, which progressively increases until it reaches a maximum stress and then declines until it eventually reaches a zero value, meaning that the adhesive or composite interface has become completely disbonded. The implementation of CZM in finite element simulations has been investigated over the last decades, targeting its application in various applications [16], including in adhesively bonded joints under mixed-mode conditions [61].

Cohesive laws trace back to the 1960's, where fracture mechanics approaches were used for understanding the plasticity phenomena near the crack tip as the crack propagates and the material interfaces gradually separated [62, 63]. Furthermore, the idea of a relative formulation between the local stress displacement and the FPZ was developed, where such relationship was first constituted as a cohesive law [2]. Cohesive laws define the relationship between interfacial traction stresses and the corresponding relative displacements across the interface. To comprehensively characterize a cohesive law, four key factors come into play: stiffness, strength, fracture energy and shape [64]. The stiffness simply represents the resistance of the interface to deformation whereas the strength defines the maximum interfacial traction before failure. As referred, the fracture energy quantifies the resistance to a crack growth along the cohesive interface. Lastly, the shape of the cohesive law redefines these previous concepts since it determines how will the cohesive elements evolve and degrade as a function of the loading or displacement imposed. The shape of the cohesive law depends on the material type and can be triangular [65], trapezoidal, such as polynomial, linear-parabolic, exponential [60] or even a combination of shapes also known as power-law, which interpolate shapes in-between pure opening and pure shear scenarios [2, 16] in

two dimensional models.

The triangular law is the simplest cohesive approach to follow and is suitable for brittle and moderately ductile materials [2, 16, 51, 60]. In addition, the trapezoidal law is also preferable for more ductile adhesives such as elastomers, for instance [60].

Figure 2.14 illustrates the triangular and trapezoidal CZM law shapes for two dimensional components.

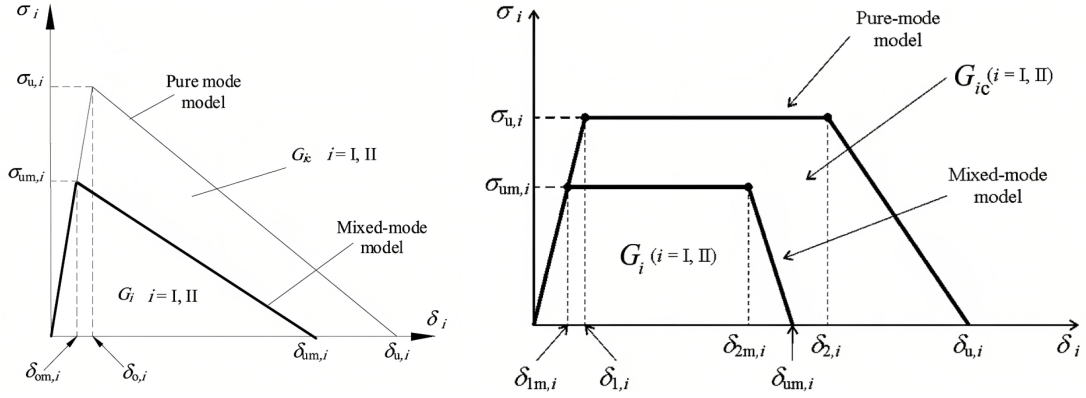


Figure 2.14: Triangular (left) and trapezoidal (right) softening laws for pure mode I and mode II cohesive damage model. Adapted from [60]

The elastic response of cohesive zone models can be described by a straightforward linear relationship between the maximum strength and the modulus. This linear relationship holds true for both tensile scenarios (referred to as I or n) and shear scenarios (referred to as II or s). The cohesive traction is determined by multiplying the stiffness matrix $\mathbf{K}$ with the corresponding strains. The stiffness matrix includes parameters for tensile and shear stiffness, where $K_{nn} = E$ represents the tensile stiffness, and $K_{ss} = G$ represents the shear stiffness. Since no tensile-shear combination was performed, we assume that $K_{ns} = K_{sn}$ has a zero value [66].

$$\sigma_u = K\varepsilon \Leftrightarrow \begin{Bmatrix} \sigma_{u,n} \\ \sigma_{u,s} \end{Bmatrix} = \begin{bmatrix} K_{nn} & K_{ns} \\ K_{sn} & K_{ss} \end{bmatrix} \begin{Bmatrix} \varepsilon_n \\ \varepsilon_s \end{Bmatrix} \quad (2.39)$$

Thus, a damage criterion must be selected as well as a softening phenomena, which occurs after the load peak is reached. As an example, for a triangular shaped CZM laws:

$$\sigma_n = (1 - d_n)\sigma_n^u \quad ; \quad \sigma_s = (1 - d_s)\sigma_s^u \quad (2.40)$$

where σ_n^u and σ_s^u are the instantaneous cohesive traction. The damage variables, denoted as d_n and d_s for tension and shear, respectively, are determined based on the triangular shape law. Their expressions are provided as follows [66]:

$$d = \frac{\delta_{um,i}(\delta_i - \delta_{0m,i})}{\delta_i(\delta_{um,i} - \delta_{0m,i})} \quad , \text{ where } i = I, II \quad (2.41)$$

which is valid for both tension and shear components.

The damage criterion for traction-separation laws in the context of mixed-mode fracture is established through an energetic approach, taking into account the critical energy release rate values for both mode I and mode II fracture modes [2]. To establish a unified mode mixity formulation, it is possible to extrapolate a relationship for mixed-mode fracture energy by combining the two defined individual laws, for two dimensional models. One approach to accomplish this is by utilizing the Power Law, which can be described as follows:

$$\left(\frac{G_I}{G_{I_c}}\right)^\alpha + \left(\frac{G_{II}}{G_{II_c}}\right)^\alpha = 1 \quad (2.42)$$

in this case, the parameter α was set to one, implying the use of a linear power law [16].

Chapter 3

Experimental procedure

3.1 The novel flexible adhesive

3.1.1 Adhesive mixture and manufacturing specifications

The two-component SPUR was provided in two separate containers: one containing part A and another part B. The first one, carbon black, contained the SPUR formulation in addition to the aminosilane, amine hardener and a filler, whereas the second one joined the epoxy resin and the catalyst formulation. The SPUR and aminosilane are moisture curing materials while the amine hardener and the epoxy resin will react, creating minute precipitates of hard epoxy, illustrated in figure 3.1.



Figure 3.1: Provided representation of the precipitates in the cured SPUR without (at the left) and with the epoxy resin part B (at the right). Adapted from Momentive Performance Materials Inc.[®]

The hardened epoxy precipitates provide more strength to the adhesive and enhance the adhesion capacity [1, 2].

To commence the adhesive fabrication, the safety data sheets provided by the company were interpreted and the safety features addressed. The adhesive mixture took place in a plastic goblet which was cleaned with acetone. The procedure of mixture was to place both part A and part B

in the right amounts inside the goblet, then mix it in a speed mixture machine at 2000 [rpm] for two minutes. Thereafter, it was reacquired to add distilled water and mix again at the same speed for 20 seconds. All mixtures were performed in a SpeedMixer DAC[®] 150.1 FVZ-K centrifugal mixer. Table 3.1 summarizes the manufacturing stages of the first batch. The final mixture should result in shiny smooth black surface.

Table 3.1: 2k SPUR manufacturing specifications

Step	Process	Mixing
1	Add part A and B to a flakdeck cup	2000 [rpm] for 2 minutes
2	Add distilled water	2000 [rpm] for 20 seconds

Since part A is more viscous, it was impossible to pour it from the original container, hence, an acetone cleaned spatula was used to withdrawn the carbon black substance minimizing the remain material contamination. On the other hand, part B was less viscous, thus it was possible to pour it from the jar. A pipette was used to introduce the distilled water to the mixture. A 4 digit digital balance (Kern[®] ALS) was used to control the weight measurements. The temperature of the first mixture to go into the mixer was checked: due to the presence of vinyl silanes, the temperature should not be risen above 50C. The samples had less than 30 minutes of pot-life, hence the adhesive pouring process into the test molds or specimens was performed quickly and with cautiousness. Furthermore, both part A and B containers were opened and subjected to a rich nitrogen environment, in order to promote a neutral storage environmental inside each container, since the chemicals in part A are mostly volatile and moisture sensible. Table 3.2 summarizes the quantities of each component added in function of part A. All tests considered only 1% of water due to the fact that the pot-life would be reduced to half whether 1.5% were used instead, and the properties were said not to be majorly affected.

Table 3.2: Mixture quantities in the two-component adhesive manufacture

	1% water	1.5% water
Part A	1.000	1.000
Part B	$0.40197 \times A$	$0.40197 \times A$
Distilled water	$0.00667 \times A$	$0.01005 \times A$
Pot life	25-30 [min]	15 [min]

3.1.2 Additives

Silquest[™] and CoatOSil[™] are trademarks of Momentive Performance Materials Inc.[®], a collection of specialty silanes that offer solutions for a wide range of applications such as coatings,

sealants, adhesives, and composites. These organofunctional silanes have unique properties that make them useful as crosslinkers, allowing for the longer duration of coatings, inks, adhesives, and sealants as well as enhancing the mechanical performance [67]. Also known as adhesion promoters, these additives improve the bonding strength between different substrates of a wide range of materials. These act as coupling agents, linking mineral surfaces with organic polymers to enhance the overall performance of the composite materials as well as acting as moisture scavengers, effectively extending the shelf-life of moisture-sensitive systems by minimizing their contact with moisture [67].

The influence of additives was studied only on the tensile and shear properties of the modified two-component formulation. For that, four additives were used:

- CoatOSil™ Flx (SF 1023) [68]
- Silquest™ A-1110 [69]
- Silquest™ A-Link 600 [70]
- Silquest™ A-Link 235 [71]

The CoatOSil™ Flx, also referred as SF 1023 [68] was present in all three mixtures: each different mixture contained a different reference of Silquest™, resulting only in three different configurations. Table 3.3 summarizes the mixture portions of each additive component.

Table 3.3: SPUR CoatOSil™ and Silquest™ additives portions per one unit of part A

	Mixture 1	Mixture 2	Mixture 3
Part A	1.000	1.000	1.000
CoatOSil™ Flx	$0.05638 \times A$	$0.06578 \times A$	$0.06265 \times A$
Silquest™ A-1110	$0.01879 \times A$	-	-
Silquest™ A-Link 600	-	$0.0094 \times A$	-
Silquest™ A-Link 235	-	-	$0.01253 \times A$
Part B	$0.4385 \times A$	$0.4385 \times A$	$0.4385 \times A$
Water	$0.00728 \times A$	$0.00728 \times A$	$0.00728 \times A$
AHEW/EEW	0.61	0.61	0.61
Ratio Part A to B	2.4:1	2.4:1	2.4:1

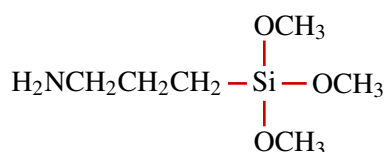
The CoatOSil™ Flx (SF 1023) [68] is a coating modifier which improves flexibility, corrosion in a salty environment and retains a glossy look under adverse weathering conditions. The other three additives belong to the silane Silquest™ line, which promotes adhesion and act as coupling agents between resins and fibres, increasing the integrity of the fibrous filaments. Under room temperature conditions, these additives can also crosslink polymer molecules improving hardness, creep resistance and thermal stability [72]. Summarizing, they act as crosslinking additives with adhesion promotion and as coupling agents [73]. The Silquest™ A-1110 is a versatile amino-functional silane coupling agent which promotes bonding capability between inorganic substrates

and silane-modified urethanes SPUR prepolymer, an organic polymer for instance [69, 72, 74]. The Silquest™ A-Link 600 is a low-yellowing amino silane [72, 75] suitable for use in SPUR formulations as adhesion promoter as well as providing flexibility and colour retention under ultra-violet (UV) radiation and thermal exposure [70, 76]. Finally, Silquest™ A-Link 235 is applicable to a wide range of RTV sealants and polyurethanes, acting as an adhesive promoter, enhancing the elasticity and adhesive strength and diminishing residual surface tack [71].

In terms of chemistry, these Silquest™ organofunctional silanes possess a bi-functional nature, incorporating both organic and inorganic reactivity within their molecular structures [73]. A typical organofunctional silane are composed by a:

- Reactive functional groups;
- A link;
- Silicon atom;
- Hydrolyzable groups.

For instance, the Silquest™ A-1110 chemical formulations follows:



gamma-Aminopropyltrimethoxysilane $\Rightarrow$ Silquest A-1110 silane

3.1.3 SPUR viscosity

A second batch of three different formulations of the part A component, the SPUR, was manufactured, having each of the formulations a different molecular weight, or, in other words, unequal viscosity levels. The labels provided by Momentive Performance Materials Inc.® were:

- L $\Rightarrow$ low viscosity;
- K $\Rightarrow$ medium viscosity;
- J $\Rightarrow$ high viscosity.

The SPUR with "L" viscosity contained the same molecular weight value than the part A component provided in the first batch, nevertheless the novel formulation was manufactured through a different process.

The mixture of these three levels of viscosity was performed by joining the epoxy resin (part B) provided in the first batch and distilled water, following the procedure listed in table 3.2.

3.2 Specimen manufacturing

3.2.1 Bulk test

The bulk test provides the tensile properties of the novel adhesive, allowing to determine the Young's modulus and tensile strength. By plotting the stress versus strain which can be captured during the tensile test (with a loading cell and an extensometer), the stress-strain curve will provide the elastic and plastic behaviour of the material. Bulk specimens can be obtained with two techniques, all seeking to create an hydrostatic pressure: pouring in the mould or creating plates under pressure. The first technique is more suitable for soft adhesives and relies on a mould with the already normalized "dog-bone" specimen shape, where it is possible to remove the bulk specimen directly from the mould [10, 37]. The second technique presented uses a rectangular shaped mould in which a plate of cured adhesive can be obtained. This methodology is usually used for more rigid or stiff adhesives when cured, as the shape of the bulk specimens will be achieved only by milling the cured bulk sheet. For softer adhesives, some rip out effects can occur due to the milling operation.

For polyurethane adhesives, some authors [2, 10] prefer the injection mould fabrication. Nevertheless, due to the existence of epoxy precipitates, the adhesive could be machined without having finishing rip out issues which led to the selection of the second approach. The mould used for this purpose is composed of 6 parts: two opposed plates which will provide a smooth shape and four steel barriers, each one located in each edge, all connected by four Allen head bolts [77]. Figure 3.2 illustrates the exploded assembly view of the bulk sheet plate mould used in the adhesive manufacturing.

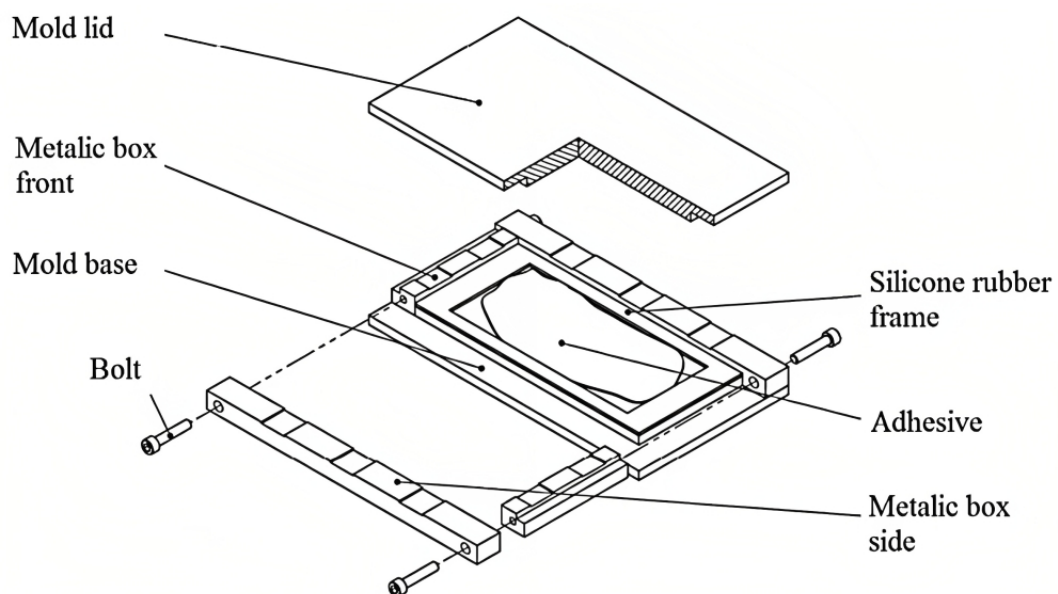


Figure 3.2: Bulk sheet mould used in the manufacture [51, 78]

The thickness of the bulk sheet is set by an auxiliary silicone rubber frame. This will prevent the adhesive from escaping the mould and, most importantly, induce pressure from the sides when compressed, generating an hydrostatic pressure. In addition, the frame will provide the final dimensions to the cured sheet. The silicone frame with a thickness of 2 [mm] was hand cut and fitted into the mould. The internal width was set to allow the manufacture of three "dog-bone" specimens for each bulk sheet manufactured. The experimental procedure to produce the bulk sheet can be described as follows:

1. Degrease the mould with acetone;
2. Apply a layer of mould release agent to all the mould components and let dry out;
3. Close the mould cage;
4. Insert the silicone rubber frame;
5. Close the mould ;
6. Insert it in a hot press and adjust pressure and temperature according to curing condition.

The release agent used was a Loctitte[®] model 770-NC Frekote.

Figure 3.3 illustrates two steps commented above: the application of release agent and the final application of the adhesive, uniformly distributed by a spatula.

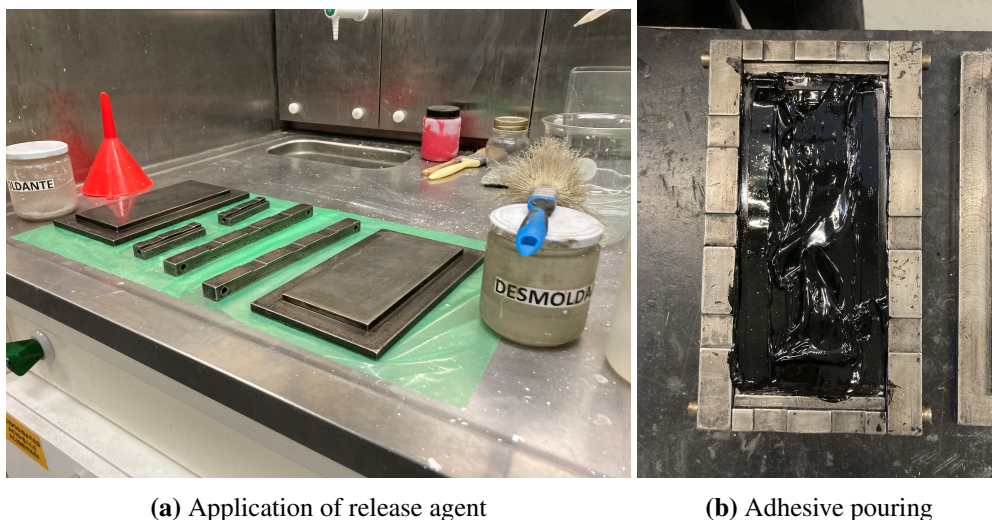


Figure 3.3: Steps in the bulk sheet mould manufacture

The pressure applied by the hot press (around 30 [bar]) will guarantee the absence of air bubbles (voids) and a good surface finish. Having the curing process competed, the mould is withdrawn from the hot press and cooled at ambient temperature for a few minutes. Thereafter, the Allen bolts can be unscrewed, the mould opened with care and the metallic case dissassembled. The bulk sheet can be easily peeled from the metallic surface and the silicone rubber frame

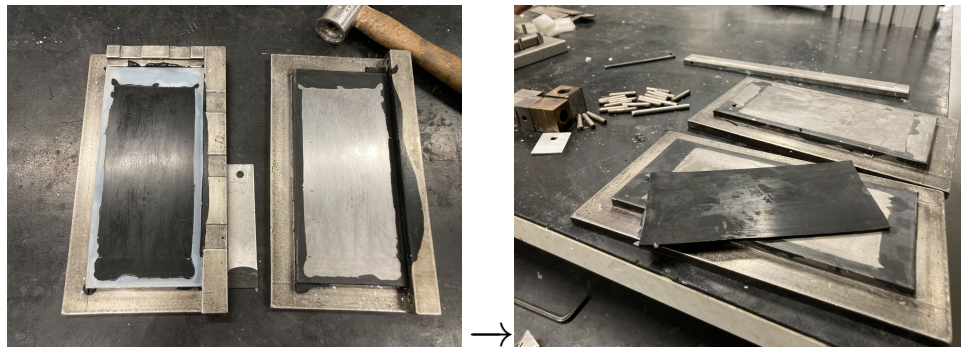
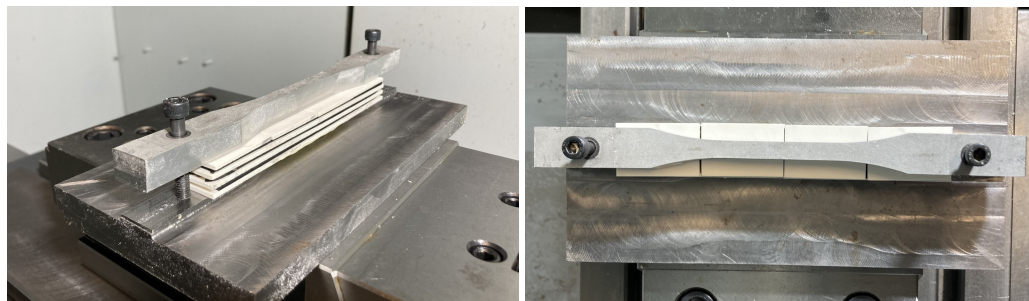


Figure 3.4: Dismantling of the bulk sheet mould

separated by applying a bending moment on the adhesive-frame interface. Figure 3.4 shows the disassembly of the final bulk sheet, being removed from the mould.

The overall dimensions of the bulk sheet were 155x70 [mm], with a thickness of 2 [mm], following the French NF T 76-142 standard [8]. Henceforward, the sheet was longitudinally cut into three separate smaller sheets, which were then machined. A CNC program already developed was computed using a HAAS® VF2 Mini with 3 milling axis and the rectangular smaller sheets were compiled in a special support, allowing their machining. Furthermore, small glass fibre tabs were inserted in-between and above the three piled adhesive sheets. Figure 3.5 shows the machining process from the adhesive glass-fibre layup, until the final bulk specimens were obtained.



(a) Staggering sequence to CNC machine

(b) Top view of the special support



(c) Machines bulk specimens

Figure 3.5: CNC machining of bulk specimens

The final bulk specimens possess the dimensions displayed in figure 3.6 in accordance to NF T 76-142 standards [8].

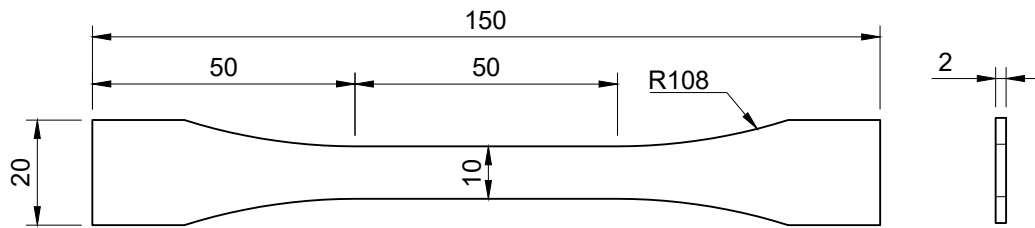


Figure 3.6: Bulk specimen drawing (dimensions in [mm]) [8]

3.2.2 Thick adherend shear test

The Thick Adherend Shear Test (TAST) serves as a valuable method to determine the adhesive's shear properties. Its primary objective is to evaluate the shear strength and enhance the shear modulus by minimizing the peel stresses since the steel substrates employed in each specimen are relatively thick [10]. Additionally, the overall configuration of the setup is designed for ease of manufacturing. While the traditional single lap shear joints with varying overlap lengths are commonly used for comparing lap shear adhesive properties, it is important to consider that the adhesive experiences a more complex stress distribution due to peel stresses, particularly when dealing with thin substrates and smaller overlap lengths [2]. In this regard, TAST specimens offer an advantage by overcoming these complex stress configurations and focus on accurately measuring the true shear strength and subsequent shear modulus [10, 37].

The mold utilized in the experiment provides dimensions consistent with the relevant European standards (ISO 11003-2) [9], ensuring consistency in the TAST specimen manufacturing process. Figure 3.7 illustrates the dimensions of the assembled TAST coupon, according to the previously cited ISO standard.

Each specimen is manufactured with an adhesive thickness of approximately 5 [mm], using 1.5 [mm] shim tabs. These tabs serve as two purposes: controlling the overlap of the adhesive and preventing, or minimizing, the occurrence of tensile stresses during testing. Figure 3.8 displays the assembly of both TAST specimens and shims.

It should be noted that the repetitive nature of the testing process can lead to the degradation of geometric tolerances specified by the standard. This, in turn, affects the accurate determination of the adhesive thickness [10]. In principle, the substrates should not be reused or retested. However, in practice the substrates can be reused with the assistance sandblasting procedure followed by acetone cleaning. A brown corundum aluminium oxide F030 at 6 [bar] was used in the sandblasting procedure. Additionally, they were sequentially numbered from one to six. Figure 3.7 illustrates the dimensions of the specimens, aligning with the specifications outlined in ISO 11003-2 [56].

Following this preparation, the adhesive thickness (t_{TAST}) was indirectly determined by carefully measuring each pair of adherends thicknesses, using a precise caliper with a resolution of 0.05 [mm].

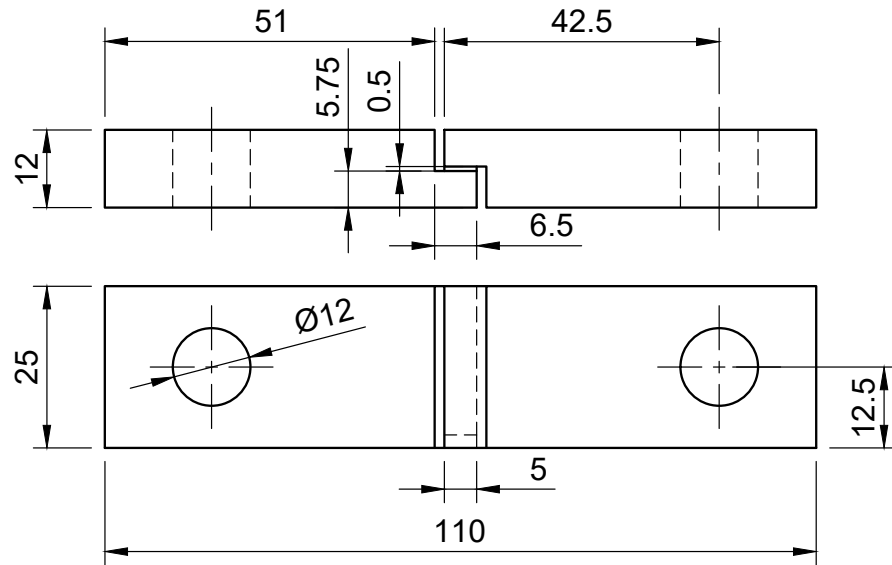


Figure 3.7: TAST specimen drawing (dimensions in [mm]) [9]

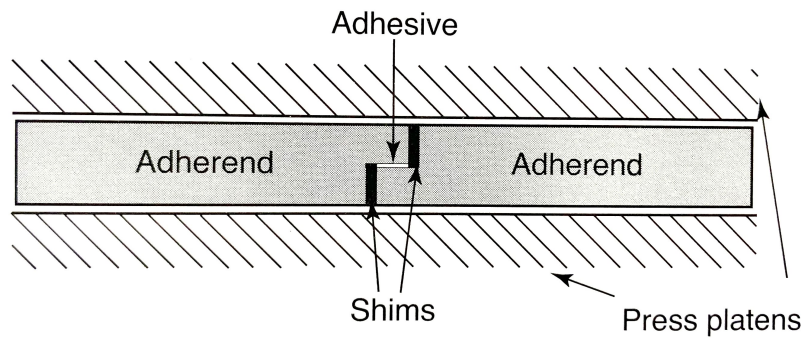


Figure 3.8: TAST specimens with the insertion of the shims. Adapted from [10]

The TAST mould incorporates guiding pins to accommodate six TAST specimens [77]. Prior to the application of the release agent, the base of the mold was thoroughly cleaned using acetone. Subsequently, the bottom TAST specimens were positioned in their designated locations. The adhesive was then carefully applied, followed by the placement of the lower shims and the assembly of the top part, as depicted in figure 3.9.

To ensure the desired shear behavior during testing, small shims with a thickness of 1.5 millimeters were inserted into the top part of each specimen. As referred, these shims prevent the adhesive from reaching any undesired surfaces, thus ensuring a predominantly pure shear stress state [10]. The shims were 3D printed with 25x6.25x1.5 [mm] dimensions, guaranteeing that the adhesive would only be present in the five millimeter overlap imposed by the ISO standards. Any excess adhesive would flow from the side of the specimens. It is important to note that removing the shims from the cured specimens can be challenging, as these come into direct contact with the

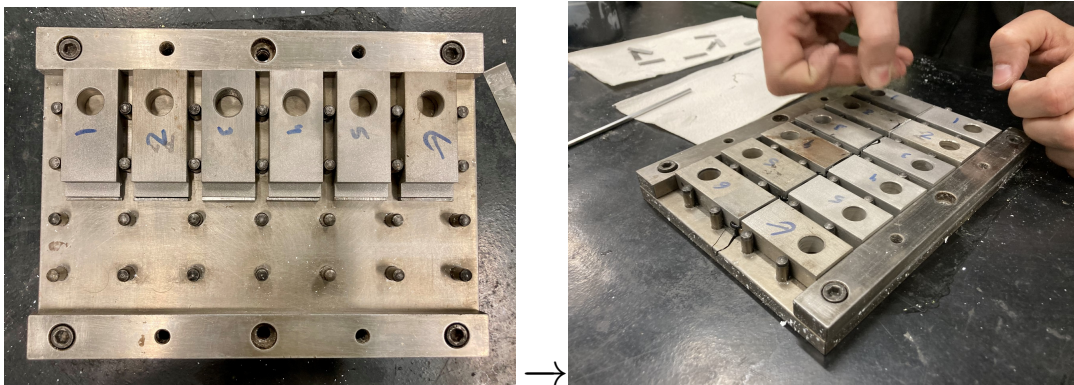


Figure 3.9: Positioning of the TAST bottom specimens (left) and top parts assembled together with adhesive and the shims (right)

adhesive. Therefore, a sufficient layer of release agent was applied to facilitate their extraction. Finally, the top platen was positioned, and the entire mold was placed in a thermal chamber under the specified curing conditions, with additional weights applied on top.

The experimental procedure for the TAST can be described as follows:

1. Degrease the mould and shims with acetone;
2. Apply mould release agent in all of the mould components, especially the shims, followed by drying in the hood;
3. Place the bottom TAST specimens with adhesive on the edges;
4. Insert the top TAST specimens with adhesive in the mould, from the inner specimens to the outer ones;
5. Insert the bottom shims as the top TAST specimens are placed;
6. Insert the top shims and clean any extra adhesive that might flow out from the top;
7. Close the mould and insert it in a hot press or in a thermal chamber with weight on top and leave at the require curing specifications.

Lastly, to remove the TAST specimens and prepare them for testing, the following steps must be taken into consideration [2, 10, 37]:

1. Retrieve the top mould metal cover;
2. Gently take out the TAST specimens: cut the adhesive with a sharp cutter or an X-acto knife to separate the specimens;
3. Withdraw the shims carefully by applying an outwards controlled force;
4. Cut any excessive adhesive on both specimen sides;

5. Clean the side with acetone;

For the sake of completeness, digital image correlation (DIC) was performed in the TAST analysis, hence the surface of one of each specimens side was prepared. A matte white paint was sprayed in a control environment, followed a thin, speckled layer of matte black paint [7]. Figure 3.10 shows the set of six TAST specimens after the paint coat application stage.

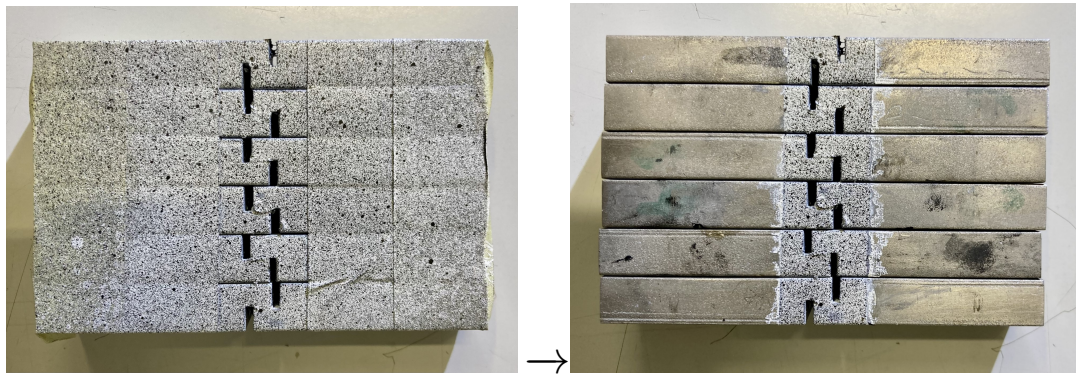


Figure 3.10: TAST specimens ready for DIC analysis

3.2.3 Double cantilever beam

The double cantilever beam test is based on pure crack opening in Mode I and aims to characterize the fracture toughness in the respective mode. The DCB test was performed under ASTM D3433 standards as well as ISO 25217:2009 [79]. The specimen consists in two high strength DIN 40 CrMnMo 8-6-4 steel bars, where a thin layer of adhesive is applied between them. Figure 3.11 displays the DCB specimen geometry, following the previous standards.

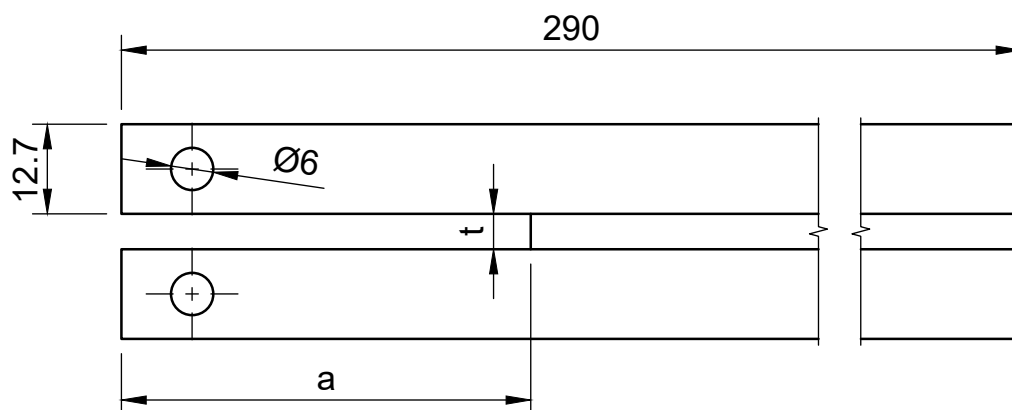


Figure 3.11: Dimensions for the standard DCB specimen (dimensions in [mm]) [79]

To facilitate the removal of adhesive residue from previous tests, each steel bar was placed in a chamber at a temperature of 200°C for approximately two hours. Following this step, the

specimens undergone a thorough cleaning process, using a scraper prior to acetone application and were subsequently sandblasted under the same condition as the TAST specimens. It was of utmost importance to ensure that the substrates remained flat and free from any bends or undulations. To verify substrate flatness, each pair of specimens was visually inspected against a light source and a flat plate of glass. If any bends were detected, a straightening procedure using a three-point bending testing setup was performed until the substrate was completely flat.

Eventually, the cleaned mould [77] with guiding pins, coated with a release agent film, was prepared to receive the bottom substrate specimens. An initial crack length a_0 of 45 [mm] was generated by inserting a thin, razor sharp blade. The thickness of the razor blade was 0.10 [mm], and to obtain the standard 0.20 [mm] of adhesive layer throughout the specimens overlap, two ribbons of 0.05 [mm] calibrated tape were glued to both blade surfaces, leaving only a minute portion of the blade edge extending outwards to mould the initial crack tip shape. At the end of both DCB adherends a single ribbon of 0.20 [mm] tape was added. These components were also coated with a release agent film to help in their removal after the curing process. Figure 3.12 illustrates the bottom adherends placed in the steel mould as well as the inserted razor assembly ribbon and adhesive application.

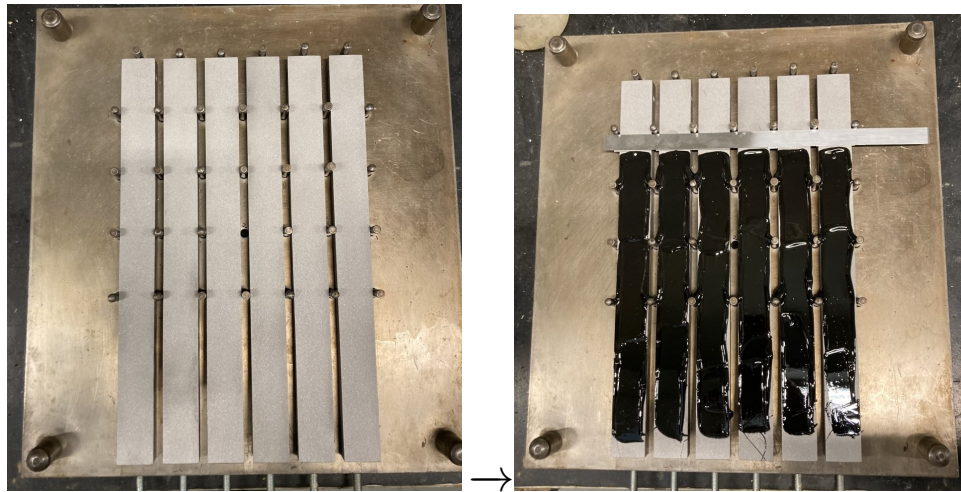


Figure 3.12: Bottom DCB bars in the mould (left) and razor ribbon together with adhesive application (right)

Subsequently, the adhesive was applied to both bottom and top substrates. The two substrates were then carefully assembled and pressed together using the top part of the mold and the 0.20 [mm] ribbon placed at the specimens end. To prevent the formation of voids and to ensure compliance with the specified curing conditions, the entire mold set was placed in a thermal chamber, with an appropriate amount of weights stacked above.

The DCB specimen fabrication was performed following the enumerated steps:

1. DCB bars were cleaned and sandblasted;
2. The adherends were checked for straightness and geometrical accuracy to the standardized dimensions;

3. Cleaning the sandblasted surface with acetone;
4. Assembly of the razor ribbon;
5. Coating the mould, razor ribbon and end tape with release agent film (and let it dry);
6. Placing the bottom adherends in the mould and the razor ribbon accordingly with the preferred initial crack length value;
7. Insert and spread the adhesive layer using a cleaned spatula;
8. Dispense a thin layer of adhesive in the top substrates;
9. Place the top adherend and apply a slight pressure by hand;
10. Insert the end 0.20 [mm] calibrated ribbon at the end of the specimens;
11. Apply a moderate pressure and close the mould;
12. Place the mould in a hot press on a thermal chamber with weights on top and set the desired curing parameters.

3.2.4 Single lap joints

SLJ, using both aluminium and carbon fibre reinforced polymer (CFRP) adherends, were manufactured for 25 [mm] and 50 [mm] of adhesive overlap length, always with an adhesive thickness of 0.5 [mm].

The aluminium alloy 6060-T6 substrates, provided from Aston Martin Lagonda[®] in a previous work, were already anodized and had an area of 25x100 [mm] with 2 [mm] of thickness. The mechanical properties are listed in table 3.4 [80].

Table 3.4: Mechanical properties for the anodized aluminium substrates

	Elastic modulus	Poisson's ratio
	[GPa]	[-]
Al 6060-T6	69	0.33

The anodized substrates were only cleaned with isopropyl alcohol (IPA) before adhesive application.

The carbon/epoxy pre-pregs were provided by layers provided by SEAL[®] Texipreg model HS 160 RM and handled in the laboratory: the manufacturing process is deeply described in section 3.2.5. The final CFRP properties are listed in table 3.5 [81].

The CFRP substrates were abraded with 240-grid sand paper in a linear $\pm 45^\circ$ path from the 0° layup fibre direction. Hereafter, the adherends were acetone cleaned and placed on a Teflon or

Table 3.5: Mechanical properties for the CFRP substrate (1 - fibre direction,; 2 - transverse direction; 3 - out of plane direction) [81]

Elastic modulus	Shear modulus	Poisson's ratio
[MPa]	[MPa]	[-]
$E_1 = 109000$	$\nu_{12} = 0.342$	$G_{12} = 4315$
$E_2 = 8819$	$\nu_{13} = 0.342$	$G_{13} = 4315$
$E_3 = 8819$	$\nu_{23} = 0.380$	$G_{23} = 3200$

paper surface for plasma treatment. The plasma treatment was performed on substrates bonded area, in a homogeneous movement during six seconds. Figure 3.13 illustrates the plasma treatment performed. The effectiveness of this treatment was previously validated using a contact angle measurement system, demonstrating an increase in the surface energy.

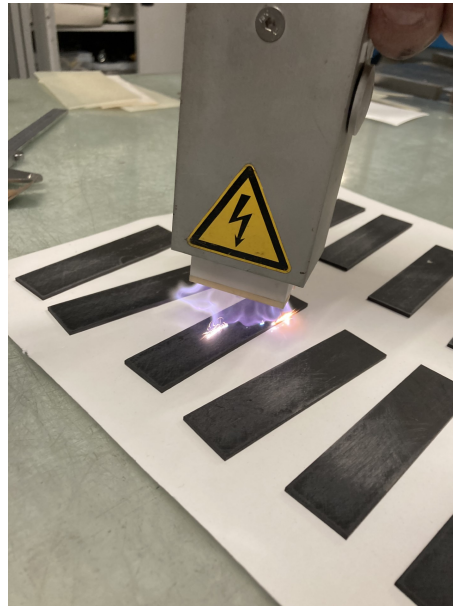


Figure 3.13: Plasma treatment for the CFRP substrates

Figure 3.14 show the drawing of both aluminium and CFRP SLJs, where the adhesive thickness t was 0.5 [mm], the same as for the aluminium SLJs.

Having the substrates ready for adhesive application, the manufacturing process becomes trivial. Traditionally, the steel mould showed in figure 3.15 is convenient since the SLJ length can be adjusted with the bottom screws. This mould is also utilized in the fabrication of DCB specimens.

Nevertheless, PETG 3D printed spacers were manufactured in order to accommodate a more lightweight and smaller aluminium mould, with guiding pins. Both spacers and the mould were cleaned with acetone and coated with a release agent before manufacturing. The lower substrates were positioned and adhesive was poured. Hence, the top substrates were coated with a thin

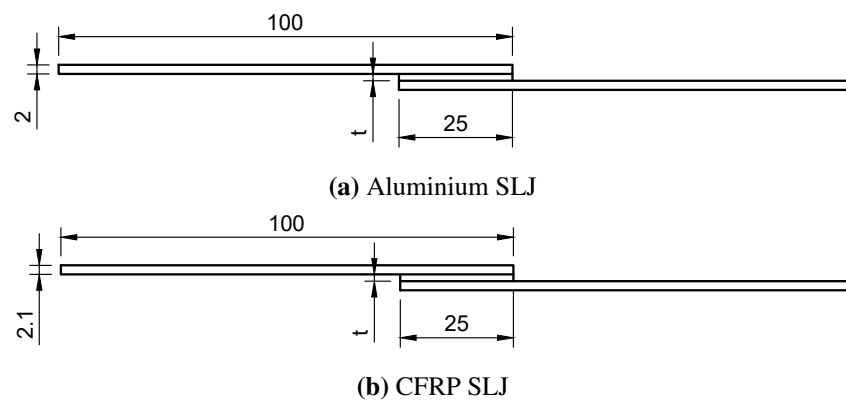


Figure 3.14: Dimension of the SLJ for aluminium and CFRP substrates in [mm]

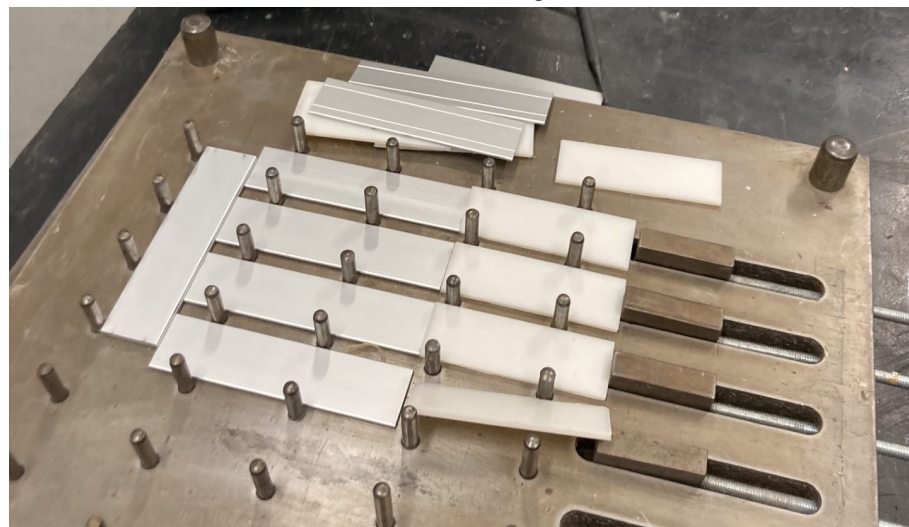
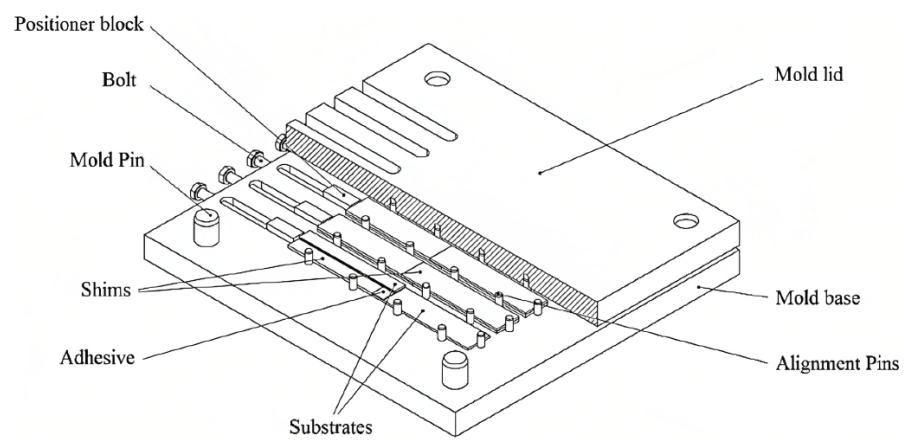


Figure 3.15: Steel mould for SLJ and DCB manufacturing [51]

adhesive layer and joined to the opposite part. The mould was closed with another aluminium plate and the assembly was inserted in a thermal chamber with some weights on top to cure. Figures 3.16 and 3.17 illustrate the open mould with aluminum and CFRP SLJ substrates, respectively.

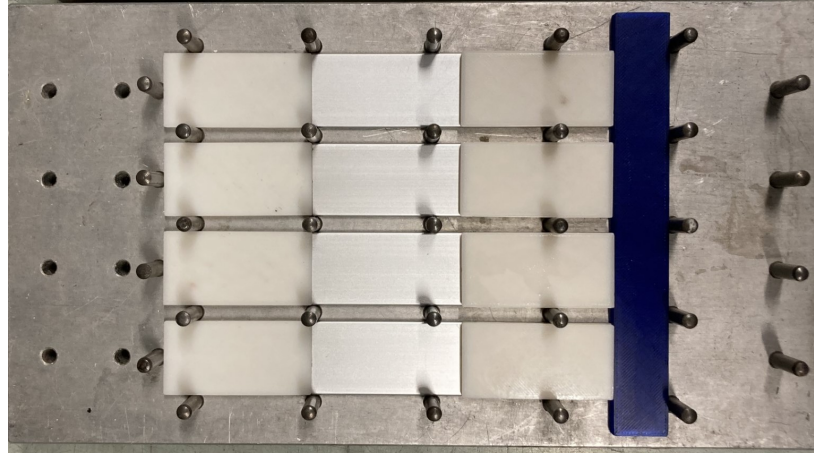


Figure 3.16: Aluminium substrates manufacturing

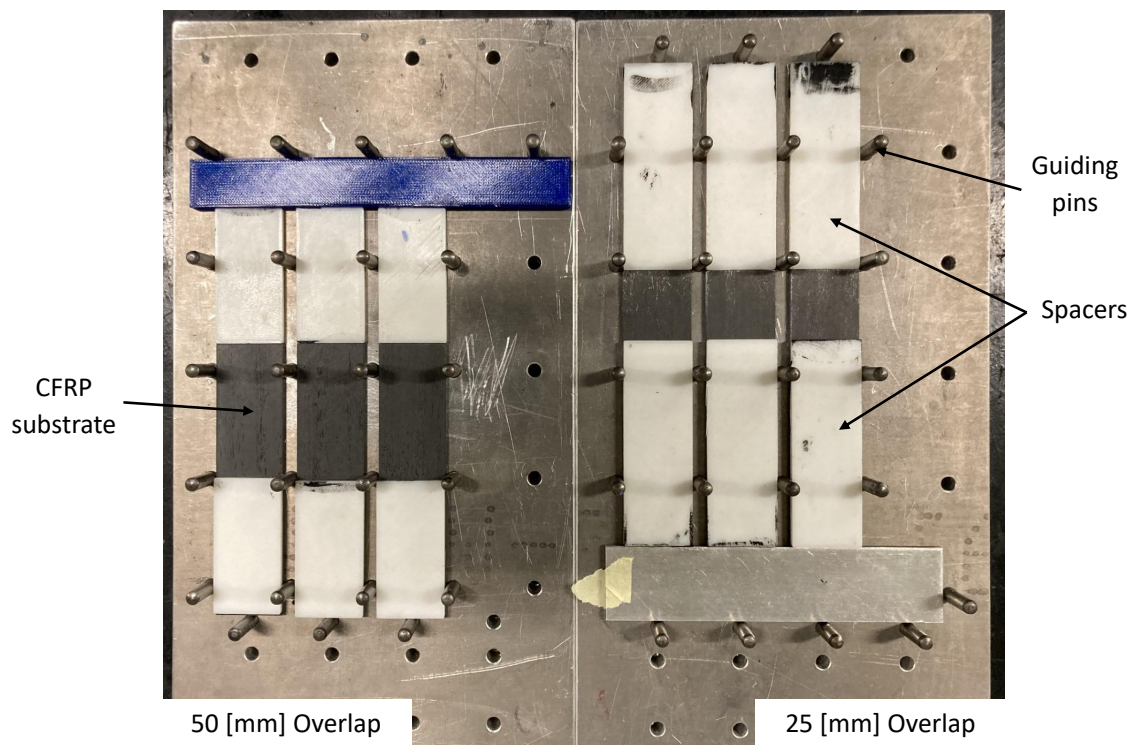


Figure 3.17: CFRP SLJ manufacturing for both 25 [mm] (right) and 50 [mm] (left) of adhesive overlap length

3.2.5 CFRP substrates

A set of SLJs with unidirectional carbon fibre reinforced polymer (CFRP) adherends and with an overlap length of 25 and 50 [mm] were also manufactured. The CFRP substrates were produced by hand laying and curing CFRP pre-preg layers. The final substrate thickness preferred was 2.1 [mm], hence seven carbon/epoxy pre-preg layers with dimension 300x300 [mm] and a layer thickness of 0.15 [mm] were staggered. Thereafter the layup was placed in the hot plate press to cure. The fabrication process of the CFRP sheet, with the final substrate thickness is described as follows:

1. The pre-preg roll was removed from the refrigerator where it was stored at -18°C and left in room temperature to warm-up for a few minutes;
2. The table and items in use were cleaned with acetone;
3. The pre-preg was unrolled and let it sat on a table where seven square sheets of 300x300 [mm] were cut using an x-acto sharp knife;
4. A Teflon layer was removed from two side-by-side sheets, where a hot gun was used to slightly and homogeneously heat the carbon/epoxy pre-preg;
5. When the pre-preg begun to get slightly sticky, the sheets were aligned and carefully laid upon the table and hand pressurized ensuring a 0° layup (a steel rounded corner mould was used to avoid voids) - this process was repeated until all 300x300 [mm] seven layers were jointed;
6. Due to mould constraints, the joint sheet was cut in half along the fibre direction having then two 150x300 [mm] sheets;
7. The two sheets were joined following the same procedure described illustrated in figure 3.18;
8. A two steel plate mould was coated with release agent and left to dry in a hood;
9. The carbon/epoxy sheet was placed in the mould and four calibrated spacers with a thickness of 2.1 [mm] were applied along the sheet edges;
10. The mould was inserted in the hot press, subjected to a pressure of 30 [bar].

The curing cycle for the carbon/epoxy pre-preg used is one hour at 145°C and then another hour at 140°C . After the two hours, the hot press heating system was turned off and the mould was withdrawn only when the temperature was below 60°C . The mould was then cooled to RT outside the press. Figure 3.19 shows the opened mould, containing a composite layup before and after the curing stage. The CFRP sheet was then cut into 100x25 [mm] substrates in a cutting machine with a diamond disc. To be noted that 25x25 [mm] tabs where also manufactured following the same procedure.



Figure 3.18: Heat application in the final stage of the sheets layup

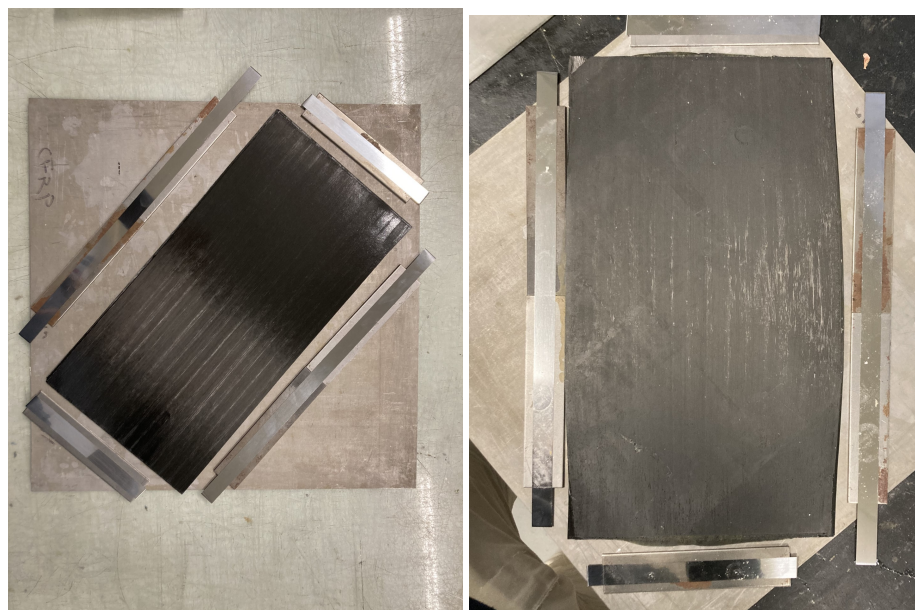


Figure 3.19: CFRP plate before and after curing

Chapter 4

Test results

The present chapter agglomerates the results obtained for the adhesive and the two-component formulation with 3 different resin modifier additives and different molecular weight. This chapter summarizes information and provides additional details from the first paper [A](#) which describes the experimental part as well as the corresponding outcomes. In this section, a detailed explanation of the most relevant results takes place.

Each test requires testing jigs to accommodate and load the specimens. Each one has an universal joint mechanism which allows the supports to be coupled with the quasi-static machine used. After the bottom and top jigs are mounted it is important to balance the load measured by the machine loading cell at the beginning of each set assembly.

4.1 Outcomes for the SPUR adhesive

4.1.1 Tensile test

For the tensile bulk test special hand tight tethers were used to accommodate the edges of each specimen. Figure [4.1](#) shows the block claws securing the specimen. These were also used when testing SLJs.

A minute pre-load (less than 3 [N]) was applied provided the elasticity of the specimen. A digital camera was mounted in a tripod and leveled with the aim of aligning the lens as normal to the specimen surface as possible. A light source (LED) was utilized in order to provided sufficient illumination for the specimen images: the distance of the light source to the test was adjusted by measuring the luminosity of the specimen in the digital camera. The global test setup is displayed in the next section in figure [4.4](#). Since the test was supposed to last a long period of time, a video recording of the specimen was not performed. Instead, the camera was programmed to photograph the specimen every five seconds. This methodology later provided a good quality strain field extrapolation with relatively lower file size, which is one constrain in the DIC process since each file can easily occupy a large amount of memory space. Before commencing the test

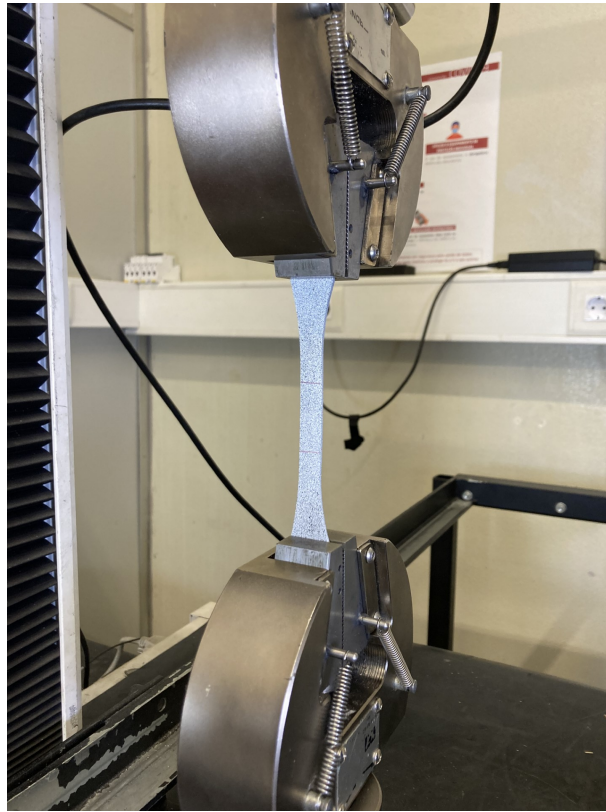


Figure 4.1: Assembly of the bulk specimen onto the quasi-static machine

procedure, the displacement of the machine was also balanced and both the camera and the test were set to begin at the same time. Figure 4.2 shows the failure points for the first three tensile specimens tested.



Figure 4.2: Bulk specimen failure modes

Two transverse line sets were previously painted which marked longitudinal dimension of 30 [mm], serving to track the extension along the test run. All bulk specimens failed within the region with 10 [mm] of width, thus all specimens were shown to be valid. To note, all bulk specimens,

from SPUR or from the adhesive with additives, possessed a similar rupture mode,

The strain field was obtained using GOM Correlate® (2019) DIC software. Here, four facet points were marked for each specimen, two longitudinally and the other in the transverse direction, close to the fracture section. The aim was to create two distances for which the software would provide the distanced points value for each picture provided (Δl). Hence, the results were exported to an *Excel* sheet where, by dividing the distances measured by the initial one, the strain along those points could be accurately determined.

$$\varepsilon = \frac{\Delta l}{l_0} \quad (4.1)$$

Henceforward, by withdrawing the strain for the transverse and longitudinal points, the Poisson's ratio could be estimated with the following relation.

$$\nu = -\frac{\varepsilon_{transverse}}{\varepsilon_{longitudinal}} \quad (4.2)$$

Figure 4.3 illustrates the points and distances chosen for a particular specimen as well as the quality of the speckle. This is important since it is the base for an accurate strain correlation: faced with a poor speckle pattern or a blurred image with low quality, the software will have issues identifying the corresponding points along the picture instances. The green surface signifies a good quality of the image and good extrapolation of the speckled points in the software used to perform DIC analysis.

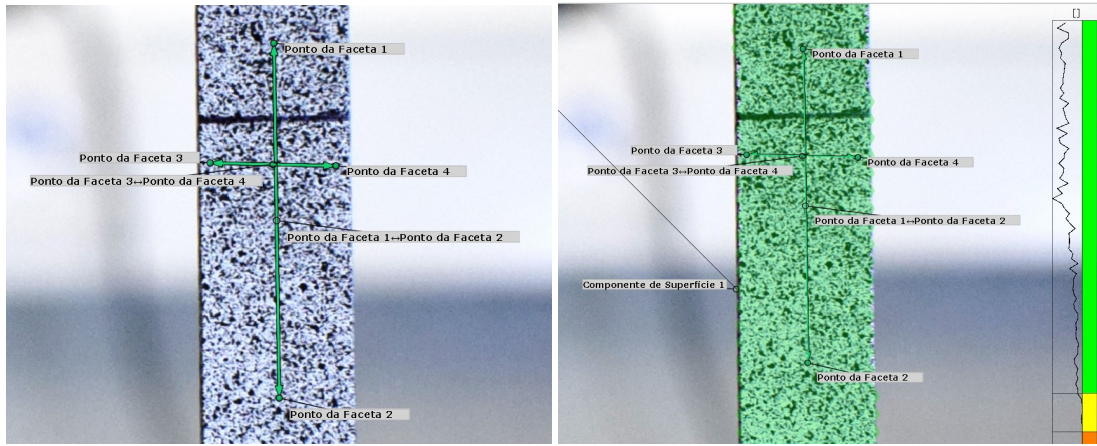


Figure 4.3: Bulk specimens during DIC analysis

Table 4.1 summarizes the tensile properties determined, as well as the Poisson coefficient obtained from DIC analysis.

Having both tensile modulus and Poisson's ratio, the shear modulus can be estimated considering the following relation, valid for isotropic materials:

$$G = \frac{E}{2(1 - \nu)} \quad (4.3)$$

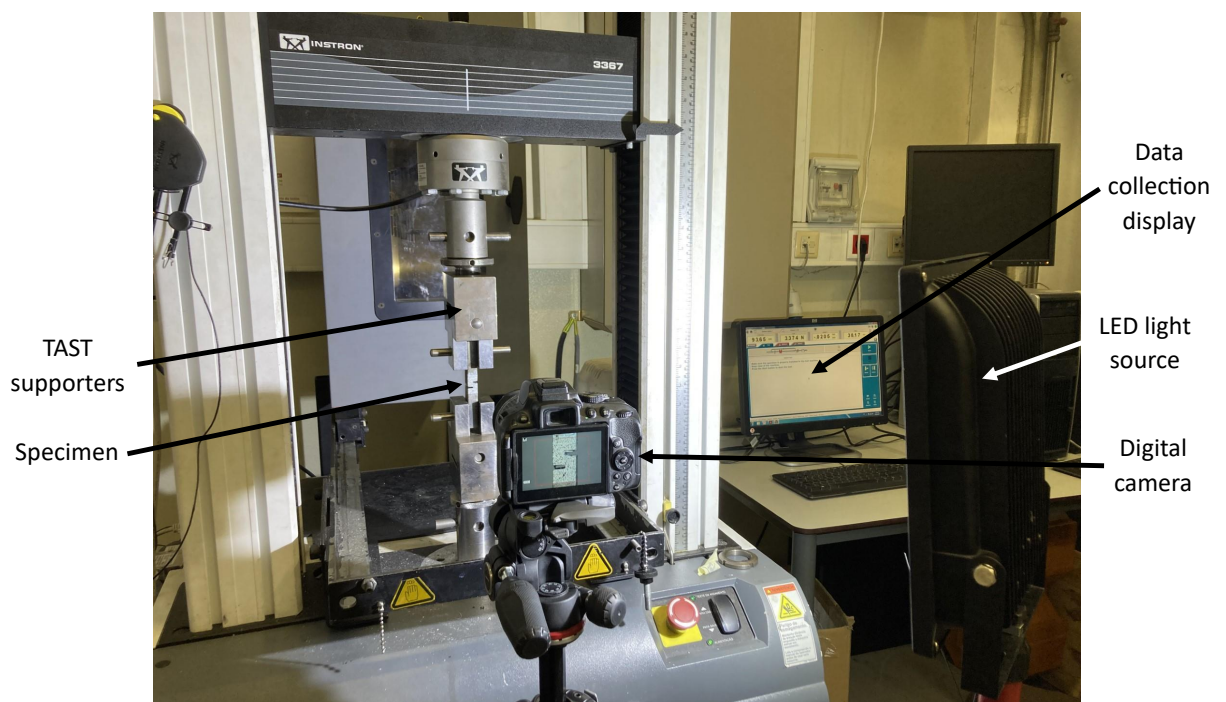
Table 4.1: 2k SPUR tensile properties

Property	Units	2k SPUR
Young's modulus, E	[MPa]	10.17 ± 0.96
Tensile failure strength, σ_f	[MPa]	4.16 ± 0.21
Tensile failure strain, ε_f	[%]	41.1 ± 5.8
Poisson's ratio, ν	[-]	0.418 ± 0.009

where a value of 3.59 [MPa] is calculated for the shear modulus.

4.1.2 Shear test

The TAST followed an assembly process similar to the bulk tensile test, where DIC was taken into consideration. The setup for the TAST run is illustrated in figure 4.4. The TAST setup guarantees stable fixation of the specimens during the test.

**Figure 4.4:** Setup for the TAST run

The two-component polyurethane adhered well to the sandblasted steel substrates. Figure 4.5 shows all the failed TAST specimens.

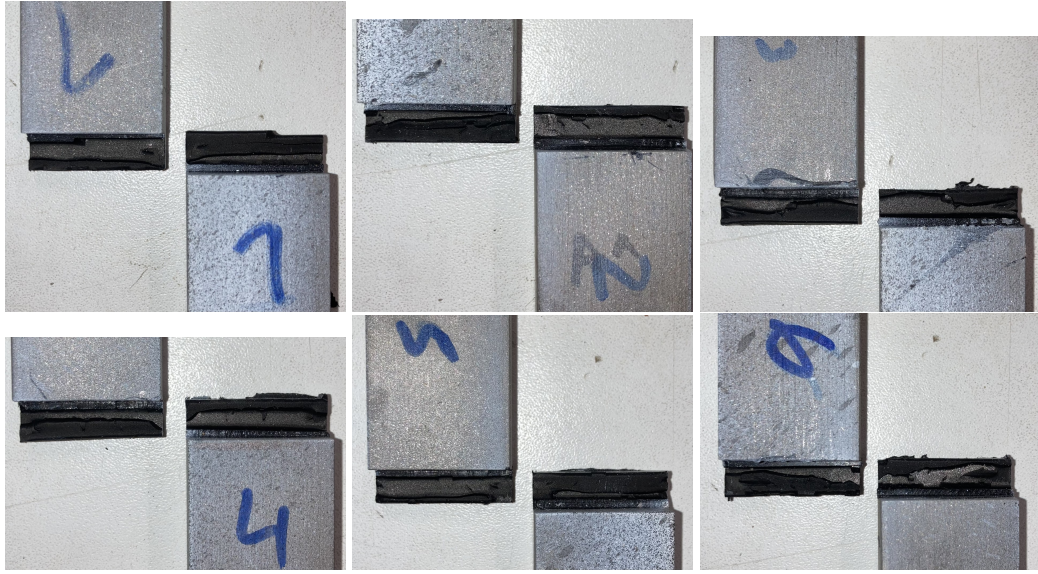


Figure 4.5: Modes of failure for all six TAST specimens tested

To ensure high quality results, the DIC extrapolated strain data was complemented with an extensometer gauge, placed at the other specimen front. In fact, when dealing with rubbery materials, the thick adherent shear test at failure may not remain stretched, thus not providing a failure in the overall 25 [mm] of width at the same instant. In reality, there exists a tilting phenomena, where one minute section of the overlap fractures before the rest of the bonded joint, provoking an unwanted rotation in the TAST specimen. This induces errors in the strain field capture for both DIC or extensometer method: that is the main reason why two strain measurement methodologies were used in opposite specimen faces, to further compare the results. In addition, the adhesive layer in TAST is much more restricted in terms of boundary conditions in comparison with the tensile test, where the material is not constrained in a thin layer, surrounded by metal.

Nonetheless, the strain results captured by the two methodologies was found to be similar. The extensometer gauge provided directly the strain measured whereas the DIC correlation allowed the capture of point distances in the full picture, which was then computed to strain by dividing those values by the initial distances. Thenceforward, this value was multiplied by the inverse of each specimen thickness (t_{TAST}), finally providing the shear strain values.

$$\gamma = \frac{\frac{\Delta l}{l_0}}{t_{TAST}} \quad (4.4)$$

Table 4.2 summarizes the shear properties determined in the TAST.

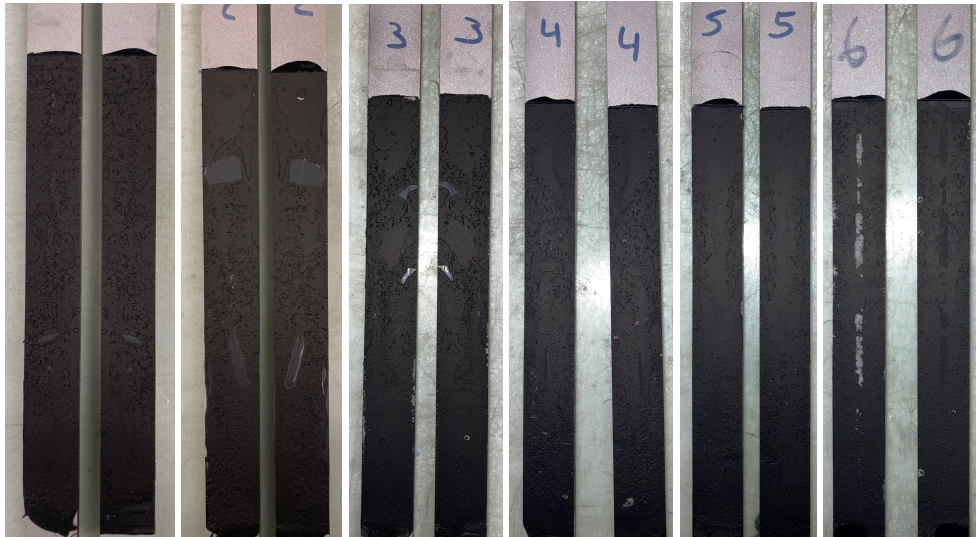
It should be noted that the shear modulus value is greater than the one extrapolated from the DIC in the tensile specimen analysis. This can be due to the different strain rates faced by the material as a function of the different adhesive layer sizes. As an example, the TAST was performed roughly under two minutes and the bulk test took around 50 minutes, although both used both under the same crosshead constant rate.

Table 4.2: 2k SPUR shear properties

Property	Units	2k SPUR
Shear modulus, G	[MPa]	7.07 ± 1.53
Shear failure strength, τ_f	[MPa]	5.47 ± 0.74
Shear failure strain, γ_f	[%]	84.7 ± 11.5

4.1.3 Fracture characterization tests

The DCB test was performed for six specimens. The test was divided into two specimen groups: the ones with a pre-crack opening stage and the ones without. In fact, to measure the critical energy release rate in mode I (pure opening), a pre-crack has to exist in the material, hence a pre-opening of the specimens is usually performed, loading the specimen until a peak is reached in the $P - \delta$ curve, as shown in the data acquisition system of the testing machine. This is enough to nucleate the crack geometry induced by the sharp razor blade. Notwithstanding, as previously referred, polyurethanes can nucleate multiple cracks instead of one and the FPZ of these materials is relatively large. In light of this knowledge, it was decided that half of the specimens should be tested without a pre-cracking stage. Figure 4.6 show all cohesive failure modes for the DCB specimens tested.

**Figure 4.6:** Modes of failure for all six DCB specimens tested

As referred in Paper A, no differences of the G_{Ic} value were found after the application of CBBM formulation [14] to both pre-cracked and not pre-cracked specimens.

Having the first fracture toughness mode determined, the following step is to characterize the adhesive under in-plane shear. The previous chapter showed that this can be accomplished with

the usage of a mixed-mode apparatus [56] which allows for the extrapolation of the G_{II_c} value from the establishment of the adhesive fracture envelope. Nonetheless, this was just performed due to the inability to test the SPUR under pure mode II conditions. The End-notch flexure (ENF) test [82], also referred as three point bending, uses the same geometry specimens as the DCB standard test [79] and allows for the estimation of the fracture toughness in mode II following a CBBM formulation for the same condition [15]. The specimens were inserted into a three point bending apparatus, where a folded Teflon sheet with oil was inserted inside the initial crack length of the specimen, as illustrated in figure 4.7, to reduce friction during the test. The lower rollers were distanced 5 [mm] from the specimen edges, whereupon the top roller was mounted to contact the specimen at midspan.

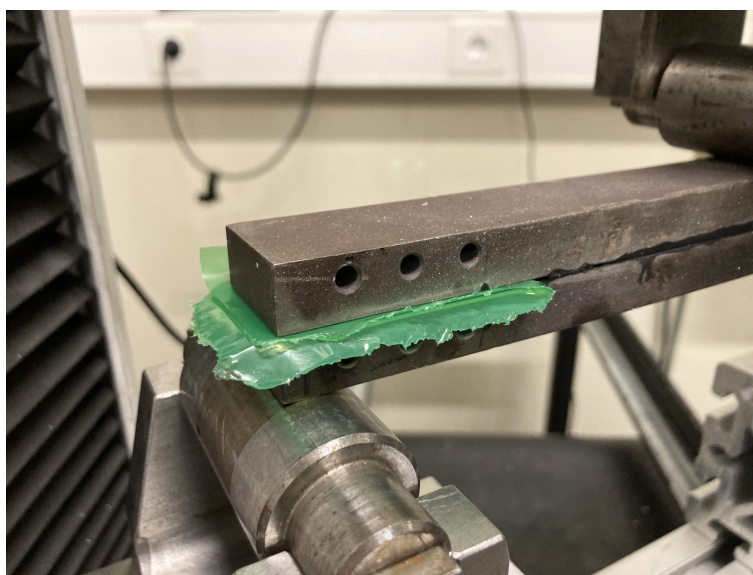


Figure 4.7: Detail of the Teflon sheet with oil in the ENF setup

In brittle adhesives, the crack propagates easily without the need for too much displacement, nevertheless, in an elastomeric adhesive the crack only begins to propagate when the steel substrates have already reached the yielding point. Since the plasticity of the ENF adherends is not taking into account in CBBM, and since there was no crack propagation before the plasticizing phenomena, all tests were considered invalid. Even using other strategies, such as the direct method supported with inclinometers [7, 50] or by performing DIC to obtain the rotation is invalid since the substrates always plasticized. Figure 4.8 shows the plasticized ENF bars in a particular trial test run.

One possible justification for this is a very large value of G_{II_c} . In fact, considering the value for the fracture toughness in mode I and literature data for other types of adhesives, a rough estimation of the toughness in mode II can be made assuming that G_{II_c} can be up to ten times larger than G_{I_c} [2]. However, a more reasonable explanation can be found by considering the large FPZ induced in these elastomeric adhesives. If the FPZ length is large enough to occupy half of the specimen's total length, the upper contact point in the ENF test will have to induce a larger displacement in

order to nucleate and propagate the initial crack. One should not that in this case this does not translate in a extreme value for G_{IIc} , but leads to conclusion that a larger displacement must be induced so that its propagation is possible. However, this can lead to impractically large, non-standard, specimen sizes, which create major problems during manufacturing and testing phases, requiring newly developed moulds and testing jigs.

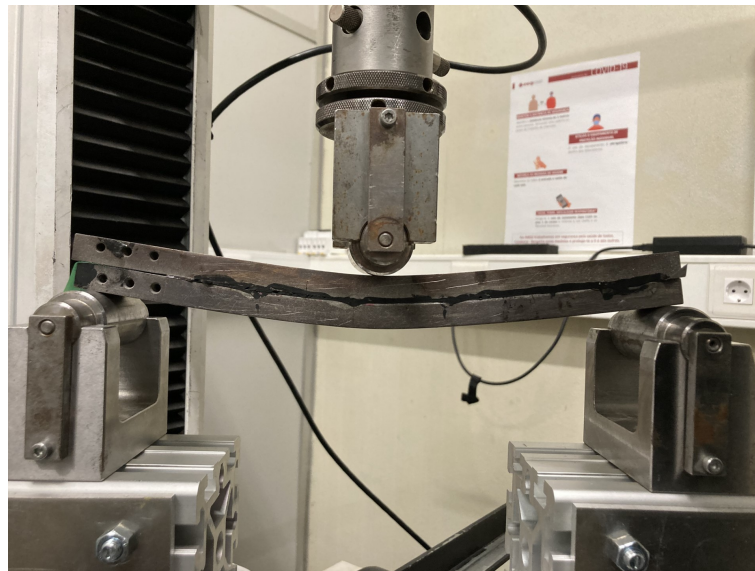


Figure 4.8: ENF invalid test

One approach to estimate the critical energy release rate in mode II is to extrapolate a fracture envelope of the material, thus the usage of the mixed-mode apparatus [56], which follows a CBBM of mode mixity formulation [13]. The displacement of each DCB substrate was measured using two LVDT's from RDP Electronics® model DCTH1000A. Both the blade and calibrated tapes were removed from the specimen prior to the test. The specimen was then fitted into the apparatus, as displayed in figure 4.9. In this case, no pre-cracking stage was performed. The apparatus was configured phase angles of 46.0° and 60.0° , where the five best DCB specimens were selected to extract the final G_{Ic} and G_{IIc} values for each respective configuration.

After the application of the mixed-mode CBBM formulation, the fracture envelope was generated by performing an estimation for the in-plane shear fracture toughness value. This was found to be around 3.3 times higher than G_{Ic} , a reasonable ratio for polyurethane adhesives [83]. Table 4.3 summarizes the fracture toughness values determined.

4.2 Single lap joints

SLJ testing and its results are discussed in detailed Paper B), appended to this thesis.

Aluminium and CFRP SLJs were manufactured with 25 and 50 [mm] of overlap adhesive length. Alignment tabs were glued to each joint adherend to minimize peel stresses on the adhesive



Figure 4.9: Mixed-mode apparatus setup [56]

Table 4.3: 2k SPUR fracture toughness in mode I and II

Property	Units	2k SPUR
Toughness in mode I, G_{Ic}	[N/mm]	1.191 ± 0.055
Toughness in mode II, G_{IIc}	[N/mm]	4

layer. The bulk tensile clamps were used to assemble the SLJ's in the quasi-static testing machine, as illustrated in figure 4.10.

The SPUR showed a good level of adhesion when bonded with the anodized aluminium substrates, whereas poor adhesion was found when bonding the CFRP substrates. More accurately, cohesive failure was obtained in the aluminium substrates while, on the other hand, a mixed-failure mode was encountered on the composite joints. Figure 4.11 shows the instances before, during and after the failure of an aluminium SLJ with 25 [mm] of overlap length. The failure is totally co-



Figure 4.10: Mounted CFRP SLJ with 50 [mm] overlap

hesive and homogeneous throughout the bonded area, where it can be noticed that multiple cracks surge all over the overlap length at the moment of failure.

The same does not can be observed in the composite joints. Figure 4.12 captures two pictures at the failure point of a CFRP SLJ with 50 [mm] overlap for better visualization. In the first one, two cracks nucleate very close to the interface of the bonded areas. The upper crack nucleates in the adhesive interface with the upper substrate whereas the lower one initiates in the adhesive interface with the bottom adherend. This nucleation point can be provided the existence of some peel joining the overlap end effect [2]. These two cracks propagate and meet in the middle of the overlap, where they eventually cause the complete failure of the adhesive layer.

Table 4.4 agglomerates the experimental values obtained for both aluminium and composite SLJs with the two overlap lengths. The lap shear strength in the aluminium joints has a greater value than the composite ones, result of the poor adhesion in this second configuration. For the sake of completeness, paper B includes a detailed discussion of the result data from the analysed SLJs.

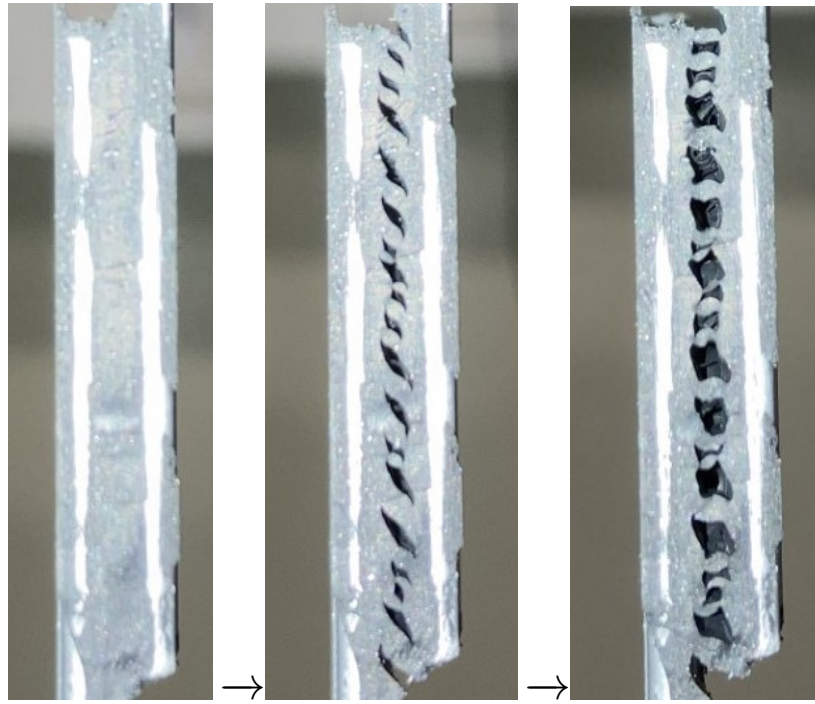


Figure 4.11: Real test instances before, at and after failure occurred

Table 4.4: Results for the aluminium SLJ

Substrate	Overlap	Maximum loading, F_{max}	Lap shear stress, σ_{lps}	Extension at F_{max}
[-]	[mm]	[kN]	[MPa]	[mm]
Al 6060-T6	25	4.04 ± 0.14	6.47 ± 0.23	1.230 ± 0.061
Al 6060-T6	50	7.13 ± 0.71	5.70 ± 0.57	1.521 ± 0.147
CFRP	25	3.51 ± 0.29	5.61 ± 0.46	1.413 ± 0.041
CFRP	50	5.27 ± 0.35	4.22 ± 0.28	1.940 ± 0.011

4.3 Outcomes for the resin modifier additives

The provided SPUR adhesive was mixed with three different Silquest™ additives and CoatOSil™ Flx. In theory these should enhance the adhesion properties. Bulk and TAST were performed, with the results being listed in table 4.5.

The failure mode for both tests was reported to be similar to the previously tested 2k formulation without the additives. The inclusion of the additives was found to diminish both the tensile and shear properties. It should be noted that the first batch was used to agglomerate the additive mixtures, two months after the first opening of the container.

For sake of completeness of paper A, figure 4.13 and 4.14 agglomerate respectively the tensile and shear strain curves for the three mixtures.

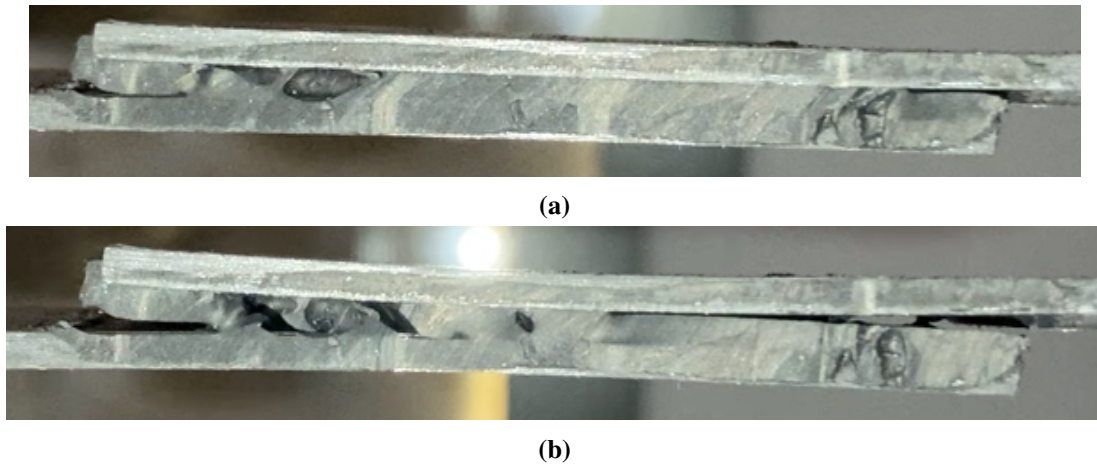


Figure 4.12: Real test instances at the failure moment for a CFRP SLJ: effect of crack propagation in each opposed bonded area from (a) to (b)

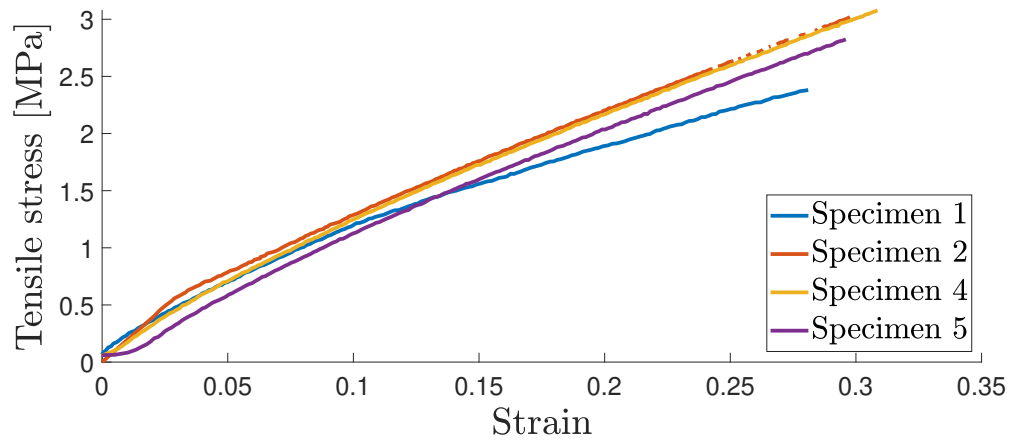
Table 4.5: Elastic and shear properties of the SPUR adhesive with three different Silquest™ additives

Property	Units	A- 1110	A-Link 600	A-Link 235
Young's modulus E	[MPa]	10.52 ± 0.50	10.28 ± 0.55	12.17 ± 0.35
Tensile strength σ_t	[MPa]	3.33 ± 0.79	1.79 ± 0.16	2.30 ± 0.19
Tensile strain ϵ	[%]	0.357 ± 0.090	0.175 ± 0.018	0.189 ± 0.014
Shear modulus G	[MPa]	3.47 ± 0.50	2.57 ± 0.29	2.71 ± 0.36
Shear strength τ_s	[MPa]	2.57 ± 0.29	2.39 ± 0.16	1.210 ± 0.132
Shear strain ϵ_s	[%]	2.71 ± 0.36	3.41 ± 0.25	1.457 ± 0.107

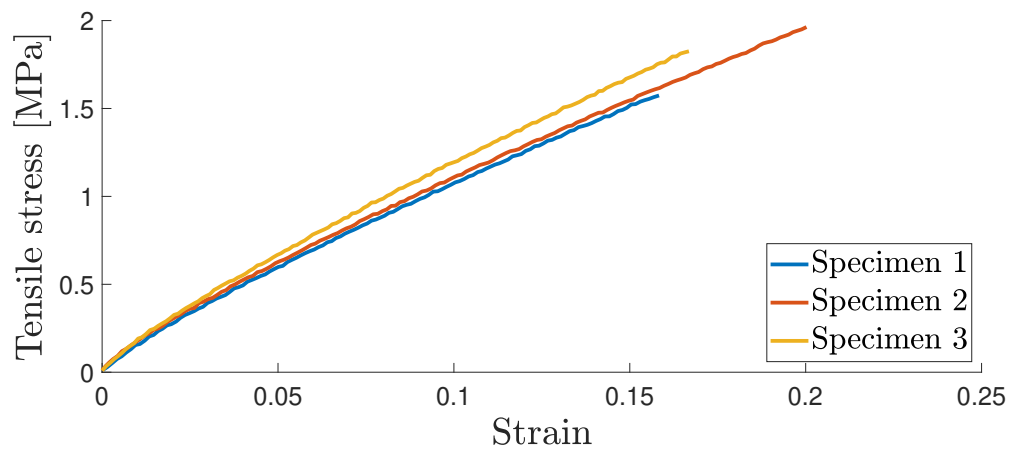
4.4 Effect of SPUR molecular weight

Three SPUR formulations with different molecular weights were characterized in terms of fracture toughness in pure mode I, without being mixed with additives. In fact, the batch referred as low viscosity, L, has the same molecular weight as the first batch of 2k SPUR, but was manufactured using a different technique. The other two batches with higher viscosities, K for intermediate and J for the highest, followed the same newer manufacturing process, differing just on the SPUR molecular weight. Table 4.6 summarizes the fracture toughness measures for each viscosity by testing at least four good DCB specimens [79] and following CBBM [14].

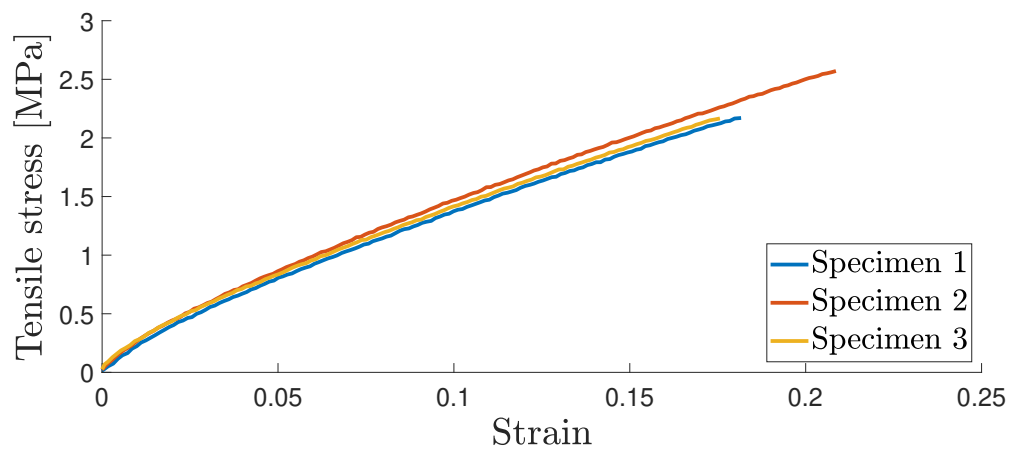
Figure 4.15, 4.16 and 4.17 show the opened specimens for the L, K and J viscosities respectively. The less viscous DCB specimens showed a cohesive failure that was sometimes oscillatory and interfacial. The other two higher molecular weight specimens showed practically cohesive failure.



(a) Bulk for mixture 1



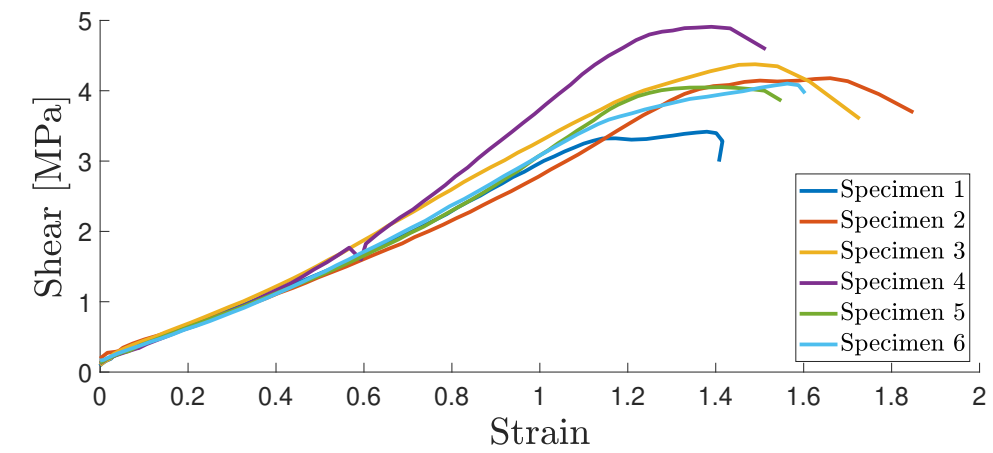
(b) Bulk for mixture 2



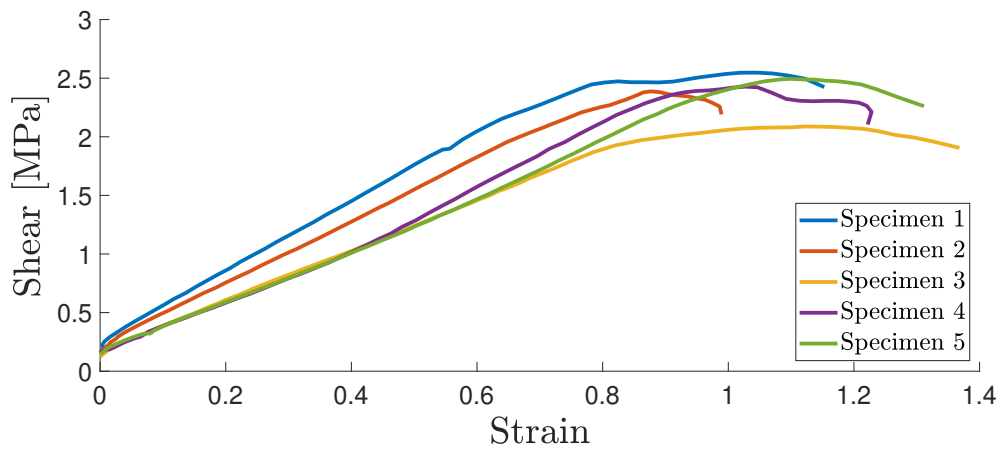
(c) Bulk for mixture 3

Figure 4.13: Stress strain curves for the three mixtures performed

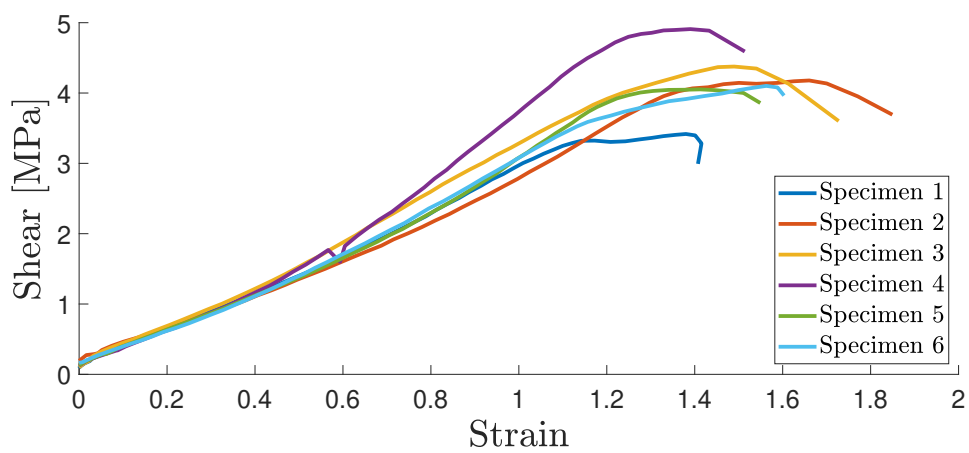
The R-curves computed recurring to CBBM are displayed bellow in figure 4.18 respectively for the lower (L), intermediate (K) and high (J) molecular weight.



(a) TAST for mixture 1



(b) TAST for mixture 2

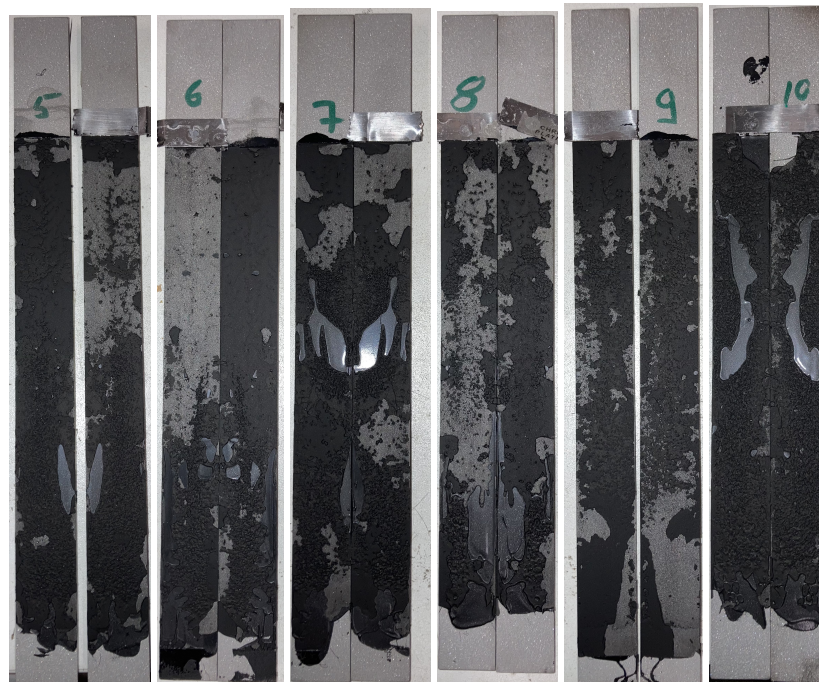


(c) TAST for mixture 3

Figure 4.14: Stress strain curves for the three mixtures performed

Table 4.6: SPUR viscosity influence in the fracture toughness in mode I

	Low viscosity	Intermediate viscosity	High viscosity
Designation	L	K	J
G_{Ic} [N/mm]	1.96 ± 0.18	2.49 ± 0.07	1.53 ± 0.08

**Figure 4.15:** Modes of failure for all six DCB specimens tested

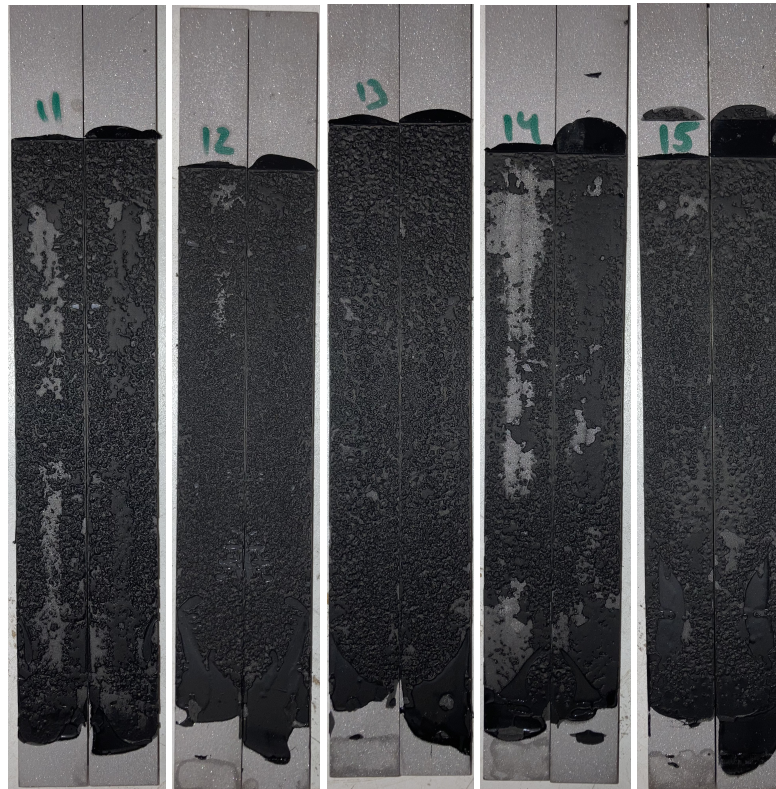


Figure 4.16: Modes of failure for all six DCB specimens tested

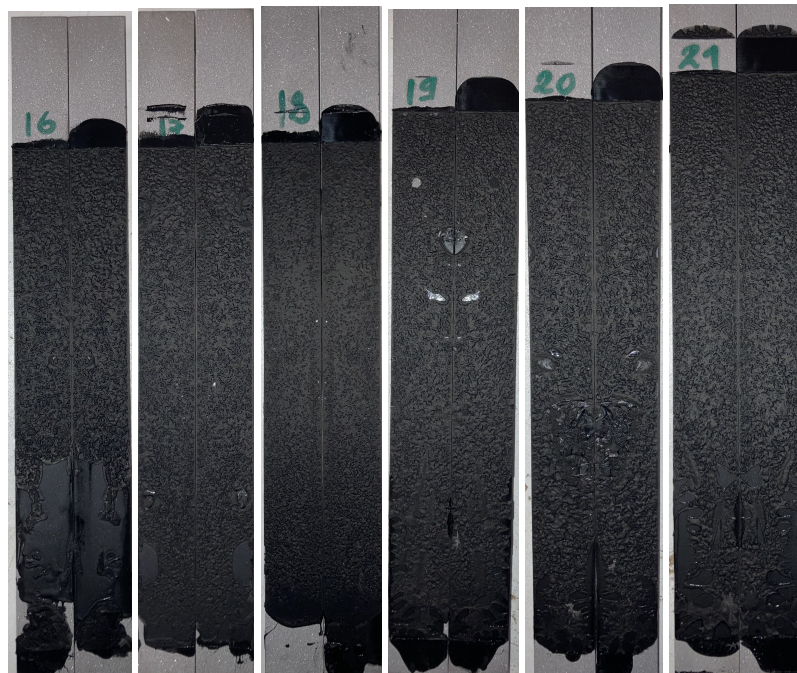
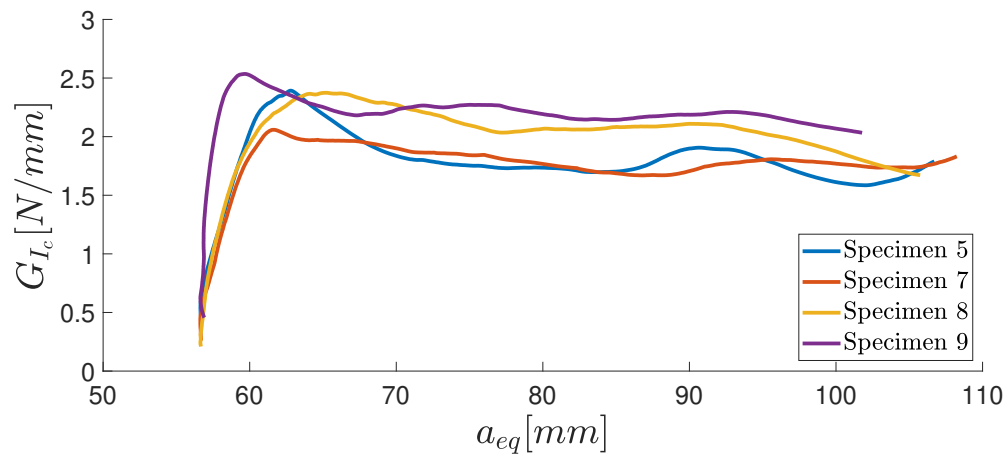
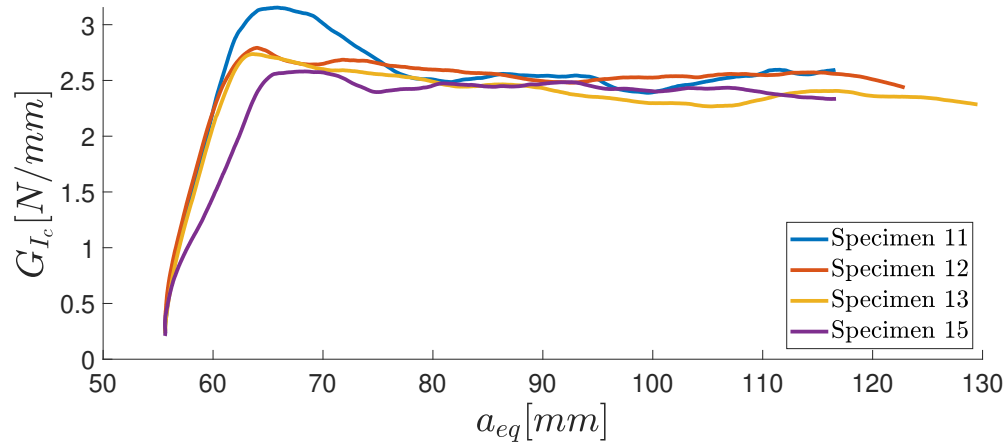


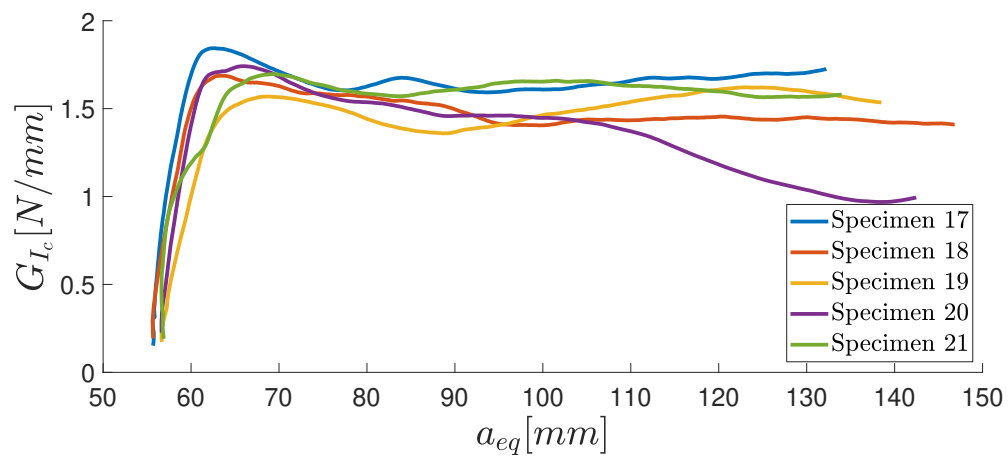
Figure 4.17: Modes of failure for all six DCB specimens tested



(a)



(b)



(c)

Figure 4.18: R-curve of the SPUR different viscosity levels: a) low (L); b) intermediate (K); c) high (J)

4.5 SEM analysis

The two-component SPUR is a blend of cured SPUR with a filler and hardened epoxy, interconnected through aminosilane. To investigate the difference in lap shear strength between SPUR part A and the 2k formulation with epoxy resin (part A+B), a scanning electron microscope (SEM) test was performed on two small samples. The aim was to examine the presence and characteristics of the precipitates, as well as analyze both surfaces using energy-dispersive X-ray spectroscopy (EDS) in various regions. The SEM report is provided in Paper A.

To investigate the grainy regions observed in both samples, a localized EDS analysis was conducted on the reference SPUR material. Two distinct zones were selected for analysis: one situated in a relatively uniform area (Z1) and the other in an area characterized by the presence of small grains (Z2), as illustrated in figure 4.19. The chemical spectra obtained from both locations was found to be nearly identical to each other and similar to the global spectra. Specifically, the concentration of silicon (Si) in both regions was comparable, making it difficult to determine whether the grainy regions or precipitates were enriched in silicon. However, the absence of spectrum variations along the thickness suggests good homogenization of the grainy area within the matrix.

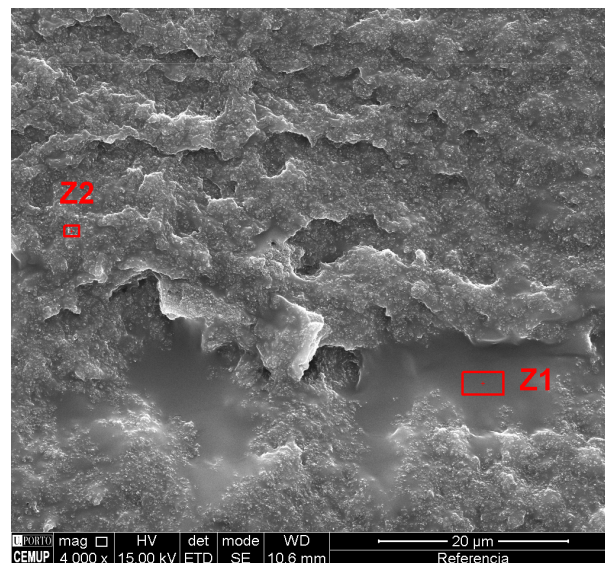


Figure 4.19: EDS location in the referenced SPUR surface

The overall SEM and EDS revealed a consistent and uniform grainy surface with no discernible variations in chemical composition across the fracture areas showing practically no variations in terms of the depth of the analysis, highlighting a good level of homogeneity throughout the material thickness.

Chapter 5

Numerical model

After obtaining the quasi-static material properties, a finite element analysis was developed to numerically validate with the experimental tests performed as a comparison base. The tensile behaviour of the material is completely elastic without a particular yield point, since the experimental tensile stress-strain curve evolves in an approximate linear shape, failing immediately at the maximum tensile strength, without showing a plateau. In light of this behaviour, a triangular cohesive law was considered to represent a suitable approach to characterize the adhesive behaviour. Nonetheless, it should be noted that common polyurethane adhesives are ductile and are usually characterized by a trapezoidal or tabular cohesive law [2, 66].

The average experimental values of the SPUR adhesive properties were inputted in ABAQUS® FE software (Dassault Systèmes, Suresnes, France) using the COH2D4 cohesive elements for the adhesive in all models, except on the bulk specimen one where a stress based approach was used to determine the failure load.

Prior to the definition of the triangular law, it is important to be critical about the mechanical characterization tests performed and the validity of the obtained properties. The TAST outputted a higher shear modulus value than the one extrapolated from the bulk tensile tests using the isotropic material relation between the elastic and shear modulus with the Poisson's ratio. Nonetheless, this can be explained by the different geometries of both tests: in the tensile run, the bulk specimen has more freedom whereas on the TAST, the 0.5 [mm] of adhesive are undergone a rapid shear condition and are much more restrict by the boundary conditions. Furthermore, strain rate distances are also in play, since although both tests follow the according quasi-static standards, being performed at a constant crosshead rate of 1 [mm/min], the duration of the tensile tests was around 20 times higher than the TAST. As a consequence, the strain rate is different in both scenarios, thus leading to different behaviour of the elastic material. Accordingly, the TAST shear value was chosen to build the triangular law for mode II in order to compute a decent correlation for more constraint adhesive tests. Figure 5.1 illustrates two cases of the triangular laws with post linear initiation response, the first using the shear modulus value extrapolated from the bulk test using DIC and a second using the direct TAST value. Here, it can be noticed the poor suitability of the

lower shear modulus, since it does not use damage under pure shear conditions. Although the application of a power-law to interpolate the two CZM triangular shapes may indeed provide a negative damage slope, the second CZM shape with G_{TAST} will be chosen due to the conditions implied in the adhesive layer in the TAST.

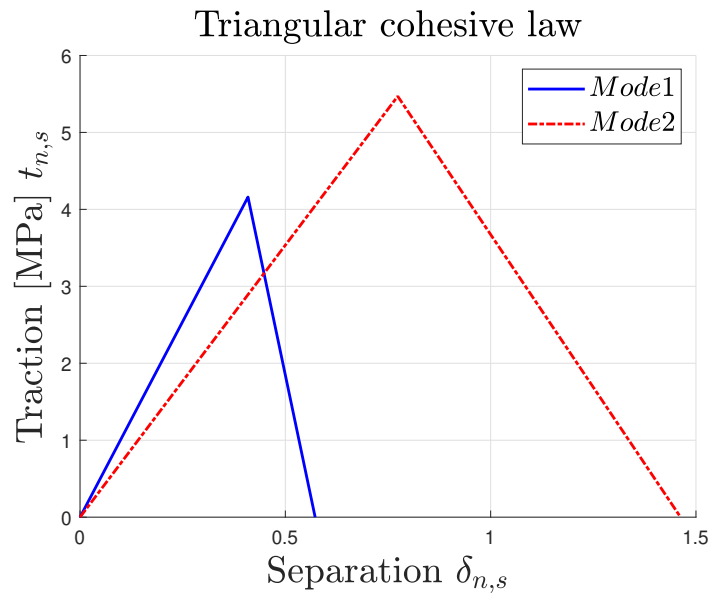
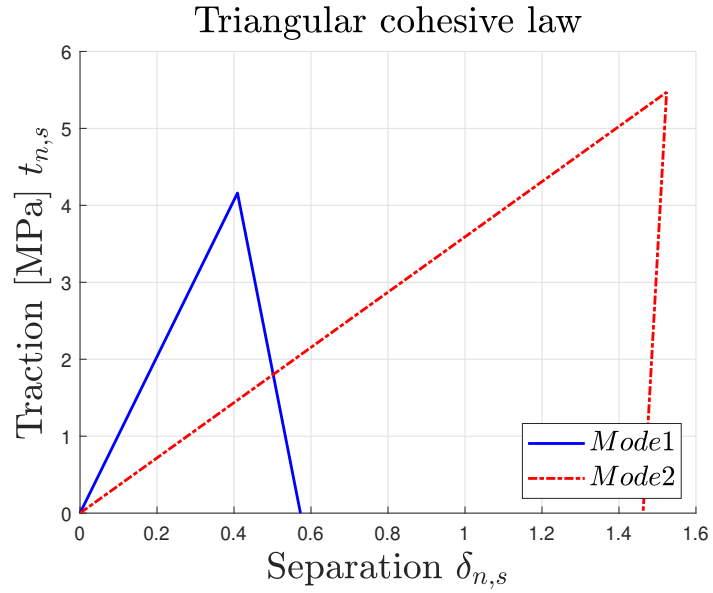


Figure 5.1: Triangular laws comparison

5.1 Numerical details

The damage criterion selected was a quadratic nominal stress formulation, which for two-dimensional models follows the relation:

$$\left(\frac{\langle \sigma_n \rangle}{N_{max}} \right)^2 + \left(\frac{\sigma_s}{S_{max}} \right)^2 = 1 \quad (5.1)$$

where N_{max} and S_{max} correspond to the maximum tensile and shear strength, respectively, and σ_i the nominal stresses. The curved parenthesis $\langle \rangle$ are the Macaulay brackets, which emphasize that a pure compressive stress will not initiate any damage [66].

The definition of the damage criterion for traction separation laws relies on an energetic formulation, which takes into consideration both the critical energy release rate values in mode I and II. Hence, having established the two triangular laws for each mode, a mixed-mode fracture energy relation can be extrapolated by combining each pure law into a mixed-law formulation. This can be achieved recurring to the Power Law for instance [84], which considers:

$$\left(\frac{G_I}{G_{Ic}} \right)^\alpha + \left(\frac{G_{II}}{G_{IIc}} \right)^\alpha = 1 \quad (5.2)$$

where the value for the α parameter chosen was equal to one. Figure 5.2 illustrates an example of the power law extrapolated for both mode I and mode II cohesive laws [85].

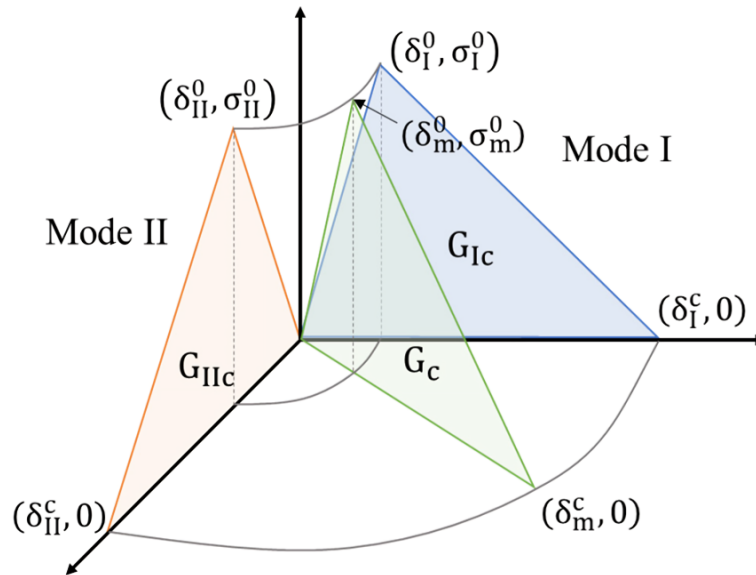


Figure 5.2: Extrapolation of a mixed-mode fracture energy power law. Adapted from [85]

The bulk specimen model employed the simplest numerical analysis. In this case, a three-dimensional linear elastic model was formulated, accounting for the properties extracted from the tensile test, such as the Young's modulus and Poisson's coefficient. Eight node hexahedron

(c3D8R) 3D elements were used with reduced integration and hourglass control. A simple failure criterion based on the experimental maximum tensile strength was established, given the linear elastic behaviour without a particular yielding point. Figure 5.3 illustrates the bulk specimen model computed in ABAQUS® FE software.

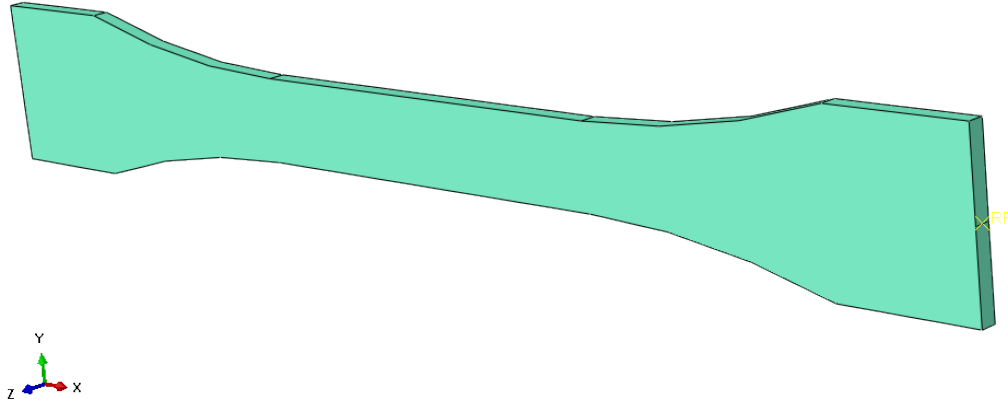


Figure 5.3: Bulk specimen

TAST specimens were modelled using elastic CPS4R plane strain elements with reduced integration and hourglass control for the steel adherends. Table 5.1 summarizes the elastic properties considered for the adherends.

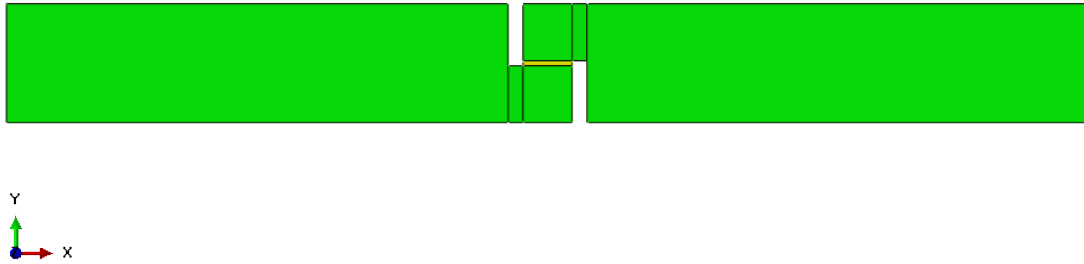
Table 5.1: Elastic properties of steel adherends

Elastic modulus [GPa]	Poisson's ratio
210	0.33

A structured mesh was applied to the adherends after the convenient partition of the adherends geometry, illustrated in figure 5.4. A mesh refinement took place at the edges of the overlap areas recurring to a double bias option. The edges of the bottom adherend were fully encastrated, whereas in the top adherend a displacement along the x axis was imposed.

For the TAST and DCB models, the shear modulus determined by the shear test was chosen. Table 5.2 summarizes the properties tuned in the finite element software, according to the laws and parameters assumed. A damage stabilization cohesive value for the viscosity coefficient was set to 10^{-5} .

The double cantilever beam specimen was modelled in order to extract the $P - \delta$ curve, from which the R-curve was generated, using CBBM [14] with the experimental data. The adherends

**Figure 5.4:** TAST specimen partitions**Table 5.2:** SPUR properties inserted in the software

Elastic		Damage		Damage evolution		
E	G	σ_f	τ_f	G_{Ic}	G_{IIc}	Mixed-mode behaviour
[MPa]	[MPa]	[MPa]	[MPa]	[N/mm]	[N/mm]	Power Law $[\alpha]$
10.17	7.07	4.16	5.47	1.191	4	1

were partitioned in order to generate a fine and structured mesh with CPS4R plane stress elements, with reduced integration and hourglass control. As in the TAST specimens, a linear static behaviour was chosen for the steel beams with the properties listed in table 5.1. Two boundary conditions were employed respecting the real test scenario. As illustrated in image 5.5, the bottom hole is pinned, allowing rotation along the normal to the image axis, whereas the upper hole is coupled to a reference point, where a displacement along the y axis (δ) was imposed. In this figure, it is also possible to visualize the partitions performed to accommodate the structured mesh.

A single bias mesh was used from the beginning of the cohesive layer (initial crack size) until the end of the overlap. To be noted, in a real scenario, there is no adhesive within 10 to 15 [mm] from the end of the overlapped length, due to the presence of the 0.2 [mm] thick calibrated tape. Nevertheless, since the aim is to capture the crack propagation along the specimen and that the specimens fails before reaching this last section with lack of adhesive, this area with no adhesive was not modelled.

Finally, models were generated to reproduce the performance of the aluminium SLJs. Table 5.3 agglomerates the aluminium substrates elastic properties inserted into the finite element software. The adhesive properties chosen were exactly the same as reported for the TAST and DCB models.

Table 5.3: Elastic properties of aluminium substrates

Elastic modulus [GPa]	Poisson's ratio
69	0.33

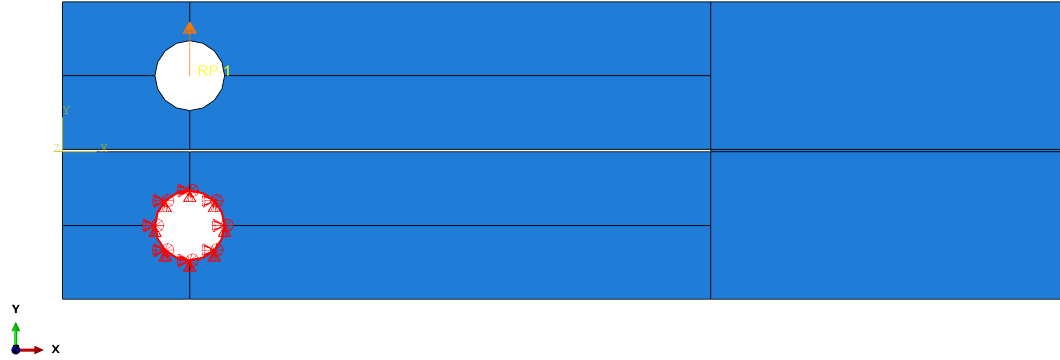


Figure 5.5: Partitions and boundary conditions imposed in the DCB specimen model

The SLJ model considered the 25x25 [mm] aluminium tabs with 2 [mm] of thickness, bonded to the real specimens. Since the thickness of the adhesive is very small, it can be negligible. The specimen was partitioned in order to establish a structured mesh throughout the model. Figure 5.6 displays both boundary conditions and the partitions introduced in the geometry. The left part of the specimen was considered as encastred in both substrate and tab faces for a length of 25 [mm], corresponding to the tabs length. The right tab faces were coupled to a reference point in which a displacement was imposed in the x direction. These conditions were similar to the ones used during the testing, where two clamps held both specimen edges.

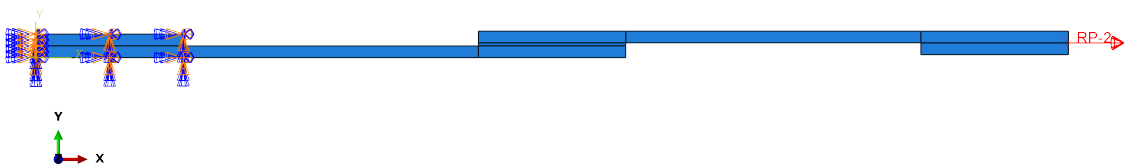


Figure 5.6: Partitions and boundary conditions imposed in the aluminium SLJ

The same four-node bilinear plane strain quadrilateral elements were considered for both substrates and tabs, using reduced integration as well as hourglass control. The cohesive layer overlap was meshed with a double bias, illustrated in figure 5.7, optimizing the number of elements in use.

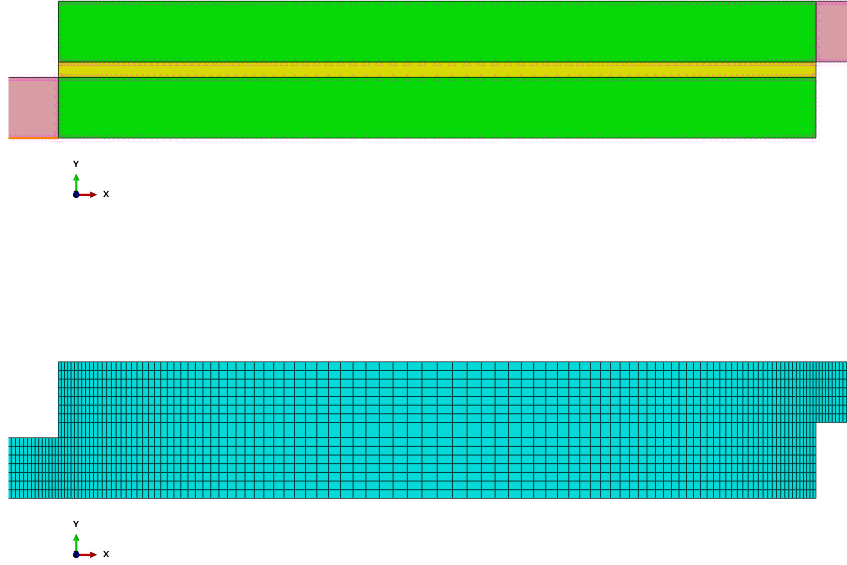


Figure 5.7: Mesh refinement along the bonded section

5.2 Numerical validation

Having laid out the numerical constitutive models and the geometries used, the validation of the hypothesis and approaches relies on a successful comparison between numerical and experimental results. All the experimental results took into consideration the compliance of the quasi-static machine used. Figure 5.8 shows the load displacement curve for both numerical and experimental data. The grey horizontal line complies with the failure criterion used, whereupon the maximum tensile strength equals to the average values measured in the tensile tests results.

The TAST model used the shear modulus value obtained from the shear test results. Hence, a numerical curve was generated and was found to be in accordance with the experimental data, as illustrated in figure 5.9.

The $P - \delta$ curve for the DCB specimen also showed a good agreement with the experimental data, as reported in figure 5.10. The $P - \delta$ curves of the specimens displayed correspond to those without a pre-crack opening procedure, since that procedure was not represented in the model. This leads to a curve which has a distinct peak before propagation. Notwithstanding, as illustrated in figure 5.11, the propagation mode is similar for both pre-cracked and not pre-cracked specimens, showing the validity of the numerical model for pre-cracked DCB specimens.

Since the anodized aluminium SLJ were found to fail cohesively, a numerical approach was possible for these joints. Figure 5.12 displays the experimental results for the four SLJ tests as well as two numerical curves, each containing a different value for the shear modulus:

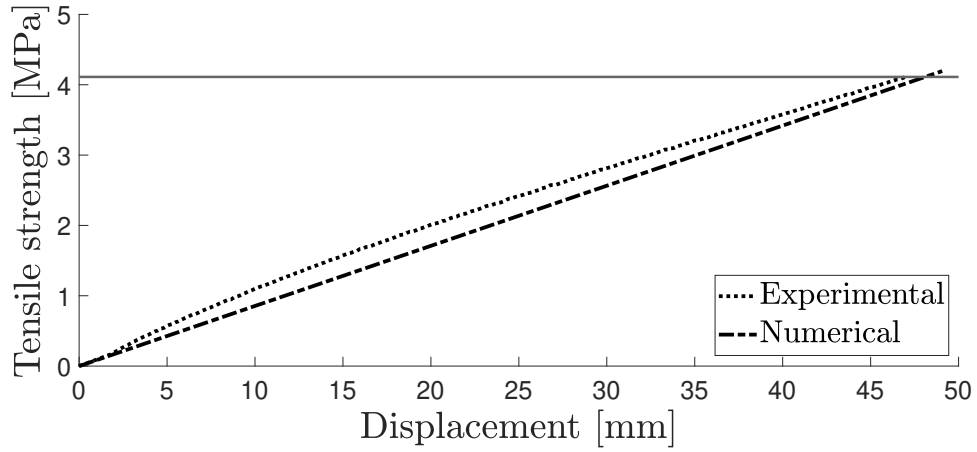


Figure 5.8: Numerical and experimental curve for the tensile test

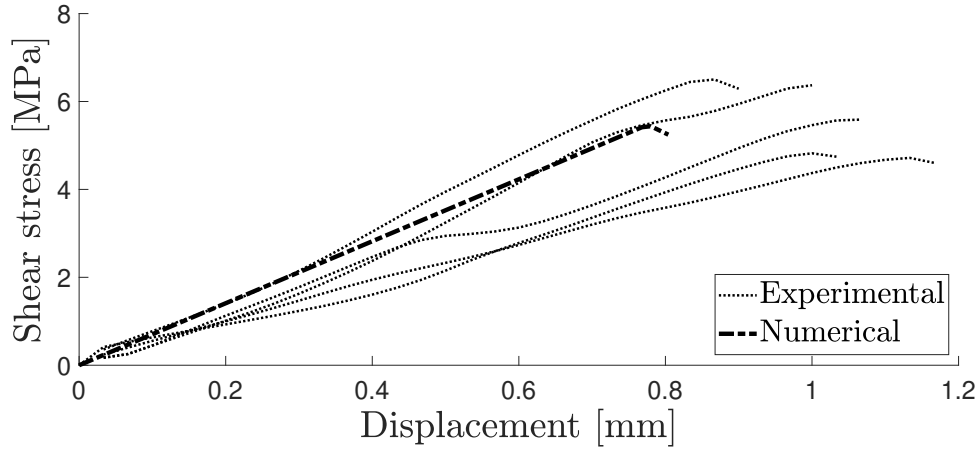


Figure 5.9: Numerical and experimental curve for the TAST

- G_{Bulk} $\rightarrow$ one in which the shear modulus G value comes from the tensile analysis, calculated from the Poisson's coefficient extrapolation from DIC;
- G_{TAST} $\rightarrow$ a second in which the shear modulus G value comes from the TAST.

In addition, since the SLJ testing conditions are different from the TAST, the maximum lap shear strength was found to be superior to the measured shear strength, hence the τ_{max} value was updated. The difference between using the lap shear strength value in the maximum shear strength is the estimation of the failure point, which means that with a lower value the joint will fail sooner, with less displacement, although showing the exact same slope.

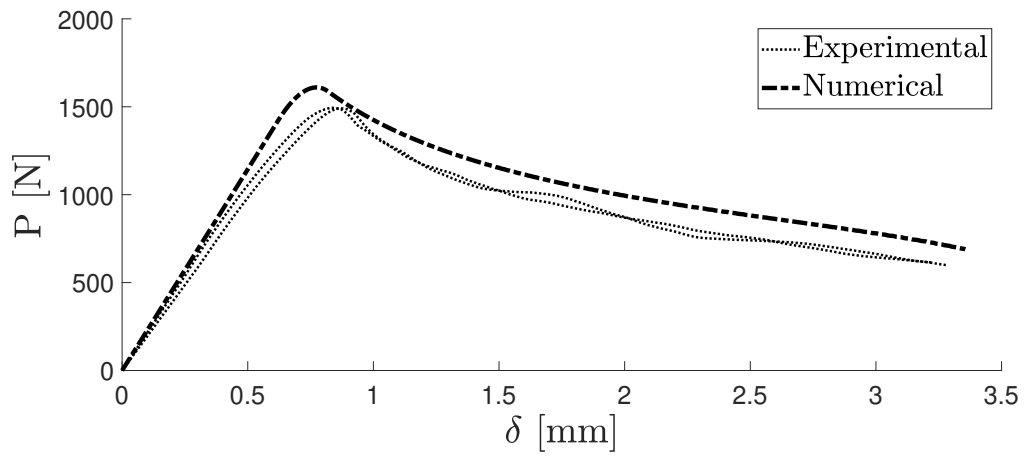


Figure 5.10: Numerical and experimental $P-\delta$ curve

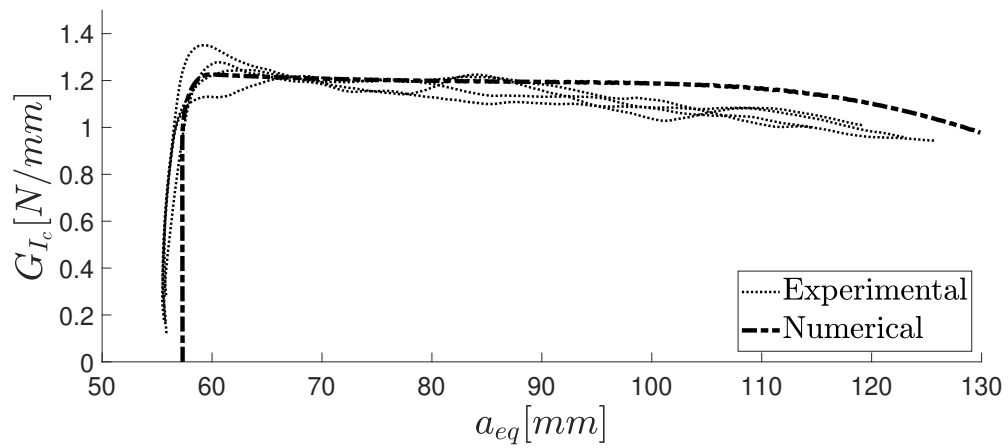


Figure 5.11: R-curve computed using CBBM for the numerical and experimental data

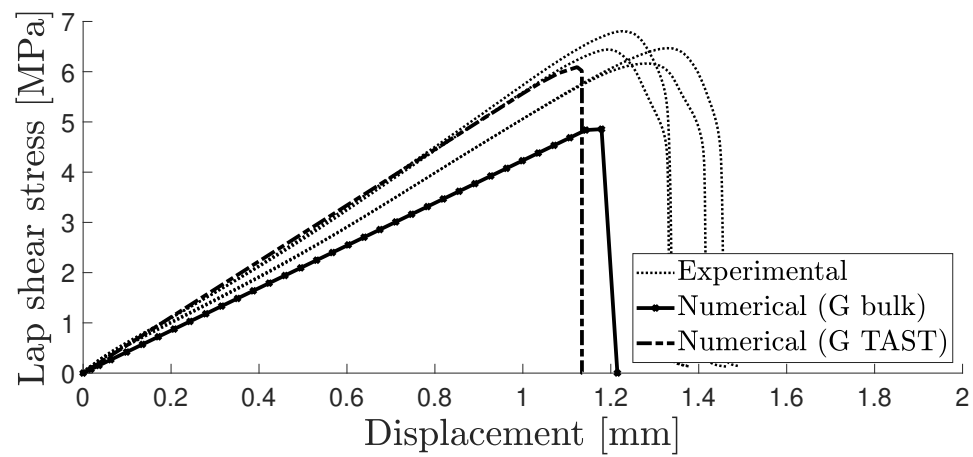


Figure 5.12: Lap shear strength vs displacement curve for both numerical and experimental 25 [mm] overlap aluminium SLJ

Chapter 6

Summary of the appended documents

6.1 Paper A

Development and study of a novel silane based polyurethane hybrid flexible adhesive - Part 1: Mechanical characterization

This paper presents a comprehensive investigation into the mechanical properties of a novel two-component adhesive that combines silylated polyurethane resin (SPUR) with standard epoxy resin. The study focuses on quasi-static conditions and employs various characterization techniques. To commence, tensile bulk tests are conducted to obtain stress-strain curve data. Additionally, the shear stiffness and strength of the adhesive are evaluated using thick adherend shear tests. Digital image correlation is utilized as a supporting tool to extract in-plane strain field information. Fracture toughness assessment is performed through double-cantilever beam and mixed-mode tests to evaluate the adhesive's performance under pure modes of fracture. The analysis also includes an exploration of shear and tensile properties influence under the incorporation of three different additives. In addition, the critical energy release rate values are examined for three distinct SPUR viscosities: low, medium, and high. Furthermore, scanning electron microscopy (SEM) is employed to examine SPUR samples, providing valuable insights into the composition and behavior of the adhesive, both with and without the presence of epoxy resin. By conducting these comprehensive experimental and analytical investigations, a deeper understanding of the mechanical properties and fracture behavior of the 2K adhesive, comprising SPUR and epoxy resin, is achieved.

6.2 Paper B

Development and study of a novel silane based polyurethane hybrid flexible adhesive - Part 2: Joint testing and numerical modelling

This paper focuses on evaluating the performance of a novel hybrid 2K SPUR adhesive in single SLJ with two different substrate materials, aluminium and carbon fibre reinforced polymer, and the numerical simulation of the already characterized adhesive. The CZM approach was chosen due to the adhesive's highly elastic nature and absence of yielding phenomena. A triangular-shaped CZM law was selected to represent the adhesive behavior. The experimental results from the previous paper served as a basis for validating the numerical model, enabling the determination of accurate parameters for the CZM. Through successful numerical validation, the tuned CZM parameters were determined, aligning with the experimental observations.

6.3 IJUP poster

Mechanical characterization of a novel silane based polyurethane hybrid flexible adhesive

The research paper titled "*Mechanical characterization of a novel silane based polyurethane hybrid flexible adhesive*" made a significant impact at the prestigious 2023 IJUP conference, earning recognition and an award. To effectively communicate the findings, a poster was meticulously designed. The poster presented a comprehensive overview of the step-by-step process involved in the mechanical characterization of the two-component SPUR adhesive under quasi-static conditions, being a brief summary of the appended Paper [A](#).

Chapter 7

Conclusion

This thesis presents a comprehensive mechanical characterization of a novel two-component SPUR mixed with epoxy resin under quasi-static conditions, at room temperature. It also outputs the mechanical properties used for the development of a numerical model, following a CZM with a triangular shape law. In terms of the properties determined, the following comments were highlighted:

- The tensile tests showed a lower Young's modulus and a low tensile strength than expected, also with a low strain to failure, below that of ductile polyurethane adhesives. Despite this, the Poisson's ratio was determined through DIC analysis and found to be 0.418;
- The shear properties of the adhesive were analyzed using the TAST procedure, revealing a shear-to-tensile strength ratio of 1.4, which is high when bench-marked with other polyurethane, elastomers or sealant adhesives. In addition, the shear properties of the adhesives were found to slightly deteriorate in two subsequent TAST runs, performed after two and three months of the adhesive storage life;
- Fracture tests were carried out to generate the fracture envelope for the 2k SPUR adhesive. Pure Mode I and mixed-mode tests were conducted, with the Mode I fracture toughness (G_{IIc}) being found to be 1.19 [N/mm] and the Mode II fracture toughness estimated to be around 4 [N/mm], approximately 3.3 times higher than the values found for common polyurethane adhesives (G_{Ic}).

SLJs were fabricated using anodized aluminum and unidirectional CFRP substrates. The adhesive demonstrated good adhesion to the aluminum substrates, resulting in a lap shear strength of 6.47 [MPa] in the joint with 25 [mm] of overlap length. However, adhesive failure was observed when bonding composite substrates, even when plasma treatment and an adhesion-enhancing additive were used in the SPUR mixture.

The second batch was used to study the eventual enhancement of the tensile and shear properties with the mixture of three different resin modifier additives, as well as the effect of the SPUR molecular weight (viscosity) in the fracture toughness value.

- All three additives showed lower tensile and shear strength with a similar tensile modulus when compared with the first 2k SPUR batch;
- The failure mode of joints bonded to CFRP substrates was the same as reported for the initial 2k formulation, still showing lack of adhesion;
- The newly formulated, low viscosity 2k SPUR showed an increase of 64% on the fracture toughness in mode I when compared to the first batch, where the molecular weight was the same, differing only on the manufacturing process;
- The intermediate viscosity SPUR showed the highest G_{Ic} value of 2.49 [N/mm];
- The highly viscous formulation showed the lowest G_{Ic} value and was the fastest to cure, being more difficult to flow and apply.

SEM and EDS analysis were performed to understand the increase in lap shear strength resulting from the addition of epoxy resin as a second component. The results showed a very similar homogeneous grainy surface with an identical chemical spectrum, regardless of the thickness.

In the numerical part of the adhesive behaviour under quasi-static conditions, the experimental tests were modeled in ABAQUS[®] FE software.

- For the bulk specimen model, a simple linear elastic approach was employed, using the maximum tensile stress as the failure criterion;
- The models for the TAST, DCB, and SLJ used the cohesive properties of the adhesive, with the shear modulus value obtained from the TAST test;
- The triangular-shaped cohesive zone model (CZM), typically suitable for brittle and stiff adhesives, was able to accurately represent the elastic behavior of the 2k SPUR adhesive without exhibiting a yielding point. The material properties and the CZM law derived from them successfully captured the in-joint behavior of the adhesive.

Comparative data analysis with other semi-structural polyurethanes revealed that the silyl-terminated polyurethanes family exhibited lower properties. While the 2k SPUR adhesive can compete with other polyurethanes in terms of critical energy release rate values, its tensile and shear properties were relatively low when compared to those reported in the literature for other silicone adhesives such as RTV 106 and AS1824. Nonetheless, it was found to be more efficient than other SPUR formulations listed in the literature [86].

Chapter 8

Future work

It would be interesting to follow the adhesive characterisation under dynamic loads, including medium rate and impact conditions.

Additionally, there is potential to enhance the developed of the adhesive properties, by changing the curing specifications and the fillers present in the mixture. Currently, the curing process does not lend itself to practical applications, hence an ambient curing followed by a high temperature post-cure for a short period of time would represent a more attractive process for industrial applications.

In the case of the application itself, these vibration damping adhesives can be suitable for filling battery packs, by possessing good thermal conductivity, which can be improved through small changes in the formulation. In this case, the importance of the adhesive dismantling, end-of-life and disposal is a future concern for the environment.

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Appendix A

Paper A

Development and study of a novel silane based polyurethane hybrid flexible adhesive - Part 1: Mechanical characterization

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Abstract: The need for more sustainable adhesive formulations has led to the use of silane-based adhesives in different industrial sectors, such as the automotive industry. In this work, a novel two component adhesive which joins silylated polyurethane resin (SPUR) with standard epoxy resin was mechanically characterized under quasi-static conditions. The characterization process was started with tensile bulk tests, conducted to determine the Young's modulus, ultimate tensile strength and strain to failure. This was followed by the thick adherend shear test, which allowed to determine the shear stiffness and strength. Testing was supported by a digital image correlation approach, allowing to withdraw the in-plane strain field. Double-cantilever beam and mixed-mode tests were performed to assess the fracture toughness under pure modes. In addition, an analysis of shear and tensile properties was studied considering three different additives. The critical energy release rate value for three different SPUR viscosities (low, medium and high) was also analysed. Finally, SPUR samples were analysed with scanning electron microscopy in order to understand and acquire more information about the 2k formulation with and without epoxy resin.

Keywords: SPUR, Silylated Polyurethane, Flexible adhesive, adhesive characterization

1 Introduction

The increased availability of high-performance adhesives has revolutionized structural design procedures. In specific applications, riveting and fastening processes can be substituted by adhesive bonding or even combined into an hybrid joint, making use of both design philosophies. Flexible adhesives also play an important role in the automotive industry, acting as sealants, structural adhesives and even in semi-structural roles, with the aim of pursuing a lightweight and eco-friendly design philosophy [1, 2]. Favourable

stress distribution and damping properties have made semi-structured adhesives good candidates for use in many applications. More specifically, the polyurethane adhesive family is widely known for its mechanical flexibility, which is of interest when bonding composite substrates, lowering stress peaks and leading to a lower risk of failure due to delamination [2, 3]. These adhesives possess a low elastic modulus and relatively low tensile strength, accompanied by a much greater elongation at failure [4, 5]. The high strain levels supported by these adhesives positively contribute for the gasket sealing properties, to the exceptional damping and good impact resistance.

Despite these advantages, common silicone and polyurethane based adhesives retain a certain level of toxicity which can be diminished [6]. Thus, although mechanical performance and cost are satisfactory, environmental concerns also play a role in adhesive formulation, necessitating a thorough analysis of life and the global life span as well as the product end of life. A result, silane terminated polymers have been developed, consisting of a hybrid material which contains lower toxicity levels, as well as similar one part (1k) polyurethane adhesives.

The adhesive under study in this work is a silylated polyurethane resin (SPUR) base, two component (2k) adhesive, inserted in the silyl terminated polyurethanes group. The hybrid chemistry of silane terminated prepolymers plays already a role in the industry supplying it from sealants, coatings and adhesives [6]. In fact, during the silane adhesive hybridisation, polyurethane-based adhesives had relatively better mechanical properties in terms of tensile strength, shear strength and elongation [7]. Silylated PUR may have special capping agents, which reduce the cross-linking density of the solution being said to provide higher mechanical properties [7]. In simple, one component polyurethane adhesives, there is a compromise of organic backbone of the polyurethane link and alkoxysilyl groups formation at the chain edges. Modified silane based polyurethanes create a free isocyanate group solution, which mitigates the toxicity hazard of the product [8].

Silyl-terminated polymers are known to be more stable and provide better adhesion and adequate storage stability. The terminated polyurethanes family is obtained by cross-linking and functionalism polyurethane with silane end-capping, obtained mainly from acrylate and aminosilane [6]. The second component of the SPUR mixture is constituted by epoxy resin and a catalyst, which slows the mixture. The influence in tensile and shear properties of the further addition of additives to the two-part component will be analysed. Furthermore, the value of the critical energy release rate in mode I will be studied by varying the molecular weight or viscosity of the SPUR in low, intermediate and high viscosity configurations.

2 Materials

A two-component formulation (SPUR plus epoxy resin) adhesive was the main target of the initial mechanical characterization carried out in this work. In a second stage, three additives were added to the mixture in order to analyse the effect of these materials on the tensile and shear behaviour of the adhesive. Finally, in a third scenario, three viscosity levels of SPUR served as base for the value analysis of the critical energy release rate in mode I. Three different viscosities were studied: one considered as a low molecular weight SPUR referred as "L", another one as an intermediate viscosity level "k" and one final more viscous "J", possessing a higher molecular weight. No additives were added to the mixtures for the viscosity influence in the G_{Ic} value.

- 2k SPUR
- 2k SPUR + 3 different additives
- 2k SPUR with 3 different molecular weights

3 Methodology

All tests were performed under quasi-static conditions at room temperature (20°C) in an INSTRON 3832 (Norwood, MA, USA) quasi-static machine with a load cell of 30 kN. For DIC measurements a digital camera (Canon EOS M5) was used. The lens equipped was a Canon EF-M 18-55mm F/3.5-5.6. The DIC was performed in GOM Correlate® (2019) software.

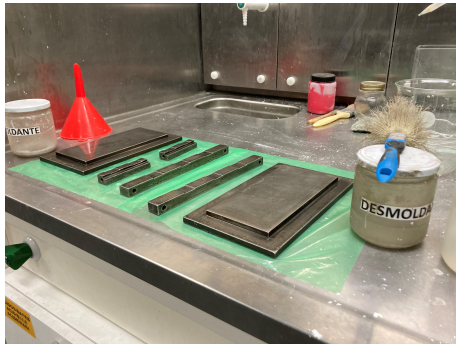
3.1 Tensile test

The bulk test provides the tensile properties of the adhesive studied, allowing both the Young's modulus and the tensile strength can be determined [9]. Bulk specimens for this procedure may be obtained by two different techniques, moulding of a plate under hydrostatic pressure which is then machined or, alternatively, the uncured adhesive is poured in a specially shaped mould. The first technique presented was chosen due to its convenience [9, 10]. All specimens were tested at a constant rate of 1 [mm/min].

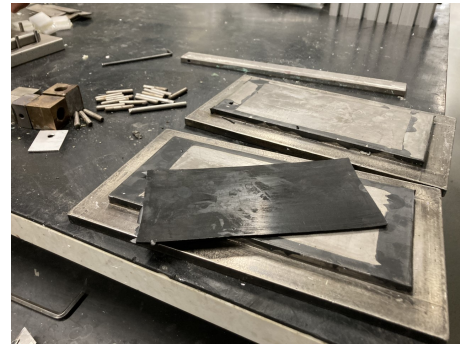
3.1.1 Bulk sheet manufacture

For polyurethane adhesives, several authors [9] have adopted the injection mould fabrication. However, due to the existence of epoxy addition, the novel adhesive studied in this work is possible to machine without having finishing rip out issues. The mould used for this purpose was the same used by [10]. The thickness of the bulk sheet is set using

a silicone rubber frame. This prevents the adhesive from flowing away from the mould cavity, while creating an hydrostatic pressure that will avoid the formation of bubbles and voids. The silicone frame with a thickness of 2 [mm] was hand cut and fitted into the mould. The experimental procedure used to produce the bulk sheet initiates with a mould degreasing process with acetone (figure 1a) followed by release agent application, using a brush. Thereafter, the mould was assembled, the silicone rubber frame was inserted and the adhesive poured. Finally, the mould was placed in a hot press, where the pressure was set to 30 [bar] and the temperature to 50°C for 24 hours, following the curing condition recommended by the adhesive formulator.



(a) Mould coated with release agent



(b) Extracted bulk sheet

Figure 1: Detail procedures during the bulk specimen fabrication

The pressure applied will guarantee the absence of air bubbles and a good surface finish. The overall dimensions of the bulk sheet were 155x70 [mm], with a thickness of 2 [mm]. The sheet, shown in figure 1b was longitudinally cut into three separate parts, which were then latter machined in a HAAS VF2 Mini with 3 milling axis and the rectangular smaller sheets were compiled to be cut. This process guarantees that the bulk specimen dimensions follow the French NF T 76-142 standard. To ensure stiffness during machining, small glass fibre tabs were inserted in-between the three stacked adhesive sheets.

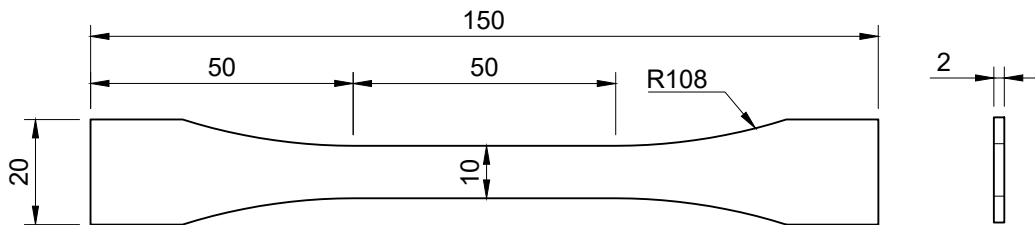


Figure 2: Dog-bone specimen dimensions [mm]

3.2 Thick adherend shear test

TAST was conducted to allow for the determination of the shear properties of the adhesive, namely its shear strength and the shear modulus. The steel substrates of each specimen are relatively thick with the aim of minimizing the peel stresses, and the overall configuration can be manufactured with ease. Single lap joint testing is often used to assess the adhesive properties under shear, but this exposes the adhesive to a complex stress state due to peel stresses, as a result of the thin substrate. TAST specimens avoid these complex stress configurations and allow to extract more accurate shear strength and shear modulus data [9,10]. All specimens were tested at a crosshead rate of 1 [mm/min].

3.2.1 Specimen manufacture

A special mould is used for manufacturing six TAST specimens, each possessing approximately an adhesive thickness of 5 [mm] and 1.5 [mm] for the shim tabs. The shims control the adhesive overlap and avoid tensile stresses when testing. The adhesive thickness was measured for each specimen pair using a caliper with a resolution of 0.05 [mm], allowing to confirm the 0.5 [mm] adhesive thickness. Figure 3 displays the dimensions of the specimens used following ISO 11003-2 standards.

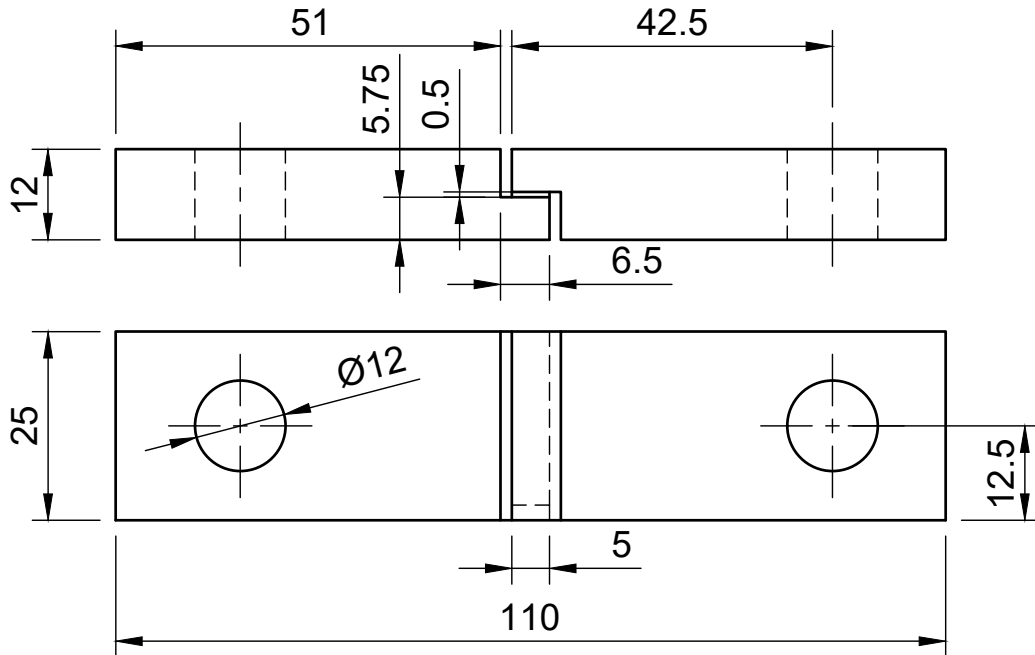


Figure 3: TAST specimen dimensions [mm]

The mould base was cleaned with acetone prior to release agent application. Hence, the bottom TAST adherends were placed accordingly, followed by the adhesive application, lower shims laid and top part assembly, as shown in figure 4c. Hereafter, 1.5 millimeter

thick shims were placed in each specimen, to prevent the adhesive to reach any unwanted surfaces, thereby guaranteeing an almost pure shear condition when testing [9]. The shims have been extracted from the cured specimens and, since they will directly make contact with the adhesive, a significant layer of release agent was applied. The top platen was placed over the assembly and the mould inserted into a thermal chamber with a weight on top, following the specified curing conditions.

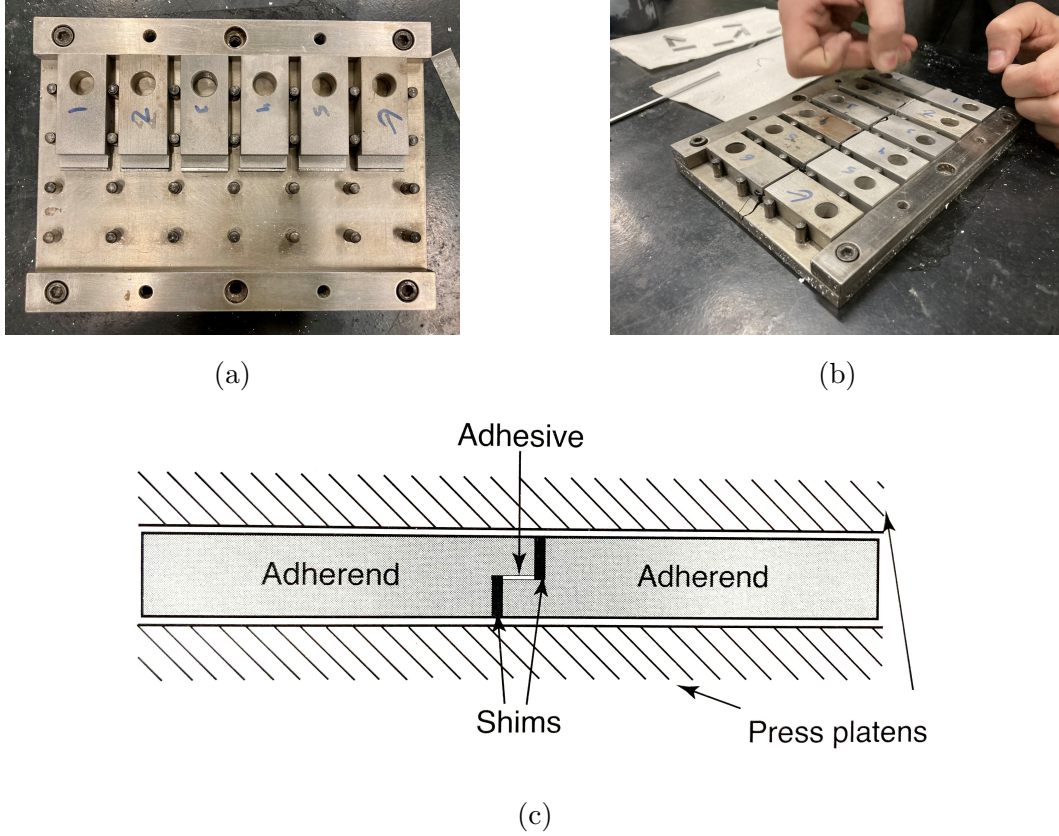


Figure 4: TAST mould preparation: (a) mould with guiding pins; (b) specimens assembly; (c) shims assemblage. Adapted from [9]

Following the conclusion of the curing process, the specimens were carefully withdrawn from the mould, the excess adhesive being removed using a sharp cutter. Finally, a fine grit of sand paper was used to smooth the side surfaces. This process was carefully performed in order not to create cracks or break the joint, which may also happen when removing the shims [9].

3.3 Double cantilever beam test

The DCB specimens were used to determine the adhesive behaviour, following a fracture mechanics based analysis. Adherends made of DIN 40 CrMnMo 8-6-4 steel have been used to estimate the critical strain energy release rate when the specimen are opened, estimating the so-called G_{Ic} or mode I fracture toughness. Extracting the load versus

displacement curve from the testing machine, it is possible to estimate the energy release rate value according to the crack size formed throughout the assay. All DCB specimens were tested at a constant rate of 0.2 [mm/min].

3.3.1 Fracture specimens fabrication and formulation

The double cantilever beam adhered used were in conformity with ISO 25217 standards, as shown in figure 5.

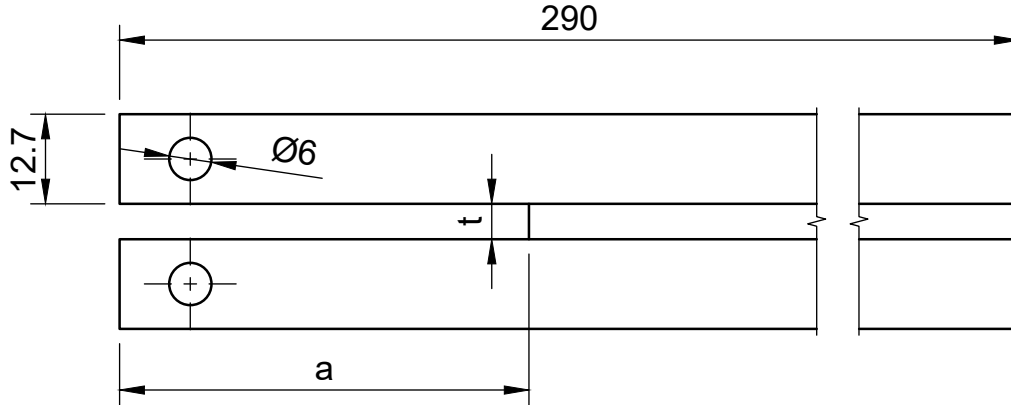


Figure 5: DCB adhesive joint dimensions [mm]

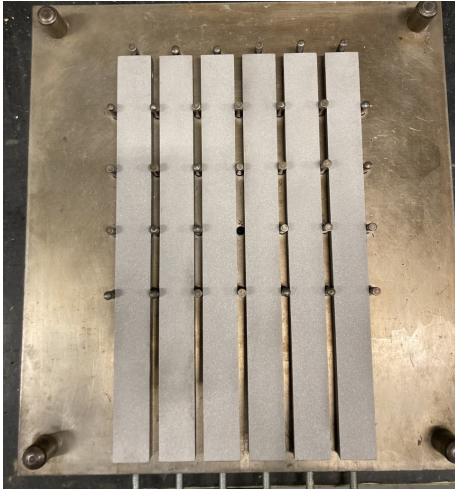
Specimens were first cleaned with acetone and sandblasted. Hereafter, the bottom substrates were inserted into a clean mould with guiding pins [9], previously coated with mould release agent (figure 6a). To guarantee an adhesive thickness of 0.20 [mm], calibrated tape was used in both specimens sides. The crack length was ensured, using a 0.10 [mm] sharp razor blade with two pieces of 0.05 [mm] calibrated tape attached on both sides. This assembly was used to guarantee an initial crack a_0 of about 45 [mm]. At the end of the specimens, a piece of 0.20 [mm] thick tape was placed. These two components were cleaned and coated with release agent film, to facilitate its removal after the curing process. The adhesive was hereafter applied in both the bottom (figure 6b) and top substrates, which were assembled over the top mould part. The mould was placed into a thermal chamber, loaded with weights to prevent voids and ensure that the curing specifications are met.

The critical energy release rate in mode I G_{Ic} was determined using the Compliance-Based Beam Method (CBBM) [11], a methodology that bases its formulation on an equivalent crack length concept which directly depends on the specimens compliance throughout the test. It is then possible to compute the R-curve based only on the P- δ data provided by the testing machine, without the need for instantaneous crack length recording, which is complex to accurately perform. Equation 1 shows the assessment of G_{Ic} .

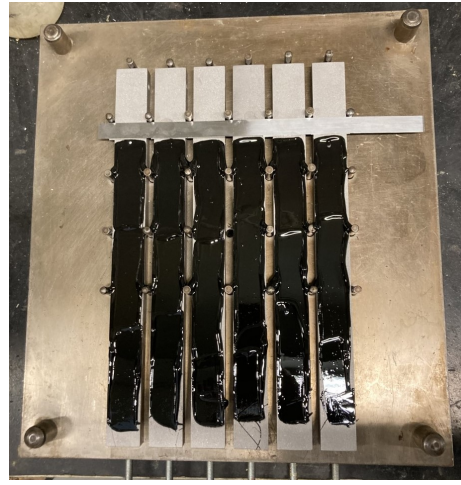
$$G_{I_c} = \frac{6P^2}{B^2t} \left(\frac{2a_{eq}^2}{t^2 E_f} + \frac{1}{5G} \right) \quad (1)$$

The geometrical parameters B and t represent the adherend width and height respectively, whereas E_f is the corrected flexure modulus, P the instantaneous loading and a_{eq} is the equivalent crack length, which assesses the real crack tip a . A crack correction factor Δ for the tip deflection and rotation phenomena as well as Δa_{FPZ} , another correction, take the fracture process zone effect into consideration [11, 12].

$$a_{eq} = a + \Delta + \Delta a_{FPZ} \quad (2)$$



(a) DCB mould



(b) Adhesive application with calibrated tape

Figure 6: Preparation of DCB Specimens

3.4 Mixed-mode fracture characterization

The End-Notched Flexure (ENF) test is usually performed [2, 9] to determine the fracture toughness in mode II. However for flexible adhesives like silicone, given the large FPZ, the crack does not propagate at all, or it nucleates after the substrates exceed the elastic regime. ENF tests were performed, but the crack only begun to propagate following plastic yielding of the steel substrates, which resulted in an excessively high G_{II_c} value. Given the inability to test this adhesive under pure Mode II conditions, a mixed-mode strategy was chosen to estimate the critical energy release rate by correlating the adhesive fracture envelope.

The apparatus for mixed-mode, developed by [13], allows to determine the $P - \delta$ curve for both modes, relying only on the load versus displacement curve provided by the testing machine and the data from two LVDT's, each one measuring the displacement of each substrate 7. The apparatus is flexible in terms of mixed-mode ratios it can test, that is,

it can easily vary the weight of each mode I or mode II preferred in the test. An angle ϕ is defined in figure 8 to take into consideration the amount of each mode loading, opening and in-plane shear, wanted.



Figure 7: Apparatus for mixed-mode [13]

$$\phi = \arctan \left(\sqrt{\frac{G_{II}}{G_I}} \right) \begin{cases} \phi = 0^\circ & , \text{ pure mode I} \\ 0^\circ < \phi < 90^\circ & , \text{ mixed mode(3)} \\ \phi = 90^\circ & , \text{ pure mode II} \end{cases}$$

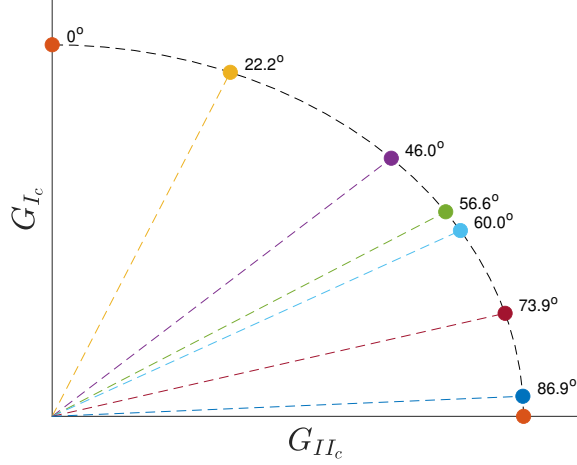


Figure 8: Example of mixed-mode testing angle phase of the apparatus

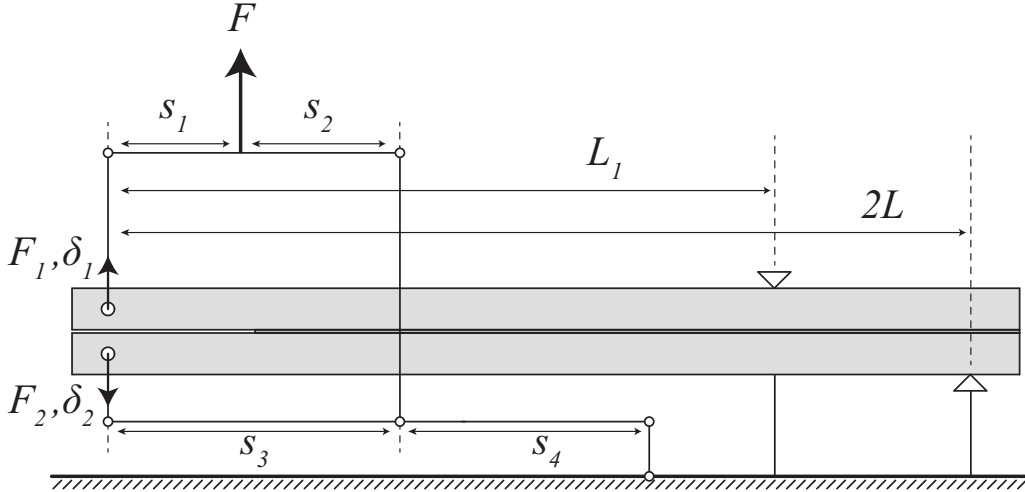


Figure 9: Representation of the specimen in the apparatus for mixed-mode [13]

The procedure used with this apparatus considers the specimens compliance, extension and loading to further estimate an equivalent crack length. This overcomes the difficulty of capturing the instantaneous crack size. In fact, in DIC correlation following a direct methodology, the FPZ (Fracture Process Zone) is not considered during calculations [14]. Thus, this methodology pursues an indirect formulation, replacing conventional crack tip measurements with equivalent crack lengths provided by the compliance's of the DCB beams throughout the test, taking the FPZ also into consideration. Figure 9 displays the forces to which each DCB specimen is subjected. The device allows for the adjustment of six geometric parameters (s_1 , s_2 , s_3 , s_4 , L_1 , $2L$) in order to accommodate different phase angle values. The estimation of the fracture energy is performed by joining the pure mode I (DCB test) and pure mode II loading cases (ENF test), combining a CBBM

formulation [13]. The compliance of the specimen beams can be written for mode I and II, respectively, as follows:

$$C_I = \frac{8a^3}{EBh^3} + \frac{12a}{5BhG_{13}} \quad (4)$$

$$C_{II} = \frac{3a^3 + 2LL_1^2}{2EBh^3} + \frac{6LL_1}{5BhG_{13}(2L - L_1)} \quad (5)$$

where B and h are geometric parameters, corresponding to the beam width and thickness; E and G_{13} are the Young's modulus and flexural modulus of each substrates. The crack length is represented by a and the geometric parameters L_1 and $2L$ are point supporters of the specimen displayed in 9. The equivalent crack length can be calculated following CBBM for mode I [11] and mode II [15].

Table 1 agglomerates the geometrical parameters values for the three different configurations tested [13]. The quasi-static test was performed at a rate of 0.2 [mm/min].

Table 1: Geometrical parameter values for each phase angle tested

Φ ($^\circ$)	s_1 [mm]	s_2 [mm]	s_3 [mm]	s_4 [mm]	L_1 [mm]	$2L$ [mm]
46.0	40	100	140	40	185	230
60.0	60	60	120	40	165	220

4 Results

This chapter presents a comprehensive analysis of the mechanical behaviour of the 2k SPUR adhesive under analysis, encompassing its complete characterization; the impact on tensile and shear properties by the introduction of three distinct additives to the adhesive mixture; the alteration of SPUR viscosity to examine its influence on the fracture toughness value.

4.1 2k SPUR

4.1.1 Tensile Test

The "dogbone" specimens were acetone cleaned and sprayed with a matte white paint prior to speckling with a dark matte paint. Two marks where drawn, distanced 30 [mm] from each other. Then, six specimens where positioned in pinned fixtures and finally tested. The strains were computed using DIC and the stress-strain curve was obtained. Figure 10 illustrates the pictures took in the DIC software. The stress strain curve is

illustrated in 11 for the six specimen tests. Table 2 agglomerates the average values as well as the standard deviation for the Young's modulus, tensile strain to failure.

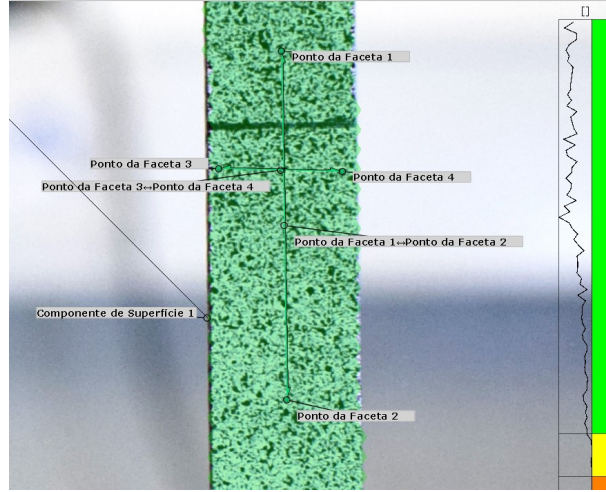


Figure 10: Speckle quality in GOM Correlate® software

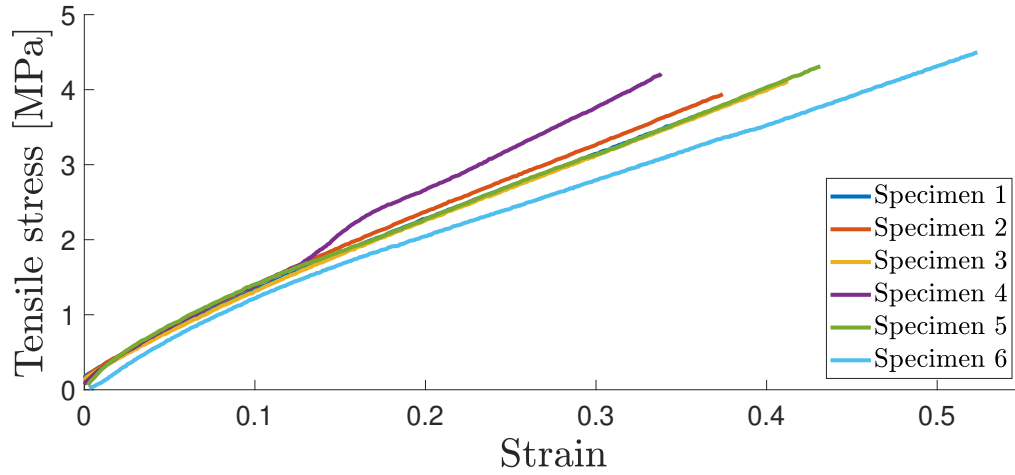


Figure 11: Tensile stress-strain curve

Table 2: Elastic data properties

Young's modulus, E	Tensile strength, σ_f	Tensile strain, ε_f
[MPa]	[MPa]	[%]
10.17 ± 0.96	4.16 ± 0.21	0.411 ± 0.058

From these results it was possible to estimate the Poisson's ratio ν considering a DIC analysis, as illustrated in figure 10, and is given by

$$\nu = -\frac{\varepsilon_x}{\varepsilon_y} \quad (6)$$

where a value of $\nu = 0.418 \pm 0.009$ was found.

4.1.2 Thick adherend shear test

The thick adherend shear test strain field was also captured following the same DIC methodology. Thus, the specimens were previously acetone cleaned prior to the application of white matte paint, followed by the application of black speckling. This shows an advantage over extensometer-based displacement measurements, where both adhesive and substrates displacements are measured [10]. DIC only allows for the capture of the adhesive displacement field in one of the specimens front. All specimens showed similar failure mode, illustrated in figure 12. The stress-strain curve is displayed in figure 13 where the shear modulus was calculated using the curve slope in the elastic regime, as well as the strength data. These results are summarized in table 3.



Figure 12: Failure mode for two TAST specimens

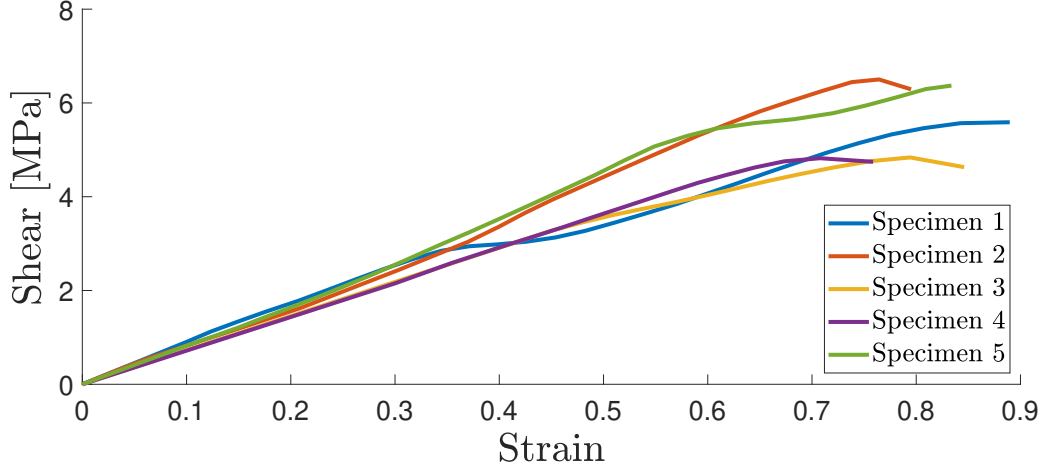


Figure 13: Stress-strain curve for the six TAST specimens

Table 3: Shear data properties

Shear modulus, G	Shear strength, τ_f	Shear strain, γ_f
[MPa]	[MPa]	[%]
7.07 ± 1.53	5.47 ± 0.74	0.825 ± 0.045

Considering the Poisson’s ratio relation between the Young’s and shear modulus in isotropic materials,

$$E = 2G(1 + \nu) \quad (7)$$

the shear modulus can be determined from the DIC analysis performed in the tensile test, which outputs a value of $G = 3.59$ [MPa]. This value does not correspond to the value measured in DIC analysis for the TAST. Should the Poisson’s ratio be calculated under the experimentally determined Young’s and shear modulus, it would lead to a value of $\nu = -0.281$, which is unrealistic [16]. This was captured both for the usage of DIC correlation together with an extensometer in the other specimen face. In fact, the thick adherend shear tests can rotate sideways when using ductile adhesives [9], and since there are layer constraints, it is hard to test the material under pure shear loading. Hence, it is believed that the Poisson’s ratio can be more accurately determined from the DIC carried out in the tensile tests. Hence, the TAST would be used solely to provide the maximum shear strength in a more accurate manner.

4.1.3 DCB test

Usually, before fracture testing is carried out, a pre-crack must be propagated in each DCB specimens. This is performed by mounting the specimen in the quasi-static machine and applying an opening load at the same test rate. When the P - δ curve reaches a peak, the crack has theoretically begun to propagate, and the test is stopped. Notwithstanding, provided the material ductility, adhesives with an elastomeric behaviour possess a considerably large FPZ, and such pre-cracking procedure could induce multiple cracks in the opening area, originating multiple energy dissipation mechanisms [17] or damaging the initial FPZ. Given the unknown values of the critical energy release rate G_{Ic} and to compare this phenomena in the novel adhesive, pre-cracking was performed in three of the six specimens, where the other three remain virgin to such procedure. Figure 14 shows the typical DCB fracture surface for the quasi-static rate. The P - δ curves are displayed in figure 15, which differentiates the three specimens with and without the pre-cracking procedure. Lastly, the critical energy release rate in mode I was determined using CBBM [11], where the same comparison took place (figure 16). A value for $G_{Ic} = 1.191 \pm 0.055$ was found, with no difference whether or not the pre-cracking stage is performed.

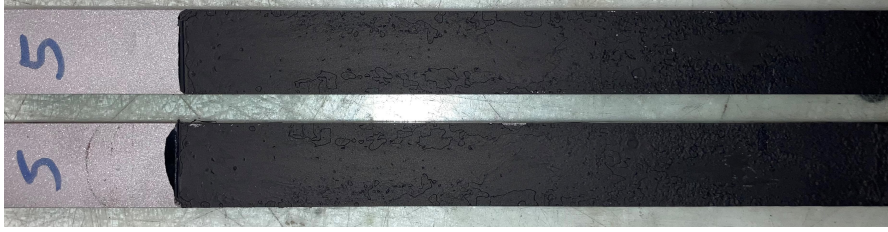


Figure 14: Typical fracture failure mode

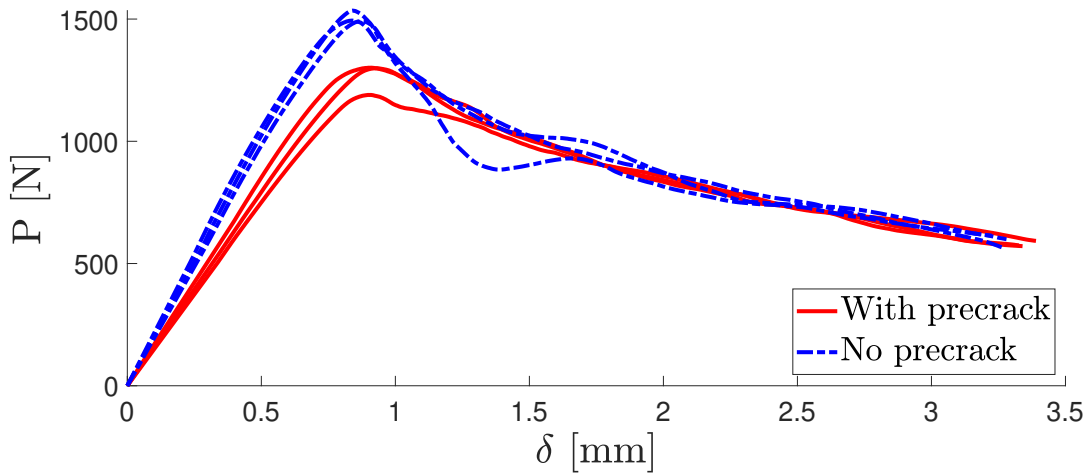


Figure 15: P - δ curve

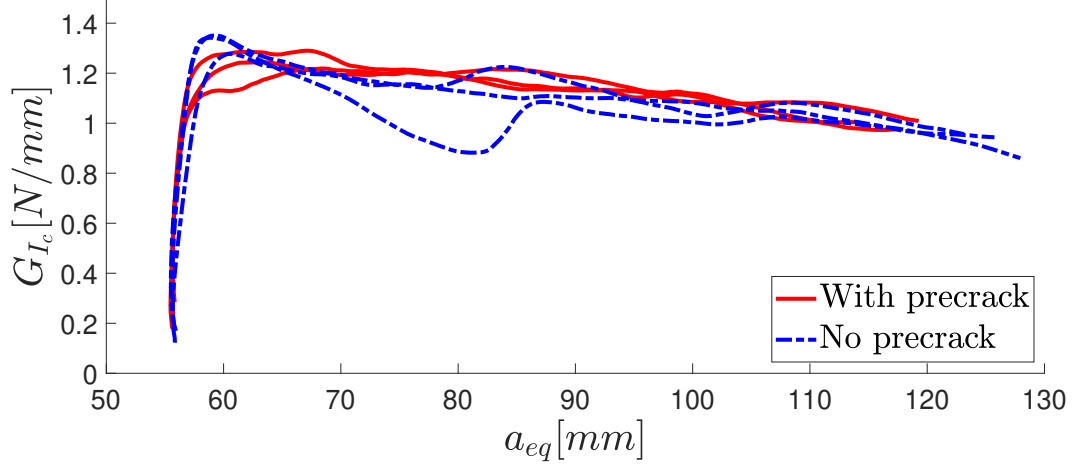


Figure 16: R-curve

4.1.4 Mixed-mode test

The DCB specimens were slightly opened in order to take out both the blade and calibrated tape, without compromising the initial crack and FPZ. The mixed-mode apparatus [13] was placed in the quasi-static machine and assembled according to table 1. The P - δ curves for the three best specimens were then retrieved from the two analysed angle values: those curves are displayed in figure 17.

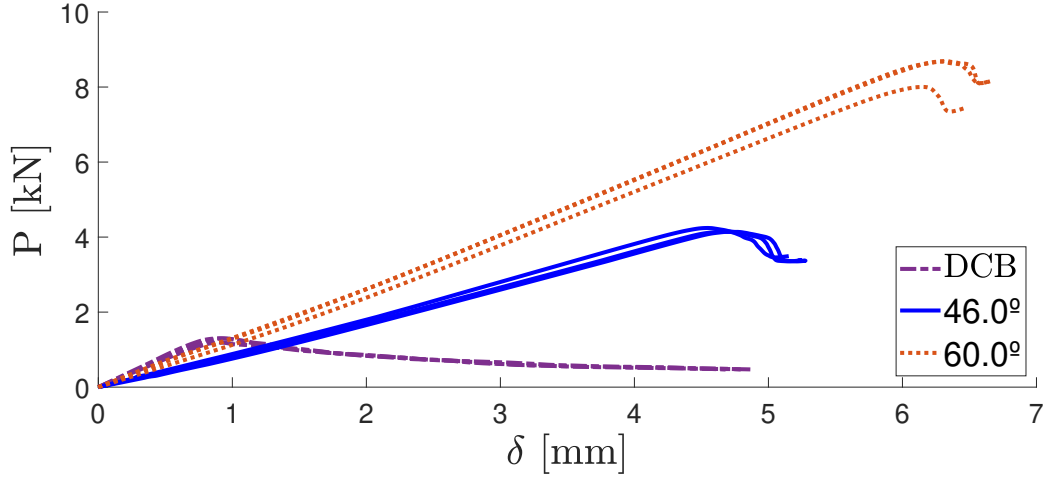


Figure 17: P - δ curves for mixed-mode at 46.0° , 60.0° and 0° (DCB)

Table 4 summarizes the values of the critical energy release rate for mode I and II for the two studied angles. Figure 18 displays the extrapolated fracture envelope of the two-component adhesive, where it is possible to estimate the value of the critical energy release rate in mode II, G_{IIc} , to be close to 4 [N/mm].

Table 4: Critical energy release rate values for mixed-mode

	46.0°	60.0°
G_{Ic}	1.50 ± 0.34	1.00 ± 0.08
G_{IIc}	1.04 ± 0.29	2.83 ± 0.49

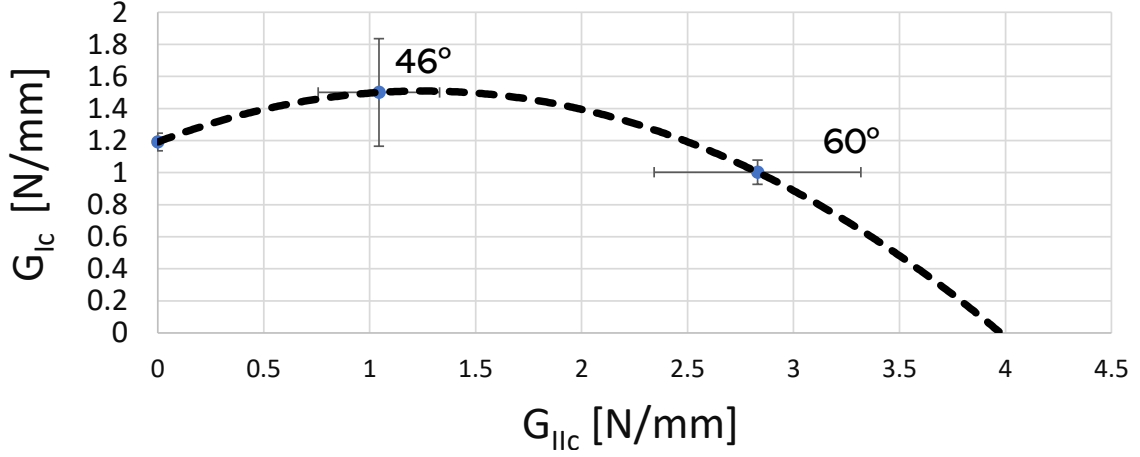


Figure 18: 2k SPUR fracture envelope

Table 5: 2k SPUR mechanical properties

Property	Units	2k SPUR
Young's modulus, E	[MPa]	10.17 ± 0.96
Poisson's ratio, ν	[-]	0.418 ± 0.009
Tensile failure strength, σ_f	[MPa]	4.16 ± 0.21
Tensile failure strain, ε_f	[%]	41.1 ± 5.8
Shear modulus, G	[MPa]	7.07 ± 1.53
Shear failure strength, τ_f	[MPa]	5.47 ± 0.74
Shear failure strain, γ_f	[%]	84.7 ± 11.5
Toughness in mode I, G_{Ic}	[N/mm]	1.191 ± 0.055
Toughness in mode II, G_{IIc}	[N/mm]	4

4.2 Influence in the use of additives

Three types of adherence promoting additives were mixed with the 2k formulation. Bulk and TAST procedures were carried out to determine and further compare both tensile and shear properties to the original unmodified silylated polyurethane resin. Table 6 summarizes the obtained tensile properties : Young's modulus, maximum tensile strength and maximum strain to failure.

Table 6: Elastic properties with the three different additives

	Young's modulus, E	Tensile strength, σ_f	Tensile strain, ε_f
	[MPa]	[MPa]	[%]
Mixture 1	10.52 ± 0.50	3.33 ± 0.79	0.357 ± 0.090
Mixture 2	10.28 ± 0.55	1.79 ± 0.16	0.175 ± 0.018
Mixture 3	12.17 ± 0.35	2.30 ± 0.19	0.189 ± 0.014

The TAST results for the different additives configurations are displayed in table 7. Both tensile and shear properties are compared in figure 19 with the normalized values of the 2k SPUR adhesive.

Table 7: Shear properties with the three different additives

	Shear modulus, G	Shear strength, τ_f	Shear strain, γ_f
	[MPa]	[MPa]	[%]
Mixture 1	3.47 ± 0.50	4.17 ± 0.44	1.610 ± 0.143
Mixture 2	2.57 ± 0.29	2.39 ± 0.16	1.210 ± 0.132
Mixture 3	2.71 ± 0.36	3.41 ± 0.25	1.457 ± 0.107

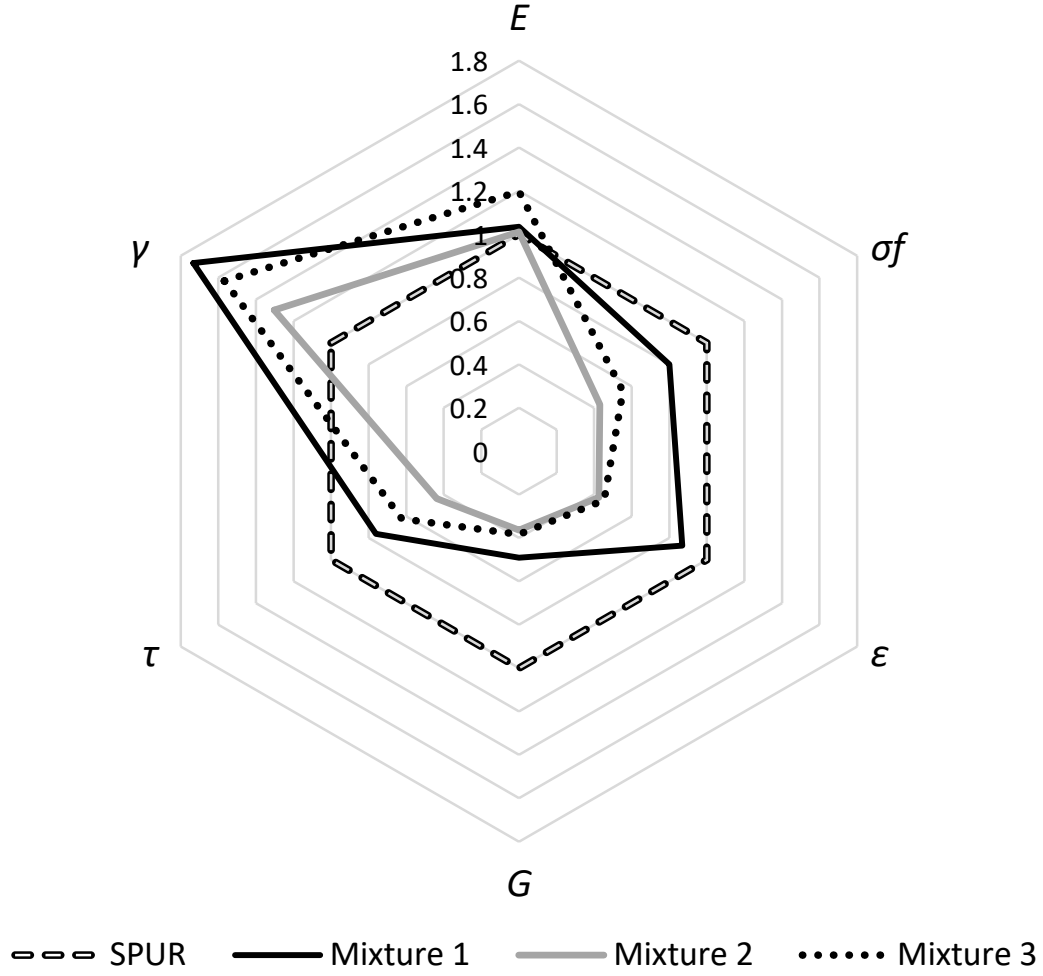


Figure 19: Comparison between tensile and shear properties of the normalized added adhesive properties to the 2k SPUR

Table 8 agglomerates the shear modulus values estimation, taking the Poisson's ratio determined in the first SPUR bulk tests.

Table 8: Shear modulus estimation for all mixtures

	Mixture 1	Mixture 2	Mixture 3
Shear modulus, G [MPa]	3.55	3.62	4.29

4.3 Influence of SPUR viscosity in G_{I_c} value

Considering the initial two-component formulation without the additives, the SPUR may be chemically rearranged to be more or less viscous. The viscosity or different molecular weight of the SPUR lead to a different critical energy release rate value in mode I. For that, three DCB tests were performed for three different SPUR viscosities: low, intermediate and high. The R-curves were computed using the CBBM [11] formulation. All considered DCB specimens had cohesive failure, similar to those the previously tested in the first 2k SPUR batch. The critical energy release rate in mode I values are agglomerated in table 9 and the results compared in figure 20.

Table 9: SPUR viscosity influence in G_{I_c} values

	Low viscosity	Intermediate viscosity	High viscosity
Designation	L	K	J
G_{I_c} [N/mm]	1.96 ± 0.18	2.49 ± 0.07	1.53 ± 0.08

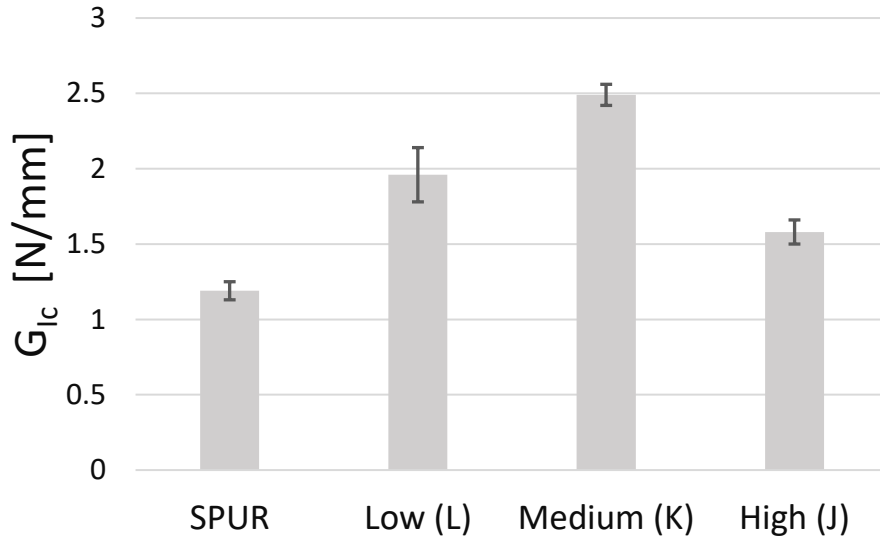


Figure 20: Influence of SPUR viscosity level in the G_{I_c} value

5 SEM analysis

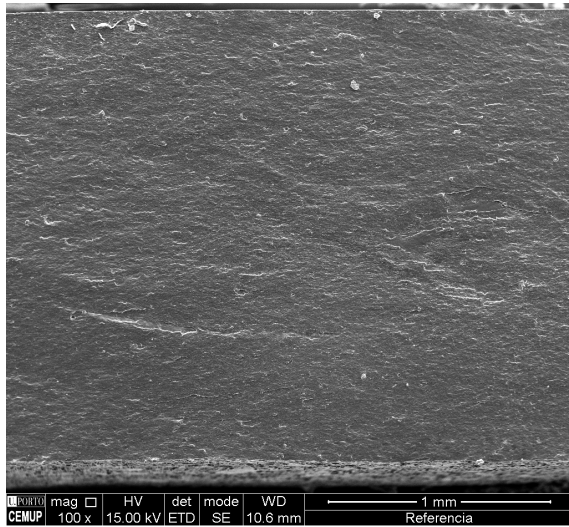
The two-component silylated polyurethane resin is a combination of cured SPUR containing a filler and hardened epoxy, where there is a coupling between the hardened epoxy and SPUR via aminosilane. In order to understand the lap shear strength difference between the SPUR and the 2k formulation with epoxy resin, a scanning electron microscope test was performed to two small samples with a smooth fracture cross section in tension of 10x2 [mm]. The aim was to investigate the presence and nature of precipitates and analyse both surfaces, as well as to perform an energy-dispersive X-ray spectroscopy (EDS) in different areas. Both specimens were cleaned with isopropyl alcohol (IPA), fixed in a plastic clip and placed horizontally submerged in IPA in an ultrasound machine to remove surface contaminants.

A High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis, specifically the FEI Quanta 400 FEG ESEM / EDAX Genesis X4M, was employed for the SEM / EDS examination. To ensure proper sample preparation, a thin film of Au/Pd was applied by sputtering using the SPI Module Sputter Coater equipment. The samples were covered for 100 seconds with a 15 [mA] current. Each image is accompanied by a databar that displays the essential analysis conditions.

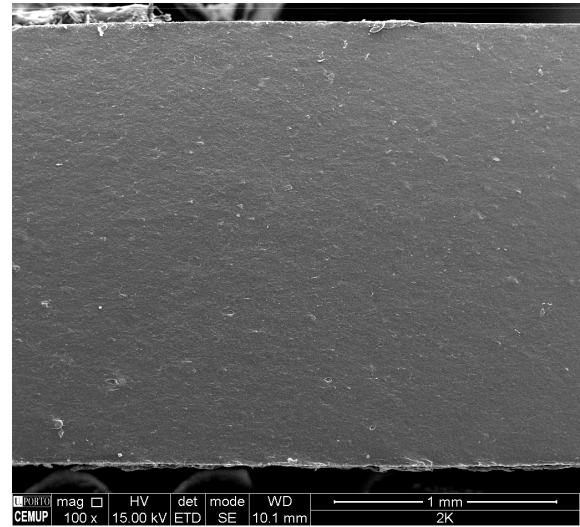
Figure 21 display the secondary field of both the reference SPUR and the two-component adhesive in X100 and X20 000 zoom magnitude. The two surfaces have an identical relief and possess very similar structures, composed of a matrix with precipitates or evenly spaced small grains, thus having an homogenised dispersion in both mixtures. It can be noted that there is an impossibility to distinguish whether the silicon (Si) was impregnated, embedded in the matrix or if it takes the form of a precipitate.

The global EDS analysis displayed in figure 22 shows normalized quantities of the chemical constituents. Since both silylated polyurethane resin and epoxy resin have constituent groups with agglomerate carbon and since it is not possible to capture any elements with an atomic number below that of carbon, it is difficult to spot other chemical continents. Notwithstanding, oxygen and silicon are present in both formulations. In fact, both spectra are similar, not being possible to ascertain any particular information from this global EDS analysis.

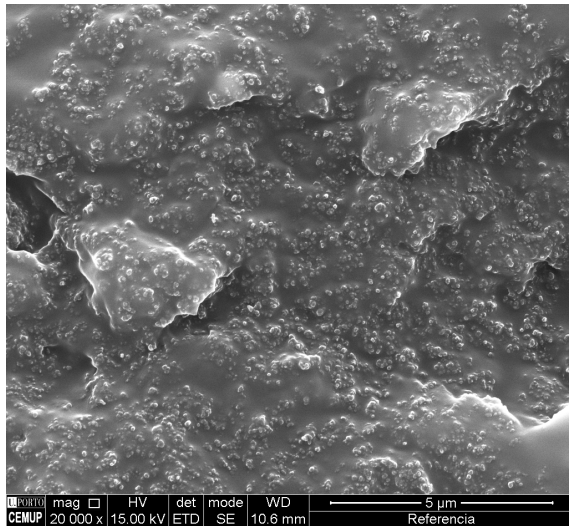
To study the spectrum of the grainy areas presented in both samples, a localized EDS was performed in the reference SPUR. One zone was located in a more uniform area, whereas the other one in an area rich in small grains. The chemical spectrum for both locations is practically the same between them and similar to the global spectres. In fact, the amount of silicon (Si) present in both locations is similar, not being possible to conclude if the grainy regions or precipitates are rich in silicon. Nevertheless, since there is no variation in the spectrum, there are no variations along the thickness, enhancing the



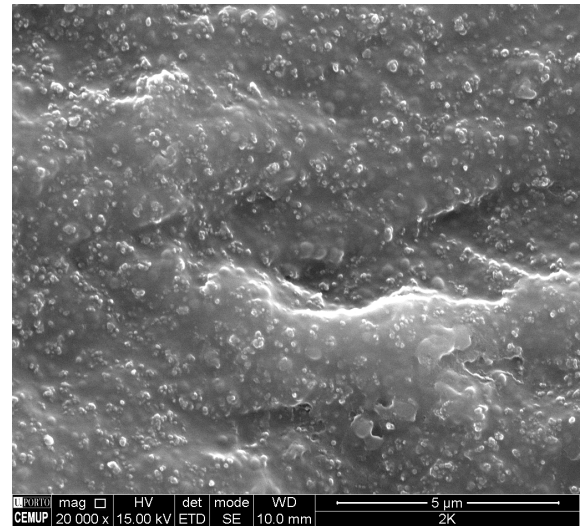
(a)



(b)



(c)



(d)

Figure 21: Surface relief of: (a) SPUR and (b) 2k mixture in secondary field with a zoom of 100X; Surface relief of (c) SPUR and (d) 2k mixture in secondary field with a zoom of 20 000X

good homogenisation of the grainy area throughout the matrix.

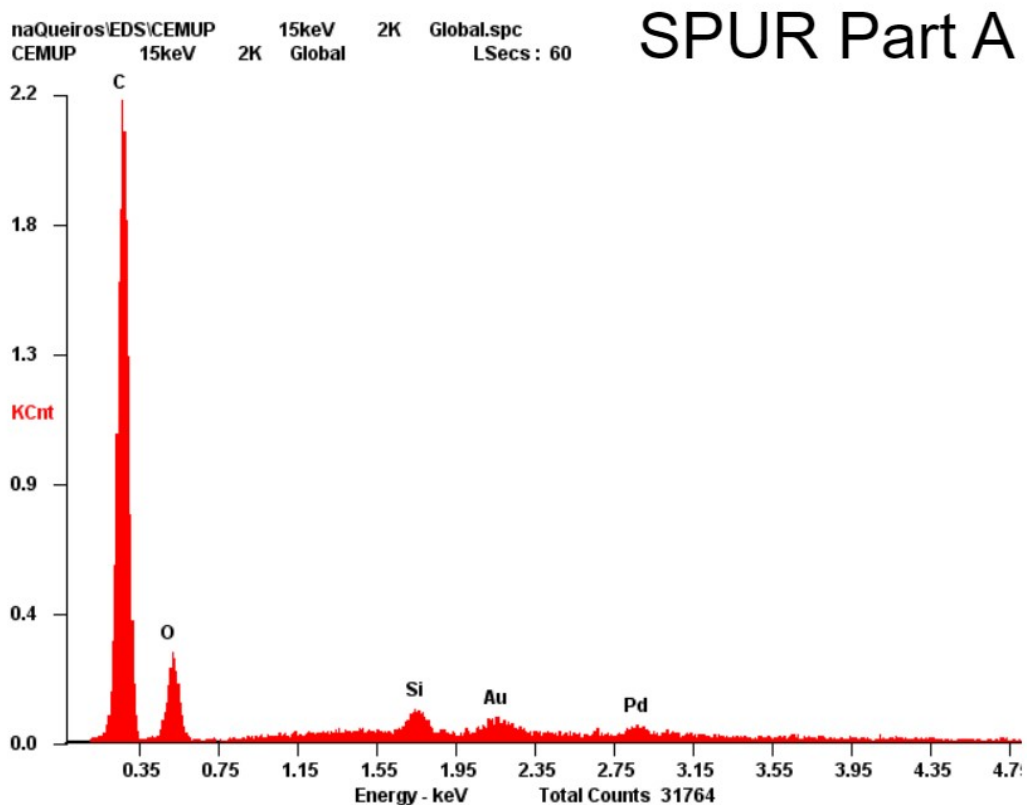
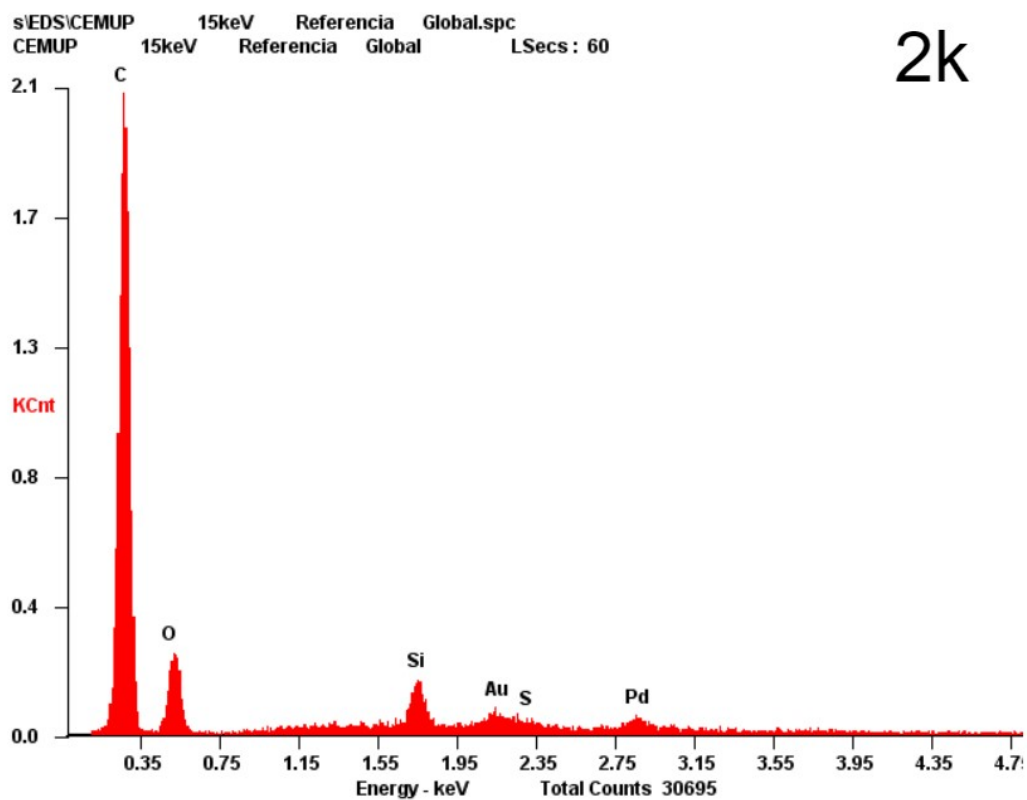


Figure 22: Global chemical spectrum of (a) SPUR (Part A) and (B) 2k adhesive (Part A+B)

6 Conclusions

In this paper, a novel two-component silylated polyurethane resin with epoxy resin was mechanically characterized at room temperature under quasi-static conditions, followed by an analysis of the effect of three different additives on the tensile and shear properties and the G_{Ic} value of the adhesive.

- Tensile bulk tests took place in order to determine the 2k SPUR tensile properties. A Young's modulus of 10.17 [MPa] and a tensile strength of 4.16 [MPa] were determined, with a failure tensile strain of 41%. The Poisson's ratio was determined using DIC analysis and was found to be $\nu = 0.418$.
- The TAST was performed to analyse the adhesive shear properties. The 2k formulation showed a shear vs tensile strength ratio of 1.4. The estimated shear modulus was 3.59 [MPa] and γ_f was 85%.
- Fracture tests were performed and the fracture envelope for the 2k SPUR generated. Tests in pure Mode I and mixed-mode were conducted, with the mode I fracture toughness, G_{IIc} found to be 1.19 [N/mm] and in mode II estimated to be 4 [N/mm], around 3.3 higher than G_{Ic} , a common value for polyurethane adhesives.

Tensile and shear tests were conducted to analyse the behaviour of the adhesive when modified with three different additives. The general tensile properties brought by the use of additives were inferior in strength and elongation, nonetheless the additive 3 showed an improved E value. Interestingly, the shear properties of the adhesive with the additives were lower, but the failure strain to failure increase from 70% of the original value up to doubling it.

To complement the study, the analysis of the fracture toughness value in mode I was conducted to three different SPUR samples with three different levels of molecular weight: low, intermediate and high. The medium viscosity SPUR had the highest value, with double of the value showed by the first batch of the 2k adhesive.

SEM and EDS analysis were performed in order to understand the lap shear strength increased with the addition of the epoxy resin as a second component. The results showed a very similar homogeneous grainy surface with identical chemical spectrum without variation with the thickness.

The data collection from other semi-structural polyurethanes show the typically low properties of the silyl-terminate polyurethanes family. In terms of critical release rate values, the 2k SPUR can compete with other polyurethanes [18], however tensile and shear properties were found to be relatively low [19,20]. Nonetheless, they are still higher than those reported in the literature for other silicone-based adhesives [18,20].

Acknowledgments

Authors have the pleasure to acknowledge the adhesive provided company as well as to INEGI, the Portuguese Foundation for Science and Technology (FCT) and CEMUP.

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Appendix B

Paper B

Development and study of a novel silane based polyurethane hybrid flexible adhesive - Part 2: Joint testing and numerical modelling

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Abstract: The need for more sustainable adhesive formulations has opened the possibility of using silane-based adhesives in the automotive industry. In this work, a novel hybrid two-component silylated polyurethane resin (SPUR) adhesive was tested in single lap joints, seeking to assess joint behaviour at room temperature under quasi-static conditions for two different substrate materials: aluminium and carbon fibre reinforced polymer. The effect of two different overlap lengths was also considered. A numerical model was created, using a cohesive zone modelling in a finite element software, to reproduce the mechanical behaviour of the joint. A triangular shaped CZM law was chosen as the adhesive behaviour is highly elastic and absent of yielding phenomena. The experimental results served as a base for the numerical validation, allowing accurate CZM parameters to be successfully determined.

Keywords: SPUR, Silylated polyurethane, CZM, Flexible adhesive

1 Introduction

The advent of adhesive technology brought significant transformations in the realm of mechanical joining. In particular, the traditional practices of riveting and fastening have been partially replaced by adhesive bonding or integrated into a hybrid joints, which combine both approaches. Flexible adhesives have emerged as vital components within the automotive industry, fulfilling various roles, acting as sealants, structural adhesives and even as semi-structural elements. These advancements align with the overarching goal of promoting lightweight designs and embracing a more environmentally conscious philosophy [1, 2]. Polyurethane adhesives are renowned for their mechanical flexibility, making them particularly suitable for bonding composite substrates. This leads to a reduced risk of delamination, a common failure mode in composite bonding found, for instance, when using brittle and stiff adhesives such as epoxies [1, 3]. This adhesive family exhibits a lower

elastic modulus and comparatively lower tensile strength, however a significantly greater elongation capacity [4], generating lower transverse strains in composite adherends. Furthermore, these levels of elastic deformation positively contribute to achieving effective gasketing and sealing properties, as well as exceptional damping and impact and fatigue resistance [5, 6].

Silylated polyurethane resins (SPUR) are a particular group of the polyurethane family, which agglomerates silyl terms to the adhesive configuration [7]. The aim of introducing silane is to adjust molecular weight (viscosity), inducing special capping agents [8] and obtain a free isocyanate formulation [9], which lowers the toxicity level. Besides having also the capability of cure in the presence of moisture, silyl-terminated polymers are widely recognized for their enhanced stability, which results in improved adhesion and satisfactory storage stability [7].

To support a wider industrial use of these adhesives, it is important to develop numerical models of the adhesive behaviour, properly validated through experimental tests. Thus, having established an effective the material model, the same adhesive can be modelled under different configuration, providing accurate failure prediction. Multiple methods of adhesive failure prediction have been analytically developed [1]. Currently, with the appearance of the finite element (FE) formulation and the cohesive zone method (CZM) as an add-in, this methodology has become the benchmark for the simulation of damage growth [10], based on a traction separation laws. This methodology considers the stress/strain behaviour as well as fracture mechanics for failure prediction. It is deemed superior to more mature formulations like the Virtual Crack Closure Technique (VCCT) or the Linear Elastic Fracture Mechanics (LEFM), which possess more limitations [11].

Cohesive zone modelling is suitable for adhesive joints since it can predict damage and failure with good accuracy in a predefined region. It reproduces an elastic loading until a peak load is reached, followed by a damage phenomena through crack initiation and propagation: the damaging technique preferred depends on the material behaviour or interface [10, 12]. The predefined law shape takes into consideration the adhesive tensile, shear and fracture toughness properties, establishing a failure and subsequently damage path [10]. Campilho et al. [10] compared the behaviour of different cohesive shape laws for brittle and ductile adhesives for different overlap length single lap joints tested under tension. The triangular shape law is generally suitable for brittle and stiff adhesives, since it converges rapidly and does not account for large yielding. Furthermore, it was concluded that the law shape effect can be negligible in these adhesives. On the other hand, for ductile adhesives, the trapezoidal law is generally more accurate than the triangular and exponential shapes. Pisavadia et al. [13] made use of a trapezoidal (trilinear) CZM shape, found to be better suitable for numerical validation of a polyurethane adhesive. The property identification methodology was previously performed in order to withdraw the mechanical adhesive properties to then establish a relation between the real and cohesive

values. For the triangular shape law, the elastic failure strength σ_f and shear failure strength τ_s correspond to the tension and shear cohesive strengths, t_n^0 and t_s^0 respectively. The shape of the law (and its area) is the result of cohesive parameters G_n^c and G_s^c , which are complemented by the critical energy release rates in pure opening (mode I) and in-plane shear (mode II).

In this work, composite and aluminium single lap joints were tested with 25 [mm] and 50 [mm] of adhesive overlap length, under quasi-static conditions. CZM elements in ABAQUS® FE software (Dassault Systèmes, Suresnes, France) were used, following a triangular shape cohesive law to simulate the adhesive. The numerical model reproduced geometries similar to those used in the mechanical tests already performed, allowing to directly compare experimental and numerical results. Although past works have used trilinear CZM shaped laws in polyurethane adhesives [1,5,10,12,13], since the experimental results of this work showed no yielding point for both tensile and shear tests, a simpler triangular shaped cohesive law was found to be more effective.

2 Materials

A two-component SPUR adhesive was mechanically characterized in a previous work under four different tests: bulk, following the NF T 76-142 French standard, thick adherend shear test (TAST) according to the ISO 11003-2 standard, double cantilever beam and a mixed-mode configuration [14] all referenced in. Table 1 agglomerates the mechanical properties for the 2k adhesive. The critical energy release rate in mode II was estimated from the mixed-mode test. All fracture characterization tests employed the compliance based beam method (CBBM) [14–17]. Poisson’s ratio was determined by DIC in the tensile bulk specimens, where a shear modulus value of 3.59 [MPa] was found, considering the elastic and shear modulus relation for isotropic materials [18]. The shear modulus presented in table 1 corresponds to value obtained from the TAST specimens, accounting for the different strain rate and different boundary conditions of both tensile and TAST experiments.

Table 1: 2k SPUR mechanical properties

Property	Units	2k SPUR
Young’s modulus, E	[MPa]	10.17 ± 0.96
Poisson’s ratio, ν	[-]	0.418 ± 0.009
Tensile failure strength, σ_f	[MPa]	4.16 ± 0.21
Tensile failure strain, ε_f	[%]	41.1 ± 5.8
Shear modulus, G	[MPa]	7.07 ± 1.53
Shear failure strength, τ_f	[MPa]	5.47 ± 0.74
Shear failure strain, γ_f	[%]	84.7 ± 11.5
Toughness in mode I, G_{Ic}	[N/mm]	1.191 ± 0.055
Toughness in mode II, G_{IIc}	[N/mm]	4

3 Experimental procedures

3.1 Aluminium SLJ

Anodized AL6060-T6 aluminium alloy substrates were used in this work to create SLJs. The adherend elastic properties of this material are displayed in table 2 and the general geometry of the aluminum joints manufactured is illustrated in figure 1, where the adhesive layer was set to be 0.5 [mm] thick and with an overlap length of 25 and 50 [mm].

Table 2: Mechanical properties for the anodized aluminium substrates

Elastic modulus, E	Poisson’s ratio, ν
[GPa]	[-]
69	0.33

SLJs were mounted in a steel mould [19], previously cleaned and coated with release agent film. To control the specimen geometry, 3D printed polymeric spacers were used, coated with release agent film to facilitate removal after adhesive curing. Since the aluminium substrates were already anodized, the surface was simply degreased with isopropyl alcohol (IPA) before adhesive application took place. Figure 1 shows a manufacturing stage of the aluminium substrate single lap joint with 25 [mm] overlap.

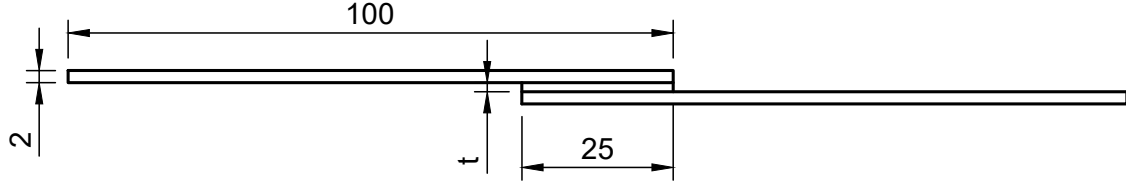


Figure 1: Aluminium SLJ geometry for 25 [mm] of overlap length

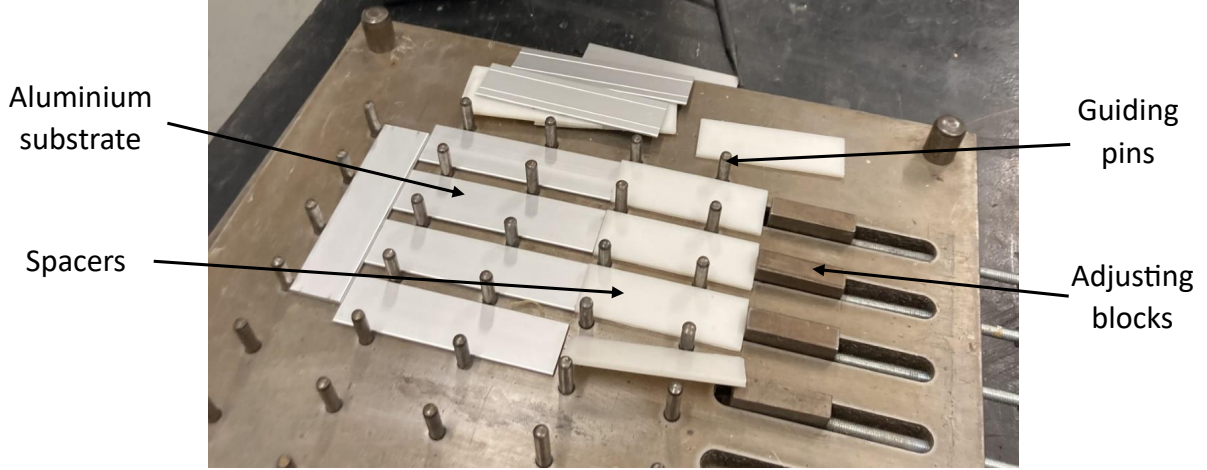


Figure 2: Aluminium SLJ geometry for 25 [mm] of overlap length

After the mould assembly, the set was inserted into a thermal chamber with weights on top and maintained at the necessary curing temperature. Hereafter, the mould was opened, the joints retrieved and the extra adhesive from the overlap area removed. Alignment tabs with 25x25 [mm] were bonded to the end of each adherend to reduce load misalignment and peel effect when testing [1].

3.2 CFRP SLJ

Unidirectional carbon fibre reinforced polymer substrates were manufactured from 14 stacked carbon/epoxy pre-preg sheets of 0.15 [mm] thickness, of the SEAL[®] Texipreg HS 160 RM type, providing a final substrate thickness of 2.1 [mm]. The mechanical properties for the composite adherends are listed in table 3 [20].

The stacked 150x300 [mm] carbon/epoxy pre-preg layers were cured in a hot press at 30 [bar] for one hour at 145°C, another hour at 140°C and then left in the press until room temperature was reached. Thereafter, the CFRP plate was cut into 100x25 [mm] substrates in a diamond disc cutting machine. The substrate surfaces were prepared with a 240-grit sand paper application, performing linear movements at a $\pm 45^\circ$ angle with the aligned unidirectional fibres. Finally, the surfaces were treated with plasma for six

Table 3: Mechanical properties for the CFRP substrate (1 - fibre direction,; 2 - transverse direction; 3 - out of plane direction) [20]

Elastic modulus, E	Shear modulus, G	Poisson's ratio ν
[MPa]	[MPa]	[-]
$E_1 = 109000$	$\nu_{12} = 0.342$	$G_{12} = 4315$
$E_2 = 8819$	$\nu_{13} = 0.342$	$G_{13} = 4315$
$E_3 = 8819$	$\nu_{23} = 0.380$	$G_{23} = 3200$

seconds each. CFRP SLJs were assembled in a simple aluminium mould with guiding pins, illustrated in figure 3. It should be noted that the curing procedure and the demoulding steps were the same as those reported for the aluminium single lap joints fabrication.

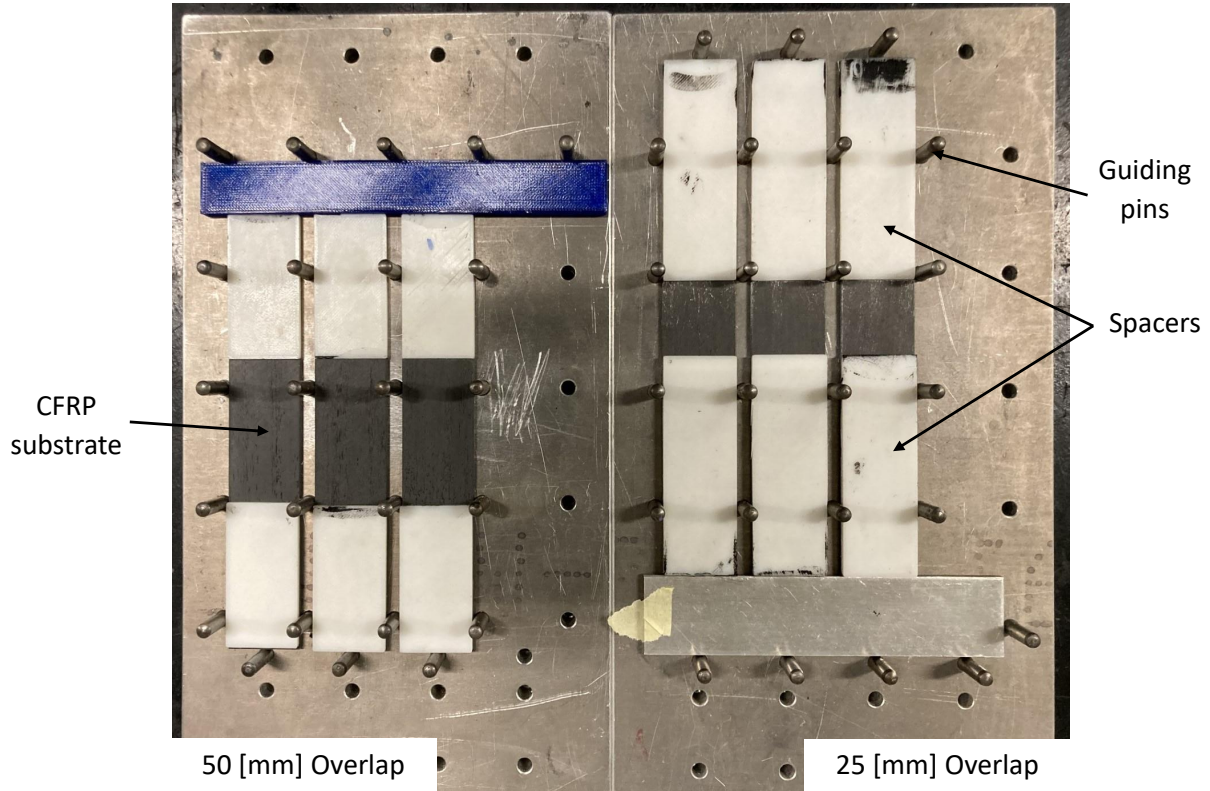


Figure 3: Mould for CFRP SLJ for both 25 and 50 [mm] of overlap length

4 Experimental results

The single lap joints were tested at a quasi-static constant crosshead rate of 1 [mm/min] at room temperature (RT) in an Instron 3832 (Norwood, MA, USA) quasi-static machine

equipped with a 30 [kN] load cell. Figures 4 and 5 display the modes of failure for both 25 and 50 [mm] overlap lengths, respectively.

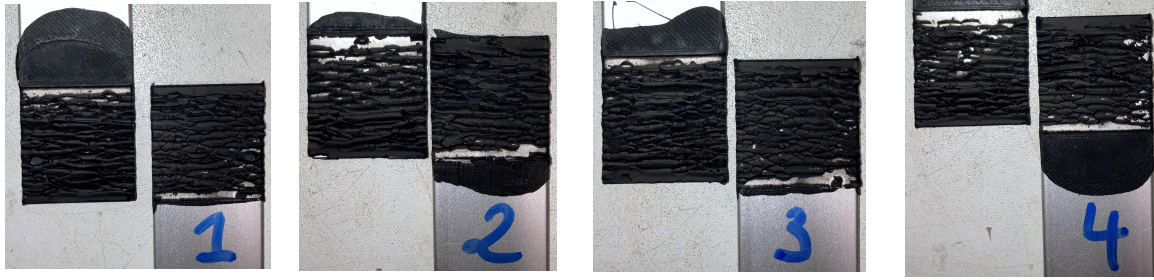


Figure 4: Modes of failure for all aluminium SLJs 25 [mm] overlap specimens

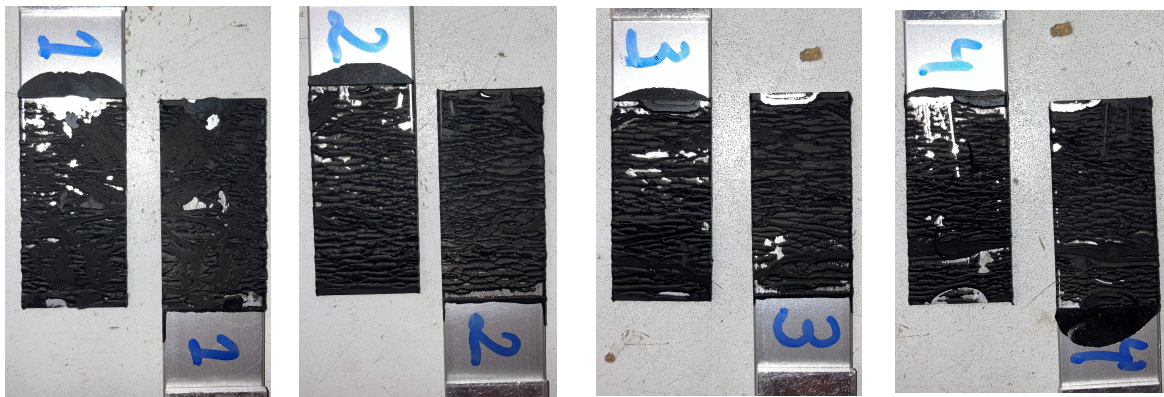


Figure 5: Modes of failure for all aluminium SLJs 50 [mm] overlap specimens

Cohesive failure occurred for all specimens and for both overlap lengths. The failure did not originate a single crack along the overlap edges, but led instead to multiple site cracking throughout the thickness. Thus, the two-component formulation showed good adhesion with the anodized aluminium substrates. Figure 6 agglomerates the load-displacement or $P - \delta$ curves as well as the lap shear stress evolution for both overlap lengths. It should be noted that the lap shear stress value generally remains very close when testing under different bonded areas, a result of the large flexibility of the adhesive.

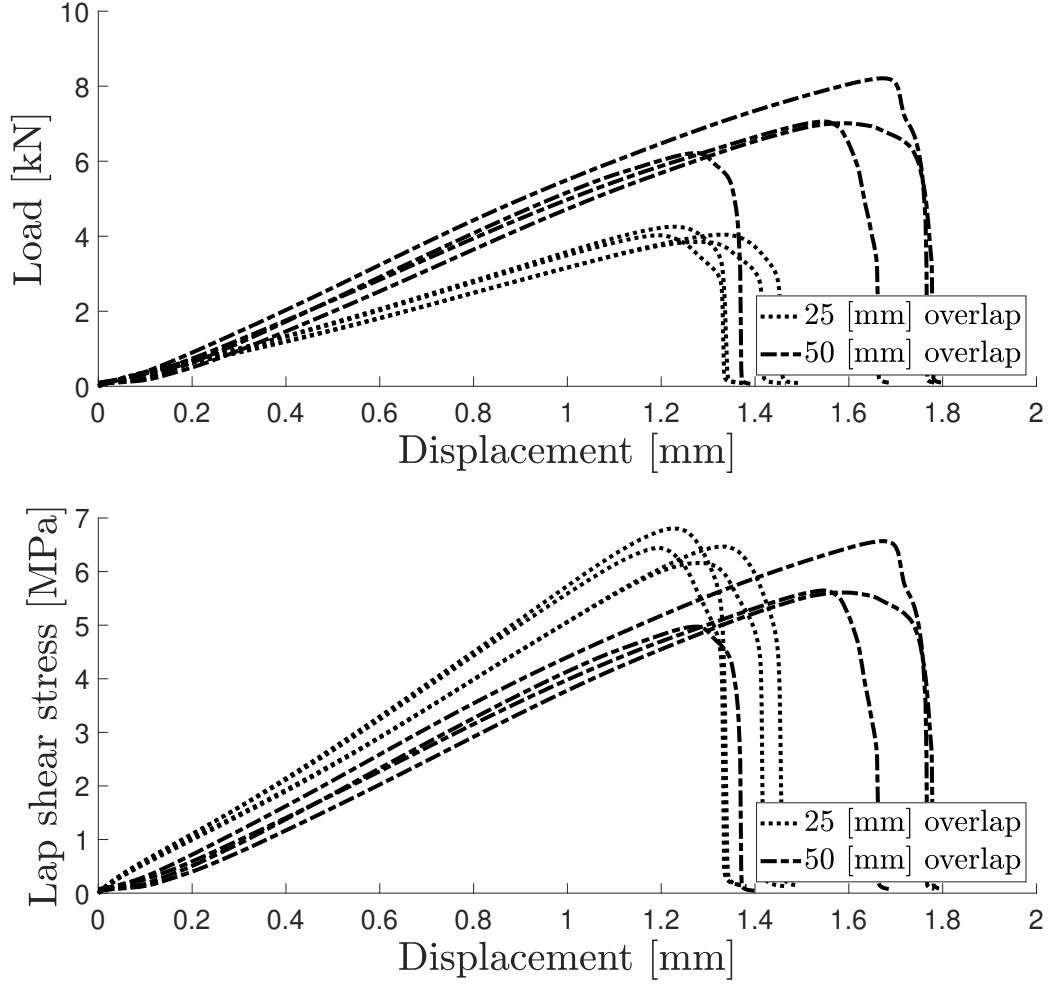


Figure 6: $P - \delta$ and lap shear stress curves for both aluminium SLJ overlap lengths

Table 4 summarizes the experimental results, showing close lap shear stress values. This close relation is detailed in figure 7.

Table 4: Results for the aluminium SLJs

Overlap	Maximum loading, F_{max}	Lap shear stress, σ_{lss}	Extension at F_{max}
[mm]	[kN]	[MPa]	[mm]
25	4.04 ± 0.14	6.47 ± 0.23	1.230 ± 0.061
50	7.13 ± 0.71	5.70 ± 0.57	1.521 ± 0.147

The composite single lap joints were fitted with CFRP alignment tabs and tested under the previously described conditions. Figure 8 and 9 display the failure modes of the specimens tested with 25 and 50 [mm] of bonded length respectively.

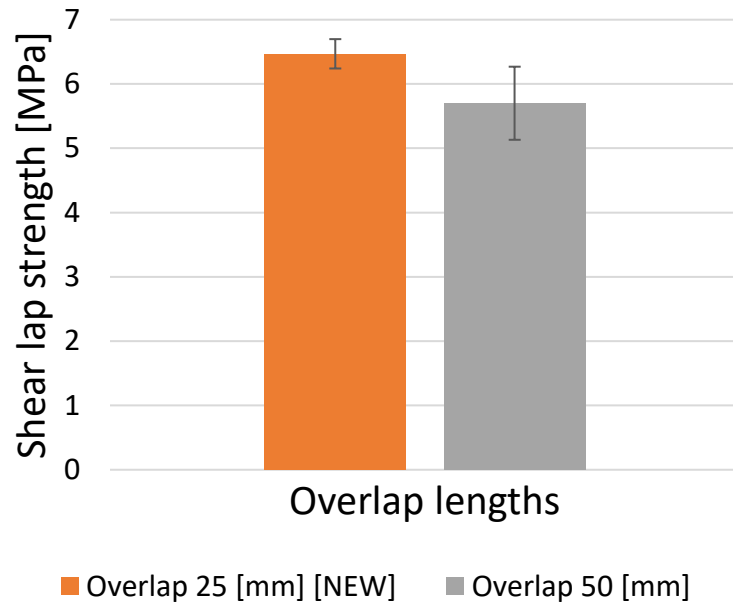


Figure 7: Comparison between the lap shear strength obtained for both overlap lengths

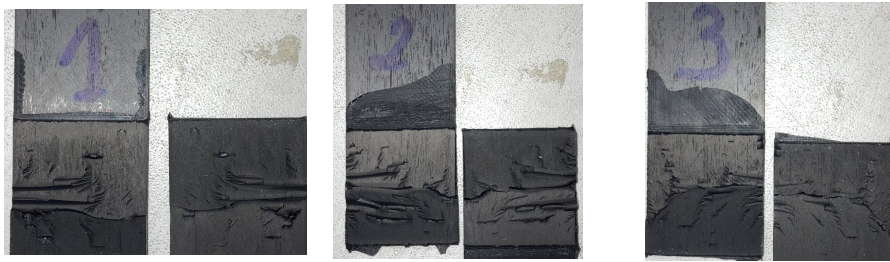


Figure 8: Modes of failure for all CFRP SLJs 25 [mm] overlap specimens

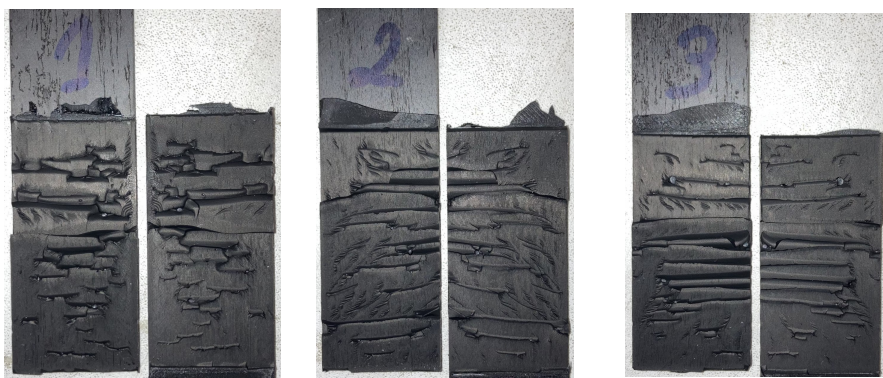


Figure 9: Modes of failure for all CFRP SLJ 50 [mm] overlap specimens

Adhesion to CFRP substrates with the plasma treatment was poor, which led to a mixed-failure mode in both joint geometries. An interfacial crack commenced to propagate at the two overlap edges, meeting in the middle of the bonded area right at the instant of failure. Seeking to address this issue, the two-component SPUR was mixed with an

additive which enhances the adhesion performance and four SLJs with 25 [mm] of overlap were fabricated and tested. However, a similar failure mode and lap shear strength value was obtained. Table 5 agglomerates the results obtained for the CFRP single lap joints tested.

Table 5: Results for the CFRP SLJ

Overlap	Maximum loading, F_{max}	Lap shear stress, σ_{lss}	Extension at F_{max}
[mm]	[kN]	[MPa]	[mm]
25	3.51 ± 0.29	5.61 ± 0.46	1.413 ± 0.041
50	5.27 ± 0.35	4.22 ± 0.28	1.940 ± 0.011

Figure 10 displays the $p - \delta$ and lap shear stress curves for both overlap lengths in the composite SLJs.

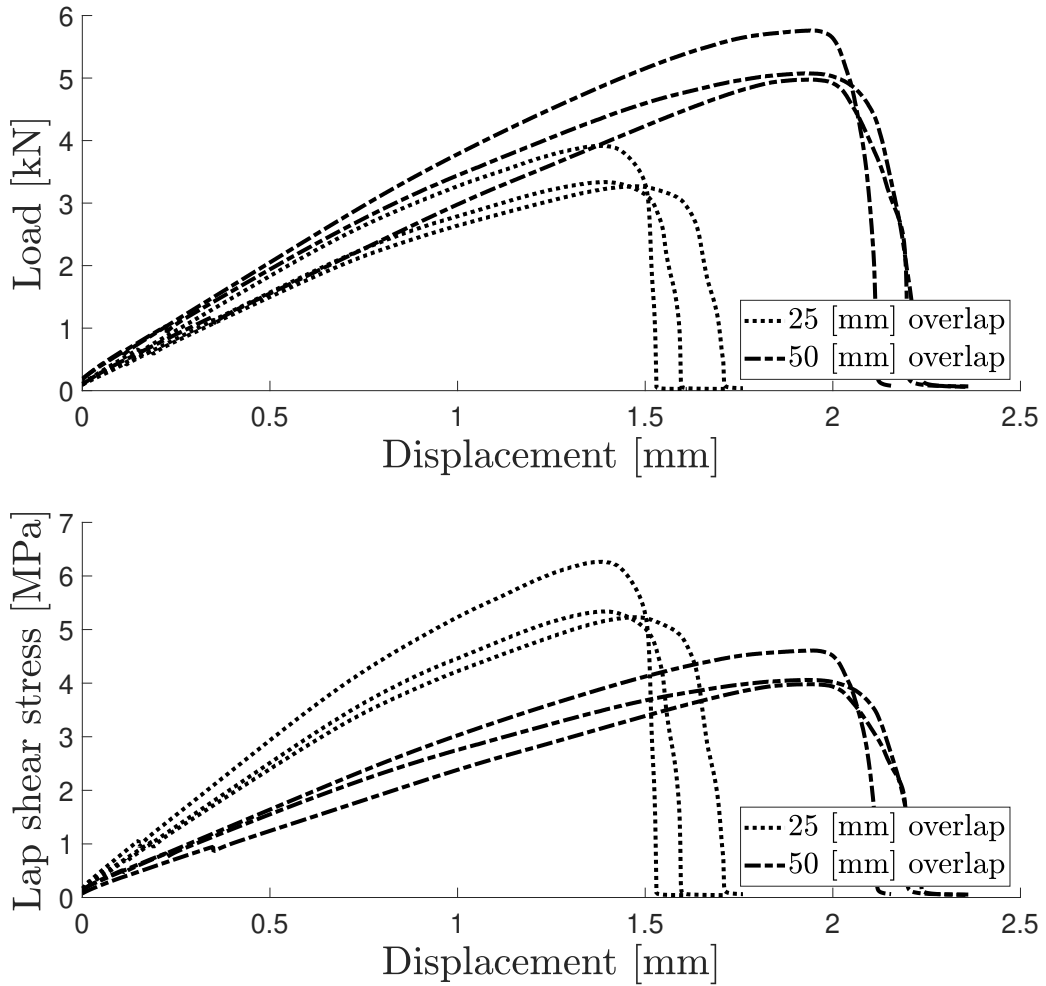


Figure 10: $P - \delta$ and lap shear stress curves for both CFRP SLJ overlap lengths

The lap shear strength was found to drop more significantly in composite joints rather than in the aluminum ones, a result of the interface failure. It is of interest to analyse the evolution of the failure load with the increase of the joint overlap length, which in theory ought to be linear. Figure 11 plots the maximum load to failure for each tested overlap, extrapolating a linear relation between them. There is a larger deviation from linearity in the composite case, again providing an indication that weak adhesion plays an important role in this case.

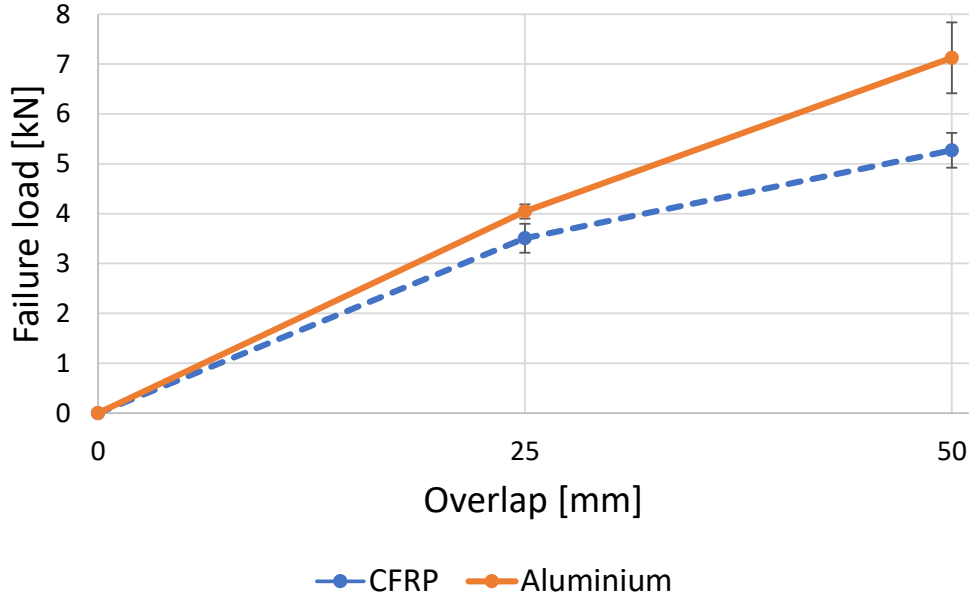


Figure 11: Evolution of failure load with the overlap length

5 Numerical modelling

5.1 Numerical details

ABAQUS® FE software was used to support a numerical analysis where a triangular shape CZM law was applied to cohesive adhesive layers. The adherents used in the TAST, DCB and SLJ testing procedures were modeled following a linear elastic approach, using ABAQUS® CPS4R plane strain elements with reduced integration and hourglass. The adhesive layer was modeled using COH2D 4-node cohesive elements, chosen due to their compatibility with the adherend selected elements. A mesh refinement procedure was performed along the adhesive overlap lengths. Unlike the bi-dimensional models, the three dimensional bulk specimen used eight node hexahedron (C3D8R) 3D elements with reduced integration and hourglass control.

The boundary conditions imposed reproduced the fixtures used in the experimental tests. An encastre was applied to the the bottom edge area of the bulk specimen and a

displacement was applied to the opposite edge. This design philosophy applies for both TAST and SLJ models, although in the latter alignment tabs were also added to the model geometry, as displayed in figure 12.

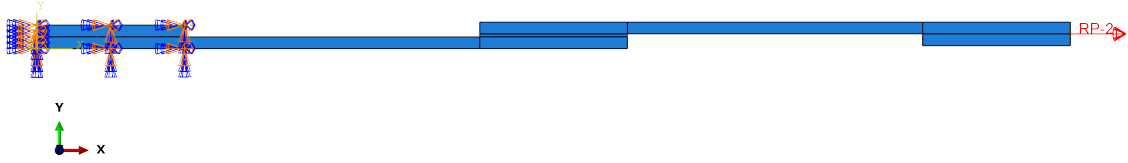


Figure 12: Boundary conditions of the single lap joint model

The lower hole of the DCB specimen was pinned, allowing for rotation along the normal to surface axis, with an induced displacement along the y axis for the upper hole, as illustrated in figure 13.



Figure 13: Boundary conditions for the DCB specimen model

The elastic behaviour of cohesive zone models is simply defined as a linear relation between the maximum strength and the modulus: this applies for both tensile (n) and shear (s) scenarios. The cohesive traction is given by the stiffness matrix $\mathbf{K}$ multiplied by the respective strains. The stiffness matrix contains the tensile and shear stiffness parameters, where $K_{nn} = E$ and $K_{ss} = G$. Since no tensile-shear mix was performed, $K_{ns} = K_{sn}$ is assumed as null [10].

$$t = K\varepsilon \Leftrightarrow \begin{Bmatrix} t_n \\ t_s \end{Bmatrix} = \begin{bmatrix} K_{nn} & K_{ns} \\ K_{sn} & K_{ss} \end{bmatrix} \begin{Bmatrix} \varepsilon_n \\ \varepsilon_s \end{Bmatrix} \quad (1)$$

The damage criterion selected was a quadratic nominal stress formulation, which follows:

$$\left(\frac{\langle t_n \rangle}{t_n^0} \right)^2 + \left(\frac{t_s}{t_s^0} \right)^2 = 1 \quad (2)$$

The softening phenomena occurs after the load peak is reached. For a triangular shaped law, as the traction follows:

$$t_n = (1 - d_n)t_n^u \quad ; \quad t_s = (1 - d_s)t_s^u \quad (3)$$

where t_n^u and t_s^u are the instantaneous cohesive traction. The damage variables referred as d_n and d_s , for both tension and shear respectively, which following the triangular shape law are given as [10]

$$d_{n,s} = \frac{\delta_{n,s}^f (\delta_{n,s} - \delta_{n,s}^0)}{\delta_{n,s} (\delta_{n,s}^f - \delta_{n,s}^0)} \quad (4)$$

which is valid for both tension and shear components.

The definition of the damage criterion for traction-separation laws is based on an energetic approach, where it considers the critical energy release rate values for both mode I and mode II [1]. Thus, there is the possibility to extrapolate a mixed-mode fracture energy relationship by combining the individual laws into a unified mixed-law formulation. One approach to achieve this is by employing the Power Law, which is described as:

$$\left(\frac{G_I}{G_{Ic}} \right)^\alpha + \left(\frac{G_{II}}{G_{IIc}} \right)^\alpha = 1 \quad (5)$$

where the value for the α parameter chosen was equal to one, hence following a linear power law. This interpolates the triangular shape laws plotted in figure 14, used in the cohesive elements [12].

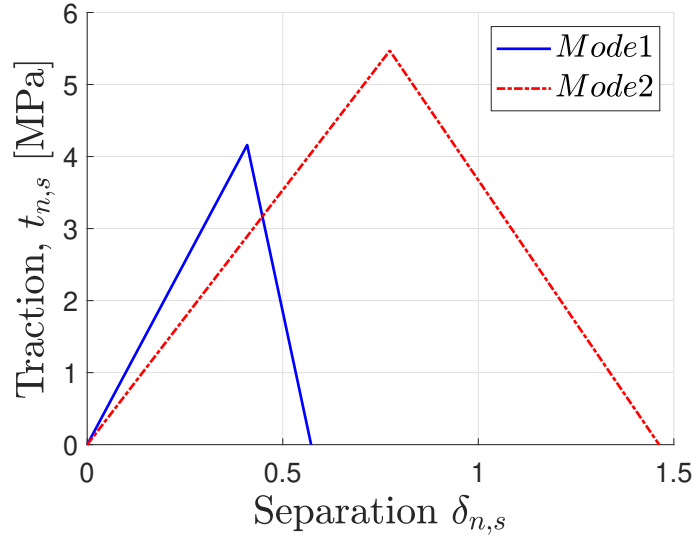


Figure 14: Triangular shape cohesive law chosen

The shear modulus value used corresponds to the one determined using the thick adherent shear test. It should be noted that this value results in a negative Poisson's ratio, being in discrepancy with the tensile test DIC results. This can be attributed to the different boundary conditions and the constrained nature of the adhesive layer found in a TAST joint. Accordingly, for modelling SLJs, where a constrained layer is present,

it was judged to be more suitable to use G_{TAST} rather than the extrapolated G_{Bulk} . Nevertheless, since the bulk specimen model is linear elastic and provides the freedom of the material the correct Poisson's ratio was chosen for this particular simulation.

5.2 Numerical validation

The tensile behaviour was set to follow simple linear elastic behaviour, as the material does not present a yield point followed by a plateau. Figure 15 illustrates the tensile strength displacement curve for a characteristic experimental run with the numerical model.

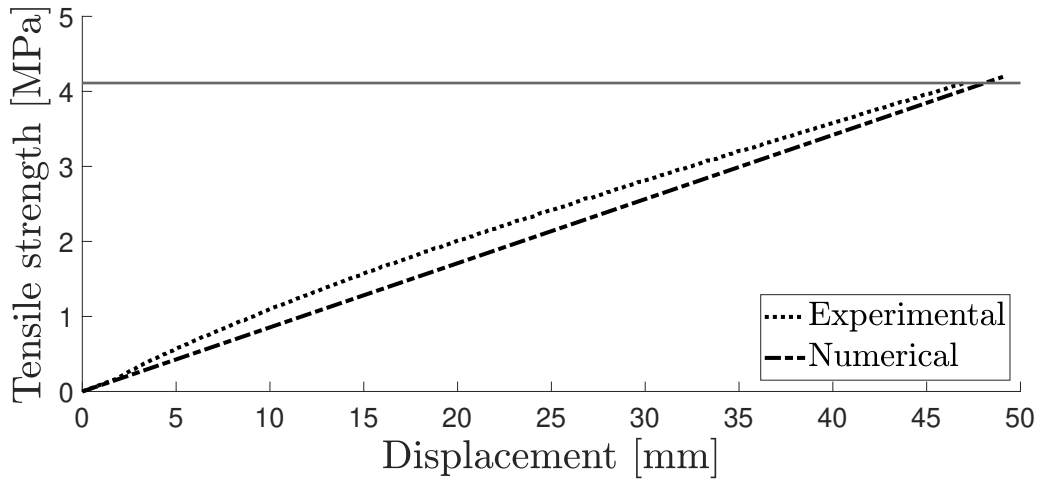


Figure 15: Numerical and experimental curve for the tensile test

For the shear test, there is some dispersion on the experimental results due to the low adhesive stiffness. Notwithstanding, a satisfactory correlation was found by employing the same triangular shape cohesive law, as shown in figure 16.

In the experimental testing process of the SPUR DCB specimen, half of the samples undergone a pre-cracking stage. DCB specimens were imposed with the same quasi-static rate but the test was stopped when a peak in the $P - \delta$ curve occurred, nucleating a crack. Then, those specimens were tested with the pre-cracking stage complete. The study showed that the critical energy release rate G_{Ic} measurement was independent of the pre-cracking or no pre-cracked specimens in this particular adhesive. The results of the numerical study were compared to both pre-cracked and no-precracked specimens. Figure 17 illustrates the damage evolution value of the cohesive layer at a particular opening stage of the specimen, whereas figure 18 displays the $P - \delta$ curve for the numerical simulation and the pre-cracked specimens. The R-curves obtained with compliance beam based method [15], for both numerical and experimental conditions are displayed in figure 19.

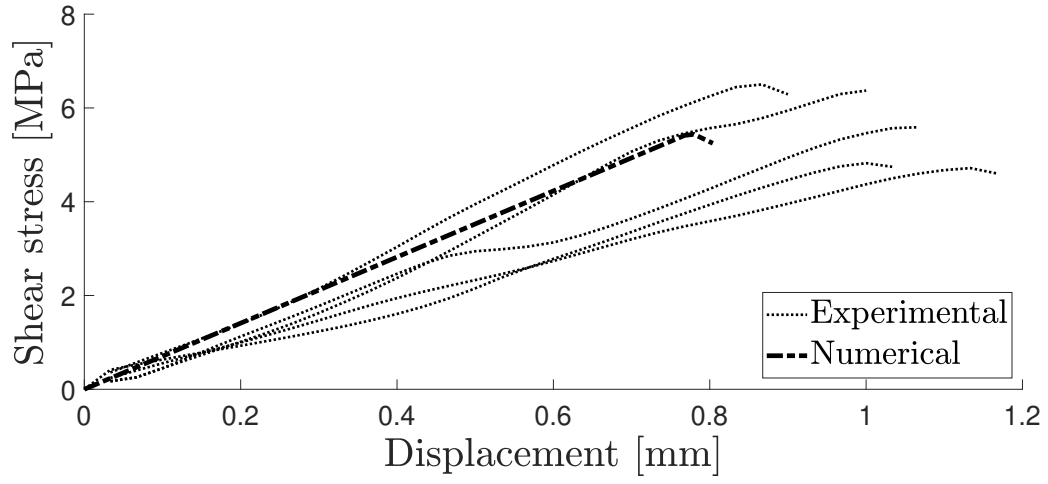


Figure 16: Numerical and experimental curve for the TAST

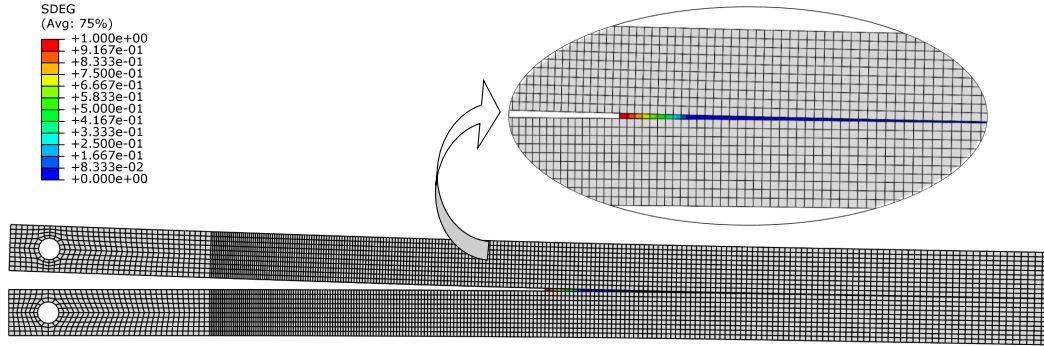


Figure 17: Damage evolution on the DCB cohesive layer

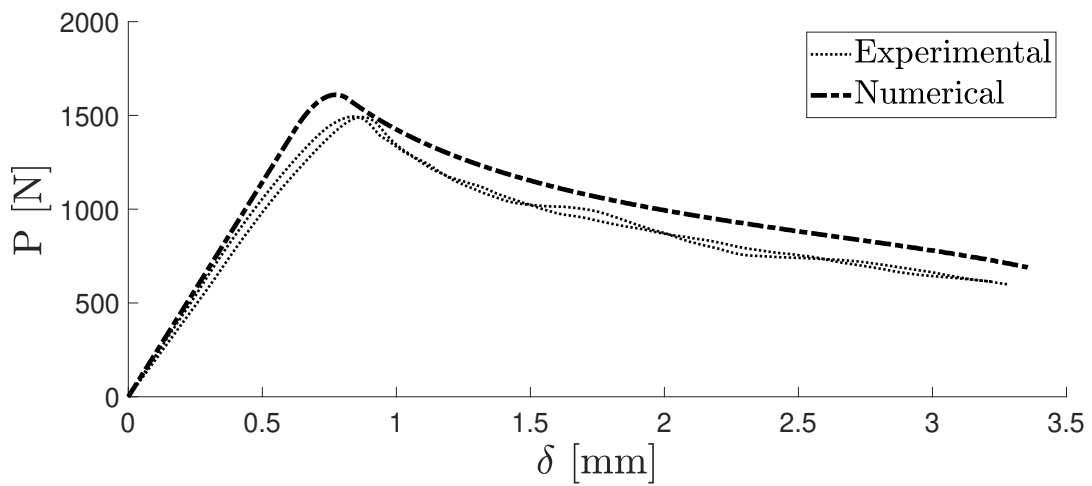


Figure 18: Numerical and experimental $P - \delta$ curve

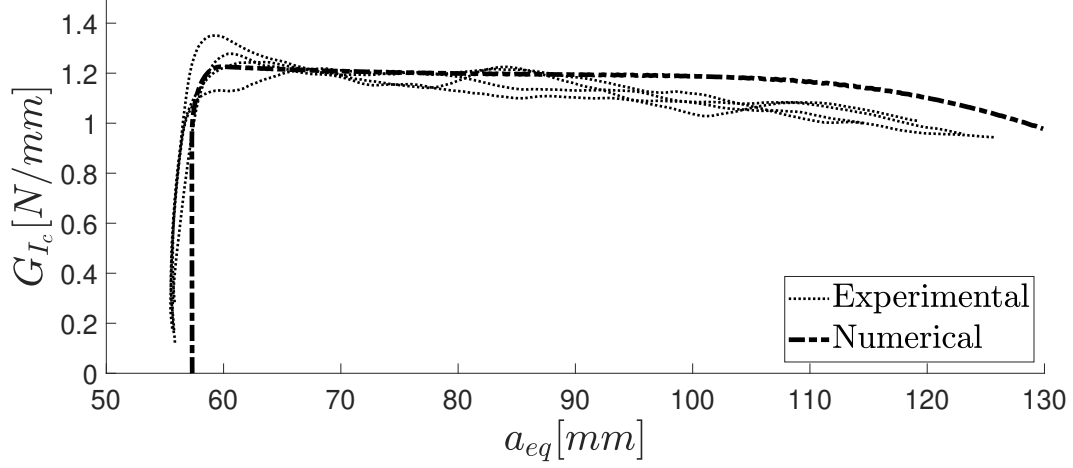


Figure 19: R-curve computed using CBBM for the numerical and experimental data

The aluminium single lap joints tested exhibited consistent testing results, with cohesive failure. Figure 20 agglomerates the experimental data as well as two numerical curves: one using the shear modulus value calculated using the thick adherend shear test and another obtained by extrapolating the value from the estimation of the Poisson's ratio from the tensile test, employing the outcomes from the DIC software. The higher shear modulus value provides a more accurate result over the bulk extrapolated value.

Composite joints were not simulated due to the lack of adhesion in the experiments, since neither the adhesive layer nor the adherend are at the root of failure.

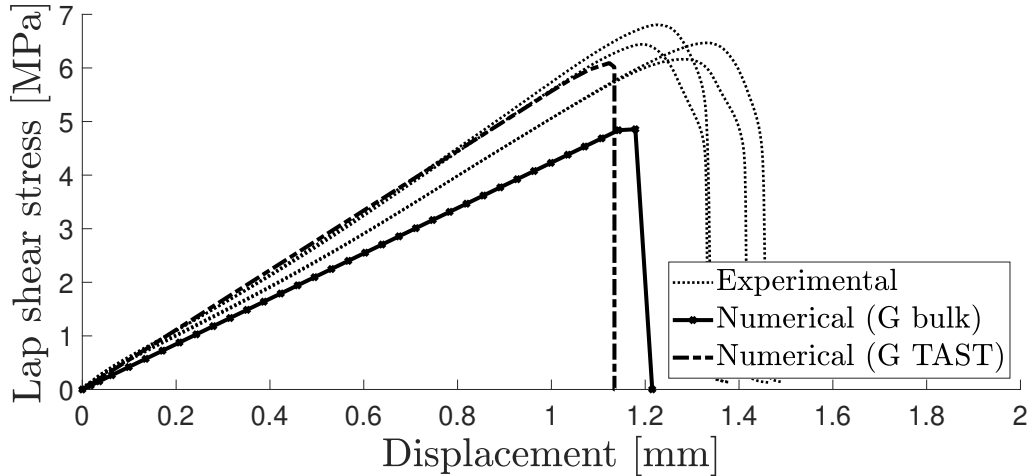


Figure 20: Lap shear strength vs displacement curve for both numerical and experimental 25 [mm] overlap aluminium SLJ

6 Conclusions

In this paper, a novel two-component silylated polyurethane resin with epoxy resin was tested for single lap joints and numerically modelled using a triangular cohesive shape law in the ABAQUS[®] FE software. Numerical models for the tensile, TAST, DCB and single lap joints were also built in ABAQUS[®] FE software, where the adhesive properties were validated, allowing to obtain a numerical curve which was in agreement with the experimental data. The bulk specimen model used a simple linear elastic approach with the maximum tensile stress serving as a failure criterion. On the other hand, the TAST, DCB and SLJ used the adhesive cohesive properties, changing the shear modulus value to the one determined in the TAST run. In fact, the influence of the tensile modulus is negligible for all the three models, since the adhesive layer is much more constrained than it is the case in a tensile free specimen scenario. The following remarks summarize the key outcomes of this study:

- Single lap joints were manufactured, using anodized aluminium and unidirectional CFRP substrates. The adhesive showed good adhesion to the aluminium substrates providing a lap shear strength of 6.47 [MPa] in joints with 25 [mm] of overlap length. In contrast, adhesive failure was found when bonding composite substrates, even after using a plasma treatment and with the addition of an adhesion enhancing additive to the SPUR mixture.
- The triangular shaped CZM law, commonly found to be suitable for brittle and stiff adhesives, was nonetheless able to reproduce the elastic behaviour of the 2k SPUR with no yielding point. The material properties and the CZM law determined from them were successfully used to reproduce the in-joint behaviour of the adhesive under quasi-static conditions.

Acknowledgments

Authors have the pleasure to acknowledge the adhesive provided company as well as to INEGI and the Portuguese Foundation for Science and Technology (FCT).

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Appendix C

IJUP poster

Mechanical Characterization of a Novel Saline Based Polyurethane Hybrid Flexible Adhesive

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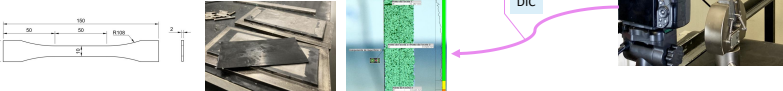


1. Introduction

In this work a novel 2K adhesive which joins silylated polyurethane resin (SPUR) with epoxy resin was mechanically characterized. The new semi-structural adhesive allows for both composite and plastic bonding. The mechanical characterization process was begun with tensile bulk tests followed by the thick adherent shear test (TAST) with DIC correlation. Furthered, for the withdrawal of the fracture behaviour, the double-cantilever beam (DCB) and a mixed-mode approach were performed to respectively acquire the value of the first fracture toughness pure mode and estimate the adhesive fracture envelope. All tests were performed under quasi-static conditions at room temperature (20 °C) and executed in an Instron 3367 quasi-static machine. The curing specifications were all set to 50 °C during 24 hours. Semi-structural adhesives like polyurethanes are an actual trend due to the elastic behaviour and damping properties versus the global shear and tensile strength. The novel saline based PU provides an adhesive possesses higher tensile and shear strength, due to the coupling between hardened epoxy and SPUR via aminosaline.

2.1 Experimental Details: Bulk

The Bulk test provides the tensile properties of the adhesive. The performed bulk sheet followed the NF T 76-142 standard, where a mould joining a silicone frame [1] were used. The assembly was cured in a hot press, where three "dogbone" specimens where later CNC machined from each bulk sheet.



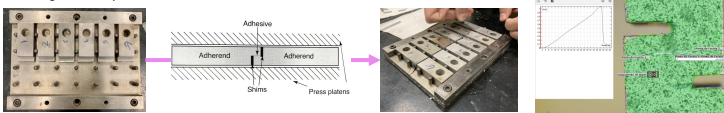
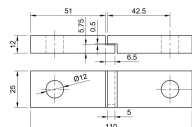
The six specimens tests where performed at RT (20 °C) in a quasi-static machine at a rate of 2 [mm/min]. The specimens where then coated with white matte paint and speckles with black dots, in order to obtain the strain field from digital image correlation (DIC) software. A digital camera photographed the specimens at a rate of one per each five seconds.



2.2 Experimental Details: TAST

The TAST provides the shear properties of the material, following ISO 11003-2:1993 standard. The steel substrates where measured to estimate the adhesive thickness, sandblasted and acetone cleaned. After, they where placed in a mould and he adhesive applied. Shims coated with release agent film where applied in order to guarantee pure shear conditions

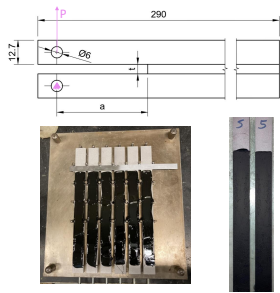
The strain field was computed using DIC, following the same methodology of the bulk test. Specimens where tested at a rate of 1 [mm/min].



2.3 Experimental Details: DCB

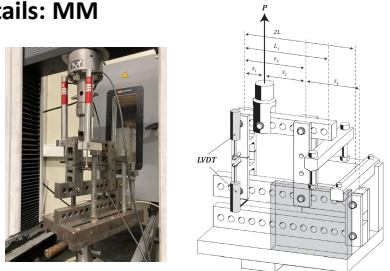
DCB specimens where manufactured using steel substrates which an adhesive thickness of 0.2 [mm] (ensured by the usage of calibrated tape) and a crack length of about 48 [mm]. A razor sharp blade was located at front to create an initial crack geometry. The six tests were performed at a rate of 0.2 [mm/min]: three of the specimens contained a pre-crack. The P-δ curve was withdrawn from the machine and the Compliance-Based Beam Method (CBBM) was used to calculate an equivalent crack length (a_{eq}) in order to estimate the critical energy release rate in pure mode I (G_{IC}) [2].

G_IC = (6P^2 / (b^2 h)) * (2a_eq^2 / (h^2 E_f) + 1 / (5G))



2.4 Experimental Details: MM

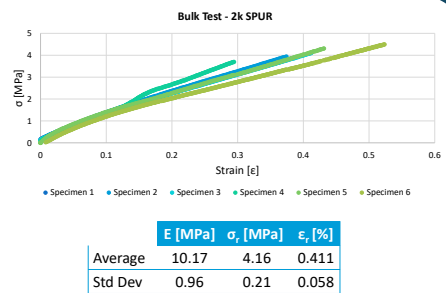
The mixed-mode test requires the same DCB specimens. A mixed-mode apparatus [3] which allows to tests under difference phase angles (φ) conditions was used. The CBBM formulation was followed, which did not require any instantaneous measurements of the crack length as it propagates through the test. Two LVDT's where used to capture the displacement of each substrate.



φ = arctan (G_IIC / G_IIIC)

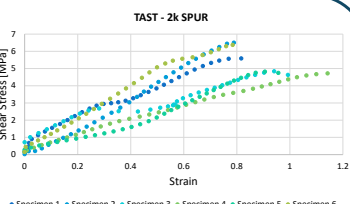
3.1 Results: Bulk

All six specimens failed within the 10 [mm] width. The DIC data provided the strain field, which was then agglomerated with the machine data to withdraw the tensile properties: Young's Modulus, maximum tensile strength and elongation to failure.



3.2 Results: TAST

The adhesive adhered well to the steel substrate, where all failure modes where mixed in between cohesive and adhesive failure. The TAST provided information in what recalls the shear modulus, maximum shear strength and elongation to failure.



Typical Failure Mode

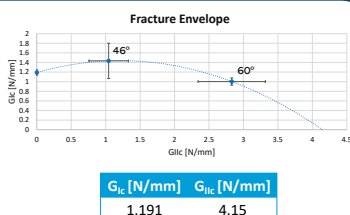
3.3 Results: DCB

Pure mode I fracture test was performed for 3 specimens without a pre-crack and other 3 with an induced pre-crack. The CBBM formulation [2] allows for a more ease test, since no crack length recording is needed. The P-δ curve and later the R-curve for all specimens where computed where the final critical energy release rate was found to be 1.19 [N/mm].

	G _{IC} [N/mm]
Average	1.191
Std Dev	0.055

3.4 Results: Mixed-Mode

The Mixed-mode approach was chosen provided the flexibility of the adhesive and the inability to perform the end-notch flexure (ENF) tests to capture the critical energy release rate in mode II. Hence, two degrees (46.0 and 60.0) and where chosen to estimate such value by extrapolating the so-called adhesive fracture envelope. Five DCB specimens were used for each phase angle. The apparatus arrangement [3] allows for testing the DCB specimens under different φ phase by rearranging the S₁, S₂, S₃, S₄, L₁ and 2L values. An estimation of 4.15 [N/mm] for mode II was achieved.



4. Conclusion

The lower lap shear strength values of polyurethane adhesives lead to the investigation of novel chemical varieties, such as inducing hardened epoxy precipitated in a saline matrix. The mechanical characterization showed decent tensile and shear values for the semi-structural adhesive, with relatively lower elongation, but higher shear strength than tensile. The critical fracture energy ratio between the second and first mode was set to 3.5, whilst in most common adhesives this value is set to be around 5 and 10. In the DCB test, when compared the pre-crack specimens with the ones where such opening did not occur, the R-curve did not vary much and both provided a decent value for G_{IC} within a minute standard deviation value. This adhesive has room for improvement, where the property characterization ought to be implemented under different curing specifications. Semi-structural adhesives are a combination of structural and elastic bonding, where an eventual application ought to be sealing or a main structural component in between battery cells in a battery pack, which is now and will be a high demand industry.



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