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Repair and end of life strategies for ecofriendly adhesive bonded joints

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Abstract

The use of adhesives has grown significantly across various industries, including aerospace, electronics, and automotive, due to their versatility. However, adhesives also raise environmental and sustainability concerns. Structural adhesive joints, in particular, rely mainly on thermosetting materials, which can be toxic and pose challenges for recycling. Once bonded, these materials cannot be efficiently recovered, and the only option is often to destroy the joint.

With the development of adhesives and their increasing industrial use, there is a growing emphasis on recyclable and bio-based materials. This concern is especially critical in structural applications, where material and adhesive waste can result in significant losses and elevated costs. Some debonding strategies, such as the application of heat, chemicals, or thermally expandable particles, have been proposed; however, these approaches are not always efficient.

This study investigates a potential solution for sustainable adhesive bonding through the mechanical characterization of a commercial vitrimer, Vitrimax VHM. Its performance under quasi-static conditions was benchmarked against a thermoplastic adhesive (T-Link) and a conventional epoxy (AV 138). For this purpose, four types of tests were carried out. Bulk tensile tests and thick adherend shear tests were performed to evaluate the mechanical properties under these conditions. Double cantilever beam (DCB) specimens were manufactured to determine fracture energy, while compact tension tests were conducted to measure fracture energy with minimal substrate influence. Creep tests and single-lap-joint (SLJ) tests were performed at 50% of the glass transition temperature to evaluate time-dependent behaviour and joint strength, respectively. Additionally, SLJ tests were also carried out at room temperature over multiple adhesion cycles on steel substrates to assess both performance retention and re-adhesion capability.

The results demonstrate that Vitrimax combines competitive mechanical strength, significant fracture energy, and effective creep resistance, while also retaining performance after re-bonding. These findings provide insight into the potential of vitrimers for structural applications and underscore their promise as recyclable, sustainable alternatives to conventional adhesives.

Keywords: Vitrimer, thermoplastic, epoxy, recyclable, adhesive joints, dynamic covalent bonds.

Resumo

O uso de adesivos tem aumentado significativamente em diversos setores, incluindo aeroespacial, eletrônico e automóvel, devido à sua versatilidade. Contudo, os adesivos levantam algumas preocupações ambientais e de sustentabilidade. As juntas adesivas estruturais dependem sobretudo de materiais termoendurecíveis, que podem ser tóxicos e são difíceis de reciclar. Uma vez colados, estes materiais não podem ser recuperados de forma eficiente, sendo frequentemente necessário destruir a junta.

Com o desenvolvimento e a crescente utilização industrial dos adesivos, tem-se verificado um maior número de investigações em materiais recicláveis e de base biológica. Esta questão é particularmente relevante em aplicações estruturais, onde o desperdício de materiais e adesivos pode resultar em perdas significativas e custos elevados. Algumas estratégias de descolagem, como a aplicação de calor, produtos químicos ou partículas termicamente expansíveis, têm sido propostas; contudo, nem sempre se revelam eficientes.

O presente estudo investiga uma solução potencial para a colagem adesiva sustentável através da caracterização mecânica de um vitrímer comercial, o Vitrimax VHM. O seu desempenho, em condições quase estáticas, foi comparado com um adesivo termoplástico (T-Link) e uma epóxi convencional (AV 138). Para tal, foram realizados quatro tipos de ensaios: testes de tração e de corte, para avaliação das propriedades mecânicas; ensaios em *double cantilever beam* (DCB) para determinação da energia de fratura; ensaios de *compact tension* (CT) para quantificar a energia de fratura sem influência do substrato; e ensaios de fluência e juntas de sobreposição simples (SLJ) a 50% da temperatura de transição vítrea, para avaliar, respetivamente, o comportamento à fluência e a resistência das juntas. Para além disso, os ensaios SLJ foram também realizados à temperatura ambiente ao longo de múltiplos ciclos de adesão em substratos de aço, de forma a avaliar a retenção do desempenho e a capacidade de re-adesão.

Os resultados demonstram que o Vitrimax combina resistência mecânica competitiva, elevada ductilidade, energia de fratura significativa e resistência eficaz à deformação, mantendo o desempenho após a readesão. Estas conclusões fornecem informação sobre o potencial dos vitrimers em aplicações estruturais, salientando o seu interesse como alternativas recicláveis e sustentáveis aos adesivos convencionais.

Palavras-chaves: Vitrímer, termoplástico, epoxy, reciclável, juntas adesivas, ligações covalentes dinâmicas.

United Nations Sustainable Development Goals

The United Nations Sustainable Development Goals (SDGs) are a global agenda established in 2015, comprising 17 interconnected objectives designed to address pressing social, environmental, and economic challenges by 2030. They aim to eradicate poverty, protect the planet, and ensure prosperity and well-being for all, while fostering innovation and sustainable practices across sectors.

This research contributes primarily to:

- **SDG 9 (Industry, Innovation and Infrastructure)** by enabling the development of sustainable and reprocessable adhesive systems for advanced structural applications.
- **SDG 12 (Responsible Consumption and Production)** as the recyclability and reprocessability of vitrimers support circular economy principles and contribute to waste reduction.
- **SDG 13 (Climate Action)** as the potential replacement of conventional thermoset epoxies with recyclable adhesives can lower the environmental footprint of industrial applications with significant adhesive consumption, such as automotive, aerospace, and electronics.
- **SDG 15 (Life on Land)** as the development of recyclable adhesive systems can mitigate pollution and limit the accumulation of non-recyclable waste in terrestrial ecosystems.

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“Às vezes ouço passar o vento; e só de ouvir o vento passar, vale a pena ter nascido.”

Fernando Pessoa

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List of Acronyms

CAN	Covalent Adaptable Networks
CBBM	Compliance-based beam method
CFRP	Carbon Fibre-Reinforced Polymer
CT	Compact tension
CZM	Cohesive Zone Model
DCB	Double-cantilever beam
DIC	Digital image correlation
FEM	Finite element method
FPZ	Fracture Process Zone
RT	Room Temperature
SDG	Sustainable Development Goals
SLJ	Single lap joint
TAST	Thick adherent shear test

Chapter 1

Introduction

With the advancement of adhesive joining techniques, their use has expanded across various industrial sectors, such as automotive, marine, electrotechnical, and aerospace, as well as in increasingly demanding applications. This is attributed to the advantages they offer over traditional methods, including the feasibility of using lightweight materials, enhanced design flexibility, and the ability to join dissimilar materials [1].

The most commonly used adhesives in these applications fall under the category of thermosets, which provide excellent mechanical properties to adhesive joints. However, due to their permanent crosslink structures, these adhesives cannot be recycled without compromising the integrity of the adhesive bond [2]. Consequently, at the end of a part's lifecycle, the only viable solution is its complete destruction, which leads to material waste, not only of the adhesive but also of the substrate.

Given that sustainability has become an increasing concern within industries, numerous scientific investigations are being conducted to develop adhesives that address these challenges while maintaining their suitability for demanding structural applications.

Therefore, this study aims to analyse vitrimers, a new class of adhesive, as a potential solution by comparing their properties with those of a thermoplastic, and a conventional epoxy, while also evaluating their behaviour under creep conditions and their re-adhesion capabilities.

1.1 Objectives

This thesis focuses on investigating solutions for end-of-life strategies in adhesive bonding. To achieve this, three main objectives were defined. The first was the mechanical characterisation of the adhesives studied in this work through bulk tensile tests, Thick Adherend Shear Tests (TAST), Double Cantilever Beam (DCB) tests, and Compact Tension (CT) tests. The second objective was the evaluation of creep behaviour, and the third was the analysis of re-adhesion performance in Single Lap Joints (SLJ).

1.2 Research methodology

To meet the goals defined in Section 1.1, the following research methodology was adopted:

- Comprehensive literature review, focusing on the state of the art of vitrimers, to gain a deeper understanding of the properties and mechanisms of vitrimers.
- Experimental testing for the characterisation of an adhesive, including bulk tensile tests, TAST, DCB, and CT tests.
- Creep tests to evaluate time-dependent deformation and stability.
- Single lap joint (SLJ) tests analyse the behaviour of the adhesive joint and evaluate the rebonding capability of the adhesives.

1.3 Thesis outline

This thesis is structured in seven chapters. Chapter 1 presents the objectives of the research, the methodology followed, and an overview of the thesis structure. Chapter 2 provides a comprehensive literature review, covering the fundamentals of adhesive joints, a brief description of thermoplastics and thermosets, and a more detailed discussion of vitrimers.

Chapter 3 describes the experimental procedures, including the materials used, the specimen manufacturing processes, and the mechanical tests performed. In Chapter 4, the results of these experiments are presented and analysed, encompassing mechanical characterisation, creep behaviour, and single lap joint performance.

Chapter 5 summarizes the thesis output presented in the appendant documents, highlighting the key contributions and outcomes of the research. Chapter 6 presents the conclusions of the thesis, discussing the implications of the results. Finally, Chapter 7 outlines perspectives for future work and potential directions for further research in the field.

Chapter 2

Literature review

2.1 Polymer classes

To provide a clearer understanding of vitrimers, this section begins with an overview of thermoplastics and thermosets, and then introduces vitrimers in detail.

2.1.1 Thermoplastic

Thermoplastics are polymers that soften or melt when heated, making them easy to shape, and then solidify again upon cooling [3]. This behaviour is possible due to their internal structure, which consists of long, linear polymer chains that do not chemically react with one another, meaning no crosslinking occurs (see [Figure 2.1](#)). When heated, these chains gain mobility, allowing the material to melt without permanent damage. As a result, thermoplastics can be reheated and reshaped multiple times, which makes them recyclable [4–6]. The linear chain structure also gives thermoplastics relatively high toughness and ductility. Although their strength is moderate, this can be improved with the use of additives [7, 8].



Figure 2.1: Molecular structure of thermoplastic [9].

Thermoplastics are most commonly used in non-structural applications where low cost, easy processability, and resistance to chemicals and environmental factors are key priorities. They are widely found in packaging, consumer and institutional products, transportation, electrical applications, furniture, as well as paints and coatings for various low-impact functions. In the automotive industry, thermoplastics are particularly valued for their impact resistance and weather durability, making them a preferred choice for interior components [10–13].

For structural applications, thermoplastics are often used in the form of foams, which provide cellular strength, high impact resistance, and energy absorption, making them ideal for car panels and protective gear [14, 15]. They are also widely employed in adhesives and repair solutions, where they enhance damage tolerance and environmental resistance. Thanks to their chemical structure, thermoplastics can be easily repaired through localized melting, enabling efficient maintenance and reusability [16–18].

Linear epoxy

Linear epoxy is a thermoplastic defined by epoxy groups located at the ends of each chain, which can react to form longer polymer chains. Although linear epoxies can be used in their native form, they can also be combined with curing agents to form a three-dimensional crosslinked network [19].

Compared to conventional thermosetting epoxies, linear epoxies generally exhibit higher toughness, extensibility, and recyclability, while having lower strength, modulus, and thermal resistance [20, 21]. Their network-free structure allows for reprocessing, repair, and recycling, addressing sustainability concerns. Linear epoxies also allow tunable transparency, mechanical performance, and improved thermal conductivity for specific applications [21, 22]. However, reduced crosslinking typically results in a lower glass transition temperature and can increase water absorption, affecting thermal stability and long-term durability [23]. Overall, linear epoxies involve a trade-off between toughness and rigidity, making them suitable for applications where reprocessability and damage tolerance are more important than maximum stiffness and strength.

These materials are widely used in recyclable and high-performance composites, serving as matrices for carbon fibre reinforced composites in aerospace, automotive, and wind energy applications [24]. They are also employed in adhesives and bonding agents, providing enhanced toughness, extensibility, and self-healing capabilities for multi-material joints, as well as in protective coatings that offer chemical resistance, durability, and recyclability for metal and infrastructure protection [25, 26].

Additionally, linear epoxies are applied in personal and structural protection, including vehicle and body armours, protective shields, helmets, and sports protective equipment, as well as in composite panels for aircraft and trim bonding for automotive components [27]. Their thermoplastic nature allows for reshaping, remoulding, and advanced manufacturing techniques such as resin transfer moulding, vacuum bagging, stamping, roll forming, and 3D printing. Across these applications, linear epoxies stand out for their balance of mechanical performance, process flexibility, and sustainability [28].

2.1.2 Thermosets

Thermosets are polymer materials that, when exposed to heat, form permanent crosslinks. These crosslinks render the material rigid and prevent it from softening again [29].

Crosslinks are chemical bonds formed either between linear polymer chains or through the polymerisation of reactive resin monomers. During this process, the monomers create a three-dimensional network structure without passing through a linear state (Figure 2.2).

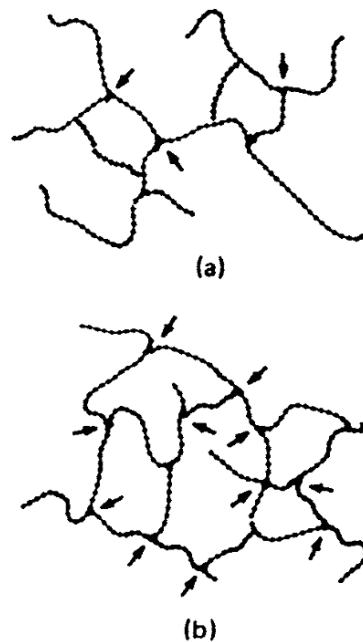


Figure 2.2: (a) Lightly crosslinked network polymer. (b) Highly crosslinked network polymer [30].

Depending on where they are used, thermosets can take on very different roles. General purpose thermosets, such as polyesters, offer moderated mechanical properties, limited temperature resistance, and low cost production, making them suitable for a wide range of standard applications. Engineering thermosets such as epoxies provide higher strength, better temperature resistance, and improved durability, which is why they are so widely used in demanding industries. Finally, special thermosets are tailored for very specific needs and often provide unique properties. For example, allyls are typically chosen for insulation applications [30].

Applications

Thermosetting polymers, particularly epoxy adhesives, are extensively employed in structural applications due to their adaptability and robust performance characteristics. The versatility of epoxy systems arises from the wide range of available formulations, which allows for precise tailoring of their properties to suit specific requirements. These adhesives demonstrate excellent bonding capabilities with a variety of substrates, including metals, ceramics, glass, wood, and most plastics

[31]. Their high cohesive strength and low shrinkage upon curing make them particularly suitable for applications such as void filling and gap bonding. In addition, epoxy adhesives exhibit notable resistance to water and chemicals, along with superior thermal stability when compared to thermoplastics, which tend to soften or melt at elevated temperatures. However, some disadvantages of epoxies include the need for high-temperature curing, their inherent brittleness, and the potential toxicity during handling [32].

Epoxy resins are also widely used as matrix materials in fibre reinforced composites, where they contribute to enhanced mechanical performance and provide excellent resistance to moisture and corrosion. They are compatible with a broad range of reinforcement fibres, including carbon, glass, aramid (Kevlar), and boron fibres. This compatibility makes epoxy composites particularly valuable in high-performance applications, such as aerospace and marine industries, where both structural integrity and environmental resistance are critical [32–35].

In addition to structural and composite uses, epoxy resins are frequently applied as protective coatings. Their strong adhesion, chemical resistance, and ability to form durable films make them effective in enhancing substrate longevity and providing barriers against water and corrosion. Some advanced formulations incorporate self-healing functionalities, enabling the autonomous repair of minor damage and thereby extending the service life of the coated materials [36–39].

Moreover, epoxy materials are extensively used in electrical and electronic applications due to their excellent insulating properties and stability under high voltage conditions. These properties help prevent short circuits and support the safe operation of electronic components. By incorporating specific additives, thermal conductivity can be improved to aid in heat dissipation, and certain formulations are designed to reduce electromagnetic interference. Additionally, flame retardants and thermal management features are often included to further enhance the safety and reliability of electronic devices.

2.1.3 Vitrimers

On one hand thermoplastic have the property to be reshaped and recycled, but do not have the mechanical properties necessary to more demanding applications. On the other hand, thermosets have higher mechanical properties, but because of the formation of permanent crosslink they cannot be reused. To resolve the problem of finding an adhesive that could be both recycled and have good properties, vitrimers started to be investigated through the years in a way to reach a greener future.

The concept of vitrimers was introduced in 2011 when Leibler and colleagues synthesized the first polymer containing dynamic covalent bonds [40]. Vitrimers are polymer networks in which chain connections undergo exchange reactions, enabling topological rearrangements while preserving the overall number of covalent bonds [41]. The following sections will explain the functioning of vitrimers and their influence on the mechanical properties, as well as thermal properties and temperature effects.

Dynamic covalent bonds

Dynamic covalent bonds are reversible chemical bonds that can break and reform when exposed to external factors such as heat, light, or changes in pH. Although they are covalent in nature, their activation energy is lower than that of permanent covalent bonds, which makes this reversibility possible. Since activation energy corresponds to the energy required to initiate a chemical reaction, in vitrimers it enables the continuous breaking and reforming of bonds. This allows rearrangements within the polymer network, something that cannot occur in materials with permanent covalent bonds.

Dynamic covalent bonds are the basis of covalent adaptable networks (CANs), which are polymers with reversible bonds that reorganise themselves when exposed to external stimuli. CANs can be dissociative, where bonds break before new ones form, reducing crosslink density and viscosity (Figure 2.3a), or associative, also called vitrimers, where a new bond forms first, allowing the network to keep its stability (Figure 2.3b).

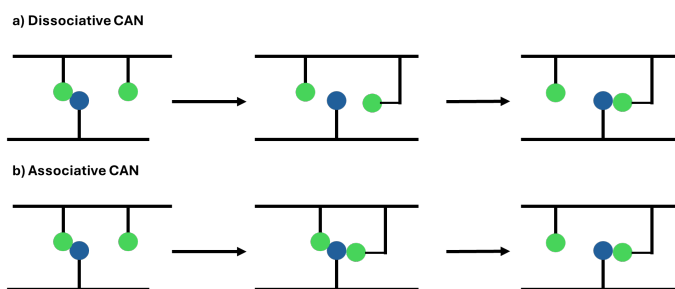


Figure 2.3: Simplified representation of (a) dissociative and (b) associative CAN.

Nevertheless, we cannot categorise CANs directly by type of bonds as there are some that may react in both ways depending on specific conditions. On the other hand, it is not feasible to classify them only by physical properties, since there are dissociative mechanisms with rheology properties similar to vitrimers. This is due to the rate of bond formation which is much higher than the bond breakage, so the viscosity-temperature of the polymer is still comparable to that of a vitrimer. For last, the crosslink network not only depends on the dynamic covalent bonds but also in intramolecular interactions, such as hydrogen bonding interactions, van der Waals interactions, and metal–ligand coordination [42].

Reversible reactions

Depending on the chemical groups involved in the material, the reversible reactions also changes. Table 2.1 shows some of the most common reactions with their functional groups and the mechanisms in CANs following the functional groups classification.

Table 2.1: Reversible reactions on vitrimers with its functional groups and CAN classification.

Reaction type	Functional groups involved	Mechanism in CANs
Transesterification	(-COOR) , (-OH)	Associative
Transimination	(C=N) , (-NH ₂)	Associative
Disulfide exchange	(S-S)	Associative/Dissociative

The transesterification reaction is the most common one and was the first reaction reported in a vitrimer by Leibler et al [40]. In this reaction, the alcohol group (-OH) attacks the carbonyl carbon in the ester group (-COOR) (Figure 2.4), forming an intermediate group. When it collapses, the alcohol group is released and a new ester bond is formed. The reaction happens when the catalyst is added, and its efficiency depends on the nature of the catalyst, the ester and alcohol structures, and the temperature [42–45].

Recent studies have developed catalyst-free transesterification vitrimers. By turning the ester groups more reactive, the Ojha et al. [46] adhesive only needed heat and, if necessary, a catalyst could be used to lower the temperature. In another study from He et al. [46], a more acidic and reactive group was used instead of the normal alcohols that resulted in faster exchanges and lower energy neededx.

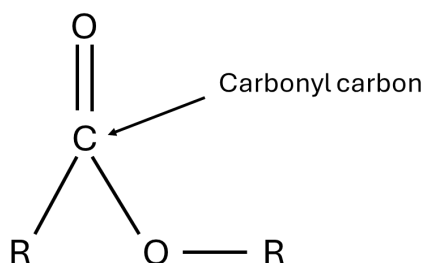


Figure 2.4: Molecular framework of the ester functional group.

The transimination occurs in a similar way as the transesterification; the amine group (-NH₂) attacks the imine carbon, forming an intermediate component, which releases the previous amine. Consequently, a new imine bond (C=N) is formed. The rate exchange or, in other words, the efficiency of the reaction depends on the solvent, temperature and chemical structure of the imine bonds, making it very dependent of the chemical environment. However, during the formation of the initial imine network, formation of water occurs, so preliminary steps to remove it or a post-reprocessing procedure are necessary [42, 47, 48].

The disulfide exchange can happen in two different ways. The first can happen naturally or with the addition of a catalyst to speed up the reaction, where an thiolate ion ($-S^-$) will attack the sulfide bond (S-S) and force it to reform and make new connections. The other way is by breaking directly the sulfide bond through light or heat, releasing a radical that will interact and break other

sulfide bonds. The second method is considered dissociative since the bonds need to be broken in order to form a radical, while the first one is associative, [49–51].

Thermal properties and temperature effects in creep and re-adhesion

Among vitrimers' thermal properties, the glass temperature, T_g , and the topology freezing temperature, T_v are particularly relevant. The T_g is an important parameter that corresponds to the temperature at which the polymer network movement happens and it affects both mechanical and thermal properties. Above the T_g , the material demonstrates flexibility and higher molecular mobility, while below it is characterised by rigid behaviour with limited molecular movement. This property can be measured by dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC) [52].

The T_v , by definition, is the temperature that delineates the threshold above which polymer network rearrangement is possible because the dynamic covalent bonds become active. It is often measured via stress-relaxation tests, where the T_v is defined as the temperature at which the polymer viscosity reaches 10^{12} Pa·s [41].

In the majority of cases where $T_g < T_v$, the material will be in a glassy solid state if the temperature is below T_g ; it exhibits rubber-like elastomeric behaviour between the two temperatures; above T_v it behaves as a viscoelastic liquid. There are rare cases where $T_v < T_g$, in which the material remains glassy below T_g and turns into a viscoelastic liquid above it [41, 52, 53]. Because these transitions determine the chemical reactivity and mechanical behaviour of vitrimers, a precise understanding of both is essential to design sustainable and reprocessable adhesives [54].

Understanding these thermal transitions is also critical for evaluating the mechanical performance of vitrimers under load. Below T_g , molecular mobility is frozen, leading to minimal time-dependent deformation and creep resistance comparable to that of conventional thermosets [55]. As the temperature increases and approaches T_v , dynamic bond exchange reactions are gradually activated, promoting network rearrangements [53]. This not only enhances reprocessability but also introduces viscoelastic or even viscoelastoplastic deformation, where the material exhibits a combination of elastic recovery, time-dependent viscous flow, and permanent network rearrangements [56]. Finally, above T_v , bond exchange dominates, enabling stress relaxation, welding, and re-adhesion [41, 52]. Thus, while low-temperature regimes ensure dimensional stability, elevated temperatures provide the key for vitrimer recyclability and repair.

Creep describes the slow, time-dependent deformation that arises when the material is subjected to a constant stress, with temperature playing a central role [57, 58]. A typical creep response begins with an initial elastic strain, followed by three main stages. In primary creep, the deformation rate decreases as the network resists further strain. Secondary creep exhibits a nearly constant deformation rate, resulting from a balance between hardening and relaxation mechanisms. Finally, in tertiary creep, the deformation rate accelerates, leading ultimately to failure [59, 60]. While these stages are common to many polymers, vitrimers present unique features because bond exchange reactions can alter the progression of creep [55, 61, 62].

Below T_g , creep is minimal because molecular mobility is frozen and bond exchange reactions remain inactive, resulting in high dimensional stability. As the temperature approaches T_v , however, the situation changes. Chain mobility increases, and bond exchange reactions begin to reorganise the network topology. This dual contribution from polymeric dynamics and bond exchange accelerates time-dependent deformation, often leading to larger non-recoverable strains [41, 52]. Above T_v , creep becomes particularly pronounced, as network rearrangement can occur continuously under stress, allowing significant deformation over time [53, 56].

Another important aspect is that creep behaviour of vitrimers cannot be explained by temperature alone. It results from the combined influence of temperature, chemistry, and stress. Higher temperatures accelerate molecular mobility and bond exchange reactions, while applied stresses can promote topological rearrangements. The chemical design of the network, including the density and nature of exchangeable bonds, also strongly influences creep resistance [58, 62]. Altogether, this coupling determines how vitrimers deform and recover under different conditions [52, 54, 55].

Above T_v , the dynamic covalent bonds in vitrimers are fully active, allowing the polymer network to undergo significant topological rearrangement. This behaviour is the basis for re-adhesion and self-welding: two previously separated vitrimer surfaces can bond together when brought into contact at elevated temperatures. Bond exchange reactions enable stress relaxation at the interface, allowing the polymer chains to interdiffuse and form new covalent connections, effectively restoring mechanical integrity [56, 62]. The efficiency of re-adhesion depends on factors such as temperature, contact time, and the chemical design of the network, including the type and density of exchangeable bonds. Furthermore, the presence of catalysts can accelerate the bond exchange process, reducing the time required for welding and enhancing the mechanical strength of the reformed interface [62]. This reversible network behaviour enables the reprocessability and repairability of vitrimers, making them highly attractive for sustainable adhesive and composite applications [56].

2.2 Adhesive joints

2.2.1 General Considerations

The first adhesives appeared in ancient times, when substances such as beeswax, rubber sap, shellac, and rosin were used to bond components in weapons. For example, they were used to attach feathers to arrows or to reinforce them [63, 64]. Around 5500 years ago, animal-based glues were developed, made from skin, tendons, cartilage, and bones, which were processed to create an adhesive that could be applied in liquid form or solidified for later use. These types of glues were widely used as sealants in paper and wood constructions, as well as in woodworking. Evidence of this has been found in the tomb of Tutankhamun, where his coffin showed several pieces that had been bonded using such adhesives [65].

Modern adhesives are used in advanced engineering applications and in various industries such as aeronautical, electrical, and marine. They have enabled significant developments and opened new possibilities for joining different materials. In addition to replacing conventional methods like bolting and riveting, which often add weight and create stress concentrations, adhesive bonding provides lighter, stronger, and more durable joints. It also allows for improved performance in environments where vibration, fatigue, or sealing are critical. Some of the main advantages of adhesive bonding include:

- Uniform stress distribution, as shown in [Figure 2.5](#), which enhances both strength and stiffness of the joint due to the absence of stress concentrations from holes or mechanical fasteners;
- The possibility to join dissimilar materials, enabling innovative hybrid structures that combine the best properties of each material;
- Cost and weight reductions, since thin sheet plates can be joined without the need for additional fasteners or adhesives, minimizing material use and simplifying assembly;
- A smooth surface finish, as the process avoids surface damage or weak weld beads, which also reduces the need for post-processing;
- Greater design flexibility, allowing engineers to optimize component shapes, material combinations, and joining strategies for improved performance and efficiency;
- Enhanced fatigue and vibration resistance, since the adhesive layer can absorb and distribute dynamic loads more effectively than rigid mechanical joints.

These benefits show why adhesive bonding has become such an important joining method in modern industries. By making structures lighter and stronger, adhesives help improve efficiency and performance in engineering applications. At the same time, they open the door to new design possibilities that traditional joining methods cannot offer. For these reasons, adhesives are now seen not only as an alternative but often as the preferred solution in many sectors.

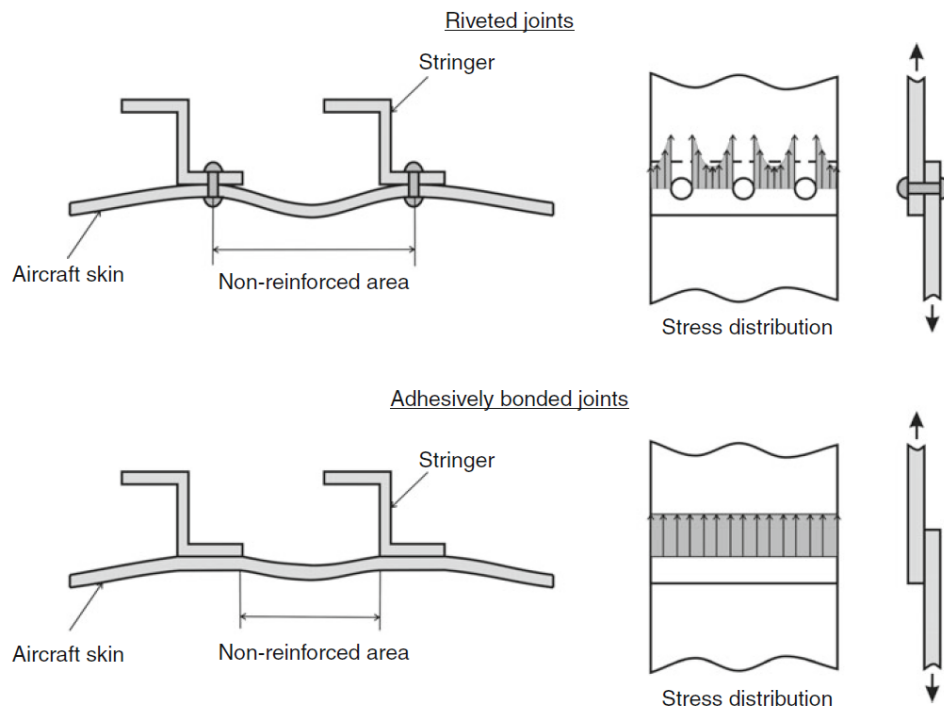


Figure 2.5: Example of uniform stress distribution and stiffness increase of adhesively bonded joints in comparison to riveted joints [63].

However, adhesives still have some challenges where further development is need, such as:

- Careful and appropriate surface preparation as it has a severe impact in the properties of the joint;
- Not suitable to cleavage and peeling loads as it induces areas with concentrated loads and weakens the joint;
- They are sensitive to moisture and temperatures so they need to be storage in certain conditions to not degrade;
- The use of moulds are necessary to maintain the joint position during the cure as it can take several days in some cases;
- The cure cycle of some materials require high temperatures which results in higher costs;
- Difficult to perform quality control, mostly because of its concern of the properties at long-term.

Despite these limitations, understanding how adhesion occurs is essential for improving adhesive technologies and their applications. Adhesion arises from several fundamental mechanisms, each contributing differently to the strength and reliability of joints. These mechanisms can be broadly categorized into mechanical, chemical, and physical adsorption, as described below.

Mechanical interlocking, represented in Figure 2.6 occurs when an adhesive flows into the surface irregularities of a material, physically locking the parts together. This phenomenon is observed in both engineering and biological systems, such as cells attaching to rough extracellular matrices [66]. Because all surfaces have microscopic peaks and valleys, this mechanism plays an important role in adhesive bonding. When an adhesive penetrates these pores or cavities and cures, it holds the adherends together through mechanical interlocking. Increasing surface roughness, either mechanically or chemically, can enhance adhesion by increasing the contact area. Mechanical roughening is effective only if the adhesive has low viscosity and wets the surface well. If abrasion does not produce a suitable topography, chemical treatments can be applied carefully to promote interlocking [67]. In some cases, such as bonding composites with hot-melt adhesives or welding thermoplastics, surface roughening may not be required because the melted material alters the surface and displaces trapped air at the interface.

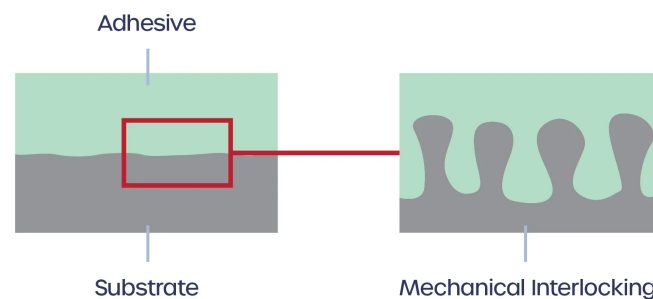


Figure 2.6: Mechanical interlocking between adhesive and substrate [68].

Another important adhesion mechanism is chemical bonding, represented in Figure 2.7, which occurs through interactions between the adhesive and substrate at the molecular level. These interactions can include covalent bonds, ionic bonds, hydrogen bonds, Lifshitz–van der Waals forces, and acid–base interactions [69, 70]. Covalent and ionic bonds provide the strongest adhesion, typically forming in cross-linked adhesives, thermoset matrices, or coatings, and can be promoted through reactions at the interface, co-curable adhesives, or the use of coupling agents. Secondary interactions, such as hydrogen bonding, are generally weaker and more common in polar materials, like polyamides, than in non polar substrates, such as polyolefins. Surface treatments, including corona or flame treatments of plastics, can be used to enhance chemical bonding by generating reactive sites and improving the overall adhesive performance [71].

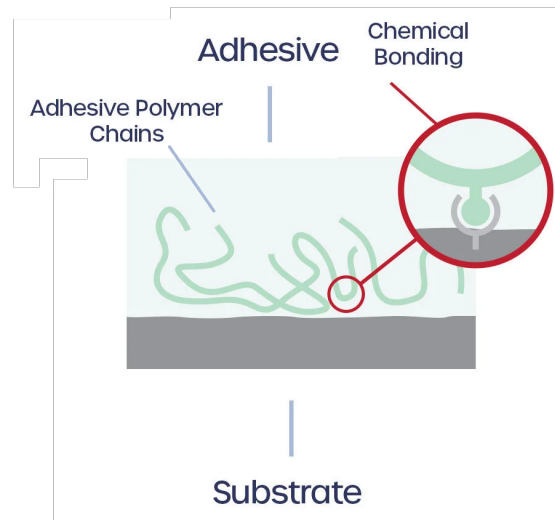


Figure 2.7: Chemical bonding between adhesive and substrate. Adapted from [68].

Finally, adhesion can result from dispersive forces, commonly referred to as van der Waals interactions (Figure 2.8). According to adsorption theory, adhesion occurs when adhesive molecules come into close molecular contact with the substrate, allowing surface forces to develop [69, 72]. These weak, short-range interactions arise from temporary fluctuations in electron density, producing attraction between molecules even in the absence of permanent charges. For van der Waals forces to be effective, the adhesive and substrate surfaces must be in intimate contact, typically within a few angstroms. This close contact, often referred to as wetting, ensures continuous interaction across the interface. In fusion bonding processes, it is similarly important that the molten materials uniformly cover the bonding region and remain free of voids after consolidation. Despite their relative weakness, these dispersive forces contribute significantly to adhesion in both natural and synthetic systems.

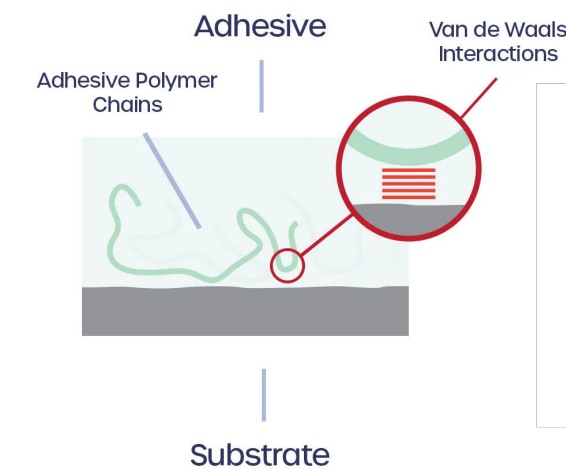


Figure 2.8: Physical adsorption between adhesive and substrate. Adapted from [68].

2.2.2 Adhesive classification

Adhesives classification is done by the polymer origin, natural or synthetic. Since it was still a broad classification, other categories have been adopted, such as functionality in the polymer "backbone", physical form, functional type, chemical family and method of application [63, 73].

Natural polymer refers to materials with an organic origin like animal or vegetal and natural rubbers, and in some cases they can also be from fully inorganic origin. The synthetic polymers are the ones that do not contain any sort of natural origin like silicones, epoxies, acrylics and polyesters [74].

As for the functionality in the polymer "backbone", they divide the adhesives into four more groups: thermoplastic, thermosets, elastomeric and hybrid. Thermoplastics are a one-part system and they do not possess a crosslink network so the adhesive does not cure or hardens with heat. Instead they melt while preserving their properties with minimal change and harden when cooled or by evaporation of a solvent [73, 75]. Regarding thermosets, they can be presented as a one or a multiple-part system, where the first requires higher cure temperatures and has a shorter shelf-life, and the second can be cured at room temperatures and has a longer shelf-life. Once cured, this adhesive cannot be heated or softened again because of the permanent covalent bonds in their internal structure [58, 75, 76]. As for the elastomers, they have distinct rheological properties that justify their own classification. These rubber-like materials are characterised by high strain capacity, toughness, and peel strength [76]. Lastly, the hybrid adhesives are a combination of the previous types with the purpose to obtain materials with better properties from each component [74, 76].

Concerning the physical form, adhesives can be applied in a liquid, paste, film/tape or powder state [75]. Liquid adhesives have very low viscosity, they tend to flow and spread during the cure cycle and, to guaranty a good wettability, they must be applied with a roll, spray or brushes. The paste adhesives have a high viscosity so they are used for filling large gaps and vertical application and should be applied with spatulas, pneumatic equipment, mastic pistols or syringe. Film or tapes adhesives are easier to handle as they provide a very defined bond line thickness and ensure a good stress distribution. For last, powder adhesives are mixed with solvents or preheat to convert them to a liquid state and gain the ability to flow [75, 76].

Adhesives are commonly classified as structural or non-structural. Structural adhesives are formulated to provide high strength and reliable performance [76], typically exhibiting lap shear strengths above 7–10 MPa, with commercial systems such as epoxies and acrylics often reaching 17–23 MPa [16, 77]. Non-structural adhesives, on the other hand, are not intended to support significant loads and generally show lap shear strengths below 7 MPa, often in the range of 1–5 MPa [77]. This category includes water-based, hot-melt, pressure-sensitive, conductive, and ultraviolet-cured adhesives, among others [58, 76].

Among the main chemical families of adhesives, epoxies, acrylics, and polyurethanes are the most widely used in structural applications. Epoxy adhesives are thermosetting systems regarded as the most versatile, offering excellent tensile and shear strength while also being adaptable to

achieve greater flexibility and toughness without compromising performance. Acrylic adhesives cure rapidly and provide high strength, although they are generally more expensive than epoxies. Polyurethane adhesives can cure at room or elevated temperatures and deliver good peel and shear strength while maintaining toughness and flexibility even at low temperatures, but they are sensitive to moisture and heat [58, 63, 76].

2.3 Loading modes and joint design

The adhesive joint is responsible for transmitting external loads. To guaranty they are not the weakest part it is important to understand the type of stress they are under [76]. The most four common loading modes in adhesive joints are tension, shear, peel and cleavage stresses, represented in Figure 2.9.

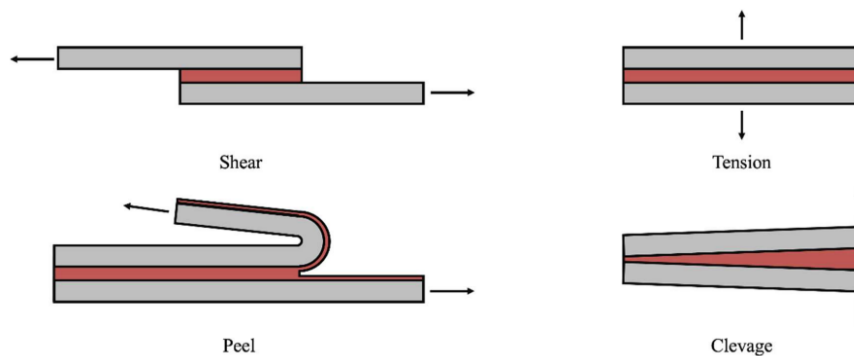


Figure 2.9: Loading modes in the adhesive joints [76].

Depending on the joint design, there can be more than one stress type and they depend on the load, the adhesive and substrates properties, and the joint's geometry. The design of the joint will affect the selection of the adhesive for two reasons. First, the adhesive must be capable of supporting the loading mode that the joint will be under. Second, the set life of the adhesive, before cure cycles, must be sufficient to provide enough time for the adhesive applications, especially in large parts [63, 76]. The Figure 2.10 represents some of the most common joint designs, being the single lap joint a popular choice because it has an easy manufacture.

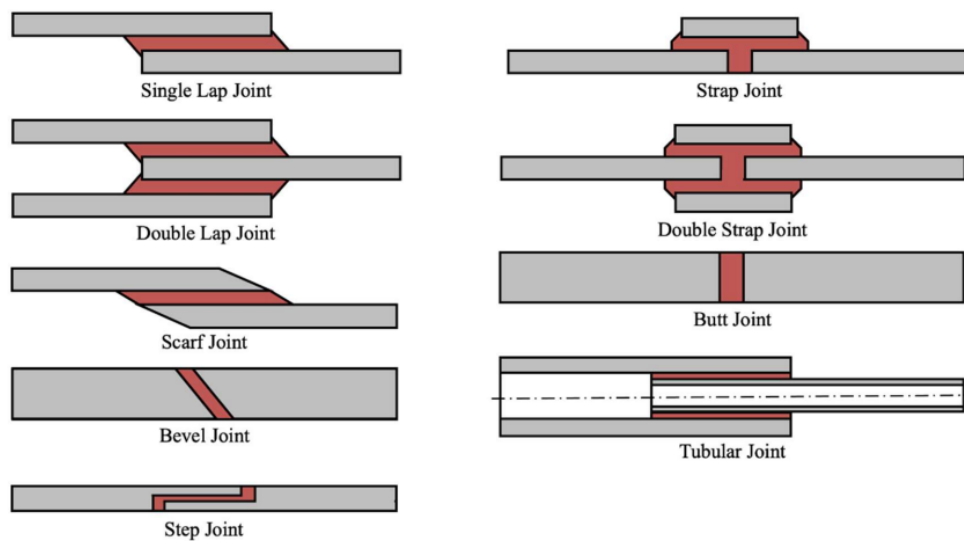


Figure 2.10: Examples of joint configurations [76].

2.4 Failure modes and joint design

The failure mode, represented in Figure 2.11, can be categorised by cohesive failure in the adhesive, cohesive failure in the substrate, mixed failure (adhesive-cohesive) and adhesive (interfacial) failure. The cohesive failure in the adhesive happens when the internal strength of the adhesive tears, leaving a layer of adhesive on the substrates. It also indicates that, in the joint, the adhesive was the weakest part between the bond of the substrate and the adhesive, and the substrate itself. The cohesive failure in the substrate occurs when the joint is correctly designed and produced and the failure occurs in the substrate. Adhesive failure is normally due to inappropriate surface preparation, thus the failure occurs between the interface of the adhesive and the substrate. The mixed failure involves a combination of adhesive and cohesive failure in the same fracture surface.

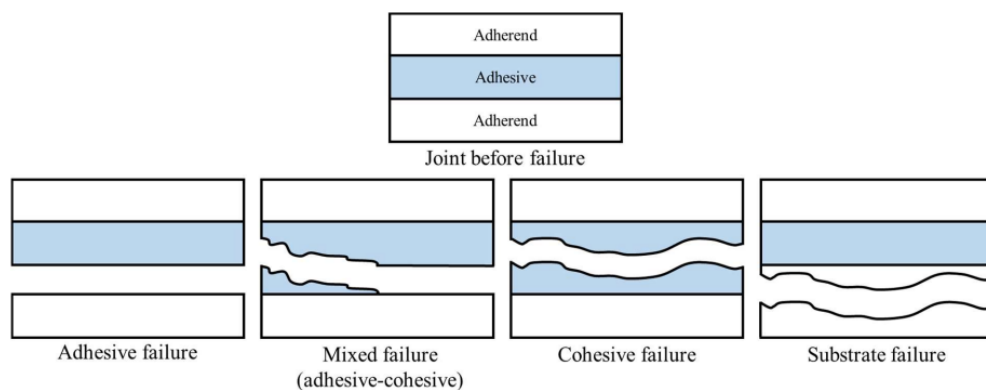


Figure 2.11: Different failure modes for adhesive joints [78].

2.5 Strength prediction approaches

To accurately predict how the joint will fail, knowing the loading mode is not sufficient as it does not take into account the possibility of defects, environmental conditions and crack formation [79]. Therefore, several approaches were developed to include this variable, such as continuum mechanics, fracture mechanics and damage mechanics [80].

2.5.1 Continuum mechanics

The continuum mechanics approach assumes an ideal bond between the substrate and the adhesive, treating both materials as continuous and neglecting the properties of the interface. Consequently, failure predictions rely solely on stress and strain. However, singularities at the overlap edges, illustrated in Figure 2.12, reduce the reliability of this method [58, 63]. In finite element analysis (FEA), stress values at these edges increase with mesh refinement, making model convergence difficult. A common strategy to mitigate these stress concentrations is the use of a filleted adhesive layer, yet studies indicate that singularities still occur and their magnitude depends on the fillet radius [81]. Furthermore, these approaches are limited to continuous structures with well-defined geometries and do not account for material defects [58, 80].

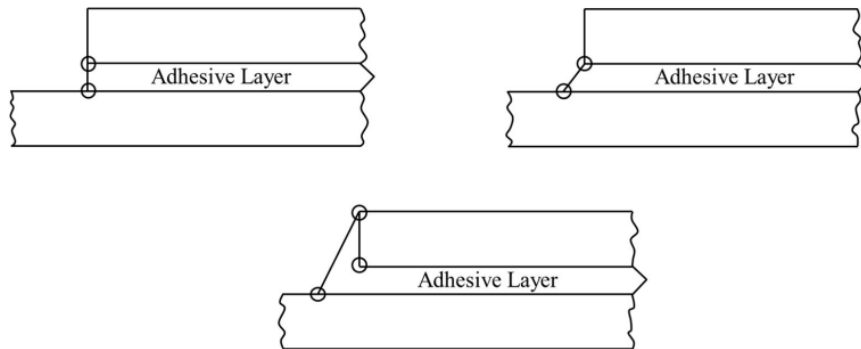


Figure 2.12: Singularities in the proximity of an adhesive edge [80].

2.5.2 Fracture mechanics

Unlike the continuum mechanics approach, fracture mechanics considers defects in the material, whether from manufacturing or during service, and describes cracks as discontinuities. This allows a quantitative analysis of whether a crack or defect may grow to a critical size that could cause failure. According to Griffith's theory, crack propagation occurs when the energy at the crack's tip, called the energy release rate G , reaches a critical value G_c , which is a material property [76, 82].

Fracture mechanics mainly uses the stress intensity factor and the energy release rate to study cracks. These criteria are more suitable for describing crack propagation than for capturing the very beginning of damage [76, 80]. In materials that can deform near the crack's tip, such as elastomers, the fracture process zone (FPZ), a localized region of inelastic deformation, must also

be considered, as it influences the energy required for crack growth [63, 83]. In all cases, these dissipation mechanisms can be described as the energy per unit of crack surface area. The energy release rate represents the change in elastic energy as the crack grows, and for a plate with constant thickness it is given by [76, 82]:

$$G = \frac{1}{B} \left(\frac{dW}{da} - \frac{dU}{da} \right) \quad (2.1)$$

where B is the specimen thickness, W is the external work, and U is the strain energy stored in the body.

The stress intensity factor, K , is a scale parameter that characterises the variation of the stress field near the crack's tip and is expressed as [76, 82]:

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

where Y is a non-dimensional factor dependent on geometry and loading distribution, σ_r is the applied remote stress, and a is the crack length. Crack propagation occurs when K reaches the material fracture toughness, K_c , which is a critical property of the material.

Irwin [84] established the relationship between the stress intensity factor and the energy release rate. For a plane stress state:

$$G = \frac{K^2}{E} \quad (2.3)$$

and for a plane strain state:

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

where E is the Young's modulus and ν is the Poisson's ratio. These relations are also valid for the corresponding critical values, K_c and G_c [76, 82, 83].

Crack propagation may occur under different loading conditions (see Figure 2.13), which are classified into three basic fracture modes. Mode I corresponds to an opening mode, while Modes II and III correspond to shear modes. In Mode II, the crack surfaces displace relative to each other perpendicular to the crack front (in-plane shear), whereas in Mode III the displacement is parallel to the crack front (out-of-plane shear). In real-world conditions, crack growth often results from a combination of these modes rather than a single pure mode [76, 80, 82].

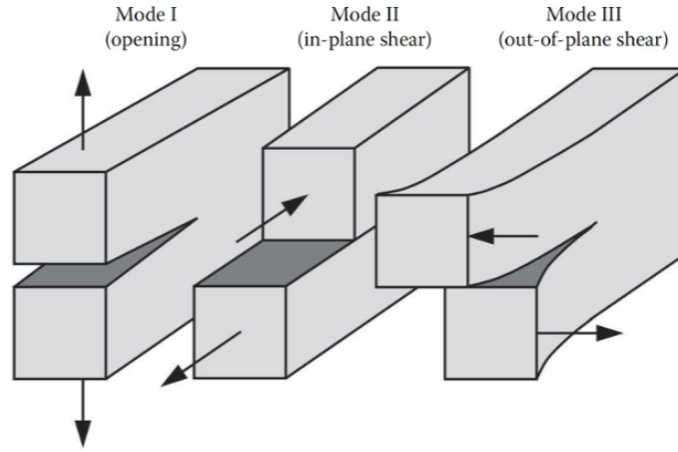


Figure 2.13: Fracture modes [65].

Each fracture mode is characterised by its own stress intensity factor: K_I for Mode I, K_{II} for Mode II, and K_{III} for Mode III. While both the stress intensity factor and the energy release rate can describe fracture, there are several advantages to using the energy release rate, G . First, G has a clear physical meaning, as it is directly related to the energy absorbed during fracture. Second, calculating K can be challenging, especially when the crack is located at or near an interface. Since adhesive joints are non-homogeneous materials, energy-based fracture approaches are better suited to describe their behaviour [57, 80].

In bulk materials, cracks typically propagate in Mode I. However, under service conditions, bonded joints rarely experience pure loading. The presence of substrates restricts deformation and creates a triaxial stress state. Therefore, Mixed Mode characterisation and analysis are essential for understanding fracture in adhesive joints, and the proper application of energetic criteria becomes fundamental.

A commonly used criterion for Mixed Mode fracture assumes that the fracture energy envelope can be represented as a sum of the normalised components of the adhesive fracture energies [76, 80]:

$$\left(\frac{G_I}{G_{Ic}}\right)^\alpha + \left(\frac{G_{II}}{G_{IIc}}\right)^\beta = 1 \quad (2.5)$$

where G_{Ic} and G_{IIc} are the critical energy release rates for Mode I and Mode II, respectively, and α and β are constants. The most commonly applied criteria are the linear criterion, where $\alpha = \beta = 1$, and the quadratic criterion, where $\alpha = \beta = 2$.

For planar problems, the Mixed Mode fracture ratio is often used and can be defined as:

$$\phi = \tan^{-1} \frac{G_{II}}{G_I} \quad (2.6)$$

This approach provides a practical way to evaluate fracture under realistic, combined loading conditions in adhesive joints.

When linear elastic fracture mechanics (LEFM) cannot be applied, alternative methods such as the J-integral are used to determine fracture toughness in adhesive joints [83, 85]. This approach is suitable for both brittle and elastic-plastic materials, and it is particularly effective for ductile adhesives like polyurethane, where the fracture process zone (FPZ) is large [86]. For brittle adhesives, the critical energy release rate (G_c) and the critical J-integral value (J_c) are nearly equivalent, while for more ductile adhesives G_c can be slightly higher due to the larger FPZ.

The J-integral method is commonly used with Mode I (opening) and Mode II (in-plane shear) fracture tests, such as the Double Cantilever Beam (DCB) and End Notched Flexure (ENF) tests. One of the main challenges of this method is the experimental complexity, as it requires continuous monitoring of the specimen. In particular, the rotation of the substrates and the instantaneous crack length must be tracked during testing. While load and displacement can be measured directly from the testing machine, rotation is usually monitored with inclinometers [78], and crack length is often captured using Digital Image Correlation (DIC) [86].

The Compliance-based beam method (CBBM) simplifies fracture testing because it does not require continuous crack length measurement, being especially useful when tests are carried out under variable conditions such as thermal chambers [87, 88]. Instead, it introduces the concept of an equivalent crack length, which is estimated from the load (P), displacement (δ), experimental compliance (C), and the fracture process zone (FPZ). This avoids errors from direct crack tracking and simplifies data processing.

The method is based on beam theory relations, where compliance is defined as:

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

and depends indirectly on the crack length. Following Irwin–Kies relations, the critical energy release rate in Mode I is given by [82, 88, 89]:

$$G_{Ic} = \frac{P^2}{2B} \frac{dC}{da} \quad (2.8)$$

where B is the specimen width and a the crack length.

To account for root rotation and FPZ effects, the equivalent crack length is introduced:

$$a_{eq} = a + \Delta + \Delta a_{FPZ} \quad (2.9)$$

Finally, the fracture energy can be expressed as [82, 88]:

$$G_{Ic} = \frac{6P^2}{B^2 h^2} \left(\frac{a_{eq}^2}{E_f} + \frac{h^2}{5G_{13}} \right) \quad (2.10)$$

where h is the substrate thickness, E_f the corrected flexural modulus, and G_{13} the shear modulus.

This formulation allows fracture energy to be determined from the P – δ curve alone, while incorporating effects through the equivalent crack length concept, making CBBM particularly effective for adhesive joints [81].

2.5.3 Damage mechanics

Fracture mechanics-based methods are limited because they do not consider the initiation of damage, assuming that failure occurs in a single planar crack propagating through undamaged material. In practice, cracks must first nucleate before propagation. To address this limitation, damage mechanics approaches were developed, with the Cohesive Zone Model (CZM) being the most widely applied [58].

In CZM, the adhesive layer is replaced by zero-thickness interface elements that transfer tractions between the substrates. These elements follow traction separation laws, describing both crack initiation and propagation without requiring a predefined defect [63, 80, 87]. This makes CZM particularly attractive, as it avoids stress singularities and allows progressive degradation of the adhesive joint to be simulated. Nevertheless, cohesive elements must be inserted in regions where failure is expected, such as within the adhesive layer or at the interfaces with the adherends, which requires prior knowledge of likely failure mechanisms [63].

The foundation of this approach is the cohesive law, which relates local tractions to the relative displacement across the interface. The response typically begins with an elastic increase in stress, reaches a maximum cohesive strength, and then decreases to zero, representing complete separation [61, 90, 91]. Four main parameters define a cohesive law: stiffness, cohesive strength, fracture energy, and shape. Any two of fracture energy, cohesive strength, or separation length are sufficient to characterise the law, except in the case of trapezoidal shapes. Stiffness and strength can be estimated through calibration with experimental data, while fracture energy can be measured directly via classical fracture mechanics tests [80].

Cohesive laws can take various shapes, including linear, bilinear, trapezoidal, exponential, and polynomial. Triangular or bilinear laws are commonly used for brittle adhesives, while trapezoidal laws better represent ductile adhesives with an extended FPZ [63, 87, 92]. Figure 2.14 illustrates these shapes for brittle and ductile adhesives.

Thanks to this flexibility in defining cohesive laws, CZM has been widely applied to model adhesive joints and delamination phenomena in polymers, composites, metals, ceramics, concrete, and multi-material systems, under different loading conditions such as static, fatigue, cyclic, and impact [58, 63].

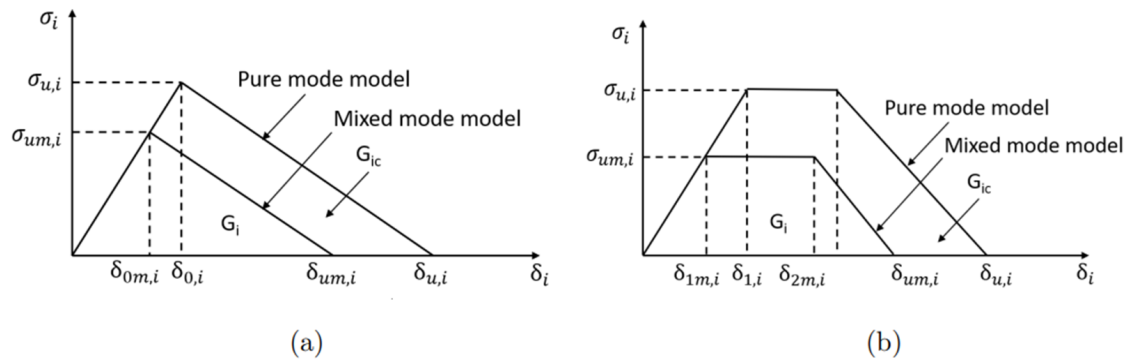


Figure 2.14: Schematic representation of traction separation laws: a) Triangular traction-separation law; b) Trapezoidal traction-separation law. $i=I,II$. Adapted from [87].

Chapter 3

Experimental procedures

3.1 Materials

Three adhesives were investigated in this study: AV 138, a thermoset; T-Link, a thermoplastic; and Vitrimax, a vitrimer. AV 138 and T-Link were selected as reference systems, while Vitrimax was the primary focus due to its reprocessible nature and dynamic covalent network, which may provide significant advantages over conventional adhesives.

3.1.1 Adherends

The adherends used in the study were aluminium, high-strength steel and duplex stainless steel. The properties of these materials are listed in [Table 3.1](#).

Table 3.1: Al 6082-T6, duplex stainless steel, and DIN 55 Si 7 properties [93–95].

Material	Yield stress (MPa)	Young's modulus (GPa)	Poisson's ratio (–)
Al 6082-T6	255	69.5	0.35
Duplex stainless steel	740	210	0.33
DIN 55 Si 7	1100	210	0.30

3.1.2 T-Link

T-Link is a commercial epoxy-based thermoplastic supplied by L&L Products in A4 sheets with a thickness of 0.127 mm.

To cure the adhesive, the hot press was pre-heated at 180°C with a pressure of 10 bar. When the temperature, monitored with a thermocouple, reaches 150°C the heating system was switched off and the cooling system was turned on while maintaining pressure.

3.1.3 Vitrimax

Vitrimax is a commercial adhesive from Mallinda Inc. (USA), and is supplied with an epoxy and a hardener. The adhesive was prepared by mixing the resin and hardener at a weight ratio of 1:2, with the hardener being the component in lower proportion. Since this material is supplied as a resin, the curing cycle required adjustment. Based on information provided by the supplier, the curing cycle adopted in this study was performed at 180 °C for 15 minutes.

3.1.4 AV 138

The adhesive AV 138 is supplied as a two-component system, consisting of Araldite AV 138 M-1 and Hardener HV 998-1, manufactured by Huntsman Advanced Materials. It was prepared by mixing the resin and hardener at a ratio of 10:4 by weight, with the hardener being the component in lower proportion. The curing cycle adopted in this study was carried out at 105°C for 1 hour and 5 minutes.

3.2 Specimen manufacture

3.2.1 Bulk test specimens

The bulk specimens were manufactured following the French NF T 76-142 standard, using a rectangular mould designed to obtain cured adhesive plates. The mould ([Figure 3.1](#)) consisted of six parts: two opposing plates providing smooth surfaces and four steel barriers positioned at each edge, all secured with Allen head bolts.

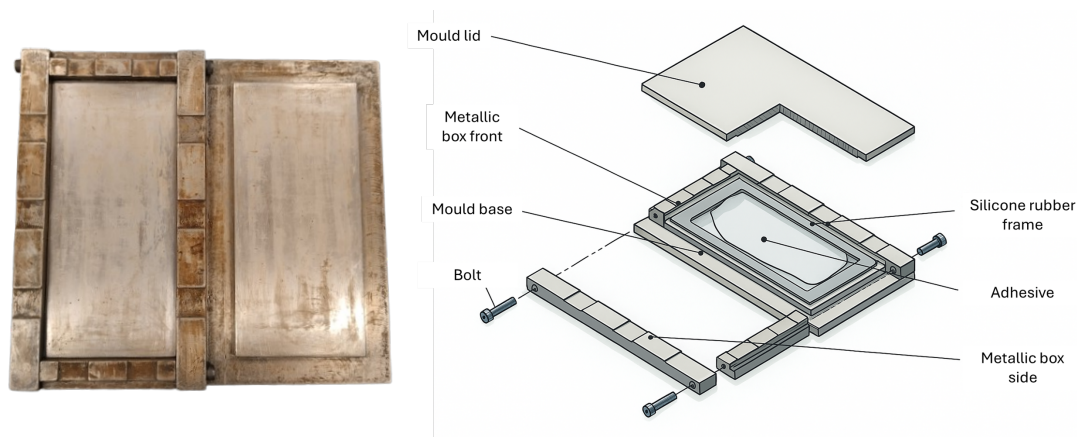


Figure 3.1: Bulk sheet mould used in the manufacture [81, 89].

The sheet thickness was controlled by a hand-cut silicone rubber frame of the required thickness. This frame not only prevented adhesive leakage but also generated lateral hydrostatic pressure during pressing, ensuring uniform consolidation and defining the final sheet dimensions. The overall sheet dimensions were 155 × 70 mm, with a thickness defined by the silicone frame.

The experimental procedure was as follows:

1. Degrease the mould with acetone.
2. Apply and dry a layer of release agent (Loctite® 770-NC Frekote) to all mould components.
3. Assemble the mould cage and insert the silicone rubber frame.
4. Close the mould and place it in a hot press.
5. Apply a pressure of approximately 30 bar and cure under the specified temperature and time conditions.

The applied pressure ensured the absence of voids and a high-quality surface finish. The curing cycle for these specimens was the same as previously described for Vitrimax and AV 138. After curing, the mould was removed from the hot press, cooled to room temperature, and carefully disassembled. The bulk sheet was peeled from the metallic surface, and the silicone frame was removed.

Finally, the cured sheet was longitudinally cut into three smaller sheets, as the internal width of the frame was set to allow the production of three “dog-bone” specimens per sheet. These sheets were then machined into specimens using a CNC milling program on a HAAS® VF2 Mini (3-axis), following the British standard BS 2782 [96], achieving the final dimensions shown in Figure 3.2.

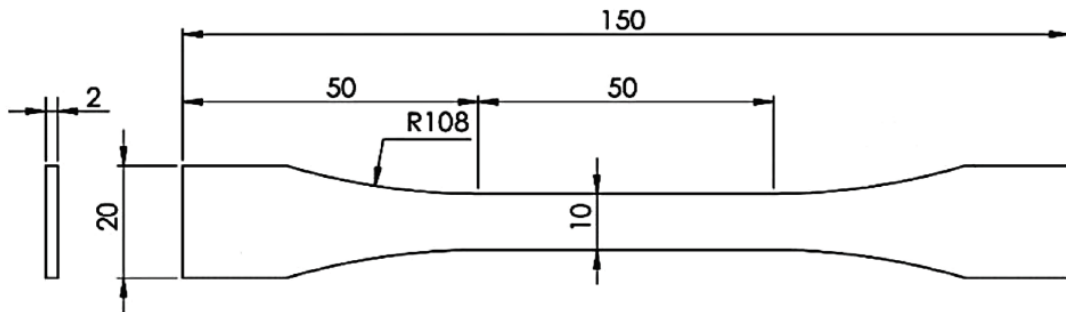


Figure 3.2: Tensile specimen geometry [mm].

3.2.2 Thick adherend shear test specimens

A specialized mould was employed to manufacture the TAST specimens, providing dimensions consistent with the ISO 11003-2 standard [97], thereby ensuring uniformity across all samples. Each specimen was designed with an adhesive overlap of approximately 5 mm, controlled by 1.5 mm-thick shim tabs ($25 \times 6.25 \times 1.5$ mm), and an overall adhesive thickness of 0.5 mm. These shims serve to both maintain the specified overlap and minimize the occurrence of tensile stresses during testing. The adhesive thickness was verified by measuring the combined thickness of each pair of adherends using a caliper with 0.05 mm resolution. Figure 3.3 illustrates the TAST specimen dimensions, while Figure 3.4 shows the assembled specimens with shims.

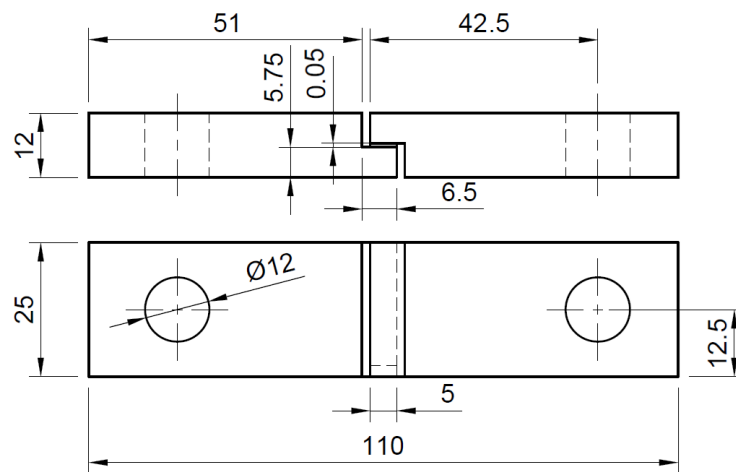


Figure 3.3: TAST specimen dimensions [mm] according ISO 11003-2 standard.

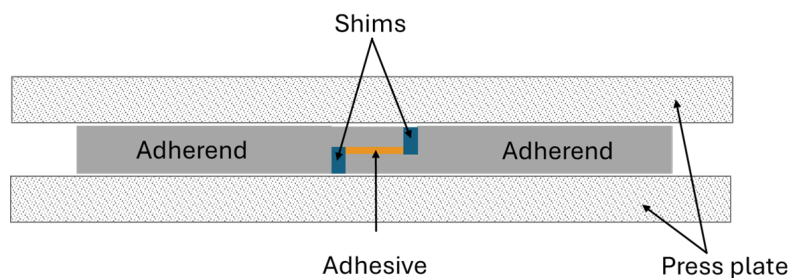


Figure 3.4: Assembly of TAST specimens + shims in the mould.

Prior to assembly, the mould and shims were thoroughly cleaned with acetone, and a release agent (Loctite® 770-NC Frekote) was applied. The adherends were also surface-treated: steel substrates, for Vitrimax, were sandblasted using brown corundum aluminium oxide F030 at 6 bar, while aluminium substrates, for T-Link, were sanded with 1000-grit sandpaper. [Figure 3.5](#) illustrates the TAST mould with the specimens correctly positioned along with the shims.

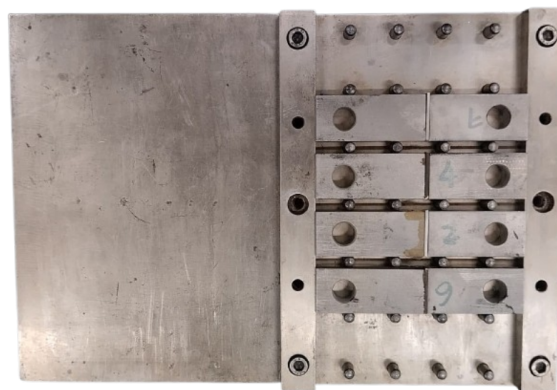


Figure 3.5: TAST specimens with shims in mould prepared to curing.

The experimental procedure for TAST specimen preparation is as follows:

1. Degrease the mould and shims with acetone.
2. Apply release agent to all mould components and shims, and allow to dry.
3. Position the bottom TAST specimens in the mould with adhesive applied to the edges.
4. Insert the top TAST specimens from the inner to the outer positions.
5. Place the bottom shims as the top specimens are positioned.
6. Insert the top shims and clean any excess adhesive.
7. Close the mould and cure in a hot press or thermal chamber under the specified temperature, pressure, and time conditions.

After curing, the top metal cover of the mould was removed, and the TAST specimens were carefully extracted. The shims were gently withdrawn to avoid inducing any damage to the specimens, and any excess adhesive along the edges was trimmed. Finally, the specimens were coated with white matte paint and speckled with black paint to enable Digital Image Correlation (DIC) analysis during mechanical testing.

3.2.3 Double cantilever beam test specimens

The DCB tests were performed in accordance with the ISO 25217 standard [98], based on pure crack opening in Mode I, with the objective of characterizing the fracture toughness in this loading mode. The specimens consisted of two high-strength DIN 40 CrMnMo 8-6-4 steel bars and Al 6082-T6 adherends. A thin adhesive layer was applied between the adherends, with the final geometry and dimensions shown in Figure 3.6, where t represents the adhesive thickness and a the initial crack length. Particular care was taken to ensure that the substrates remained flat and free from bends or undulations, especially when handling film adhesives.

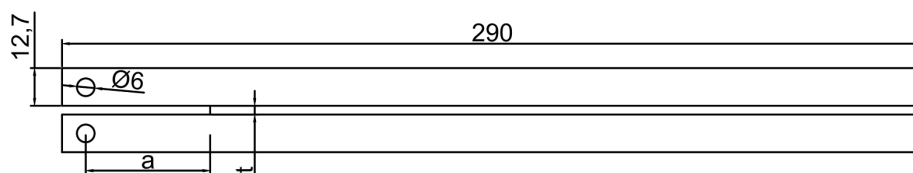


Figure 3.6: Dimensions [mm] for the standard DCB specimen [98].

The DCB specimens were prepared using the following steps:

1. Adherend preparation: steel adherends (Vitrimax and T-Link) were sandblasted, and aluminium adherends (T-Link) were sanded, followed by cleaning with acetone to remove contaminants.
2. Initial crack definition: a 0.10 mm-thick razor blade was used to establish the initial crack length ($a_0 = 45$ mm). Two 0.05 mm calibrated tape strips were attached to either side of the blade to maintain a uniform adhesive thickness of 0.20 mm. The razor-tape assembly was coated with release agent for easy removal post-curing.
3. Mould preparation: the mould, equipped with guiding pins, was cleaned and coated with release agent, including the razor-tape assembly and calibrated tape, then allowed to dry.
4. Placement of bottom adherends and adhesive application: the prepared bottom adherends were positioned in the mould, and a thin, uniform layer of adhesive was applied to their bonding surfaces using a clean spatula.
5. Placement of top adherends and end tape: a thin layer of adhesive was applied to the upper adherends, which were then carefully positioned over the lower adherends with slight hand pressure to ensure proper contact. The razor-tape assembly was inserted in the overlap to generate the predefined crack, and a 0.20 mm calibrated ribbon was placed at the specimen ends to maintain consistent adhesive thickness.
6. Mould closure: moderate pressure was applied to allow excess adhesive to flow out, and the mould was securely closed.
7. Curing: the mould was placed in a hot press or thermal chamber and cured under the specified temperature, pressure, and duration.

After curing, two blocks ($20 \times 20 \times 20$ mm) were bonded to the substrates using a two-component epoxy. Prior to bonding, the blocks were sandblasted and cleaned with acetone, and the substrates were sanded to ensure proper adhesion. These blocks serve to facilitate gripping during testing and ensure proper load transfer, as shown in Figure 3.7.

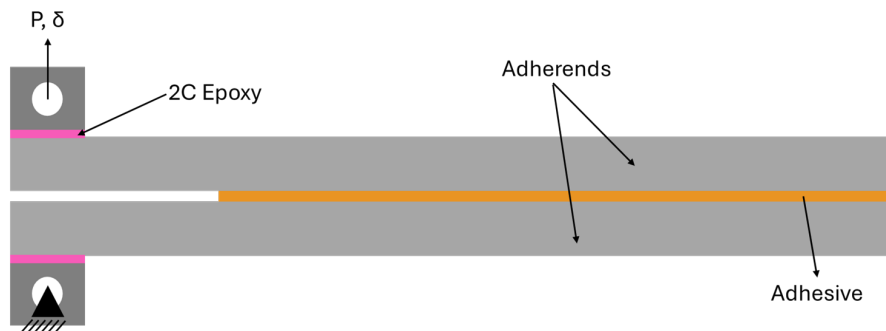


Figure 3.7: Representation of the DCB specimen with loading blocks.

3.2.4 Compact test specimens

The compact tension (CT) tests were conducted in accordance with the ASTM D5045-14 standard [99]. Specimens were manufactured from plates produced according to the French NF T 76-142 standard, using the same processing route previously described for adhesive casting. Silicone frames were cut to dimensions of 165×70 mm and were used to control plate thickness during fabrication. Two different thicknesses were obtained (2 mm and 4 mm) by employing silicone frames of varying thickness.

After curing, each plate was cut transversally and subsequently machined to the standardized geometry and dimensions required for CT testing using a HAAS® VF2 Mini CNC milling machine, as illustrated in Figure 3.8.

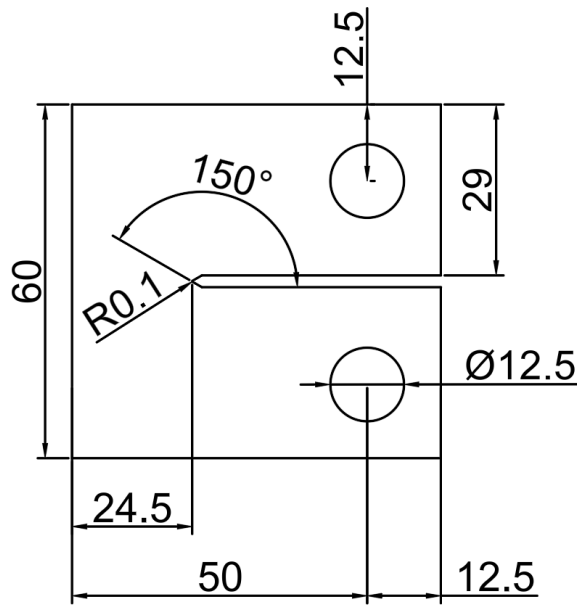


Figure 3.8: CT specimen dimensions [mm] according to the ASTM D5045-14 standard.

The fracture initiation process was performed in two stages. First, the notch length was measured with a caliper to set the initial reference. Then, a sharp blade was used to introduce a rough notch, and a razor blade was subsequently employed to refine the crack tip and produce a sharp pre-crack. The final crack length was verified using an Emspira 3 digital microscope to ensure compliance with the required dimensional precision. Figure 3.9 presents the microscope images of the notch after refinement of the crack tip.

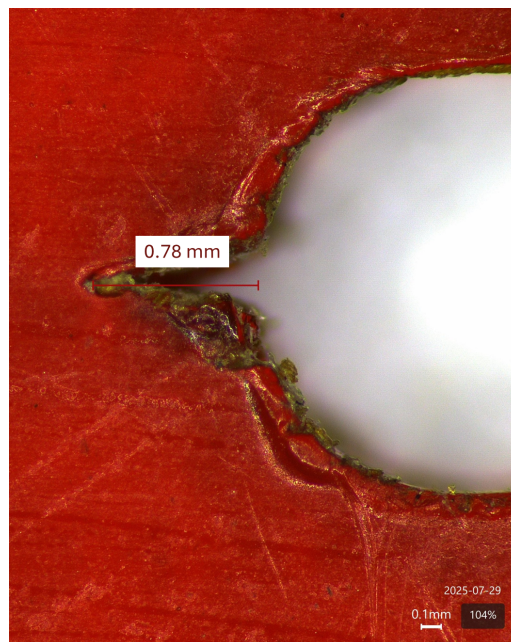


Figure 3.9: Refined crack tip of the CT specimen under microscope ($a_0 = 0.78$ mm).

The CT specimen preparation is summarized in the following steps:

1. Plate casting: Adhesive plates were produced according to NF T 76-142 using silicone frames cut to 165×70 mm. The frame thickness was selected to obtain either 2 mm or 4 mm plates.
2. Sectioning: After curing, each plate was cut transversally into two sections. At this stage, only the external dimensions were defined, leaving the internal geometry to be finished during machining.
3. Machining: Each section was then machined to the final CT geometry.
4. Notch preparation: The notch length was first measured with a caliper. A rough notch was introduced with a sharp blade, followed by refinement with a razor blade to produce a sharp pre-crack. Both operations required constant monitoring under the microscope to ensure accurate positioning and geometry of the crack.
5. Crack verification and cleaning: The final crack length was measured with the digital microscope, and the specimens were cleaned with acetone prior to testing.

3.2.5 Creep specimens

To ensure good repeatability of the results, three tests were performed for each adhesive. Bulk plates were manufactured following the same process described in previous sections, with a thickness of 0.5 mm. For the T-Link samples, the thickness was the same as that of the film. The samples were then cut to their final dimensions using a blade, and the final measurements were

taken with a caliper (Figure 3.10). Since the width of each sample varied, it was not represented in the figure. Figure 3.11 shows the final bulk plates and the cut samples for Vitrimax and AV 138. T-Link samples, in contrast, were cut directly from the film.

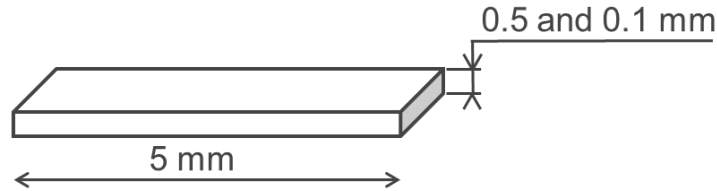


Figure 3.10: Creep specimens geometry [mm].



Figure 3.11: Bulk plates cut of Vitrimax (left) and AV 138 (right).

3.2.6 SLJ specimens

To evaluate re-adhesion and the influence of temperature on joint behaviour, additional SLJs were produced using duplex stainless steel substrates with a thickness of 2 mm, a length of 107.5 mm, and an overlap of 12.5 mm (see Figure 3.12). Prior to adhesive application, the substrates were sandblasted and cleaned with acetone to ensure proper surface preparation.

The SLJ tests were performed under two conditions, with and without temperature. In the first case, a temperature of $50\%T_g$ was applied to evaluate the joint strength and correlate the results with the creep behaviour. In the second case, the SLJs were tested at room temperature (RT) to assess the joint strength after several re-adhesion cycles. For this condition, SLJ specimens of Vitrimax were produced with adhesive thicknesses of 0.1 mm and 0.5 mm; in the 0.5 mm specimens, the thickness was reduced by 0.1 mm after each re-bond to ensure proper adhesion. For T-Link, SLJ specimens were manufactured at the original adhesive thickness using the hot press method described in subsection 3.1.2.

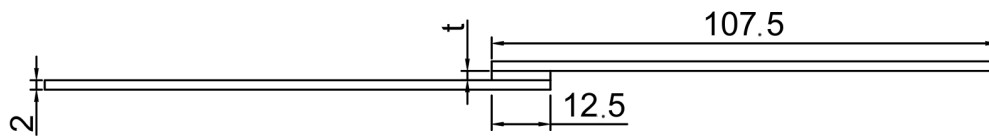


Figure 3.12: SLJ geometry for 12 [mm] of overlap length.

The manufacture of the specimens is described in the following steps:

1. The adhesive application and specimen assembly were carried out as follows:
2. Clean the aluminium mould and spacers with acetone, then apply a layer of release agent.
3. Adjust the mould length using the bottom screws, if applicable.
4. Position the lower substrates in the mould and apply adhesive to their bonding surfaces.
5. Coat the upper substrates with a thin adhesive layer and carefully place them onto the lower substrates, ensuring proper alignment (see [Figure 3.13](#)).
6. Close the assembly with the upper part of the mould.
7. Insert the mould into a hot press and cure the adhesive under the specified temperature and pressure conditions.

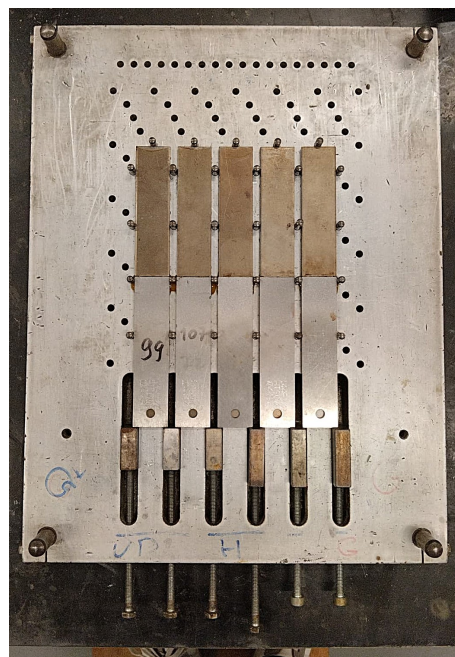


Figure 3.13: Manufacturing in the SLJ specimens.

Chapter 4

Results

This section provides an overview of the testing setup and presents the results of the mechanical characterization, creep, and single-lap joint (SLJ) tests. The results reported in the appended paper are summarized for each test, while additional results generated in this study are also presented and discussed.

4.1 Mechanical characterization

4.1.1 Bulk tests

Bulk tensile tests were performed at room temperature (20 °C) under quasi-static conditions, using a displacement rate of 1 mm/min, in an INSTRON® 3367 testing machine (Illinois Tool Works, Hopkinton, MA, USA). Special hand-tight tethers were used to grip the specimen edges, and block claws were employed to secure the specimens, as shown in [Figure 4.1](#).

To enable Digital Image Correlation (DIC), a Nikon® D5300 digital camera equipped with a Canon EF-M 18–55 mm f/3.5–5.6 lens was mounted on a tripod, levelled, and aligned as close as possible to the specimen normal. A LED light source was used to ensure homogeneous illumination, with its distance adjusted by monitoring the luminosity of the specimen on the camera. Since photographs provide higher quality for DIC analysis compared to continuous video, the camera was programmed to capture one image per second. Before starting the test, the machine displacement was balanced, and synchronization between the camera and the testing machine was verified.



Figure 4.1: Tensile Bulk test setup.

Load–displacement curves were recorded throughout all tests, while the images acquired during testing were processed using GOM Correlate®.

Engineering stress was calculated as the applied load divided by the initial cross-sectional area of the specimen, while engineering strain was obtained by dividing the displacement measured via DIC by the original gauge length, L_0 , as shown in Equation 4.1.

$$\varepsilon = \frac{\Delta L}{L_0} \quad (4.1)$$

From the strain results obtained by DIC, both longitudinal and transverse strains were extracted. The Poisson's ratio, ν , was then estimated using Equation 4.2, where $\varepsilon_{\text{longitudinal}}$ corresponds to the strain in the loading direction and $\varepsilon_{\text{transverse}}$ corresponds to the strain perpendicular to it:

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

For T-Link, tests were also performed at a higher displacement rate of 10 mm/min and compared with those at 1 mm/min. As shown in Figure 4.2, the load–displacement curves reveal that the higher rate leads to greater strain to failure, while the maximum stress increases only slightly. This contrasts with the typical behavior of thermoplastics, where higher strain rates usually result in reduced ductility. Similar observations have nevertheless been reported in the literature,

including the works of Mian et al. [100], Fatemi et al. [101] and Cidlina et. al [102]. A likely reason for this deviation is thermal softening: at higher strain rates, internal friction within the polymer chains generates localized heating, which elevates the material's temperature and softens the polymer. This softening enhances ductility and allows greater elongation before failure.

In addition, since the specimens were cut directly from sheets without thermal conditioning, residual manufacturing effects may have influenced the response, contributing to the high scatter in results. This suggests that the observed behaviour may differ if tests are performed on bulk plate samples.

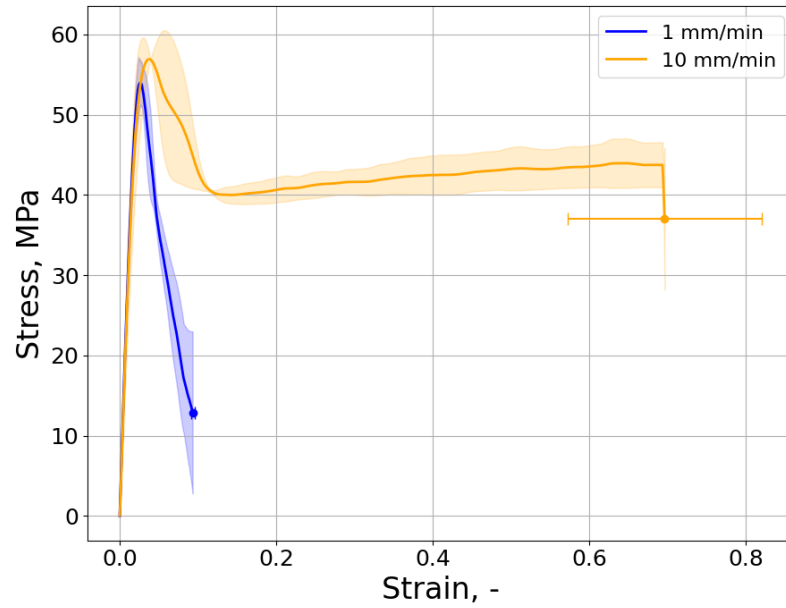


Figure 4.2: Load-displacement curve of T-Link for strain rates of 1 mm/min and 10 mm/min.

Table 4.1 presents the average values of Young's modulus, tensile strength, and tensile strain at failure, as reported in the appended paper in the section B.2.3.1. The Poisson's coefficient for the AV 138 adhesive was obtained from the TAST tests, as described in the next section.

Table 4.1: Tensile properties of T-Link, Vitrimax, and AV 138 adhesives.

Property	Units	T-Link	Vitrimax	AV 138
Young's modulus, E	MPa	2878 ± 78	1992 ± 51	4615 ± 240
Poisson's ratio, ν	—	0.37 ± 0.01	0.40 ± 0.02	0.48 ± 0.03
Tensile strength, σ_f	MPa	56.8 ± 0.6	48.7 ± 0.5	47.6 ± 1.7
Tensile strain to failure, ϵ_f	%	9.3 ± 0.4	15.2 ± 0.8	1.42 ± 0.16

4.1.2 Thick Adherend Shear Test

The strain field in the thick adherend shear test was measured using two different techniques depending on the adhesive type. For T-Link, a film adhesive, Digital Image Correlation (DIC) was employed. Since film adhesives are generally more sensitive to local strain gradients and stress concentrations, DIC provided a more accurate and detailed characterization of the strain distribution across the joint. For Vitrimax, a paste adhesive with higher tolerance to deformation irregularities, an extensometer (2630-100 Series, Instron, Norwood, MA, USA) was used. The use of DIC was not required for Vitrimax, as it demands precise camera alignment and can be affected by specimen rotation, potentially compromising measurement accuracy. In fact, a tilting phenomenon may occur, where a small portion of the overlap fractures before the rest of the bonded joint, inducing an undesired rotation in the TAST specimen and affecting strain measurement precision.

The measured shear modulus, shear strength, and shear strain to failure for the adhesives obtained in [section B.2.3.1](#) are summarized in [Table 4.2](#), providing a comparative assessment of their mechanical performance under thick adherend shear conditions.

Table 4.2: Shear properties of T-Link, Vitrimax and AV 138 adhesives.

Property	Units	T-Link	Vitrimax	AV 138
Shear modulus, G	MPa	191	462 ± 5.0	1560 ± 35
Shear strength, τ_f	MPa	27.9	28.5 ± 0.3	32.9 ± 0.9
Shear strain to failure, γ_f	%	53	110 ± 10.0	5.0 ± 1.0

To relate the measured shear modulus, G , to the bulk elastic properties of the adhesive, the Poisson's ratio, ν , can be estimated for isotropic materials using the following relation:

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

where E is the Young's modulus obtained from the bulk tensile tests and G is the measured shear modulus. This provides a consistency check between shear and tensile measurements.

Table 4.3: Comparison of Poisson's ratios of T-Link and Vitrimax from bulk and TAST tests.

Material	Bulk Test (ν)	TAST Test (ν)	Relative Error (%)
T-Link	0.37	0.76	105.4
Vitrimax	0.40	0.31	22.5

Using the relation between Young's modulus and shear modulus for isotropic materials ([Equation 4.3](#)), the relative error between the TAST and bulk test results was acceptable for Vitrimax, whereas for T-Link it was extremely high and physically unrealistic, since the Poisson's ratio of an

isotropic material cannot exceed 0.5. Therefore, T-Link was used only to determine the maximum shear strength.

4.1.3 Double cantilever beam test

The double cantilever beam (DCB) specimens were tested using an INSTRON[®] 3367 universal testing machine, equipped with a load cell of appropriate capacity to ensure accurate force measurement, at a crosshead speed of 0.2 mm/min. The specimens were mounted in specially designed supports, which were connected to the machine using stiff steel pins in order to guarantee precise load transfer and to minimize undesired rotation or misalignment during testing.

To evaluate the fracture toughness of the adhesives, the mode I critical strain energy release rate (G_{Ic}) was calculated using the Compliance Based Beam Method (CBBM) [103]. This method has become widely adopted in adhesive joint characterization due to its robustness and reliability. Unlike traditional approaches that require direct optical monitoring of crack propagation, CBBM eliminates the need for instantaneous crack length measurement, which is often difficult to measure accurately because the crack front is not always easy to see clearly in the adhesive layer or may not propagate in a perfectly straight line. Instead, the method introduces the concept of an equivalent crack length (a_{eq}), which is inferred directly from the specimen compliance. This ensures that all non-linear effects associated with crack growth and plasticity at the crack tip are inherently taken into account, providing a more consistent estimation of fracture energy.

The resistance curve (R-curve) was constructed using only the load–displacement (P – δ) data recorded during testing, enabling the evolution of G_{Ic} to be tracked throughout crack extension. This approach not only reduces experimental uncertainties but also makes the methodology more accessible, as no external instrumentation such as clip gauges, cameras, or extensometers are required.

The critical strain energy release rate is determined from the following expression:

$$G_{Ic} = \frac{6P^2}{B^2t} \frac{2a_{eq}^2}{E_f t^2} + \frac{1}{5G} \quad (4.4)$$

where B and t represent the adherend width and thickness, E_f is the corrected flexural modulus, P is the applied load, G is the shear modulus of the adhesive, and a_{eq} is the equivalent crack length approximating the actual crack front position a .

In the case of T-Link bonded to aluminium substrates, the DCB specimens exhibited interfacial failure, as shown in Figure 4.3. This failure mode, attributed to insufficient adhesion between the adhesive and the substrate, resulted in unreliable fracture energy measurements. From the R-curve in Figure 4.5, the fracture energy was determined as 0.39 ± 0.085 N/mm; however, this value cannot be considered accurate due to the interfacial debonding. To address this issue, the appended Paper shows the results of a complementary study that was conducted within the group using sandblasted steel substrates. The change of adherend material improved the adhesion quality and, although the failure mode was still mixed, it enabled a more reliable evaluation of the fracture energy.

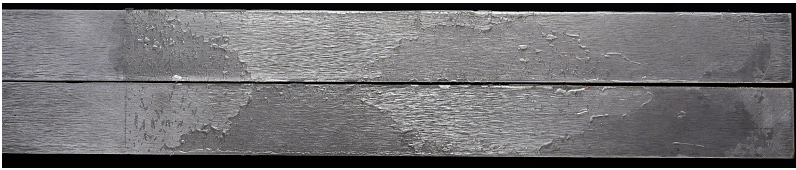


Figure 4.3: Failure mode for DCB specimens of T-Link.

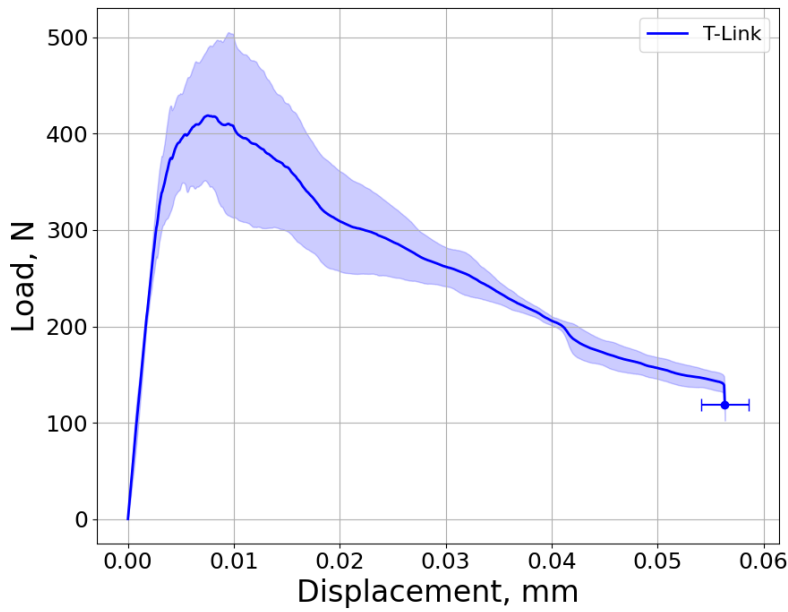


Figure 4.4: Load–displacement curves from the DCB test of T-Link.

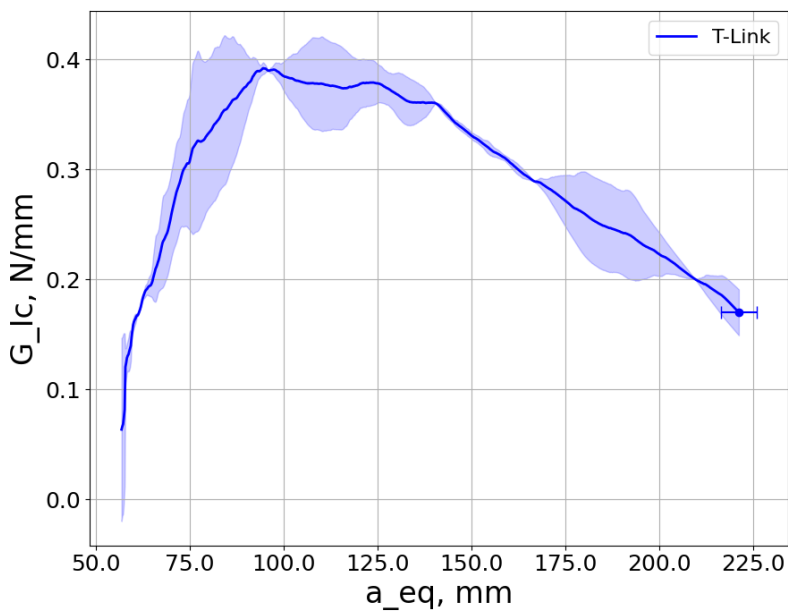


Figure 4.5: R-curve on aluminium substrates for T-Link, illustrating crack growth resistance.

The Table 4.4 summarizes the fracture energy values considered in this study.

Table 4.4: Fracture energy release rate in Mode I.

Property	Units	T-Link	Vitrimax	AV 138
Fracture energy in Mode I, G_{Ic}	N/mm	2.3	0.4 ± 0.06	0.37 ± 0.04

4.1.4 Compact test

This test allows the determination of the plane-strain fracture toughness, K_{Ic} , a parameter indicative of the resistance of a material to fracture, and the critical strain energy release rate, G_{Ic} , a parameter based on the energy required to propagate a crack [99].

The specimens were secured to the testing machine using steel pins, and to prevent bending, thick tabs were 3D-printed. The assembly configuration is shown in Figure 4.6.

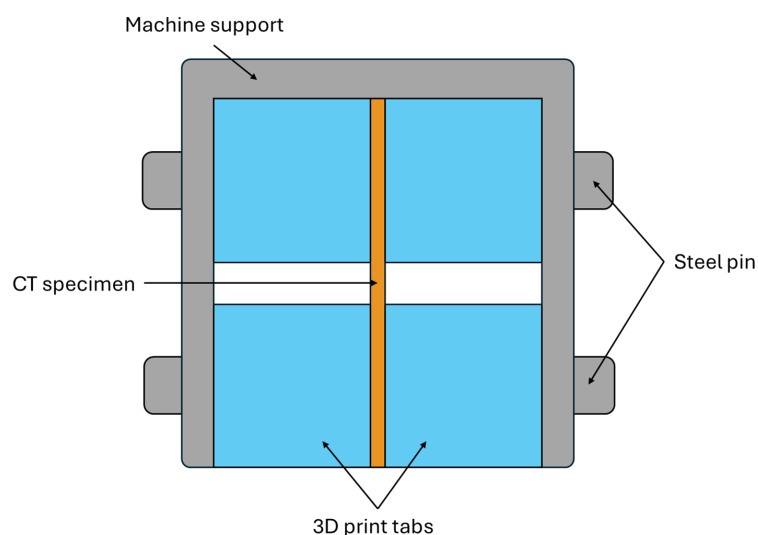


Figure 4.6: CT configuration.

During testing, the specimens were continuously observed to ensure proper execution and to identify potential anomalies. To support this, a LED light source was positioned to provide homogeneous illumination, and images were captured at 5-second intervals instead of recording continuous video. An example of the captured images is shown in Figure 4.7.



Figure 4.7: Fracture propagation during test.

The final values of the critical strain energy release rate, G_{Ic} , obtained from the tests are summarized in Table 4.5.

Table 4.5: Critical strain energy release rate in Mode I.

Property	Units	Vitrimax
Critical strain energy release rate, G_{Ic}	N/mm	3.39 ± 0.12

4.2 Creep tests

The creep tests were carried out on a DMA Triton 2000 equipped with a 10 N load cell, under constant force. The applied load corresponded to 3% of the maximum stress of each adhesive, using specimens with 5 mm length and 0.5 mm thickness. Tests were performed at a frequency of 1 Hz, following a two-step temperature protocol: a first stage at $50\%T_g - 5^\circ\text{C}$, used as a pre-conditioning step, and a second stage at $50\%T_g$. A heating rate of $5^\circ\text{C}/\text{min}$ was used to reach each test temperature.

Regarding the adhesive performance, in Figure 4.8 T-Link was unable to withstand the applied conditions, losing structural integrity shortly after the beginning of the test and entering a rubbery state, which invalidated the results. In contrast, both the AV 138 and the Vitrimax showed stable behaviour during the first stage, with low deformation and the establishment of a plateau. At the higher temperature, AV 138 remained stable, although with higher overall deformation. Vitrimax also resisted creep under these conditions, but without reaching a clear plateau, suggesting that this temperature represents the upper limit at which the adhesive maintains effective creep resistance.

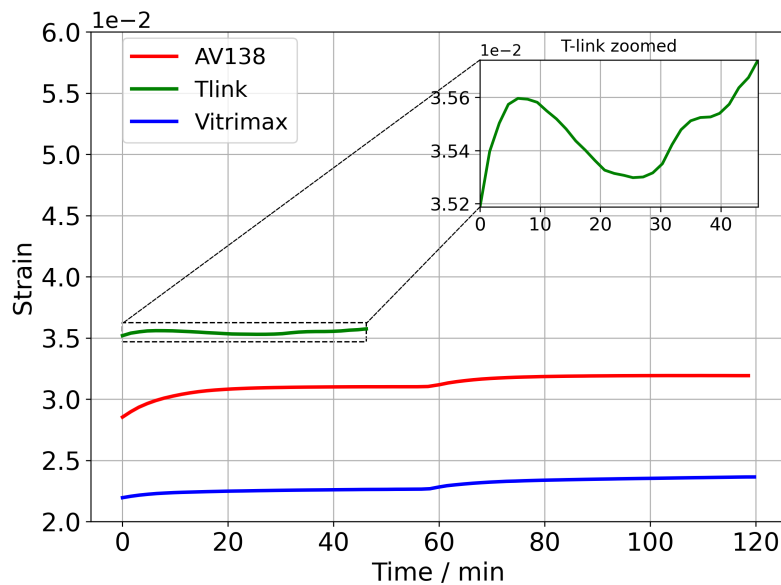


Figure 4.8: Creep results after 2 hours for T-Link, Vitrimax and AV 138.

4.3 Single Lap joint tests

The specimens were clamped in grips and aligned using steel pins. This assembly was then fixed to the machine supports, also with pins. To ensure proper alignment and to compensate for the thickness introduced by the overlap region, tabs were bonded to the substrates. For the tests conducted with temperature, a hot chamber was used, in which each sample was kept for 10 minutes to guarantee uniform heating. The complete setup is shown in Figure 4.9.

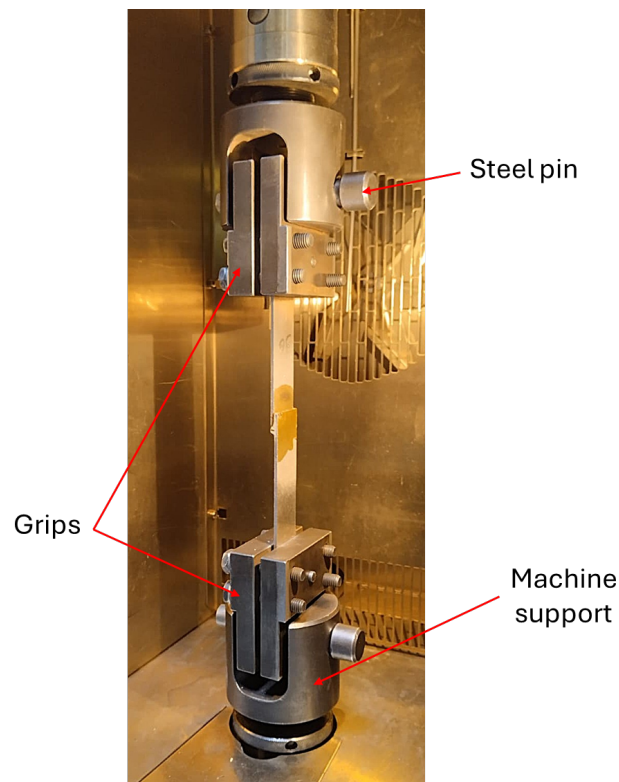


Figure 4.9: Setup used for SLJ tests.

4.3.1 Temperature effects

SLJ tests were performed at the same temperature as the creep tests to capture how the joint behaves under the thermal conditions that affect creep, ensuring the strength results are consistent with the creep test conditions.

Figure 4.10 to Figure 4.12 show the results for the three adhesives for $50\%T_g$. In both Vitrimax and T-Link there was a decrease in the load as it was expected. In AV 138 the behaviour remained the same which was expected, since it's an adhesive resistant up to 140°C [104].

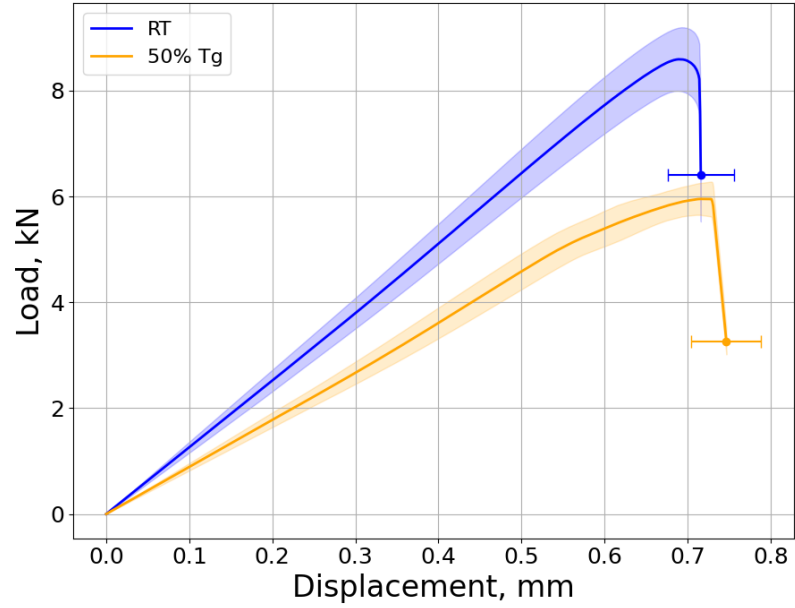


Figure 4.10: Load-displacement of T-Link SLJs tested at 50% T_g .

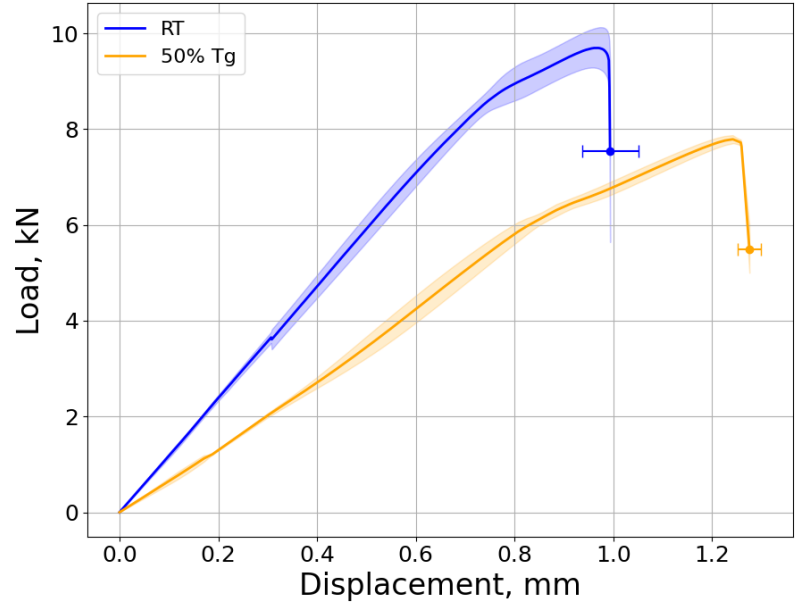


Figure 4.11: Load-displacement of Vitrimax SLJs tested at 50% T_g .

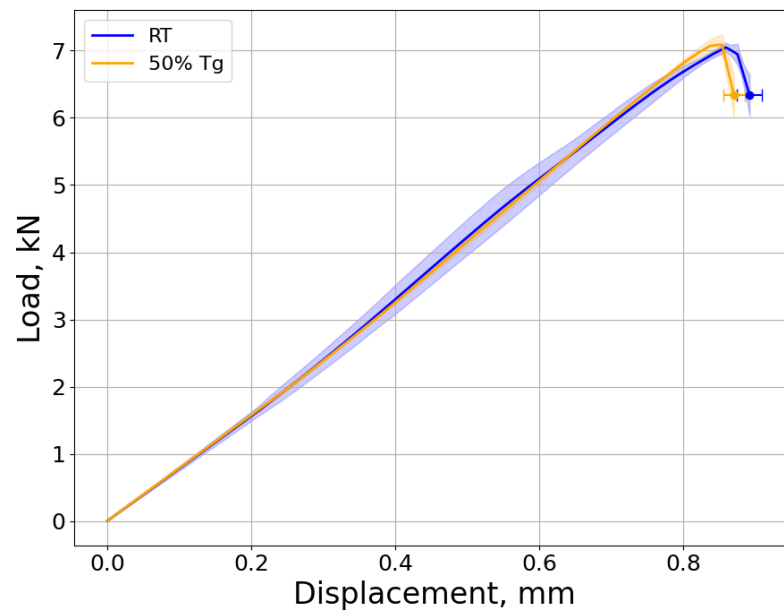


Figure 4.12: Load-displacement of AV 138 SLJs tested at 50% T_g .

4.3.2 Re-adhesion

Figure 4.13 to Figure 4.15 present the average curves obtained for each rebond cycle of T-Link, and for Vitrimax with adhesive layer thicknesses of 0.1 mm and 0.5 mm, respectively. For clarity, these graphs display the results individually. However, in the appended Paper, the values are presented in percentage form to facilitate interpretation and comparison between different conditions.

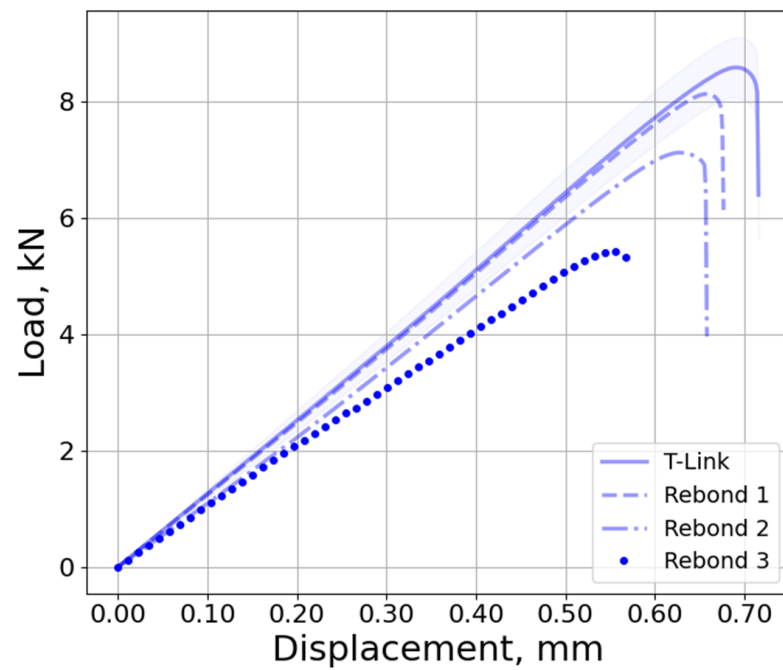


Figure 4.13: Load-displacement curve of T-Link SLJ during re-adhesion.

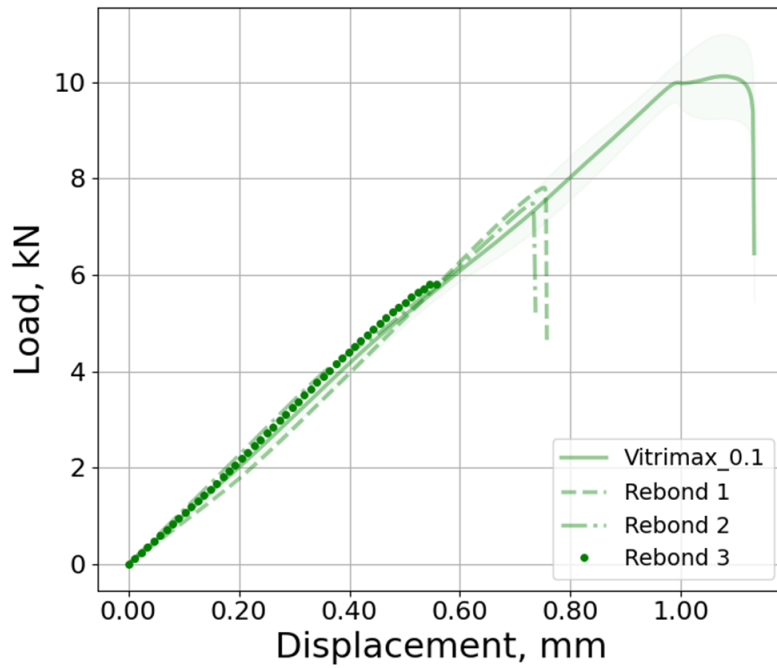


Figure 4.14: Load-displacement curve of Vitrimax SLJ with 0.1 thickness during re-adhesion.

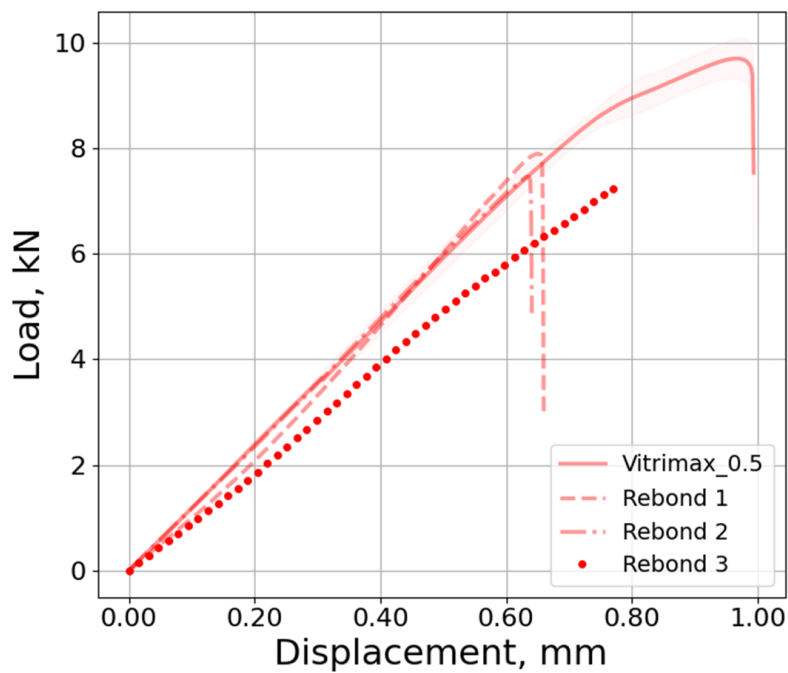


Figure 4.15: Load-displacement curve of Vitrimax with 0.5 thickness during re-adhesion.

Figure 4.16 shows the failure modes observed for both adhesives across all cases. From the initial test up to the third rebond, the failure mode remained consistent: mixed failure for T-Link and interfacial failure for Vitrimax.

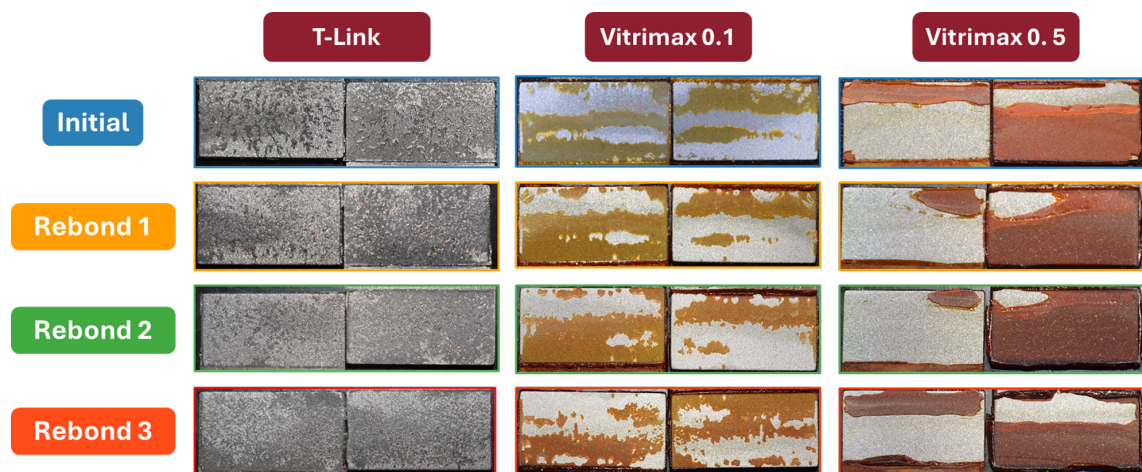


Figure 4.16: Failure mode for T-Link and Vitrimax in each cycle.

Chapter 5

Summary of the appended documents

CLBA Conference - Repair and end of life strategies for ecofriendly adhesive bonded joints

This thesis resulted in participation in the 6ª Conferência Luso-Brasileira de Adesão e adesivos (CLBA2024), held on December 12–13, 2024, where a bibliographic review on vitrimers was presented. The first part of the work outlined the state of the art, covering their advantages, external stimuli, bonding strategies, and the current limitations of bio-based vitrimers. The second part focused on the experimental procedure for the V_{DER332} adhesive and the results of mechanical and thermal tests, with particular emphasis on its rebonding ability. While the adhesive performance proved modest compared to conventional adhesives, the tests confirmed its recyclability. Future work will focus on optimizing the production process to enhance its practical applicability.

Paper - Mechanical Performance of Vitrimer, Thermoplastic, and Epoxy Adhesives: A Comparative Study

This paper presents a comprehensive investigation into the mechanical properties of a vitrimer adhesive (Vitrimax VHM), with its performance benchmarked against a thermoplastic adhesive (T-Link) and a conventional epoxy (AV 138). The study focuses on quasi-static conditions and employs a range of mechanical characterization techniques. To begin, bulk tensile tests are conducted to obtain stress–strain data and evaluate elastic properties, including Poisson’s ratio. The shear stiffness and strength of the adhesives are then assessed through thick adherend shear tests, using both extensometer and digital image correlation depending on the adhesive type. Fracture toughness was assessed through compact tension and double-cantilever beam tests, allowing determination of the critical energy release rate, G_{Ic} . In addition, creep tests and single lap joints are performed below the glass transition temperature T_g to study the long-term deformation response of the adhesives and the joint strength, respectively. Finally, the recyclability of the vitrimer is examined through single lap joint tests, where specimens are re-bonded and re-tested over multiple cycles to assess re-adhesion capability. By combining these complementary experimental approaches, this study provides a detailed understanding of the mechanical, fracture, and time-dependent behaviour of vitrimers, offering insights into their potential application as sustainable alternatives to conventional structural adhesives.

Chapter 6

Conclusion

This thesis presents the mechanical characterization of Vitrimax VHM, a commercial vitrimer adhesive, benchmarked against a conventional epoxy (AV 138) and a thermoplastic adhesive (T-Link). The study covered bulk tests, shear and fracture characterization, creep evaluation, and joint-level performance, providing insights into the potential of vitrimers as structural adhesives.

Bulk tensile tests demonstrated that Vitrimax exhibits tensile strength comparable to AV 138 but with significantly greater ductility, a result of its lower crosslink density and dynamic covalent network. While AV 138 showed higher stiffness, its limited strain capacity contrasted with the ability of Vitrimax to sustain large deformations, making it more suitable for applications requiring energy dissipation and toughness. T-Link presented the highest stiffness and tensile strength, though these values are provisional due to its manufacturing history and lack of thermal pre-conditioning. In addition, strain-rate sensitivity tests showed that T-Link displayed greater strain to failure at higher displacement rates, a behaviour contrary to typical thermoplastics, likely thermal softening.

In shear, Vitrimax displayed a moderate modulus and strength similar to T-Link, but its exceptional ductility set it apart, allowing it to accommodate large deformations and dissipate energy effectively prior to failure. Fracture characterisation further reinforced this behaviour. DCB tests on both Vitrimax and T-Link generally resulted in interfacial failures, though in the case of T-Link, more reliable results were obtained when tested on steel substrates. CT tests, which eliminate substrate influence, highlighted the intrinsic toughness of Vitrimax, with high G_{Ic} values confirming its ability to undergo significant energy dissipation before fracture.

Creep tests performed over short durations further illustrated the advantages of Vitrimax's dynamic covalent network. While AV 138 maintained greater dimensional stability due to its permanent crosslinks, Vitrimax resisted creep effectively, balancing structural stability with adaptability. T-Link, however, rapidly entered a rubbery state and lost dimensional stability under similar conditions, confirming its unsuitability for long-term creep resistance.

In SLJ tests at 50% of the T_g , the vitrimer showed intermediate performance between the epoxy and thermoplastic. While it lost some strength compared to room temperature, its dynamic covalent network enabled partial stress redistribution, preventing the sharp drop observed in the

thermoplastic. This indicates that vitrimers can retain good joint performance under moderate thermal loading, offering a balance between stability and adaptability.

Re-bonding experiments using single lap joints showed that Vitrimax retained a higher proportion of its initial strength over multiple cycles compared to T-Link, particularly when applied in thicker layers. While both adhesives experienced some reduction in performance due to material degradation and adhesive loss, Vitrimax maintained substantial residual strength after repeated cycles, underscoring its potential for reuse and its suitability for recyclable structural applications.

This thesis shows that Vitrimax stands out as a next-generation structural adhesive by combining three key advantages rarely achieved together. First, it exhibits superior creep resistance compared to conventional thermoset adhesives like AV 138, making it highly reliable under long-term loading. Second, it maintains excellent mechanical properties, including high ductility and fracture toughness below its glass transition temperature. Finally, its dynamic covalent network allows reprocessing and recyclability, offering a sustainable alternative to permanent adhesives. Together, these features position Vitrimax as an ideal adhesive for applications demanding both durability and environmental responsibility.

Chapter 7

Future work

Future studies could focus on improving the quality of T-Link bulk specimens by producing plates under vacuum, in order to avoid bubble formation, and by performing complementary analyses to verify whether any volatile components vaporise at certain temperatures. It would also be valuable to extend creep tests to longer durations and under different conditions, as well as to carry out creep recovery experiments to better distinguish between recoverable and permanent deformation.

For the Vitrimax, stress-relaxation tests should be conducted to determine the T_v , which is a distinctive property of this material. Additionally, strategies to enhance adhesion, such as the use of primers or surface treatments, could be explored to improve joint performance and reliability.

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Appendix A

Abstract - CLBA conference

Repair and end of life strategies for ecofriendly adhesive bonded joints

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Abstract: Adhesives have become essential in various industries, with increasing demand for sustainability while retaining high-performance properties. Vitrimers offer a promising solution, combining the robust mechanical characteristics of thermosets with the reusability of thermoplastics. Through reversible exchange reactions, such as transesterification, vitrimers enable dynamic covalent bonding, allowing for topological rearrangements without affecting the overall cross-link density. In this study, a vitrimer was synthesized using DGEBA (epoxy), sebacic acid, and zinc acetylacetonate. Three samples were prepared, each containing the same quantities of these materials, with the only variable being the solvent used. The first sample had no solvent, the second used acetone, and the third contained ethanol and water to dissolve Zn and SA. Using the third sample, test specimens were fabricated to conduct differential scanning calorimetry (DSC) and tensile tests. However, the adhesive performance was low compared to other adhesives. Another test involved heating two specimens to the reaction temperature to assess whether they would retain adhesion after cooling. The outcome was a rigid vitrimer that could not be separated, demonstrating its recyclability. To enhance performance, future work will focus on optimizing the vitrimer production process to develop a more practical adhesive, with adjustments to solvent concentrations and reaction temperature for improved properties.

Appendix B

Paper

Mechanical Performance of Vitrimer, Thermoplastic, and Epoxy Adhesives: A Comparative Study

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Abstract: With the development of adhesives and their growing use in industry, the concern for employing recyclable and bio-based materials has been steadily increasing. This issue becomes even more critical in structural applications, where material and adhesive waste can result in significant losses and elevated costs. Some debonding solutions have been proposed, such as the use of heat, chemicals, or even the incorporation of thermally expandable particles; however, these approaches are not always the most efficient. In this study, the mechanical characterization of a commercial vitrimer, Vitrimax VHM, was performed under quasi-static conditions, and its properties were compared with those of a thermoplastic (T-Link) and an epoxy (AV 138). The characterization included the evaluation of tensile, shear, and fracture energy properties. In addition, creep tests were carried out to assess the performance of the vitrimer under conditions below its glass transition temperature (T_g). For a more comprehensive analysis, the same tests were also conducted on the other adhesives. Finally, to investigate the recyclability of the vitrimer, single lap joint (SLJ) tests were performed. After the initial tests, the specimens were re-bonded and tested again to evaluate re-adhesion capability. This study provides insight into whether vitrimers can be applied in structural contexts and offers an outlook on potential applications where they may replace conventional adhesives.

Keywords: Vitrimer, re-adhesion, thermoplastic, recyclable, dynamic covalent bonds

B.1 Introduction

The use of adhesives has been expanding rapidly, particularly in the automotive, electronics, aerospace, and marine industries [1, 2]. In contrast to conventional joining methods such as riveting or welding, adhesive bonding enables the joining of dissimilar materials while ensuring a more uniform stress distribution. It also offers greater flexibility in joint design and contributes to lighter structures with reduced energy consumption [1, 3]. Among adhesives, thermosets, especially epoxy-based systems, are the most widely used in demanding applications due to their excellent mechanical performance, chemical and thermal stability, and resistance to creep [4–6].

However, the high demand for these adhesives has also raised some concerns. First, thermoset materials involve the use of solvents or hardeners during the curing process, which are toxic and can cause irritation, leading to health risks and environmental challenges [7, 8]. Second,

thermosets are characterized by permanent covalent bonds that form a stable three-dimensional network after curing, which prevents the material from softening or being reshaped and represents a major drawback at the end of its lifetime. As a result, thermosets are often incinerated or treated as waste and disposed of in landfills, increasing material waste and exacerbating environmental problems [6, 9].

There are already several techniques for the debonding of thermoset adhesives, including thermal (heat), chemical, electrical or magnetic methods, and the use of thermally expandable particles (TEPs) [10–12]. However, these approaches present certain drawbacks, such as poor adhesion, potential damage or contamination of the substrate, and, even when dismantling is successful, they often do not allow complete removal of the adhesive, which can hinder substrate reuse [12, 13].

To achieve a greener and more sustainable society, efforts have been made to develop adhesives that can be recycled while maintaining good mechanical properties. One approach involves the incorporation of dynamic covalent bonds into thermosets, which, when exposed to an external stimulus, soften and gain flexibility and thermal processability through bond exchange reactions that rearrange the network topology. Polymers containing dynamic bonds are known as covalent adaptable networks (CANs) and can be classified according to their exchange mechanism. The first type is CANs with a dissociative mechanism, in which a bond breaks before another forms, resulting in a temporary loss of crosslink density [4, 14]. The second type, known as vitrimers, was introduced by Leibler and his team in 2011 [15]. Vitrimers undergo associative bond exchange reactions, which do not reduce the crosslink density and preserve the network integrity of the adhesive. Since the development of the first vitrimer, in which transesterification served as the reversible exchange reaction, numerous studies have investigated other alternatives, including transimination, disulfide exchange, and boronic ester exchange [16–19].

Thermal properties play a central role in defining the behaviour of vitrimers, with the glass transition temperature (T_g) and the topology freezing temperature (T_v) being particularly important. The T_g corresponds to the temperature at which the polymer network gains sufficient mobility to exhibit flexibility, while below this temperature the material behaves as a rigid, glassy solid [20]. In contrast, T_v marks the onset of network rearrangements due to active dynamic covalent bonds and is typically determined via stress-relaxation experiments, corresponding to the temperature at which the polymer viscosity reaches 10^{12} Pa·s [21]. When $T_g < T_v$, vitrimers exhibit a glassy solid state below T_g , a rubber-like elastomeric behaviour between T_g and T_v , and viscoelastic liquid characteristics above T_v [20–22]. Understanding these transitions is critical for designing adhesives that balance dimensional stability at low temperatures with reprocessability at elevated temperatures [23].

These thermal transitions also govern time-dependent deformation and re-adhesion. Below T_g , molecular mobility is restricted and bond exchange reactions are inactive, resulting in minimal creep and high dimensional stability [24]. As temperature approaches T_v , chain mobility and bond exchange promote viscoelastic and viscoelastoplastic behaviour, while above T_v bond exchange dominates, enabling stress relaxation, welding, and re-adhesion as polymer chains interdiffuse and form new covalent connections [8, 25, 26].

Building on these features, this study mechanically characterizes a commercial vitrimer and compares its properties with a linear epoxy and a conventional thermoset. Creep tests were performed at temperatures below 50% of the T_g to assess long-term loading behaviour, and multiple rebonding cycles on single-lap joints (SLJs) at room temperature and with temperature were conducted to evaluate residual strength and reusability, contextualized with literature data.

B.2 Experimental details

B.2.1 Materials

In this study three materials were used: the Vitrimax VHM resin, a two component adhesive from Mallinda Inc.; T-Link, a thermoplastic film provided by L&L Products; and AV 138, a two component epoxy from Huntsman.

For the vitrimer, mechanical characterization included creep testing and re-bonding evaluations. Other adhesives were used as benchmarks, enabling comparisons across the three categories: thermosets, thermoplastics, and vitrimers. High-strength steel (DIN 55 Si 7, $\sigma_y = 1100$ MPa [27]) was employed as the substrate for all DCB tests. The same steel was also used for TAST tests of Vitrimax, while aluminium (Al 6082-T6, $\sigma_y = 255$ MPa) [28] was used exclusively for TAST tests of T-Link. Duplex stainless steel ($\sigma_y = 550$ MPa, according to ASTM A240 [29]) served as the substrate material for SLJ tests.

B.2.2 Specimen manufacturing and test condition

B.2.2.1 Mechanical characterization

Tensile bulk test

Bulk specimens were manufactured according to the French NF T 76-142 standard. The mould was first degreased with acetone and coated with a release agent. Sheets with overall dimensions of 150×70 mm were produced, with the thickness controlled by a 2 mm silicone rubber frame, which also prevented adhesive leakage.

The curing conditions depended on the adhesive: the vitrimer was cured in a hot press at 180°C for 45 minutes under 30 bar, while AV 138 was cured at 105°C for 1 hour and 5 minutes. For T-Link, dog-bone specimens were directly cut from the sheet using a 3D-printed template. For the vitrimer and AV 138, the sheets were divided into three parts and machined into the final dog-bone geometry (Figure B.1) using a HAAS VF2 Mini. All specimen surfaces were cleaned, coated with matte white paint, and speckled with dark paint for Digital Image Correlation (DIC) analysis.

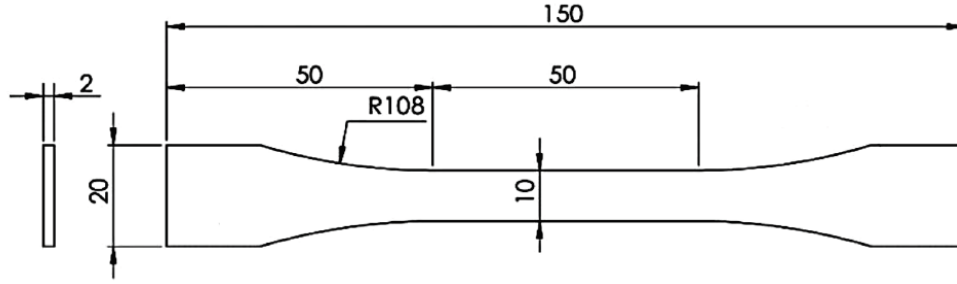


Figure B.1: Dog-bone dimensions [mm].

Bulk tensile tests were conducted at room temperature (20 °C) under quasi-static loading, using a displacement rate of 1 mm/min in an INSTRON® 3367 testing machine (Illinois Tool Works, Hopkinton, MA, USA). Load–displacement curves were recorded throughout. To correct for machine compliance, strain was measured by DIC using images captured with a Nikon® D5300 camera and processed in GOM Correlate®. Engineering stress was calculated as the applied load divided by the initial cross-sectional area, and engineering strain as the DIC-measured displacement divided by the original gauge length L_0 .

B.2.2.2 Thick adherend shear test

A dedicated mould was used to manufacture the TAST specimens, designed with a 5 mm overlap and an adhesive layer thickness of 0.5 mm, controlled by 1.5 mm shim tabs. The thickness was verified with a micrometer. The specimen dimensions followed the ISO 11003-2 standard, as shown in Figure B.2 [30].

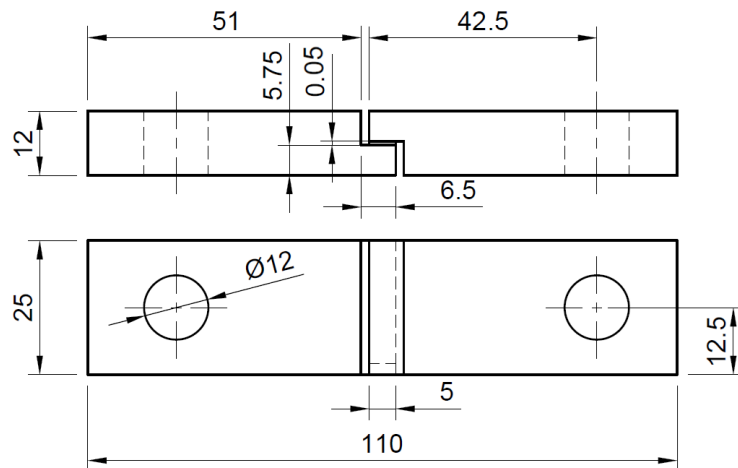


Figure B.2: TAST specimen dimensions [mm] according to ISO 11003-2 standard.

Before use, the mould was degreased with acetone and coated with a release agent. The adhesive was applied to the lower adherends, followed by the shims and upper adherends. Careful positioning of the upper shims prevented adhesive overflow and ensured suitable testing conditions

[31]. The assembly was then closed with the top plate and cured in a hot press under the same conditions described previously.

After curing, excess adhesive was trimmed, and the shims were carefully removed to avoid introducing cracks or damage. The specimens were then prepared for DIC analysis by applying a white matte paint base with a black speckle pattern.

TAST tests were performed under quasi-static loading at a displacement rate of 0.5 mm/min. Engineering strain was measured using two methods: an extensometer (2630-100 series, Instron, Norwood, MA, USA) for Vitrimax and DIC analysis for T-Link. Engineering stress was obtained by dividing the applied load by the overlap area, and the shear modulus G was determined from the initial slope of the stress–strain curve in the elastic region.

B.2.2.3 DCB specimens

The DCB tests were conducted according to the ISO 25217 standard [32], using DIN 40 CrMnMo 8-6-4 steel substrates. The substrates were first sandblasted, cleaned with acetone, and then placed in a mould coated with release agent. An adhesive thickness of 0.2 mm was achieved by applying calibrated tape to both sides of the joint, and an initial crack length of 45 mm was introduced with a 0.1 mm razor blade positioned between two 0.5 mm calibrated tapes, both coated with release agent for easy removal.

After curing, two loading blocks (20 × 20 × 20 mm) were bonded to the substrates using a two-component epoxy. To ensure adhesion, the blocks were sandblasted and cleaned with acetone, and the bonding surfaces of the substrates were sanded. The final specimen geometry is shown in Figure B.3, where t denotes the adhesive thickness and a the initial crack length.

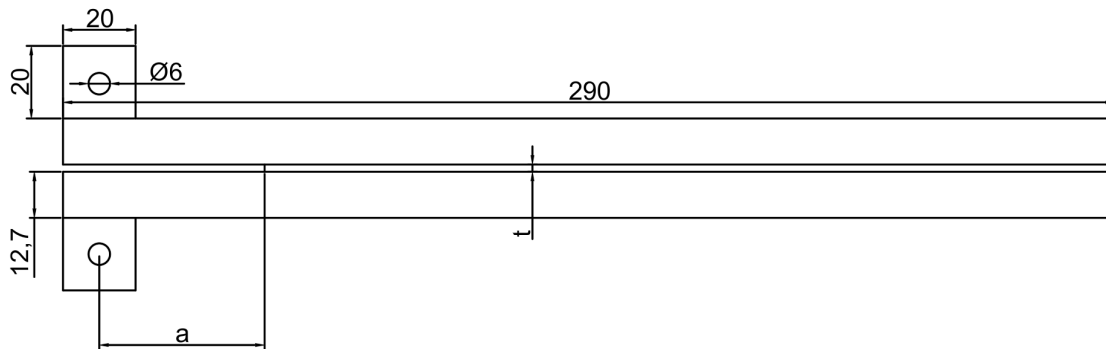


Figure B.3: DCB specimen dimensions [mm] with loading blocks.

The tests were carried out on an INSTRON[®] 3367 machine, with specimens mounted in steel supports secured by stiff pins. Fracture toughness was evaluated using the Compliance-Based Beam Method (CBBM) [33], which introduces an equivalent crack length derived from specimen compliance. This method requires only load–displacement (P – δ) data, avoiding the direct measurement of crack propagation, which is often challenging.

The mode I critical energy release rate, G_{Ic} , was calculated as:

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

where B is the adherend width, t the adherend thickness, E_f the corrected flexural modulus, P the applied load, and a_{eq} the equivalent crack length approximating the real crack tip a .

B.2.2.4 Compact tension test

The compact tension (CT) tests were carried out according to the ASTM D5045-14 standard [34]. Specimens were manufactured as plates following the French NF T 76-142 standard, using the same procedure described previously. Two thicknesses, 2 mm and 4 mm, were produced by varying the silicone frame. Each plate was cut in half and machined to the final dimensions shown in Figure B.4. To introduce the crack, an initial notch was made with a sharp blade and sharpened with a razor blade. The final crack length was measured using an Emspira 3 digital microscope.

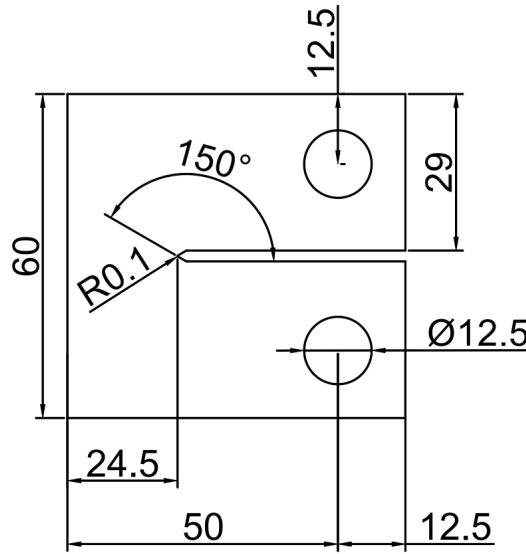


Figure B.4: CT specimen dimensions according to the ASTM D5045-14 standard [34].

To induce the final crack, a sharp blade was first used to create an initial rough crack, followed by a razor blade to refine it. The final crack length was then measured using the Emspira 3 digital microscope.

The CT tests were performed under quasi-static loading at 1 mm/min on the INSTRON® 3367 machine. Specimens were fixed with steel pins, and 3D-printed thick tabs were used to avoid bending.

This method allows determining the plane-strain fracture toughness, K_{Ic} , which characterizes resistance to crack propagation, and the critical strain energy release rate, G_{Ic} , which quantifies the energy required for crack growth.

According to ASTM D5045-14, fracture toughness is given by:

$$K_{Ic} = \frac{P_Q}{B\sqrt{W}} \cdot f(x) \quad (\text{B.2})$$

where P_Q is the load, B the specimen thickness, W the specimen width, and $f(x)$ a geometry factor defined as:

$$f(x) = \frac{6\sqrt{x} [1.992 - x(1-x)(2.152 - 3.93x + 2.7x^2)]}{(1-2x)(1-x)^{3/2}} \quad (\text{B.3})$$

The critical strain energy release rate is then obtained as:

$$G_{Ic} = \frac{(1-\nu^2)K_{Ic}^2}{E} \quad (\text{B.4})$$

where ν is the Poisson's ratio and E the Young's modulus. To ensure consistency and avoid viscoelastic uncertainties, fracture tests were performed under controlled temperature conditions.

B.2.2.5 Creep test

To ensure repeatability, three creep tests were performed for each adhesive. Bulk plates with a thickness of 0.5 mm were manufactured following the procedure described previously. The plates were cut into rectangular specimens 5 mm in length using a blade, and final dimensions were measured with a calliper.

The tests were conducted on a DMA Triton 2000 equipped with a 10 N load cell. According to the literature, the applied stress should be at least one order of magnitude lower than the tensile strength at the testing temperature [26]. Therefore, the load was set to 3% of the maximum stress of each adhesive, with the exact value adjusted according to the specimen's cross-sectional area.

Creep testing was carried out in two consecutive 1 hour stages at a frequency of 1 Hz. The first stage, at $50\%T_g - 5^\circ\text{C}$, served as a pre-conditioning step to assess the adhesive response prior to the main test. The second stage was performed at $50\%T_g$. A heating rate of $5^\circ\text{C}/\text{min}$ was applied to reach each test temperature. The glass transition temperatures of the adhesives were 70°C for T-Link, 67.2°C for Vitrimax, and 100°C for AV 138.

B.2.2.6 Single lap joint

To analyse adhesive performance in joint configurations, single lap joints (SLJs) were manufactured using duplex stainless steel substrates with a thickness of 2 mm, a length of 107.2 mm, and an overlap of 12.5 mm (Figure B.5). The substrates were placed in an aluminium mould coated with a release agent.

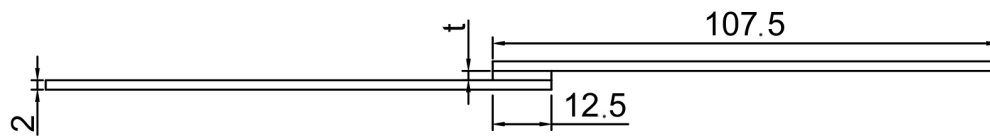


Figure B.5: SLJ geometry for 12.5 mm of overlap length.

For the SLJs tested with temperature, the adhesive thicknesses were set to 0.1 mm for T-Link, 0.5 mm for Vitrimax, and 0.2 mm for AV 138.

Re-adhesion performance was assessed through three additional bonding cycles. For Vitrimax, specimens were prepared with thicknesses of 0.1 mm and 0.5 mm. In the latter case, the thickness was reduced by 0.1 mm after each cycle to ensure proper bonding. For T-Link, the joints were manufactured with the original adhesive thickness, which was measured after each cycle.

All SLJ tests were carried out on the same testing machine described in the previous section. Load–displacement curves were continuously recorded until failure at a constant crosshead speed of 1 mm/min. When temperature control was required, specimens were placed inside a hot chamber for 10 minutes prior to testing to ensure thermal equilibrium.

B.2.3 Results

B.2.3.1 Mechanical characterization

Bulk tensile test

Dog-bone specimen surfaces were first cleaned with acetone, coated with matte white paint, and then speckled with dark matte paint. Three specimens were tested for both Vitrimax and T-Link, while the results for the AV 138 adhesive were taken from previous internal studies that have not yet been published. Strains were measured using DIC software, and the stress–strain curves were subsequently plotted. Figure B.6 shows the average curves for the tested adhesives, and Table B.1 presents the average values of Young’s modulus, tensile strength, and tensile strain at failure.

With the results present in Table B.1, the Poisson’s ratio was determined through DIC analysis using the following equation:

$$\nu = -\frac{\varepsilon_x}{\varepsilon_y} \quad (\text{B.5})$$

where ε_x and ε_y correspond to the strains measured along the x- and y-axes, respectively. The Poisson’s ratio of $\nu = 0.370 \pm 0.010$ was obtained for the T-Link adhesive, while the Vitrimax adhesive exhibited a value of $\nu = 0.400 \pm 0.020$. The Poisson’s coefficient for the AV 138 adhesive was obtained from the TAST tests, as described in the next section.

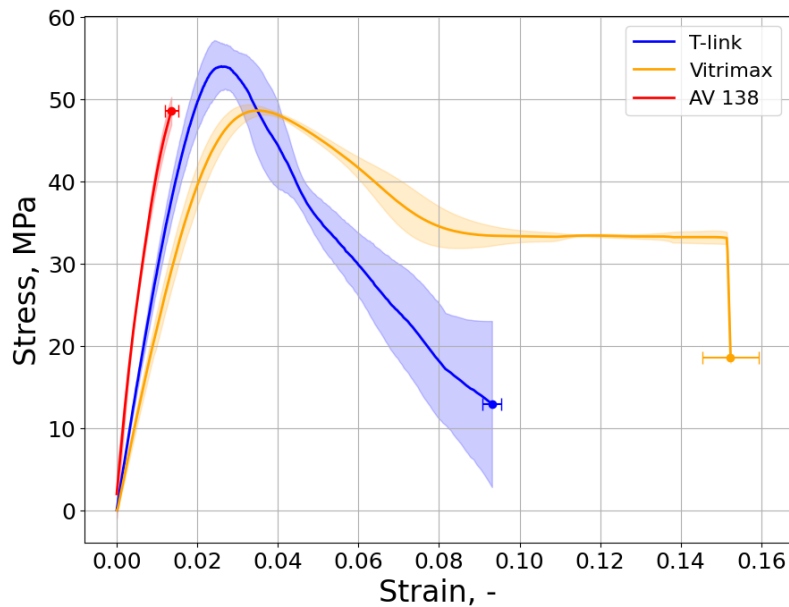


Figure B.6: Tensile stress–strain curve of T-Link, Vitrimax and AV 138.

Table B.1: Elastic properties of Tlink, Vitrimax, and AV 138 adhesives.

Property	Units	Tlink	Vitrimax	AV 138
Young's modulus, E	MPa	2878 ± 78	1992 ± 51	4615 ± 240
Poisson's ratio, ν	–	0.37 ± 0.01	0.40 ± 0.02	0.48 ± 0.03
Tensile strength, σ_f	MPa	56.8 ± 0.6	48.7 ± 0.5	47.6 ± 1.7
Tensile strain to failure, ϵ_f	%	9.3 ± 0.4	15.2 ± 0.8	1.42 ± 0.16

Thick adherend shear test

The strain field in the thick adherend shear test was measured using DIC for T-Link and an extensometer for Vitrimax. Since T-Link is a film adhesive and more sensitive than a paste adhesive, DIC was used to obtain more precise strain measurements. For Vitrimax, an extensometer was sufficient because DIC requires precise camera alignment and can be affected by specimen rotation during testing, potentially reducing measurement accuracy.

Figure B.7 shows the failure modes of the two adhesives. In both cases, failure occurred at the interface. For T-Link, most of the tests showed poor adhesion, which caused variability in the results; therefore, only one test was considered. The shear modulus, shear strength, and shear strain to failure are summarized in Table B.2

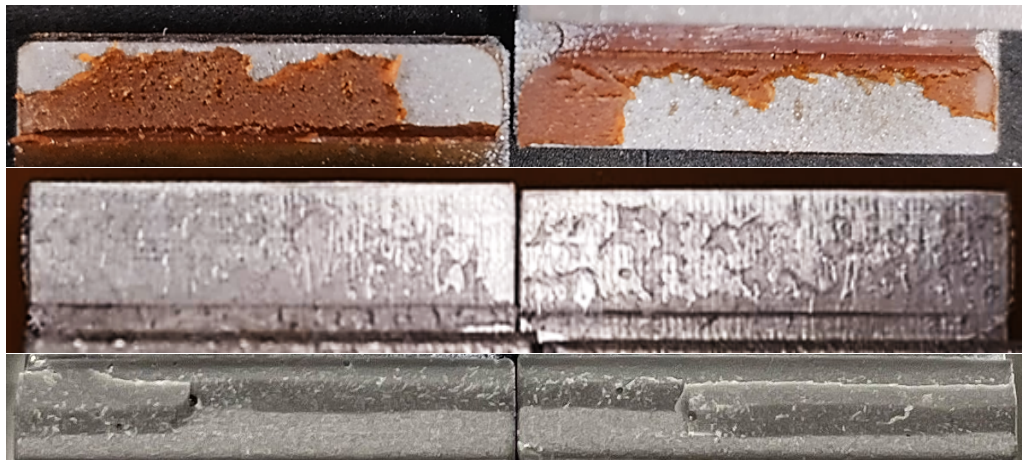


Figure B.7: Failure mode for Vitrimax (top), T-Link (middle) and AV 138 (bottom).

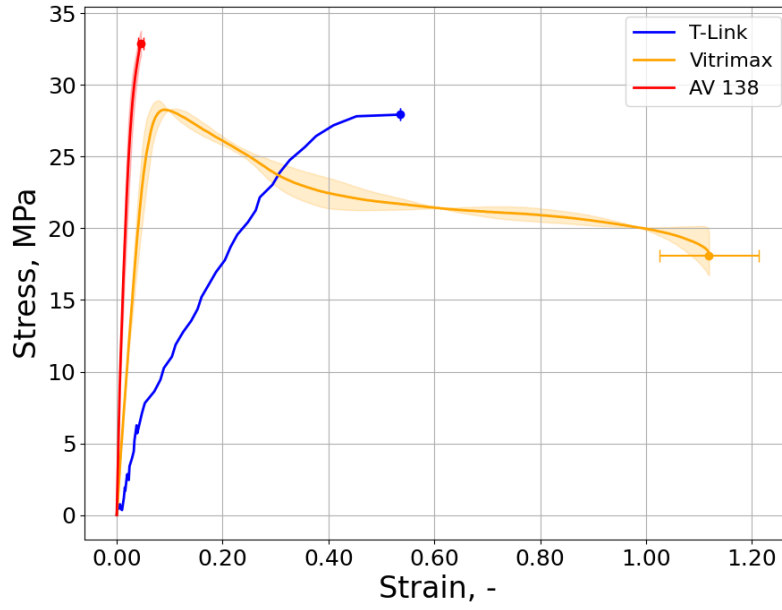


Figure B.8: Stress–strain curves for the TAST specimens of Vitrimax, T-Link and AV 138.

Table B.2: Shear properties of Vitrimax and AV 138 adhesives.

Property	Units	T-Link	Vitrimax	AV 138
Shear modulus, G	MPa	191	462 ± 5.0	1560 ± 35
Shear strength, τ_f	MPa	27.9	28.5 ± 0.3	32.9 ± 0.9
Shear strain to failure, γ_f	%	53	110 ± 10.0	5.0 ± 1.0

The shear modulus obtained from the TAST was 191 MPa for T-Link, 462 ± 5.0 MPa for Vitrimax, and 1560 ± 35 MPa for AV 138. Using the relation between Young’s modulus and shear modulus for isotropic materials (Equation B.6), the calculated Poisson’s ratios were 0.76 for T-Link and 0.31 for Vitrimax. The latter differs from the bulk test result by about 20%, which is considered acceptable, whereas the former is physically unrealistic, since the Poisson’s ratio of an isotropic material cannot exceed 0.5. Therefore, T-Link was used only to determine the maximum shear strength.

$$E = 2G(1 + \nu) \quad (\text{B.6})$$

DCB test

For the determination of the fracture energy, steel substrates were used for Vitrimax and T-Link. For AV 138, the fracture energy is 0.37 ± 0.04 N/mm according to Correia et al., with cohesive failure [35]. During testing, both Vitrimax and T-Link failed at the interface, as illustrated in

Figure B.9. This failure mode is primarily due to poor adhesion between the adhesive and the substrate, which leads to inaccurate values and prevents the formation of a plateau, as observed in **Figure B.10**.

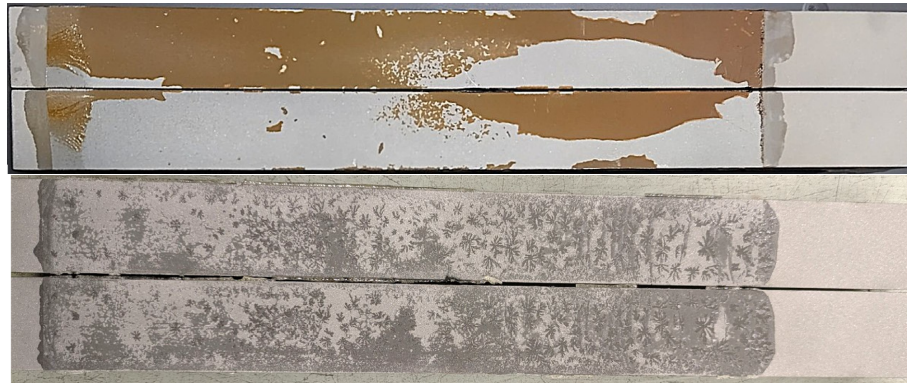


Figure B.9: Failure mode for DCB specimens of Vitrimax (top) and T-Link (bottom).

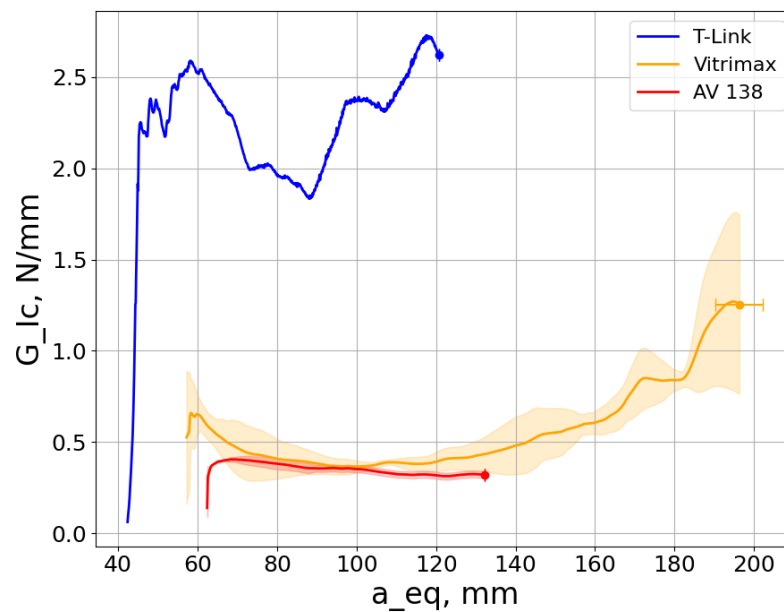


Figure B.10: R-curve.

The fracture energy for Vitrimax was determined as 0.40 ± 0.06 N/mm. However, due to the invalidity of the DCB test, a compact tension (CT) test was subsequently performed to obtain more reliable results. The CT configuration ensured that crack propagation occurred within the adhesive, without influence from the substrates. For T-Link, the fracture energy values were obtained from a complementary study conducted internally within the group, which yielded a fracture energy of 2.3 N/mm.

The fracture property is summarized in **Table B.3**.

Table B.3: Fracture energy release rate in Mode I.

Property	Units	T-Link	Vitrimax	AV 138
Fracture energy in Mode I, G_{Ic}	N/mm	2.3	0.4 ± 0.06	0.37 ± 0.04

Compact tension test

Compact tension (CT) tests were carried out to determine the critical strain energy release rate G_{Ic} of Vitrimax. Three CT specimens were tested for a thickness of 2 mm, and six specimens were tested for a thickness of 4 mm at room temperature, to analyse the influence of bending in the specimen. Figure B.11 shows uniform crack propagation in the CT specimens.

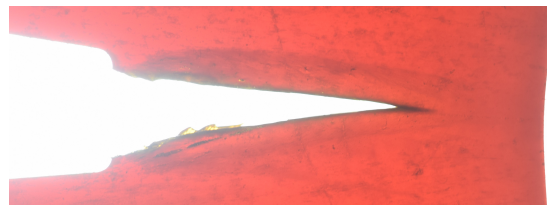


Figure B.11: Crack propagation of CT specimens.

The measured G_{Ic} values were 2.83 ± 0.38 N/mm for the 2 mm specimens and 3.39 ± 0.12 N/mm for the 4 mm specimens, representing a 16% increase with specimen thickness. This trend indicates that thicker specimens develop greater constraint at the crack tip, which confines the plastic zone and reduces the influence of bending, resulting in a toughness value closer to the intrinsic G_{Ic} of the material.

According to ASTM 5045_14 [34], fracture toughness must be measured under plane strain conditions, which only occur when the specimen is sufficiently thick. Thin specimens, such as the 2 mm ones, behave closer to plane stress, where plastic deformation spreads more easily and the measured toughness does not fully represent the material's intrinsic property. By contrast, the 4 mm specimens are thick enough to approach valid plane strain conditions, as also confirmed in Figure B.12, where they required almost twice the maximum force compared to the 2 mm specimens. Similar observations have been reported in previous studies, showing that increasing thickness reduces the effect of plasticity and brings the test closer to plane strain conditions [36, 37].

For these reasons, the value obtained from the 4 mm CT specimens ($G_{Ic} = 3.39 \pm 0.12$ N/mm) is taken as the effective fracture toughness of Vitrimax.

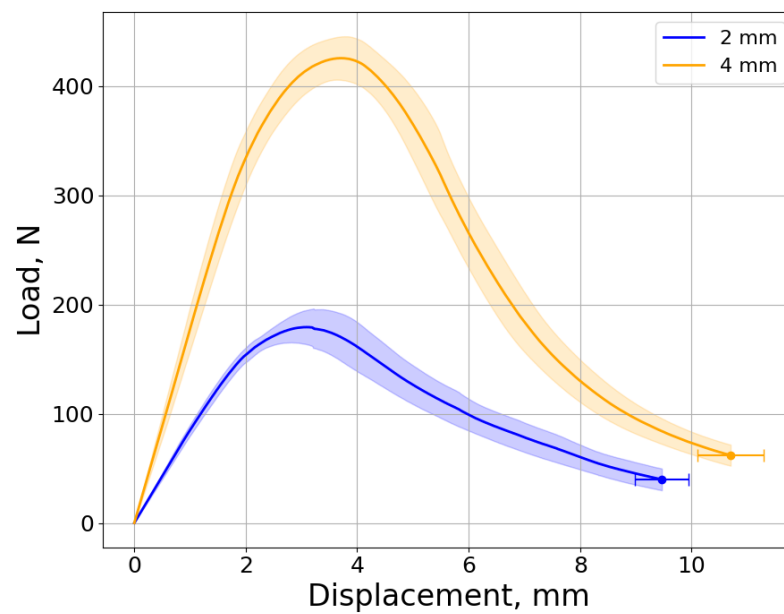


Figure B.12: Load-displacement curve of CT specimens.

B.2.3.2 Creep test

Figure B.13 shows the creep results for the three adhesives, Vitrimax, T-Link and AV 138.

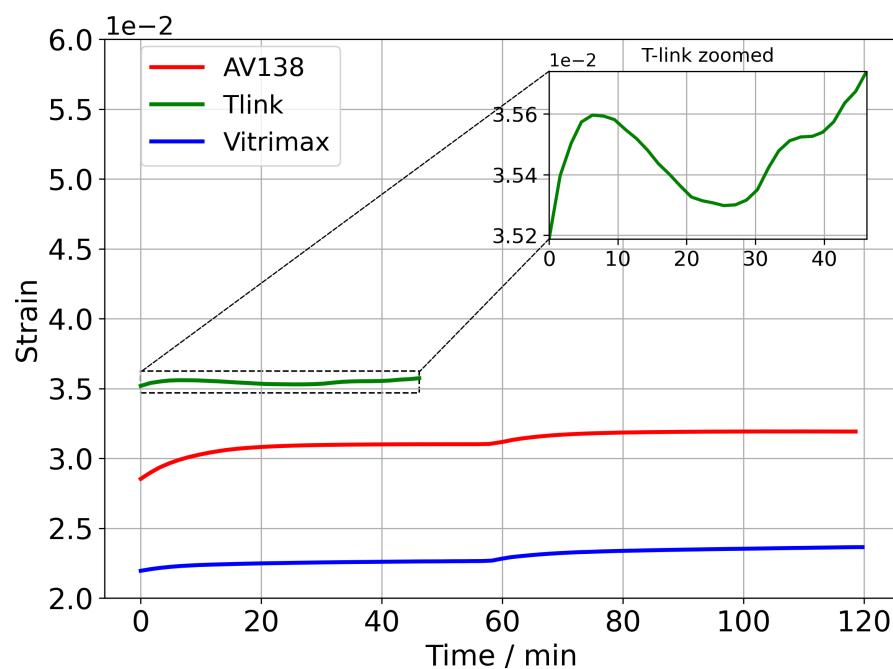


Figure B.13: Creep results after 2 hours for T-Link, Vitrimax and AV 138.

In the creep test, the T-Link adhesive initially deformed under the applied constant load as expected, with strain increasing steadily. After approximately 10 minutes, the adhesive began to

lose its structural rigidity, entering a rubbery state. At this stage, the measured strain appeared to decrease, reflecting the adhesive's inability to sustain the applied load rather than a true recovery. As the material continued to soften, the force effectively transmitted to the specimen gradually declined, leading to a transition into a relaxation-like regime where the adhesive could no longer maintain a stable deformation response under the testing conditions.

When comparing the Vitrimax and AV 138 at the first temperature ($50\%T_g - 5^\circ\text{C}$), both adhesives exhibited low deformation and reached a plateau after 60 minutes: about 2.9% for AV138 and 2.2% for Vitrimax. At the second temperature ($50\%T_g$), AV138 again reached a plateau at a slightly higher strain (3.2%), demonstrating stable behaviour under these conditions. In contrast, Vitrimax showed only a slight increase (2.3%) without reaching a clear plateau, indicating that this temperature represents the upper limit at which the vitrimer still provides good creep resistance.

Similar creep behaviour to our results has been reported in the literature [25, 26], where the vitrimers generally showed better performance; however, depending on the testing temperature, the epoxy materials sometimes exhibited superior creep resistance. These studies suggest that, in vitrimers, creep is primarily governed by the network structure, bond exchange rate, and catalytic conditions, so even small differences in these factors can noticeably affect creep resistance.

B.2.3.3 Single lap joint

Temperature effects

Figure B.14 shows the load values for the adhesives at room temperature and at 50% of the T_g of each adhesive.

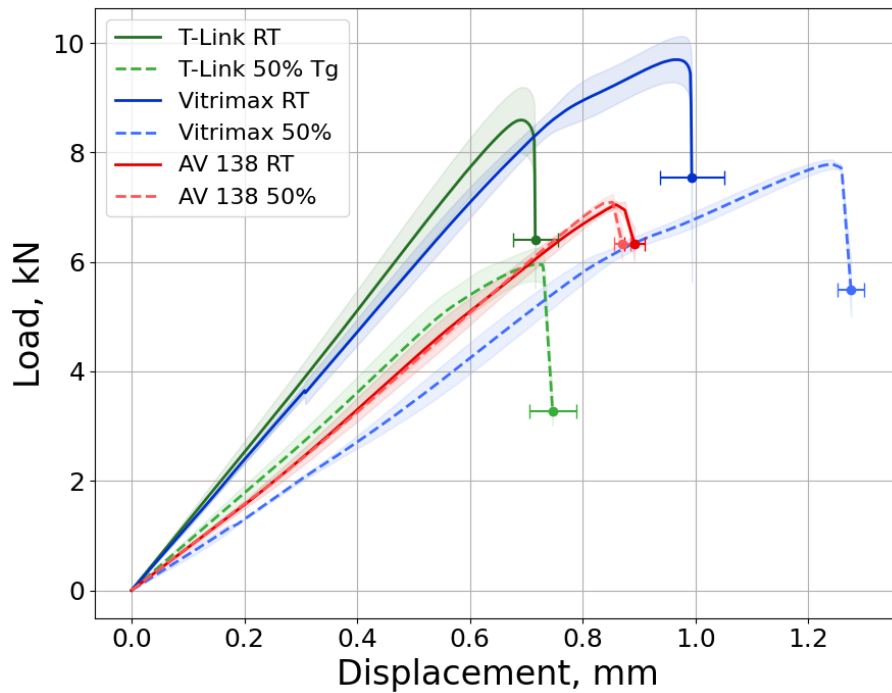


Figure B.14: Temperature effects in load-displacement curves for T-Link, Vitrimax and AV 138.

Re-adhesion

For each adhesive, at least three specimens were tested to ensure repeatability of the results. Figure B.15 shows the lap shear strength (LSS) results for T-Link, Vitrimax with thicknesses of 0.5 mm and 0.1 mm, and AV 138. Regarding rebonding, since AV 138 is an epoxy and re-adhesion is not possible, the rebond values were considered 0 MPa. Comparing the different single-lap joints (SLJs) of Vitrimax allowed the assessment of thickness as a key parameter influencing rebond behaviour.

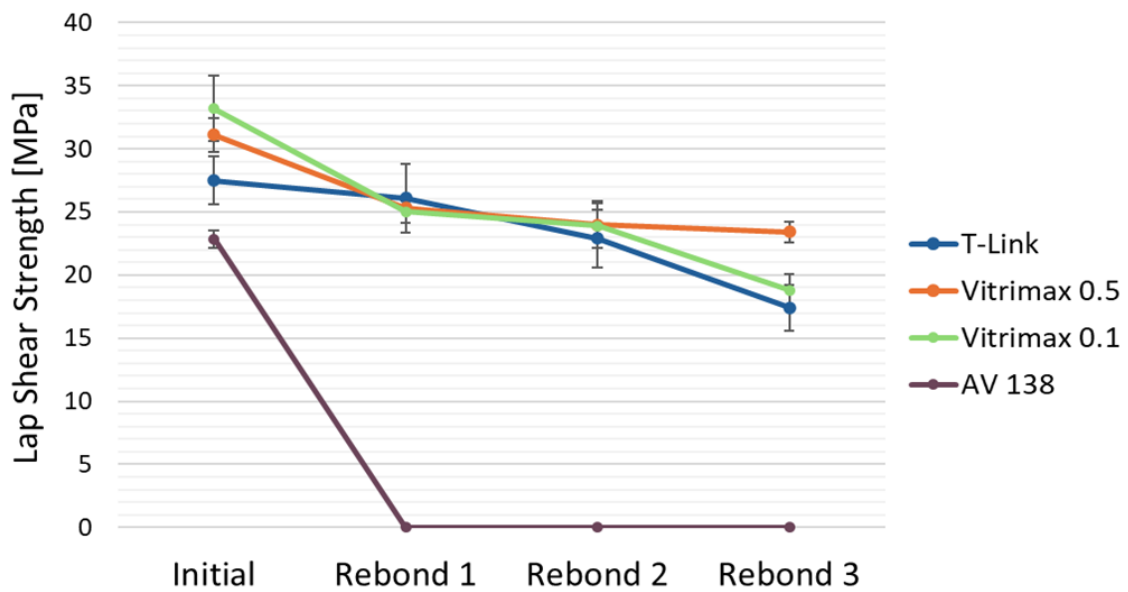


Figure B.15: Lap Shear Strength values for re-adhesion tests.

B.3 Discussion

Vitrimax and AV 138 have similar tensile strengths, but AV 138's higher Young's modulus makes it stiff and brittle, while Vitrimax is tougher and more ductile, suitable for damping. These differences arise from crosslink density: Vitrimax's lower density allows greater strain, whereas AV 138's higher density limits deformation. T-Link shows the highest modulus and tensile strength, but since it wasn't thermally exposed and given its manufacturing history, these values are provisional; its epoxy groups still confer greater stiffness than typical thermoplastics.

Vitrimax exhibits a moderate shear modulus and shear strength comparable to T-Link, but it is distinguished by its exceptionally high shear ductility, exceeding the other two adhesives. This suggests that, although it is neither the stiffest nor the strongest, Vitrimax can accommodate large deformations and effectively dissipate energy prior to failure. This behaviour is also supported by the G_{Ic} values obtained from compact tension tests, where the influence of the substrates and poor adhesion was minimized, providing more accurate measurements. Moreover, similar trends have been reported in the literature for adhesives and polymeric materials with comparable dimensions

and thicknesses. For instance, Gardan et al. [38] observed improvements in fracture resistance for ABS parts reinforced through structural modifications, while Silva et al. [39] reported consistent mechanical and fracture behaviour in fibre-reinforced polymers under comparable testing conditions. In both cases, the reported fracture toughness values were of the same order of magnitude as those obtained in the present study, reinforcing the validity of the G_{Ic} results.

In terms of creep, both AV138 and Vitrimax showed limited deformation at $50\%T_g - 5^\circ\text{C}$, reaching plateaus of 2.9% and 2.2%, respectively, within 60 minutes. At $50\%T_g$, AV138 again stabilized at 3.2%, whereas Vitrimax did not reach a clear plateau, though its strain remained low (2.3%). This highlights the different network chemistries: AV138's permanent crosslink promote stability, while Vitrimax's dynamic covalent bonds allow structural rearrangements that enhance its short-term creep resistance under load.

These differences are further illustrated when comparing bulk and creep behaviour. In bulk tests, Vitrimax showed larger displacements than epoxy, yet under creep conditions, it exhibited better strain resistance. This superior behaviour is due to the dynamic covalent bonds in Vitrimax, which allow the network to reorganize and gradually relax stress over time. In contrast, epoxy, despite showing the lowest strain in bulk tests, accumulated more deformation under constant stress during creep because its rigid network cannot redistribute stress, leading to progressive strain. These observations highlight that Vitrimax combines flexibility with stress-relaxing mechanisms, making it the better-performing material under long-term loading.

In the SLJ tests conducted at 50% of T_g , clear differences were observed between the three materials. The AV 138 maintained nearly constant strength, showing little variation. This reflects its highly crosslinked, permanent network, which provides excellent thermal and mechanical stability, making it largely insensitive to moderate temperature increases. Its rigidity and low chain mobility prevent significant deformation under the test conditions.

The T-Link exhibited the largest decrease in strength, likely due to its limited thermal resistance and lower modulus at elevated temperatures. Being a thermoplastic, its chains gain mobility as temperature rises, reducing its ability to transfer load effectively in the lap joint, which results in a pronounced drop in strength even at 50% of T_g .

The vitrimer showed intermediate behaviour: it lost some strength, but less than the thermoplastic. Its dynamic covalent network allows some stress redistribution, which helps retain better performance at this temperature, though it does not reach the epoxy's stability. Nevertheless, Vitrimax still demonstrates higher toughness than the other two adhesives, even when exposed to temperature.

As for the re-adhesion of the adhesives, Table B.4 summarizes the results obtained, showing the residual force, in percentage, for each rebond condition.

Table B.4: Lap shear strength values expressed as percentages.

Adhesive	Thickness (mm)	Initial (%)	Rebond 1 (%)	Rebond 2 (%)	Rebond 3 (%)
T-Link	0.1	100	94.9	83.3	63.3
Vitrimax	0.5	100	81.4	77.2	75.2
Vitrimax	0.1	100	75.3	72.0	56.6
AV 138	0.2	100	0.0	0.0	0.0

When comparing Vitrimax at 0.1 mm thickness with T-Link, the latter shows good initial performance but progressively loses strength with each rebond, while Vitrimax remains more stable. Nonetheless, both adhesives experience a significant reduction in strength due to material degradation and progressive material loss. The 0.1 mm Vitrimax specimens, despite a higher initial maximum LSS, lose more strength across rebonds than the 0.5 mm specimens, whose greater adhesive volume helps retain performance. After the third rebond, the 0.5 mm specimens lost 24.8% of their strength, while literature reports losses as low as 22% [40, 41], and in some cases strength can increase [42]. This greater reduction is likely due to adhesive failure, as shown in Figure B.16, which reduces rebonding efficiency compared to bonding between adhesive layers.

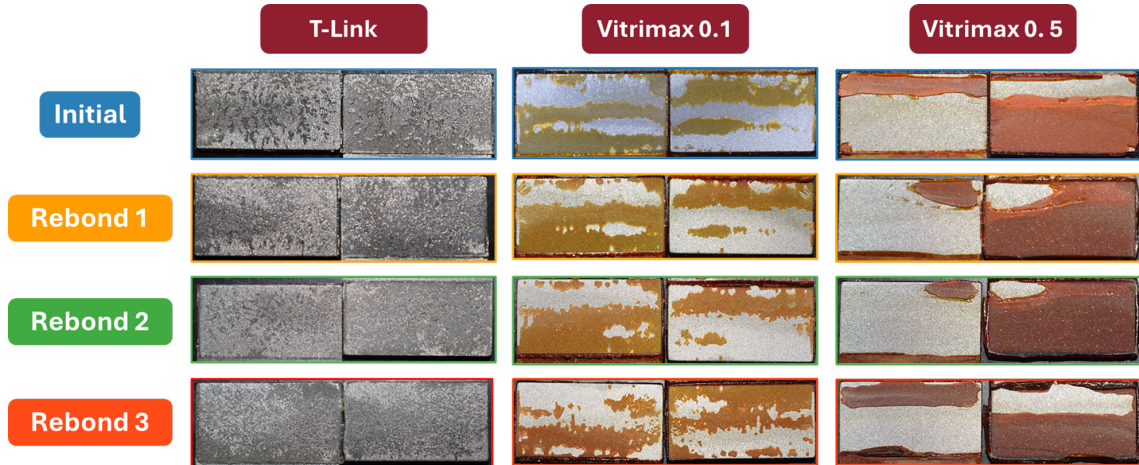


Figure B.16: Failure mode for T-Link and Vitrimax in each cycle.

B.4 Conclusion

This study investigates the creep behaviour, mechanical performance, and recyclability of Vitrimax VHM, a commercial vitrimer, in comparison with conventional adhesives, providing insight into whether vitrimers can be applied in structural contexts and offering an outlook on potential applications where they may replace conventional adhesives. While Vitrimax exhibits tensile strength comparable to the epoxy AV 138, its lower crosslink density gives it higher ductility and

toughness, making it better suited for applications requiring energy dissipation and damping. In shear, Vitrimax stands out due to its exceptional ductility, which indicates its ability to effectively dissipate energy prior to fracture, corroborating the high G_{Ic} values obtained from compact tension tests.

Creep tests further demonstrated that, although AV138 shows greater dimensional stability due to its permanent crosslink, Vitrimax maintains low strain levels and resists creep effectively over the tested time frame thanks to its dynamic covalent network. This adaptability enables it to balance structural stability and creep resistance, an important consideration for structural applications.

At 50% of T_g , AV 138 SLJs maintained nearly constant strength due to its rigid, highly crosslinked network. The T-Link showed the greatest strength loss from increased chain mobility. The vitrimer displayed intermediate behaviour, with partial strength retention from its dynamic network but less stability than the epoxy.

Re-bonding experiments using single lap joints revealed that Vitrimax retains a higher proportion of its initial strength over multiple cycles compared to T-Link, particularly when applied in thicker layers, highlighting its potential for reuse. Although some reduction in strength occurs due to material degradation and adhesive loss, the ability of Vitrimax to maintain substantial residual force after repeated re-bonding underscores its suitability for recyclable structural applications.

This study shows that Vitrimax stands out as a next-generation structural adhesive by combining three key advantages rarely achieved together. First, it exhibits superior creep resistance compared to conventional thermoset adhesives like AV 138, making it highly reliable under long-term loading. Second, it maintains excellent mechanical properties, including high ductility and fracture toughness below its glass transition temperature. Finally, its dynamic covalent network allows reprocessing and recyclability, offering a sustainable alternative to permanent adhesives. Together, these features position Vitrimax as an ideal adhesive for applications demanding both durability and environmental responsibility.

Future studies could focus on improving the adhesion of vitrimers, as adhesive failure remains one of the main drawbacks of this promising class of materials, potentially enhancing their performance and reusability in structural applications.

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