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ABSTRACT

Adhesive joints have been increasingly used in automotive applications because they offer a potential for reduced weight and cost [1]. However, with the current tendency to manufacture more low-weight and low-emission vehicles, the manufacturers are increasingly using low-density materials such as carbon fiber reinforced polymers (CFRP) or super alloys, usually expensive materials, which lead to a higher demand for recyclability. Thus, for environmental and economic reasons, the development of new technologies and processes that enable easy disassembly of the adhesive joints (without damaging the components) is becoming of great interest for the industry.

To follow this tendency, the possibility of debonding on command of adhesive joints was investigated during this research, using single lap joints (SLJs) bonded with adhesives modified with thermally expandable particles (TEPs'). Two different adhesives were used to compare the TEPs' effect on both adhesives and strength tests were performed to find the ideal TEPs' percentage to achieve an easy disassembly, if needed, of the bonded joints, while guarantying the joint strength requirements. All the results were compared with single lap joints (SLJs) of those adhesives without any TEPs'. An evaluation was performed with this comparison and it was concluded that with the increase of %wt of TEPs' the lap shear strength decreases.

To determine the best/faster way to disassemble the joints, they were locally heated for a few seconds and the joint disassembly effectiveness due to TEPs' activation was evaluated and compared between different %wt of TEPs'. As was expected, with the increase of %wt of TEPs' the temperature needed to dissemble the joints decreases.

KEYWORDS: Adhesives, Thermally Expandable Particles, Nanoparticles, Recycle, Automotive Industry, Single Lap Joints, Disassembly of Joints

II Debonding on command of adhesive joints for the automotive industry

RESUMO

O uso de juntas adesivas em aplicações automóveis tem vindo a aumentar uma vez que oferecem potencial para redução tanto do peso como do custo de fabricação. Contudo, com a tendência actual para construção de veículos mais leves e com reduzidas emissões de CO_2, os construtores automóveis estão a aumentar o uso de materiais de baixa densidade, tais como, polímeros reforçados com fibra de carbono (CFRP) ou super ligas, materiais dispendiosos, que levam à necessidade de reaproveitamento dos mesmos. Assim, por razões ambientais e económicas, o desenvolvimento de novas tecnologias e procedimentos capazes de desunir facilmente as juntas adesivas (sem danificar os componentes a ligar) assume um grande interesse por parte da indústria automóvel.

Seguindo esta tendência, a possibilidade de desunir quando necessário ligações adesivas foi investigada ao longo desta tese, usando juntas simples unidas com adesivos modificados com partículas termo expansíveis (TEPs’). Foram usados dois adesivos diferentes para comparar o efeito dos TEPs’ em cada um. Foram também efectuados ensaios de tracção para perceber qual a percentagem ideal de TEPs’ de forma a permitir, se necessário, uma fácil desunião de junta sem comprometer os requerimentos de força de adesão. Os resultados são comparados com juntas simples dos mesmos adesivos sem qualquer adição de TEPs. Desta comparação concluiu-se que com o aumento de % de TEPs no adesivo a força de resistência de sobreposição diminui.

Para descobrir o melhor/mais rápido procedimento para desunir as juntas foi aplicado calor localmente durante alguns segundos, determinou-se a eficiência de desunião de juntas através da expansão dos TEPs’ para cada percentagem de TEPs’ utilizada.

Como era esperado com o aumento da percentagem de TEPs’ no adesivo faz com que a ligação adesiva quebre a temperaturas mais baixas.

Palavras Chave: Adesivos, Partículas Termo Expansíveis, Nanopartículas, Reciclagem, Indústria Automóvel, Juntas de Sobreposição Simples, Desunião de Juntas

IV Debonding on command of adhesive joints for the automotive industry

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VI Debonding on command of adhesive joints for the automotive industry

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LIST OF ACRONYMS

CFRP – Carbon Fiber Reinforced Polymers
DLJs – Double Lap Joints
SEM – Scanning Electron Microscopy
SLJs – Single Lap Joints
TEPs – Thermally Expandable Particles
FEUP – Faculdade de Engenharia da Universidade do Porto
CNFs – Carbo Nanofibers
PEG – Polyethylene Glycol
PDMS – Polydimethylsiloxane

LIST OF SYMBOLS

T_g - Glass Transition Temperature
mins – Minutes
E – Young's Modulus
T – Temperature
P – Applied Load
δ – Displacement
RT – Room Temperature
secs – Seconds
wt% – Weight Percentage
t – substrate thickness
ta – adhesive thickness
w – Joint width
L_0 - Overlap Length

1. INTRODUCTION

Adhesive joints are becoming more relevant in the automotive industries because they offer great potential to reduce weight and cost [1]. From a sustainable development perspective, growing concerns have been raised about the environmental impacts of automotive vehicles and the increasing numbers to which they are related, including those regarding energy consumption, greenhouse gas emissions, waste generation and End-of-Life Vehicle Recycling. With the current rules for low-emission automotive vehicles [2], the manufacturers are increasingly using low-density materials such as CFRPs or super alloys, usually expensive materials, which demand more recyclability. Bearing that in mind, both environmental and economic reasons, the development of new technologies and processes that enable easy disassembly -without damaging the components - just the adhesive - is becoming the focus of interest from the manufacturers. For the automotive industry, some priority must be given to the reuse and recovery of vehicle components, because recent mandatory rules state that all vehicles must be 95% recyclable until 2015 [3].

In this thesis, a method of debonding on command of adhesive joints for the automotive industry will be investigated by using thermally expandable particles, in order to enable material recovery. Single lap joints will be used with different concentrations of TEPs and the joint disassembly effectiveness due to TEPs’ activation will be determined.

This method, as mentioned before, will increase the automobile recyclability, through the reuse and recycling of a component that remains valuable into specification-grade commodities that can be used in the manufacturing of new basic materials such as steel, aluminum, plastic, copper and brass. With this method, heat has to be applied on the joint, in order to disassemble undamaged parts/components for reusing or recycling.

1.1. OBJECTIVES

The objective of this thesis is to investigate a method of debonding adhesive joints for automotive applications by using thermally expandable particles, without damaging the bonded parts. Single lap joints will be used with different concentrations of TEPs and the joint disassembly effectiveness due to TEPs’ activation will be determined.

1.2. TASKS

- Literature review
- Specimen manufacturing

Manufacturing of SLJs with structural adhesives typically used in the automotive industry (an epoxy adhesive supplied by Dow and a polyurethane adhesive supplied by Sika) with different concentrations of expandable particles (supplied by Expancel)

- Experimental testing

Debonding of the joints. Testing of specimens manufactured during the previous task

1.3. THESIS OVERVIEW

This thesis is divided in six chapters that describe in detail the theoretical and experimental work made.

Chapter 1 introduces the subject as well as the aims of this study.

Chapter 2 (Literature review) describes the theory about adhesives:

- History
- Definitions
- Functions
- Advantages/disadvantages
- Requirements for a good bond
- Adhesion theories

Joints:

- Types
- Failure modes

Technologies for adhesive debonding on command:

- Thermally expandable particles and additives used for adhesive debonding
- Nanoparticles used in adhesive debonding
- Diels-Alder chemistry
- Electrical disassembly of adhesive joints.

Chapter 3 content (Experimental work) is about the materials used to manufacture the joints, the joint geometry and joint fabrication process and preparation (surface and mould).

Chapter 4 (Experimental testing) describes the tests performed:

- Strength tests
- Electromagnetic induction method
- Preliminary tests.

Chapter 5 (Results) describes the experimental results achieved through this study and the comparison between the adhesive joints modified with different TEPs wt%.

Chapter 6 (Conclusions) summarises the main conclusions taken from the study made for this thesis.

Chapter 7 (Future work) directions that may be taken to build on the knowledge gathered on this subject.

2. LITERATURE REVIEW

2.1. ADHESIVE BONDING

The science and technology of adhesive joints is a truly multidisciplinary field that requires mastering fundamental concepts of a number of scientific disciplines. Figure 1 illustrates the various aspects or matters which may be relevant.

The primary sciences are physics, mechanics and chemistry that join in certain areas to form other disciplines such as surface science, polymeric materials and joint design that are important in the science of adhesion. These sciences contain more specific disciplines such as fracture mechanics which is also very important. Each of these specialized sciences contributes significantly to the science of adhesion and its application in industrial products. The combination of all these disciplines can be considered the knowledge needed to apply adhesives successfully. It is obviously impossible to cover all these topics in depth in only one work. However, in the current business environment, the person responsible for the application of adhesives should be aware of all relevant technologies. In addition to the areas shown in Figure 1, the management and the economy components should not be forgotten as they are equally important [4].

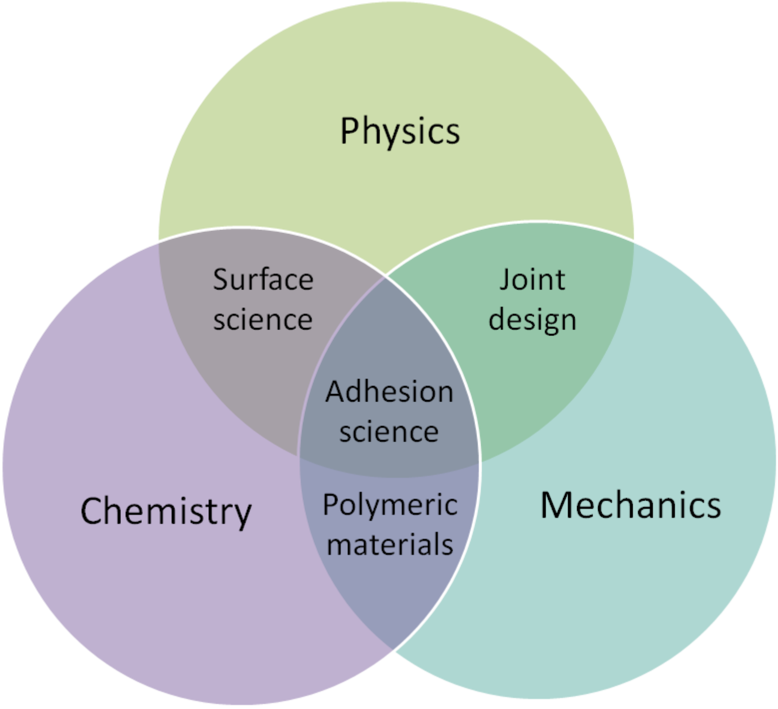


Figure 1 – Technologies involved in adhesion science [4].

2.1.1. HISTORY

Adhesives have been used since ancient times, according to Mittal & Pizzi humans observed and used the techniques and materials of many species. As humans lack the capacity of producing mucous bodily fluids suitable for gluing, such as fish, insects and birds, they had to resort to the examples nature offered. The load carrying capacity of the hardened glue used for egg-fastening and nest building is similar to that of modern structural adhesives [5].

With the development of tools and weapons stones had to be fastened to pieces of wood to manufacture axes and spears. Smearing the knots with sticky materials improved the joining process.

Some early adhesives used by humans include beeswax, rosin, rubber, shellac, sulfur, tar and vegetable gums. Prehistoric pottery was repaired using rosin, as was discovered from archaeological findings.

The Egyptians used animal and casein glues to laminate wood for the manufacturing of furniture and bows, the Greeks used slack lime as a mortar and the Greeks and Romans used a mix of lime with volcanic ash and sand to create what is still known as pozzolamic cement. These were the beginnings of adhesive bonding technology. In Table 1 further developments of adhesives in the United States are presented.

Table 1 – Chronological Developments of Adhesives in the United States [5]

Year	Material
1814	Glue from animal bones
1872	Domestic manufacture of fish glues
1874	First U.S. fish glue patent
1875	Laminating of thin wood veneers attains commercial importance
1909	Vegetable adhesives from cassava flour
1912	Phenolic resin to plywood
1915	Blood albumin in adhesives for wood
1917	Casein glues for aircraft construction
1920-1930	Developments in cellulose ester adhesives for wood
1927	Cyclized rubber in adhesives
1928	Cloroprene adhesives
1928-1930	Soybean ahdesives
1930	Urea-formaldehyde resin adhesives
1930-1935	Specialty pressure sensitive tapes: rubber base
1935	Phenolic resin adhesive filmes
1939	Poly(vynil acetate) adhesives
1940	Chlorinated rubber adhesives
1941	Melamine-formaldehyde
1942	Cycleweld metal adhesives
1943	Resorcinol-fornaldehyde adhesives
1944	Metal-bond adhesives
1945	Furane resin adhesives

Modern adhesives have had very important advances. Mittal & Pizzi refer that the first commercial glue factory was established in Holland in 1690, while casein glues were manufactured in Germany and Switzerland in the early 1800s [5].

There is no consensus on the exact introduction date of several types of adhesives, due to their simultaneous development on different geographical locations, however some say that modern adhesive technology has its origins on the discovery by Charles Goodyear in 1839 that a rubber and sulfur mixture changed from a plastic to an elastic state when heat was applied. This process was named vulcanization by Thomas Hancock in 1843, and the resulting product called ebonite. It was used for many years as the only way of bonding rubber to metal, as ebonite bonds to both. Still bonding rubber to metal was a difficult process that in the late 19th century involved vulcanization in a heated press. Research into bonding rubber to metal without metal plating led to the development of surface preparation prior to adhesive bonding. These bonds were necessary for rubber shock mounts for automobiles in the 1920s. In 1927 solvent-based thermoplastic rubber cements were developed for metal-to-rubber bonding without need of vulcanization.

Several other adhesives and adhesives technologies were developed throughout the 20th century, increasingly improving the adhesives bonding strength, heat resistance, as can be seen in figure 2.

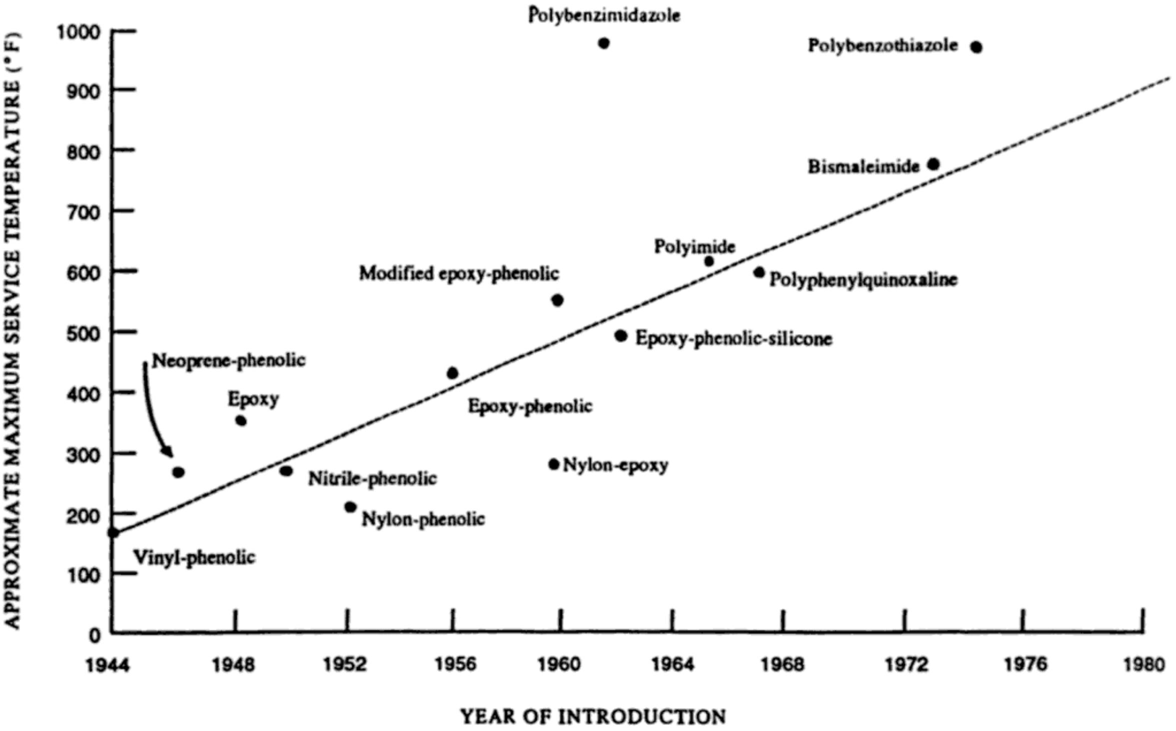


Figure 2 – Development of heat-resistant adhesives [5]

The adhesive families used in this study were developed around the time of WWII, a patent for epoxy resins was applied to in Germany in 1934 and were first sold in the United States in 1942. Polyurethanes were introduced by Otto Bayer in Germany in 1937.

2.1.2. DEFINITIONS

Ebnesajjad [6] defines an adhesive as "a material that is applied to the surfaces of articles to join permanently by an adhesive bonding process. An adhesive is a substance capable of forming bonds to each of the two parts when the final object consists of two sections that are bonded together". An important feature of adhesives is its relative small quantities compared to the weight of the bonded objects. The Adhesive and Sealant Council offers an alternate definition: "Adhesive - a substance capable of holding materials together by surface attachment" [7].

Although adhesion is a difficult concept to define in a satisfactory manner, Wu [8] offers the following definition:

"Adhesion refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. The interfacial holding the two phases together may arise from van der Waals forces, chemical bonding, or electrostatic attraction. Mechanical strength of the system is determined not only by the interfacial forces, but also by the mechanical properties of the interfacial zone and two bulk phases" [8].

In figure 3 a schematic representation of cohesive and adhesive forces in an adhesive bond is presented.

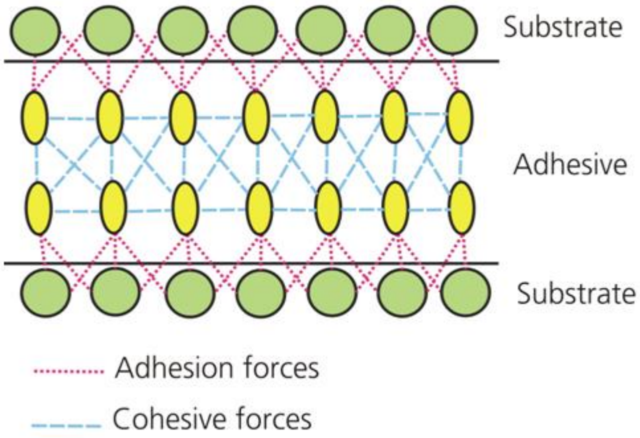


Figure 3 - Adhesive bond [9]

Still according to Ebensajjad, there are two main types of adhesive bonding:

-Structural adhesive bonding - is used for applications where the adherends may experience large stresses, possibly reaching their yield point. Structural adhesive bonds should transmit the stresses involved without loss of integrity within design limits. Simultaneously these bonds must be durable and last the useful life of the part. To be considered a structural adhesive a bond must withstand shear strength greater than 7 MPa;

-Non-structural adhesive bonding – are only required to hold lightweight materials in place. For example, pressure-sensitive tapes and packaging adhesives.

2.1.3. FUNCTIONS

The primary goal of using adhesives is to join parts. This is achieved distributing stresses from the joined parts in a more uniform manner than by using traditional mechanical solutions. The resulting structures often provide a bond as strong if not stronger than mechanical fasteners with reduced weight and cost. Mechanical structure's strength is limited to that of the area of the members in contact with the fasteners, while in adhesive bonding the load is spread out over a greater area avoiding stress concentrations.

Joining parts with adhesives allows smoother surfaces, not disturbed by bolts or rivets, with obvious advantages for applications where aerodynamics are relevant. Adhesives allow the joining of dissimilar materials, such as plastics, metal, rubber and cork.

Another important advantage of adhesives is to accommodate different thermal expansion coefficients of dissimilar adherends. This can be achieved using flexible adhesives and is not attainable with the use of conventional mechanical fasteners where the differences in expansion would cause damage.

Adhesives also perform well as sealants, and if are designed with the goal of absorbing shocks are also able to provide mechanical damping. In properly designed joints they present higher fatigue resistance than the adherends, due to their capability of withstanding cyclic shocks without the appearance of cracks [6].

2.1.4. ADVANTAGES

The main advantages pointed out to structural adhesive bonding are:

1. More uniform distribution of stress along the bonded area, which allows a greater rigidity and load transmission, thus enabling a weight reduction and therefore a lower cost. Figure 4 compares the theoretical stress distributions in a riveted joint and a glued joint. The more even distribution of tension on the glued joint (rather than the concentration observed in the riveted joint tension), contributes for a better resistance to fatigue.

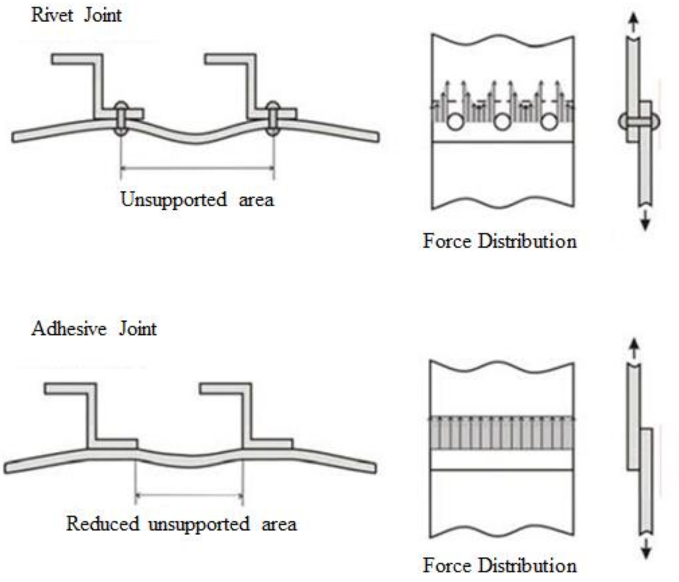


Figure 4 – Force Distribution - rivet joint versus adhesive joint [4]

2. Vibration absorption- this allows tensions to be partially absorbed, thereby improving the resistance to fatigue of the connected components themselves.

3. Connection of different materials with different composition and expansion coefficients (the flexibility of the adhesive makes up the difference).

4. Efficiently linking of thin plates, which can be an important application of adhesives for bonding metal material. In fact, for metal substrates, adhesives based on organic polymers have much lower mechanical strength and cannot join, successfully, large blocks with high strength. But when used to bind thin plates, their resistance are, generally, more than sufficient.

5. The most convenient and effective method to connect two materials, as it can be automated. The mixture and application of the adhesive can be performed by a robot.

6. The most flexible design allowing the use of new concepts and materials. A good example are the structures in which the honeycomb core is bonded to two metal or composite skins resulting in excellent specific stiffness.

7. It allows structures with regular contours, because it avoids holes (rivets, screws) and marks due to welding.

8. It creates a continuous contact between the bonded surfaces.

9. It can reduce costs because projects involving connections with adhesives tend to be lighter and more economical [5].

10. Provide joints with smooth contours.

11. Provide sealing against the elements.

12. Thermally or electrically insulate the substrates, or if required, provide electrical conductance.

13. The heat required for the adhesive bonding process is usually far below the temperature that alters the metal substrates properties.

14. Quicker and less expensive than mechanical alternatives [6].

2.1.5. DISAVANTAGES

The main disadvantages with adhesives' connections are:

1. It is mandatory to project an adhesive joint that eliminates the peel forces as much as possible (main enemy of adhesive bonds). When one of the two materials is not rigid, the connection may be subjected to peel forces and when the two materials are hard, the link may be subjected to cleavage forces.
2. It is important to use geometrics that avoid localized stresses and to ensure uniform stress distribution. If the tensions are not perfectly perpendicular to the adhesive, stresses can appear due to tearing or cleavage forces. The best solution is to design a connection in which the adhesive is subjected to shear stresses. In this case, tensions are parallel to the adhesive bond and are better distributed.
3. Having limited resistance to extreme conditions such as heat and humidity due to the polymeric nature of the adhesive.
4. The connection is not instantaneous, which leads to the use of clamping tools to keep the parts in the correct position. This can be a great economic disadvantage.
5. A careful surface preparation is required to get good results, for example mechanical abrasion, solvent degreasing, chemical treatments, primers, etc.
6. The adhesives are often cured at high temperatures (oven, press, etc.).
7. Quality control and safety are more difficult although appropriate non-destructive techniques have been recently developed.
8. There isn't a universal criteria design that allows projecting any kind of structure. There are many methods that are accurate but only in certain situations [4].
9. The bond does not allow visual inspection of the joint area
10. Long cure times may be necessary.
11. Natural or vegetable origin adhesives may be susceptible to degradation by bacteria, rodents, mold or vermin.
12. Exposure to solvents may present a health hazard, both in cleaning or solvent cementing [6].
13. There are a lot of different adhesives, which makes the selection process difficult for a specific application.
14. Adhesives are hard to debond, most of the time the boundary material is not reusable after debonding.

2.1.6. REQUIREMENTS FOR A GOOD BOND

In order for a good adhesive bond to be attained, several conditions must be attended. The proper adhesive must be selected after taking into consideration what are the adherends, the performance requirements of the bond and the process selected. Also, an adequate joint design is fundamental, as it combines the advantages of mechanical design with adhesive bond strength.

The adherends surfaces must be clean, (dirt, oil, moisture and oxide layers must be removed), or the adhesive will create a bond with this weak boundary layer instead of the substrate. Surface treatments are available to remove, or at the very least strengthen, this boundary layer, either by physical processes, chemical processes or a combination of the two.

Displacing air or other gases on the surface of the substrates is very important to attain the maximum contact area and maximize the bonding forces between the substrate and the adherends. This process is called wetting.

Finally, the appropriate adhesive bonding process must be selected. The application of the adhesive is not the end of the process. It must be subjected to the proper temperature, pressure and hold time. Once the adhesive is applied it must be capable of being converted to a solid form by:

-chemical reaction by any combination of heat, pressure and curing agents;
-cooling from a molten liquid;
-drying as a result of solvent evaporation [6].

2.1.7. ADHESION THEORIES

According to Ebnesajjad [6], the main theories used to describe adhesion mechanisms are: mechanical interlocking, electrostatic, diffusion and adsorption/surface reaction. Recently other approaches are being developed, as can be observed in table 2. Different scales of action occur for each phenomenon, and although adhesive-adherend interactions always occur at the molecular level, the microscopic parameter of note in mechanical interlocking is the contact surface of the adhesive and the adherend, surface roughness is the way in which interlocking is believed to occur and can be quantified with the use of microscopy. In electrostatic bonding the macroscopic factor in question is the surface charge.

Table 2 – Theories of adhesion [6]

Traditional	Recent	Scale of Action
Mechanical Interlocking	Mechanical Interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
Adsorption/surface reaction	Wettability	Molecular
	Chemical bonding	Atomic
	Weak boundary layer	Molecular

Mechanical theory

Adhesion occurs with the penetration by adhesives into cavities, pores and surface irregularities on the surface of the adherend. Air is displaced by the adhesive at the interface and bonds the adherends by mechanical interlocking. Often stronger bonds are formed between porous or abraded substrates, however this is not universally applicable as in some cases good adhesion also occurs between smooth surfaces.

A better bond after abrading the surface of an adherend may be due to:

-mechanical interlocking;
-formation of a clean surface;
-formation of a reactive surface;
-increase in contact surface area.

It is debatable if mechanical interlocking is responsible for enhanced bond strength or if the increase in surface contact area brings into play other mechanisms. There are diverging views on whether an increase in surface roughness will produce stronger bonds, although there is data supporting this view there are also observations to the contrary.

Electrostatic theory

A bond is formed between the adhesive and the substrate due to electrostatic effects. Electron transfer occurs because o unlike electronic band structures. Electrostatic forces are created at the interface, and resist separation. This theory is supported by observations of electrical discharges when adhesives are peeled from the substrates. It offers a plausible explanation for polymer-metal bonds, but the electrostatic forces in non-metallic systems is thought to be very small.

Diffusion theory

The interdiffusion of molecules between the adhesive and the substrate creates the bond. This can happen with polymers with long chain molecules capable of movement. Materials and bonding conditions will determine whether and to what extent diffusion takes place. There are no areas of stress concentration because there is material continuity.

An example of diffusion adhesion mechanism takes place when bonding polyethylene and polypropylene to a butyl rubber. The resulting bond lacks strength when it takes place below the melting point of polyethylene (135ºC) and polypropylene (175ºC), but increases sharply above these values, as can be evaluated in figure 5.

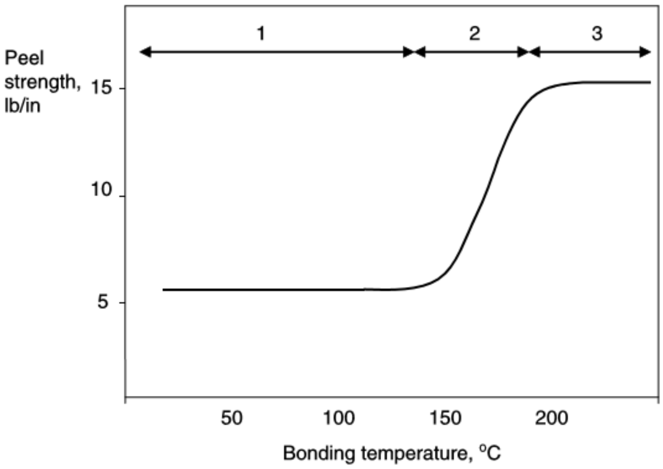


Figure 5 – Peel strength of polypropylene and butyl rubber vs. bonding temperature [6]

Wetting

This theory implies that adhesion is attained from molecular contact between two materials and the surface forces that develop between them. Wetting is the process of establishing continuous contact between the adhesive and the adherend. For this to occur, the adhesive should have a lower surface tension than the critical surface tension of the solid.

In figure 6, on the first case complete wetting and on the second case incomplete can be seen. When wetting is complete, the best possible joint strength may be achieved. Incomplete wetting generates interfacial defects reducing joint strength.

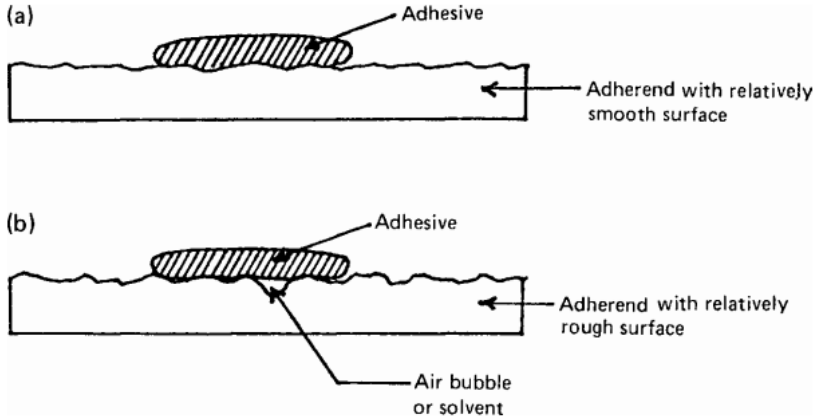


Figure 6 - a) good and b) poor wetting by an adhesive spreading across a surface [6]

Most organic adhesives easily wet metal adherends, but solid organic adherends have surface tensions below those of the most common adhesives. It is necessary for good wetting that the adhesives surface tension is below that of the substrate, which explains in part why epoxies form good bonds with metals but offer weak adhesion to untreated polymeric substances. To achieve good adhesions with polymers its surface tension can be increased by surface treatments.

Chemical bonding

This mechanism forms an adhesion bond due to surface chemical forces. Hydrogen, covalent and ionic bonds formed between adhesive and adherends are stronger than the dispersion attractive forces. Generally speaking, there are four types of interactions that take place during chemical bonding:

-covalent bonds;
-hydrogen bonds;
-Lifshitz-van der Waals forces;
-acid-base interactions.

2.2. JOINTS

2.2.1. TYPES

Adhesive joints can have many configurations as can be seen in figure 7. The most common are the single lap joints (SLJs), the double lap joints (DLJs), together with the chamfer (scarf joint) and stepped joints. The SLJ has been the most studied in literature, on experimental and theoretical terms, due to its facilitated fabrication. But that does not mean the tensions present in the joint are easy to analyze. In fact, the load is not collinear which introduces bending of the substrate. Therefore, the adhesive is subjected not only to shear forces but also to traction forces at the end of the joint [4].

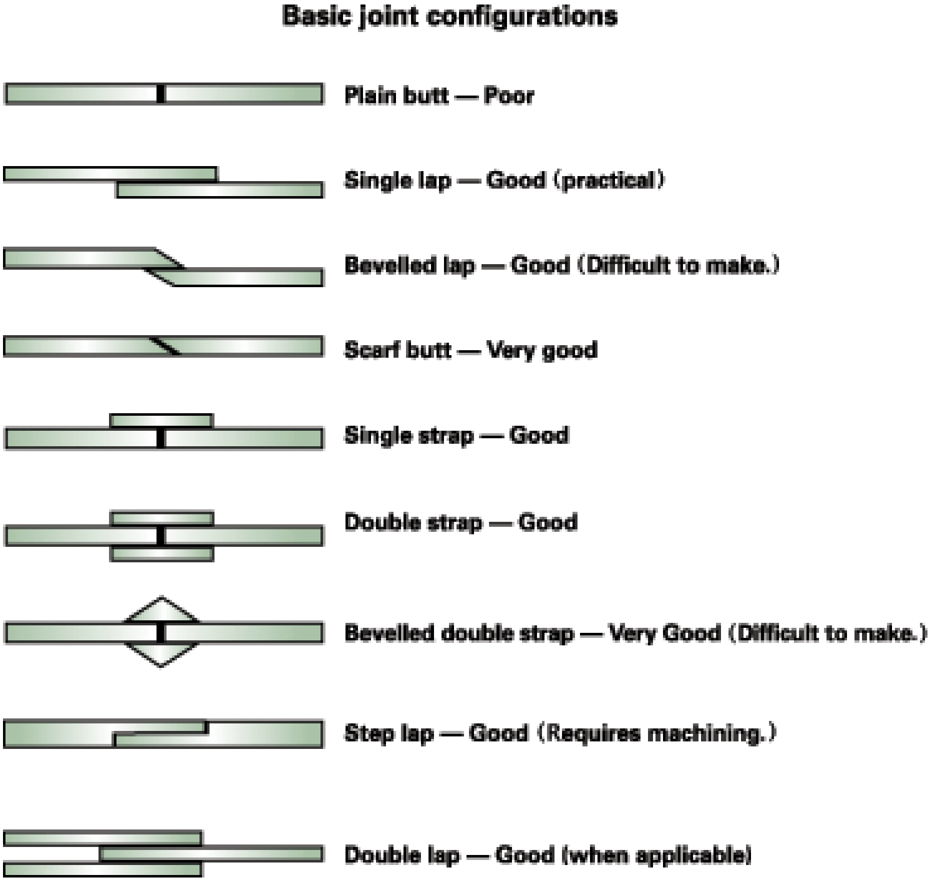


Figure 7 – Types of Joints [10]

2.2.2. FAILURE MODES

There are several reasons an adhesive bond may fail, but to begin to understand them first the failure mode must be determined. In figure 8 a schematic of the three possible failure modes when applying peeling forces to the adherends are represented.

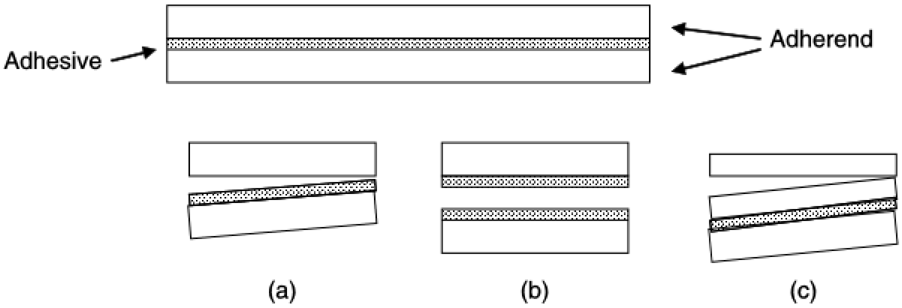


Figure 8 – Adhesive bond failure modes: a) adhesive failure; b) cohesive failure in the adhesive; c) cohesive failure in the adherend [6]

In the first case the bond failed adhesively at the adhesive-adherend interface (a) – adhesive failure. A cohesive failure occurs on the second case (b), separation occurred in the adhesive layer in such a way that both the adherends surfaces were covered with adhesive. When the adhesive bonds strength is greater than the adherend cohesive, failure in the adherend may happen (c).

Adhesive bond failures usually involve more than one mode, and are evaluated in percentages of cohesive-adhesive failure. The fraction of the area covered in adhesive is determined and a percentage attributed. A correct identification of the failure mode is essential to correct the underlying cause and save money.

100% cohesive failure within the adhesive layer is the ideal mechanism for the bond to fail.

The causes of premature failure are difficult to evaluate, incomplete wetting may cause suboptimal joint strength, different thermal expansion coefficients cause internal stresses during thermal cycling or after cooling flowing the curing process. To avoid this, fillers are often used or elastic adhesives.

The types of loads that act on bonds, their direction and rates at which they are applied are factors in determining a joint longevity. Sustained loads may cause premature failure, although some adhesives may fail under no load, particularly if they have been subjected to heat or humidity. Most adhesives exhibit very poor tolerance to peeling or cleavage loads. Rigid adhesives may have good shear strength but poor impact strength.

The way in which an adhesive bond fails should not be the only criterion used to determine how a joint should be dimensioned. Some adhesive-adherends may fail adhesively but exhibit greater bond strength than a similar bond that fails cohesively.

Ebnesajjad [6] defends that candidate adhesive bonds should be tested under simulated operating loads in a similar environment to that in which they will be operating, whenever possible [6].

2.3. TECHNOLOGIES FOR ADHESIVE DEBONDING ON COMMAND

2.3.1. THERMALLY EXPANDABLE PARTICLES (TEP$_S$) AND ADDITIVES USED FOR ADHESIVE DEBONDING

One of the technologies developed for adhesive debonding on command involves adding thermally expandable particles to the adhesive layer. Thermally expandable particles, microcapsules or microspheres, were developed by Dow Chemical Co in early 1970's [11] and are particles made up of a thermoplastic shell filled with liquid hydrocarbon. With the application of heat, the thermally expandable particles will suffer two stages (Figure 9): one is the softening of the shell material and the other is the gasification of the hydrocarbon liquid inside it. As a consequence, the shell will expand as the gas inside pushes the softened shell causing it to grow in size. When fully expanded, the volume of the particles can increase 50 to 100 times. When the heat is removed, the shell hardens and the particles remain expanded. This expansion occurs in the interval between 70ºC and 285ºC [12, 13].

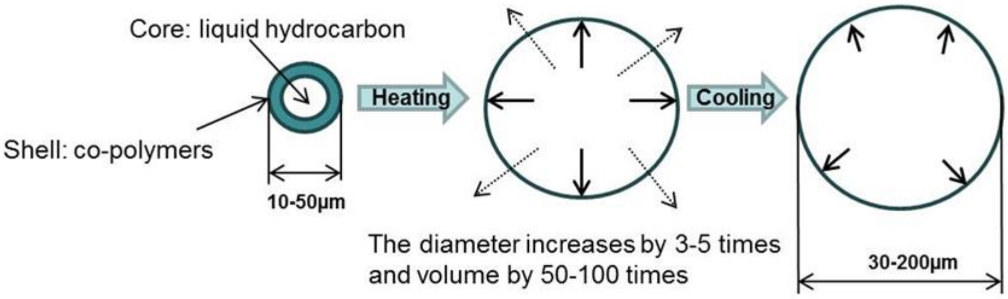


Figure 9 - Model of the expansion mechanism [12]

Due to this unique behaviour, TEPs are used by the industry in a wide variety of applications [1]. The simple heating of the joint over 100ºC leads to an easy separation of the bonded materials. The mechanism of separation can be seen in Figure 10. The adhesive expansion may be up to 400% according to the study of Nishiyama and Sato [14]. However, the high temperature performance in tests was poor since the particles began to expand around 60ºC and the glass transition temperature (T_g) of the adhesive was lower than the expansion temperature of the particles. High temperature performance is vital for structural applications such as in the automotive and aerospace fields. To overcome this problem, Kishi et al. [15, 16] used expandable graphite (which begins to expand at 200ºC) with an epoxy adhesive to study the debonding of CFRP and steel plates adhesive joints and reached a good dismantling level at 250ºC . However, presently TEPs' producers develop particles with higher expansion temperatures. Recently, Kim et al. [17] used TEPs with a polyurethane adhesive and found that the dismantlement of the joint was possible with microwave treatment for 4 mins.

Another technology for debonding by applying heat to structural adhesives is called INDAR Inside®, developed and patented by Rescoll Technological Center [18-19]. This technique is based on adding specific additives to bulk adhesives or primers. When the heat is applied at a specified temperature the additives start to decompose and release gases which migrate by diffusion from the bulk adhesive to interfaces generating local stresses leading to the debonding of the joint. The temperature needed depends on the additive, so several temperatures are possible. This technology has been implemented for ground proof tests of the structure of the GAIA, in spacecraft and in the dismantling of plastic tailgates. A great advantage of this technology is that the parts are easy to clean due to interfacial failure, but a big difference between the maximal service temperature and the debonding temperature must be guaranteed in order to avoid premature activation of the additives [12, 13].

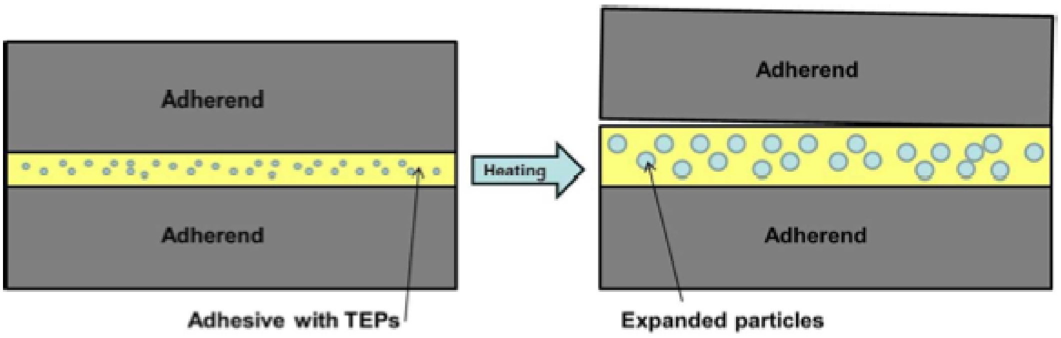


Figure 10 - Mechanism of separation (debonding) [13]

2.3.2. NANOPARTICLES USED IN ADHESIVE DEBONDING

Nanoparticles can also be used in adhesive debonding. The bonded joint has at least one primer layer which contains nanoscale particles with ferromagnetic, superparamagnetic or piezoelectric properties. As a result of the alternating electromagnetic fields, large amounts of localized heat are produced in the primer layer of the bonded joint. This localized heat input causes the softening of the thermoplastic binder, in the case of adjacent thermoplastic adhesive layers. If thermoset adhesives are adjacent to the boundary layer of the primer, then the cross-linked structure in the matrix is broken up due to the high degree of localized warming. In both cases, quasi-adhesive substrate separation is enabled with a low energy input as a result of the high localized warming of the boundary layer.

A similar system has been presented by Kolbe et al. and generally follows the principle of an alternating magnetic field introducing heat into the adhesive. Moreover, this approach can be used for any application where at least one non-metal substrate is bonded. Preferably, both substrates should be non-metallic, as metal by itself is strongly heated in the magnetic field and shield field [12, 13].

Another application is the modification of an epoxy adhesive by the addition of different contents of CNFs for bonding carbon fiber/epoxy composite adherends. It was concluded that the addition of nanoreinforcements did not significantly affect the lap shear strength of single lap joints [20]. The problems found were associated with the difficulties of obtaining a suitable dispersion of the nanoreinforcements. Good dispersion of the nanoreinforcements in the adhesive reduces the stress concentrations and enhances uniformity of stress distributions.

Another application of nanoparticles is to self-heal in polymeric materials, that are used to repair cracks, is an emerging approach to create self-healing materials, so solid state healing agents can be part of the material to create self-healing material so liquid healing agents can be avoid and to avoid the destruction and rebonding the joints. This phenomenon uses a dispersed particulate phase to fill cracks as they occur.

These phenomenon was studied by Lee [21] using computer simulations. The nanoparticles were dispersed in polymer films within a composite and a self-healing mechanism was suggested via nanoparticles migration in the crack and pre-crack region, figure 11.

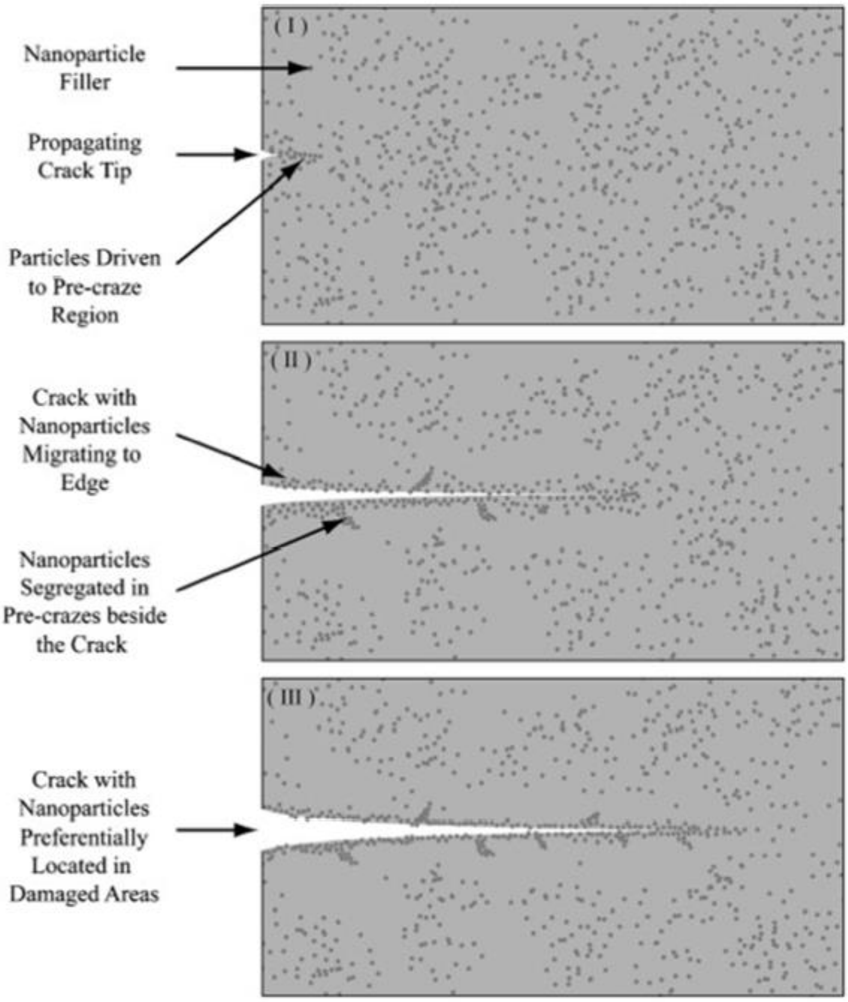


Figure 11 - Schematic representation of the nanoparticle movement during crack growth in thermoplastics [13]

2.3.3. DIELS-ALDER CHEMISTRY

Sandia National Laboratories have developed a removable adhesive that reacts to temperature change. This technology is based on the use of a reversible chemistry, figure 12, (Diels-Alder bonds) that breaks apart the adhesive at elevated temperatures, resulting in a low adhesive molecular weight and low bond strength. The adhesive bond breaks at 90º-130ºC depending on the formulation. Then, the adhesive rebonds between 20º and 60ºC. However, the rebonding capability is finite. The adhesive will bond and debond a number of times but will at some point become non-removable. It was claimed that these adhesives may be advantageous for bonding expensive electrical or electromechanical components [12, 13].

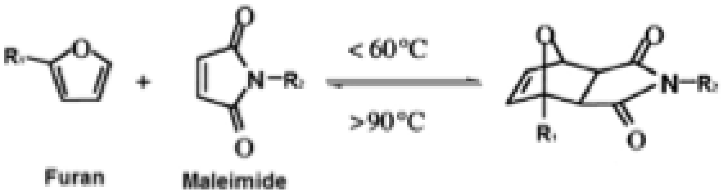


Figure 12 - Reversible Diels-Alder reaction between furan and maleimide [22]

2.3.4. ELECTRICAL DISASSEMBLY OF ADHESIVE JOINTS

Electrically induced debonding of adhesive is a technique in which adhesives can be released at command with the help of an applied potential, figure 13. Depending on the potential applied to the adhesive joint (10-50 volts recommended), the substrates can fall apart in seconds. This technology called ElectRelease^{TM} was developed by EIC Laboratories. The adherend surfaces must not be in contact to prevent any short circuit between substrates. However, the technology can be applied to non-conductive or coated substrates using an aluminum foil patch pre-bonded with ElectRelease^{TM}. A number of adhesive formulations were patented. Two of these, epoxy based, are on the market as E4 and M4 [12, 13].

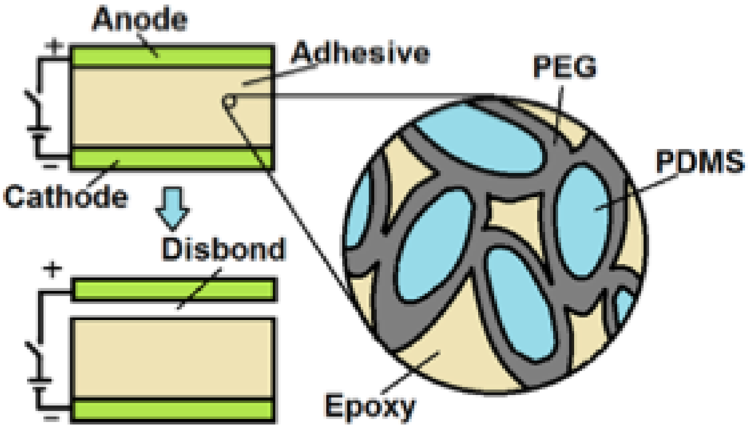


Figure 13 - Microscopic structure of ElectRelease [21]

3. EXPERIMENTAL WORK

3.1. MATERIALS

3.1.1. ADHERENDS

Hard steel substrates were used for the single lap joint specimens, in order to ensure an elastic behavior of the adherends. The mechanical properties of the DIN EN10132-4 hard steel are given in Table 3 (data provided by the supplier).

Table 3 - Mechanical properties of steel substrates

Tensile failure strength [MPa]	-
Yield Stress [MPa]	1050
Elongation %	-
Young's modulus, E [GPa]	210

3.1.2. ADHESIVES

For this study two adhesives used in the automotive industry were selected, with good crash durability and high lap shear and dynamic impact strength, as claimed by the manufacturers. A two-component ductile structural polyurethane adhesive SikaForce®7888, supplied by Sika (Sika, Portugal), whose properties were previously obtained in 2015 by Banea Banea, M.D., et al [23]:

Table 4 – Properties of adhesive SikaForce 7888 [23]

Property	
Young's Modulus, E [GPa]	2.5
Tensile failure strength, σ_f [MPa]	30
Tensile failure strain, ε_f [%]	46
T_g[1] [ºC]	40

[1] Data provided by the manufacturer (esp.sika.com)

And a two-component ductile epoxy adhesive Betamate^{TM}2098, supplied by Dow Automotive (Dow Europe, Switzerland):

Table 5 – Properties of adhesive Betamate 2098 [23]

Property	
Young's Modulus, E [GPa]	0.93
Tensile failure strength, σ_f [MPa]	18
Tensile failure strain, ε_f [%]	56
T_g [ºC] [2]	60

[2] Data provided by the manufacturer (www.dowautomotive.com)

3.1.3. THERMALLY EXPANDABLE PARTICLES

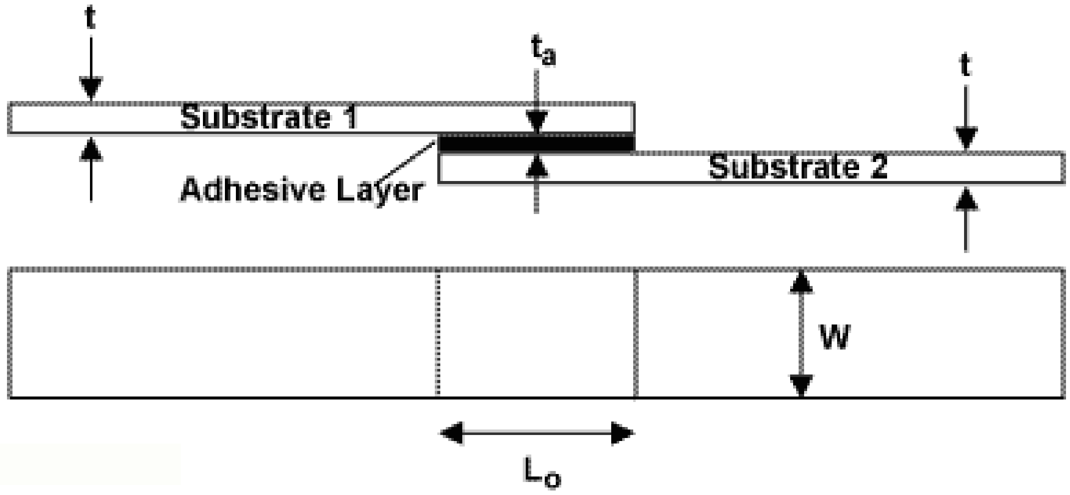
Expancel 031 DU 40 particles supplied by Expancel Nobel Industries (AkzoNobel, Sweden) were used. The diameter of these particles ranges mainly from 10 to 16 µm. Data provided by the manufacturer is given in Table 6 [23]. T_{start} represents the temperature at which the particles begin to expand and T_{max} the point of maximum expansion.

Table 6 – Characteristics of Expancel 031 DU 40

Particle size [µm]	10-16
T_{start} [ºC]	80 - 95
T_{max} [ºC]	120 - 135
Density	≤12

3.2. JOINT GEOMETRY

The joints were manufactured with steel substrate thickness of 2mm (t), the adhesive thickness selected was 0.2mm (t_a), and the width was 25mm. The geometry was chosen based on the standard procedure in use at the facilities of FEUP and can be seen in Figure 14.



t=2mm; ta=0.2mm; w=25mm; L_0=25mm

Figure 14 - Joint Geometry

3.3. JOINT FABRICATION

The steel substrates were fabricated separately respecting the previously defined dimensional requirements.

3.3.1. SURFACE PREPARATION

A surface treatment was performed after the manufacturing of the steel plates, to increase the adherence of the adhesive, to clean the surface and clear the oxides that usually accumulate there. The surface was treated with sand (SiO_2) in a Sand Blaster (Figure 15).

Figure 15 - Sand Blaster

After the sand blasting surface treatment, the specimens were subjected to a cleaning process, in order to eliminate possible contaminations of the surface. Thus, paper soaked in acetone was used, vigorously wiping the specimen treated surface. The final result can be seen in figure 16.

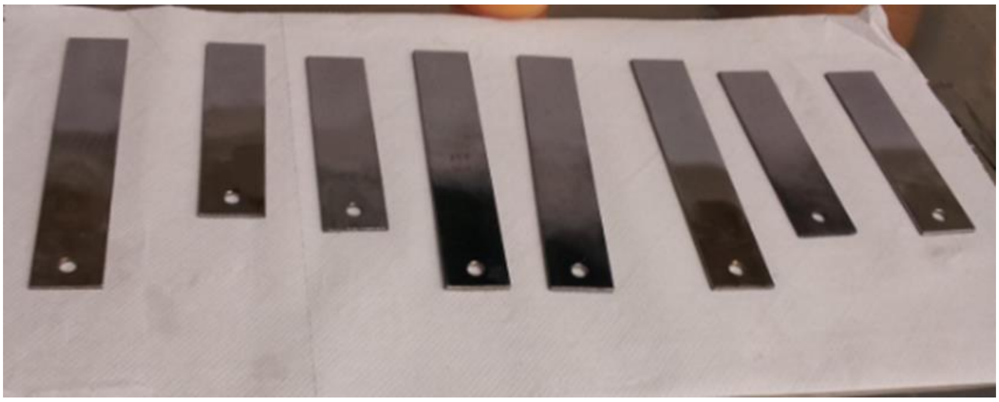


Figure 16 - Specimen after Sand Blaster

3.3.2. MOULD PREPARATION

In order to guarantee uniform and consistent thickness along the adhesive joint, the fabrication of the joints was done using a mould, figure 17.

It was ensured that the mould had a mould release agent layer thick enough to avoid bonding between the specimen and the mould (glossy surfaces indicate that they no longer have mould release agents).

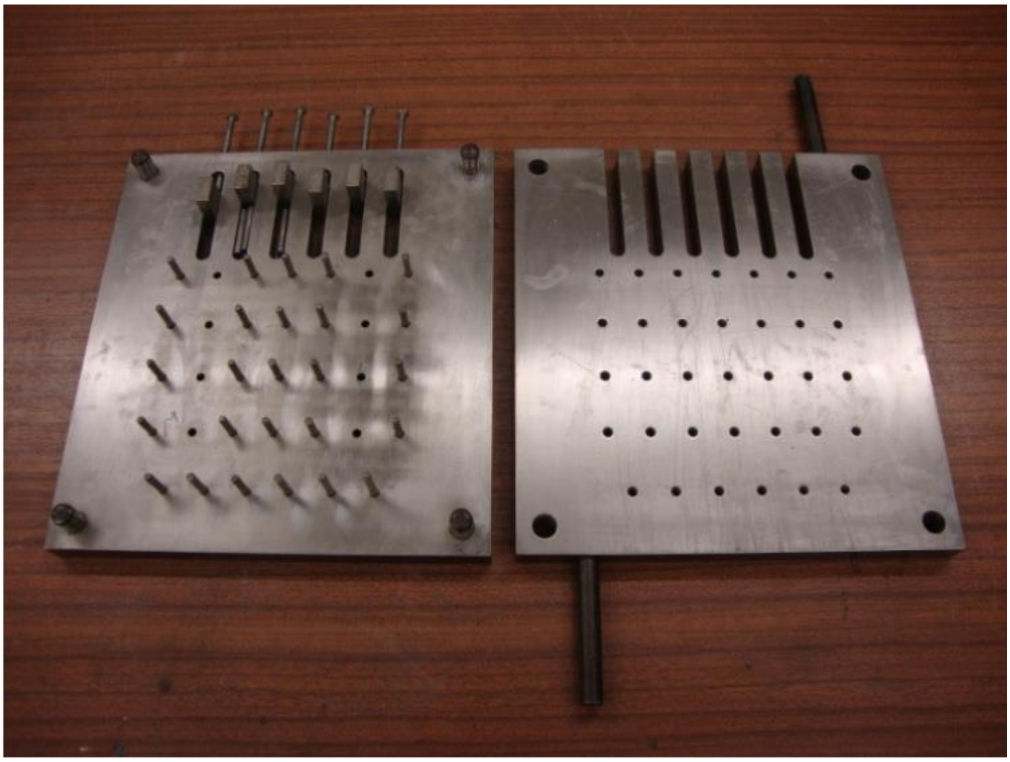


Figure 17 - Mould used to manufacture the specimens

The first half of the substrates and spacers were placed onto the mould. These spacers were used to guarantee the correct alignment of the substrate, figure 18 and figure 19.

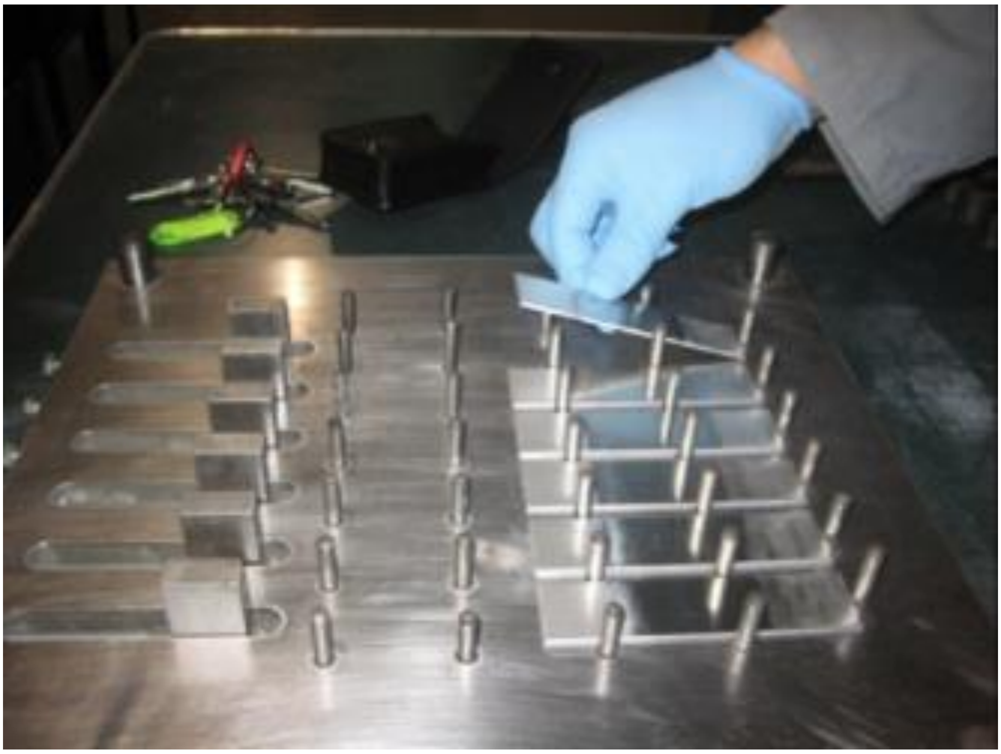


Figure 18 – Adherends’ placement

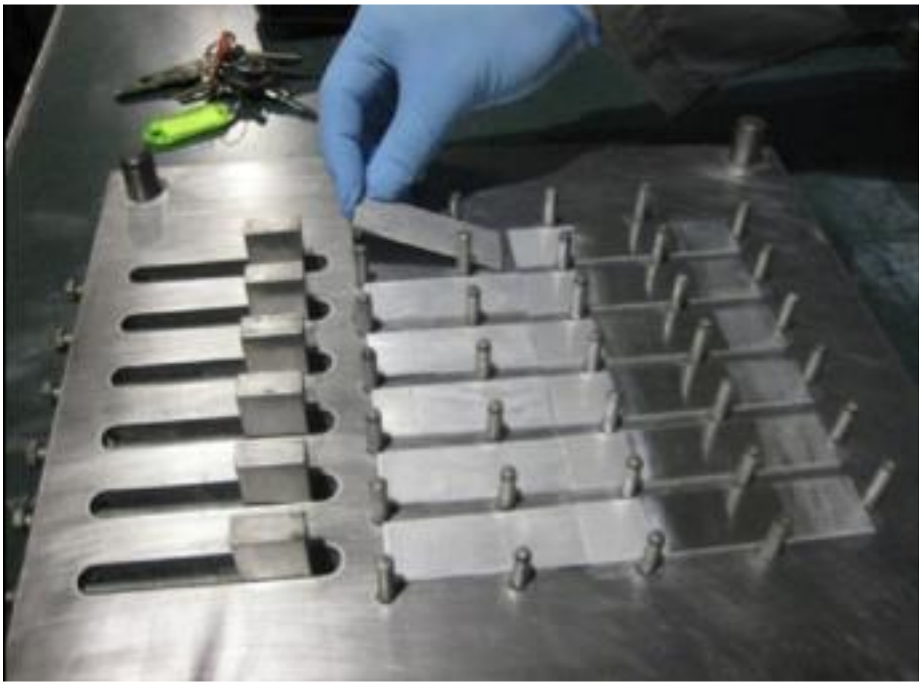


Figure 19 – Spacers' placement

3.3.3. JOINT FABRICATION

TEPs were added to the chosen adhesives in different weight percentages (wt%). For a uniform and controlled mixture of all the samples, a Speed Mixer (DAC 150.1 FVZ Speedmixer, Hauschild, Germany - figure 21) was used, and careful dosing of the components with the use of an electronic scale (figure 20) to guarantee the right quantity of each component. The mixing speed selected for the manufacturing of the adhesives was approximately 2500RPM's for one minute.

Figure 20 - Electronic Scale

Figure 21 - Speed Mixer

With the help of a spatula, a good amount of adhesive was placed on the overlap and on the middle of the tab ends' bonding area, figure 22. Then, the remaining adherends and spacers, top side, were placed in position, figure 23. To conclude this stage, the top cover of the mould was put in place, figure 24.

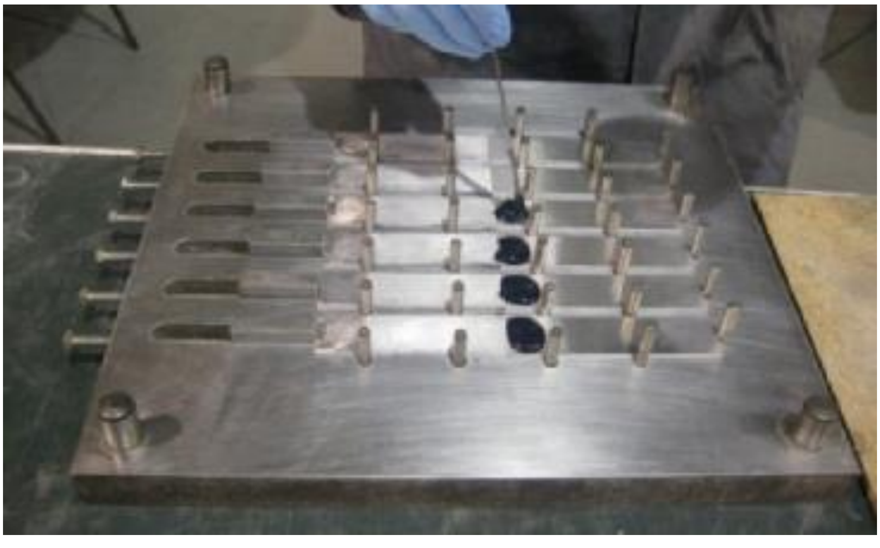


Figure 22 - Adhesive application

Figure 23 – Adherends' placement

Figure 24 - Placement of the mould's top cover

The mould was then placed on hot plated press (figure 25). The same pressure was applied for SikaForce 7888 and Betamate 2098, a force of 2000N for 24 hours. The mould was then removed from the press and left at room temperature to complete the curing process (eight days in total).

Figure 25 - Hot plated press

Figure 26 - Hot plated press (detail of how the moulds were pressured)

Once the cure cycle was complete, the specimens were separated from the mould, removing the mould pins, (figure 27) and from each other, when needed, with the assistance of a saw (figure 28). To remove the excess of adhesive, a woodworking file was used (figure 29).

Figure 27 - Mould pin removal

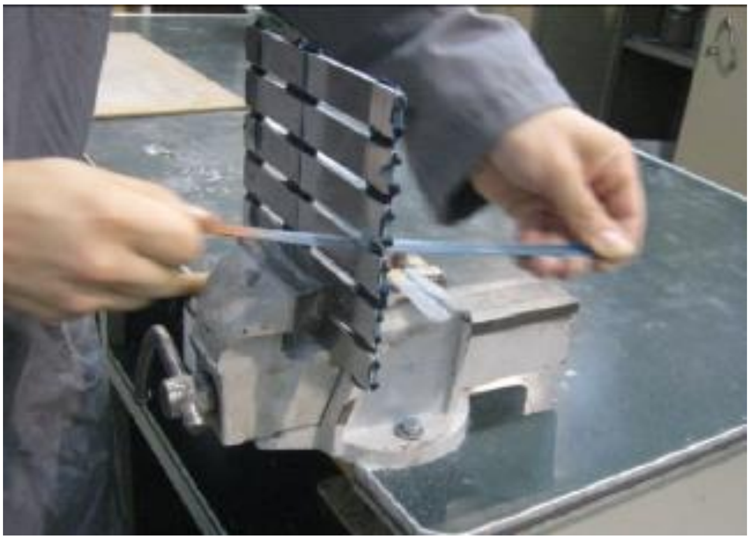


Figure 28 - Specimen separation

Figure 29 - Adhesive excess removal

After these steps the specimens were finished and ready for the test cycle.

4. EXPERIMENTAL TESTING

4.1. STRENGTH TEST

After the adhesive excess removal the verification of the joint thickness was performed with the use of calipers. Then the single lap joint tests were conducted at RT at a constant displacement rate of 1 mm/min using a MTS 312.31 servo-hydraulic machine, figure 30. The values were monitored and registered with the help of a load cell of 100 KN.

Three specimens for each adhesives TEPs wt% were tested to failure.

Figure 30 - MTS 312.31 servo-hydraulic machine

4.2. ELECTROMAGNETIC INDUTION (EVALUATION OF DEBONDING)

Induction heating is a process of heating an electrically conducting object (usually a metal) by electromagnetic induction, where eddy currents (also called Foucault currents) are generated within the metal and resistance leads to Joule heating of the metal. An induction heater (for any process) consists of an electromagnet, through which a high-frequency alternating current (AC) is passed. Heat may also be generated by magnetic hysteresis losses in materials that have significant relative permeability. The frequency of AC used depends on the object size, material type, coupling (between the work coil and the object to be heated) and the penetration depth [25].

As was previously mentioned, debonding of adhesive joints was achieved by providing heat to the TEPs, increasing the particles size up to 400% of their initial dimension [14].

To achieve this goal, the chosen solution was heating through an artisanal electromagnetic induction coil (as can be seen in figure 31).

Figure 31 - Artisanal electromagnetic induction coil

Representation of this process (figure 32) and its advantages:

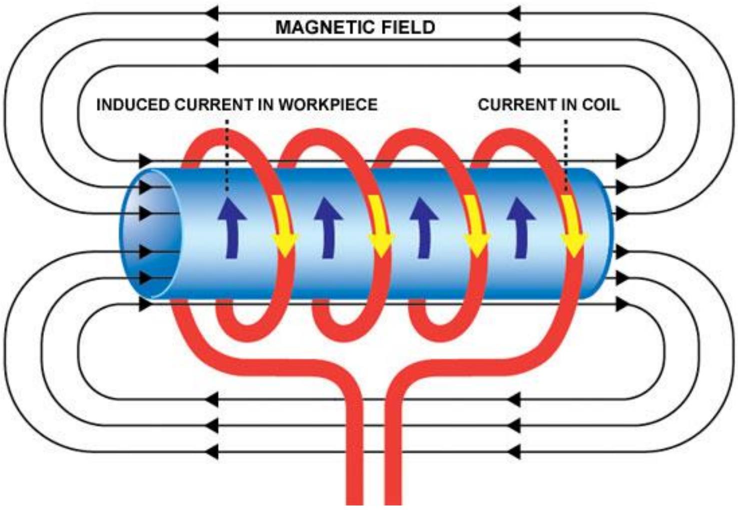


Figure 32 - Electromagnetic induction representation

This solution provides several advantages:

- No physical contact
- Heat can be focused on the adhesive bond line.
- It is fast, cheap and accurate.
-When properly set up, the process becomes very repeatable and controllable.

The elements of the induction heating machine can be seen in figure 33:

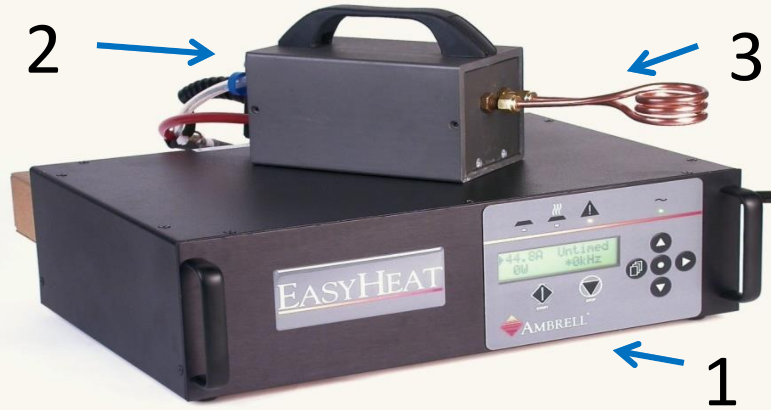


Figure 33 - Elements of the system

1- *Power source*: receives, rectifies and regulates the AC
2- *Heating station*: adjusts the frequency and voltage
3- *Induction coil*: creates the electromagnetic field

For a specific application, the design of a suitable induction coil is very important. Experience acquired from previous research formed the basis for the design of the induction coil [26, 27].

The SLJs specimens were placed in the fixture inside the induction coil and then a 100 N mass was applied in tension. The alternating magnetic field induces eddy currents in the SLJs overlap region and heats it.

Some trials (figure 34) were performed to discover the temperature needed to reach debonding, using the expanding properties of the TEPs.

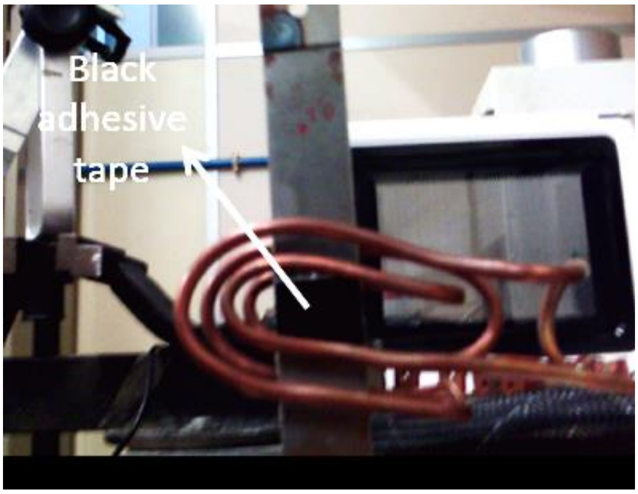


Figure 34 – Test setup

The temperature was monitored with a thermographic camera (Fluke FLK-Ti25, Eindhoven, Netherlands) by using a temperature profile as can be seen below, figure 35. This setup directly allows determining the temperatures that the TEPs-modified adhesives are subjected to. When the power supply is switched on, the timer is started in order to measure the time to failure for each joint tested.

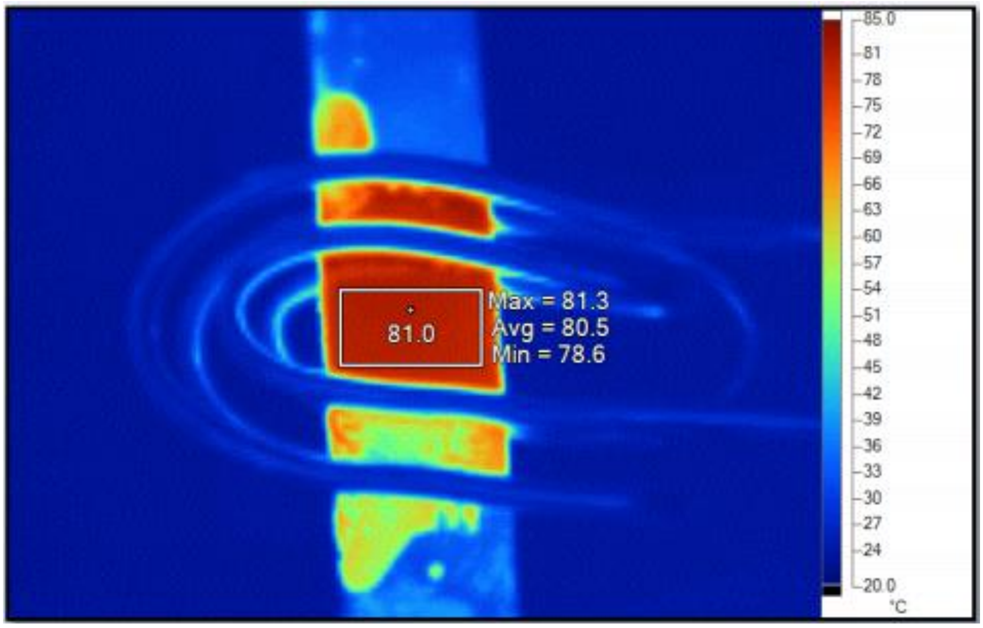


Figure 35 - Infrared (temperature profile)

This setup directly allows determining the temperatures that the TEPs'-modified adhesives are subjected to. When the power supply is switched on, the timer is started in order to measure the time to failure for each joint tested.

Debonding evaluation was made with the following sequence:

- If the joint broke, then the temperature and the time of the failure were recorded.

- If the joint did not break, the residual strength was measured.

At least three specimens from each wt% TEPs (from 0% to 25%) were tested.

To find the best setup to perform the previous sequence, some preliminary trials were done to investigate which parameters should be setup into the induction heater (power and frequency), as well as the influence of the geometry of the SLJs (adherend and adhesive thickness) on the debonding time and temperature to break the connection.

4.3. PRELIMINARY TESTS

4.3.1. INDUCTION HEATING METHOD PARAMETERS

The optimization of the induction heating system for this specific application depends on several factors: the characteristics of the part itself, the design of the induction coil, the capacity of the power supply and the temperature change required for the application [28]. The optimizations were essentially based on direct experimental tests performed on specimens of SikaForce7888 SLJs with 20 wt% TEPs subjected to different induction heating parameters. It was found that a too high heating rate, augmenting the power and frequency of the electromagnetic field, does not allow the TEPs to expand and consequently separate the joint and the bond breaks due to the thermal degradation of the adhesive.

Experimental test 1:

Power: 40kA
Temperature: 240 ºC
Comment: After 40 secs, the debonding occurred due to adhesive thermal degradation.

Experimental test 2:

Power: 30 kA
Temperature: 140ºC
Comment: The joint failed after 80 secs.

Experimental test 3:

Power: 20 kA
Comment: The joint failed after 7 mins.

Chosen setup:

Power: 30 kA
Frequency: 360 kHz

With these parameters the temperature achieved coincides with the TEPs temperature of maximum expansion, and thus provides a good basis for experimentation.

4.3.2. JOINT GEOMETRY

To check the influence of the joint adherend thickness some trials were performed with 1.5mm and 2mm adherend thickness of SikaForce 7888 SLJs with 20 wt% TEPs. As previously mentioned, the temperature of the specimens' debonding was 140 ºC, and the only difference was the time to debond (with 1.5mm adherend thickness, the debonding occurred after 60secs and with 2mm it occurred after 80secs). This increase on the time to debond was expected due to the transfer of induction heating energy that directly depends on penetration depth.

Some trials were performed with 0.2mm and 0.4mm adhesive thickness and no significant difference in the debonding temperature and time was registered. So it can be concluded that the adhesive thickness does not influence the debonding of the joint.

Hence, analyzing these preliminary tests, the 0.2mm adhesive thickness and 2mm adherend thickness were chosen (as mentioned before) and used in the tests.

5. RESULTS

In order to achieve a better understanding the influence of TEPs combined with adhesive, the specimens were modified with different concentration of TEPs and compared to the unmodified joints. Strength tests were performed with 0%, 5%, 10%, 15%, 20% and 25% of TEPs with each adhesive.

5.1. SLJS

5.1.1. FAILURE MODES

After the tests, the failure modes of the specimens were visually evaluated. As expected, the increase of TEPs created an effect of bubbles and an irregular surface, due to the expandable nature of TEPs that weakened the adhesive structure.

As can be seen in Figure 36, all the failure modes on the SLJs specimens were cohesive and no plastic deformation of the adherends was visible.

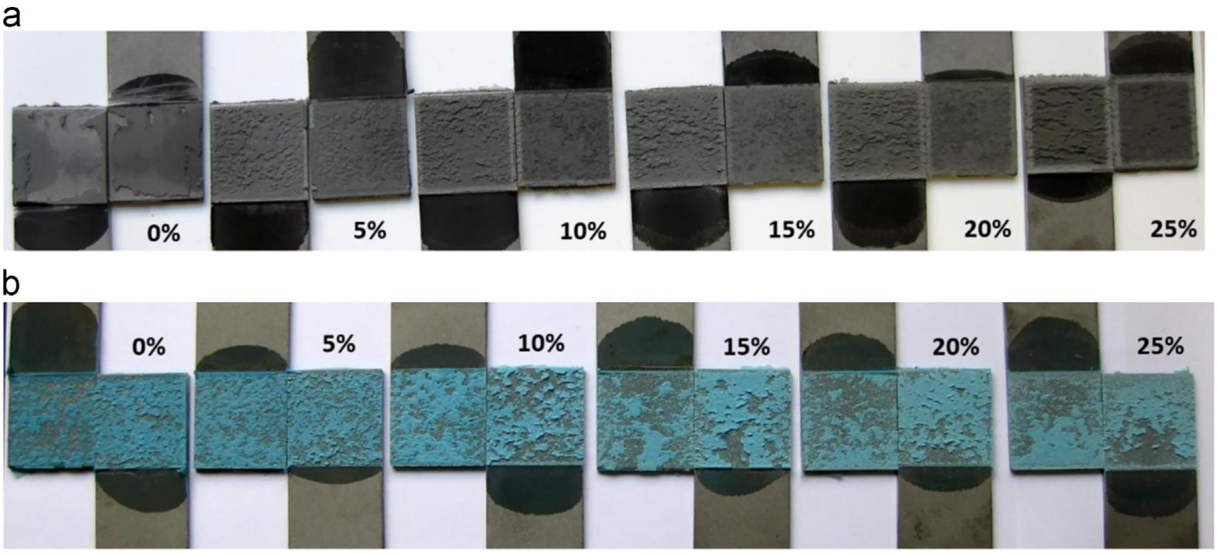


Figure 36 - Typical SLJs' failure modes as a function of wt% TEPs: a) SikaForces7888, b) Betamate™2098.

5.1.2. *P*-δ CURVES

Tensile strength tests were performed at RT on all specimens (3 specimens from each wt% TEPs). For each specimen, a load-displacement was recorded, as can be seen in the graphic below.

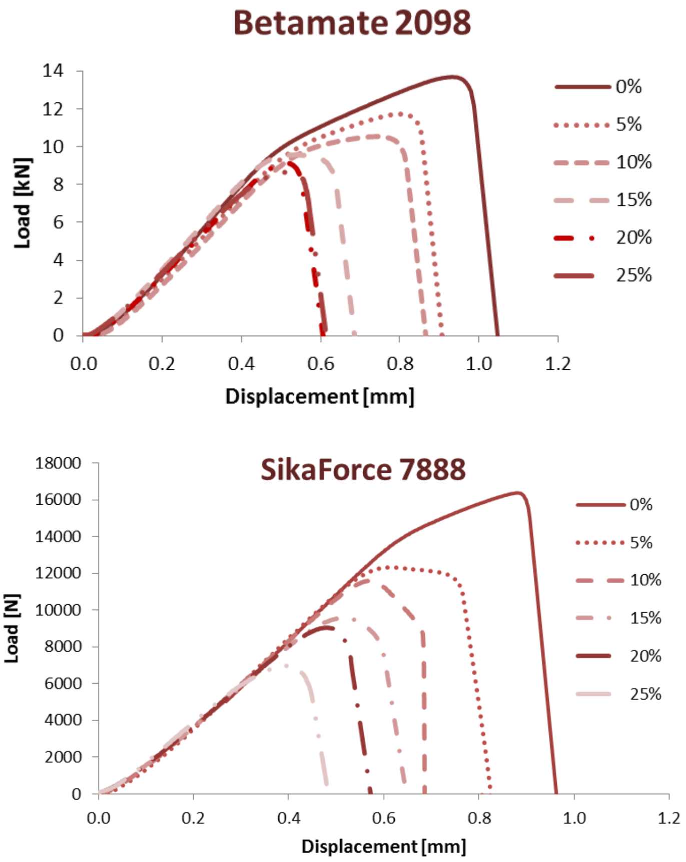


Figure 37 - Betamate 2098 & Sikaforce 7888 Load vs Displacement

As shown in Figure 37 the increase of wt% TEPs causes a decrease in both the maximum load and displacement.

Lap shear strength was evaluated using the following formula:

$$Lap\ shear\ strength = \frac{Loadforce}{Area}$$

$$Area = wL;$$

Where w=width and L=overlap length

For SikaForce 7888, tensile strength tests were performed on all specimens (3 specimens from each wt% TEPs) in the same conditions as for Betamate 2098. For each specimen, a load-displacement was recorded as can be seen in the graphic above, figure 37.

The variation of the displacement and lap shear strength as a function of wt% TEPs is presented in figure 38.

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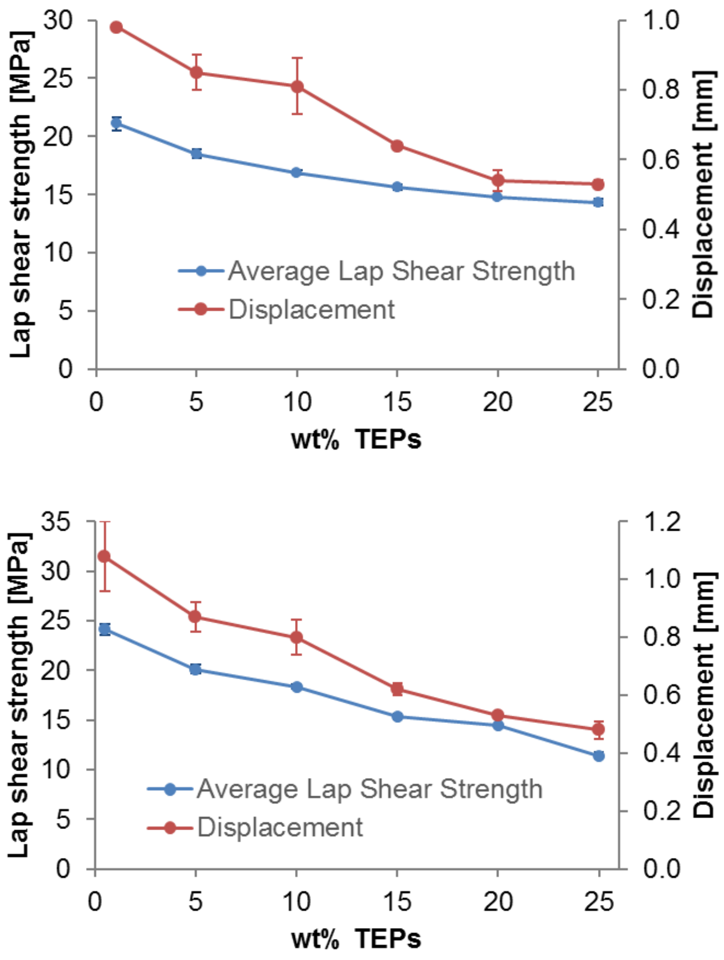

Figure 38 - Betamate 2098 & Sikaforce 7888 Lap shear strength and displacement as a function of wt%

The average loss in lap shear strength and displacement due to wt% TEPs, in percentage, was calculated and can be seen in the tables 7 and 8, respectively.

wt% TEPs	loss in lap shear strength Betamate 2098
5%	13.98%
10%	21.45%
15%	27.29%
20%	31.46%
25%	33.28%

Table 7 - Comparison of wt% TEPs and average loss in lap shear strength

wt% TEPs	loss in displacement Betamate 2098
5%	13.51%
10%	18.24%
15%	35.14%
20%	45.27%
25%	46.28%

Table 8 - Comparison of wt% TEPs and average loss in displacement

The same evaluation was performed for SikaForce 7888, to calculate the average lap shear strength and displacement loss. The decrease, in percentage, can be seen in the tables 9 and 10.

Table 9 - Comparison of wt% TEPs and average lap shear strength loss

wt% TEPs	average loss in lap shear strength SikaForce 7888
5%	16.60%
10%	23.92%
15%	36.34%
20%	40.23%
25%	52.74%

Table 10 - Comparison of wt% TEPs and average loss in displacement

wt% TEPs	loss in displacement SikaForce 7888
5%	19.44%
10%	25.62%
15%	42.28%
20%	51.23%
25%	55.25%

The decrease in lap shear strength might be explained by the drastic change in the volume occupied by the particles in the adhesive structure. On the other hand, TEPs might act as hollow voids in the adhesive, becoming the sites of stress concentration [29].

Table 11 – Comparison between the adhesives behaviour

	wt% TEPs	5%	10%	15%	20%	25%
Loss in Lap Shear Strength	Betamate2098	13.98%	21.45%	27.29%	31.46%	33.28%
	SikaForce 7888	16.60%	23.92%	36.34%	40.23%	52.74%
Loss in displacement	Betamate2098	13.51%	18.24%	35.14%	45.27%	46.28%
	SikaForce 7888	19.44%	25.62%	42.28%	51.23%	55.25%

On table 11 we can compare the behaviour of the adhesives for each wt% TEPs used. It is immediately apparent that SikaForce 7888 has a bigger loss in lap shear strength with the added %wt of TEPs than Betamate 2098. Although for 5 and 10% wt% TEPs the difference is not significant between the adhesives, for higher TEPs content this difference increases sharply.

This is also true when we compare the displacement loss, but in this case the initial difference between the adhesives is apparent from low wt% of TEPs.

5.2. EVALUATION OF DEBONDING

5.2.1. FAILURE MODES

After the debonding tests, the failure modes of the specimens were visually evaluated. The ideal would be for the debonding to happen with an adhesive failure, to avoid, as much as possible, the restoring or preparation of new joints.

To show/compare the failure mode depending on each wt%, their pictures are shown in Figure 41-43.

As can be seen in the picture below, an unmodified SikaForce 7888 specimen had a cohesive failure near the interface. The temperature for debonding was 230ºC.

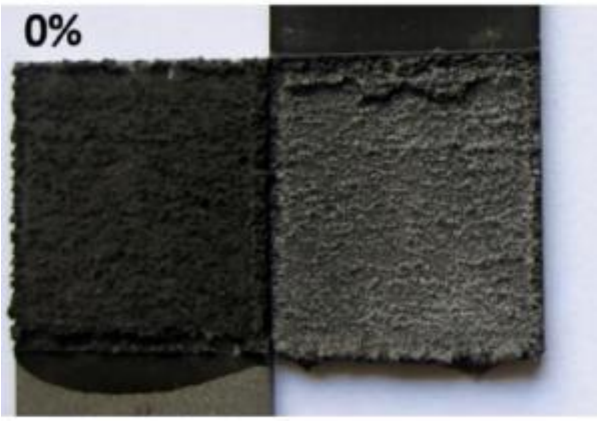

Figure 39 - SikaForce 7888 with debonding temperature of 230ºC

For 10 wt% the failure was mixed, cohesive and adhesive, as the picture below shows. The temperature for debonding was the same, 230ºC.

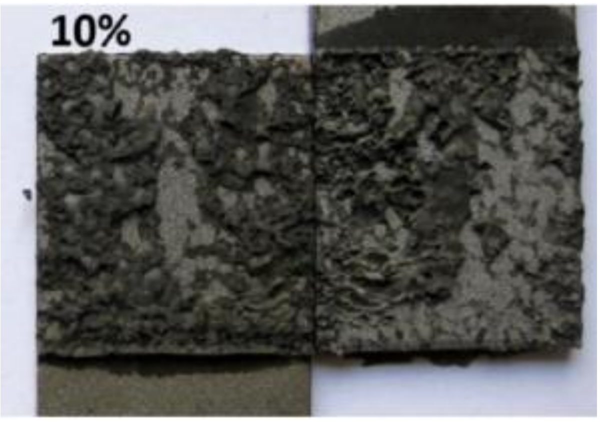

Figure 40 - Sikaforce 7888 with debonding temperature of 230ºC

For 20 wt% and for 25wt% it was still a mixed failure, as can be seen in the pictures below. For this wt% the debonding temperature was around 140ºC.

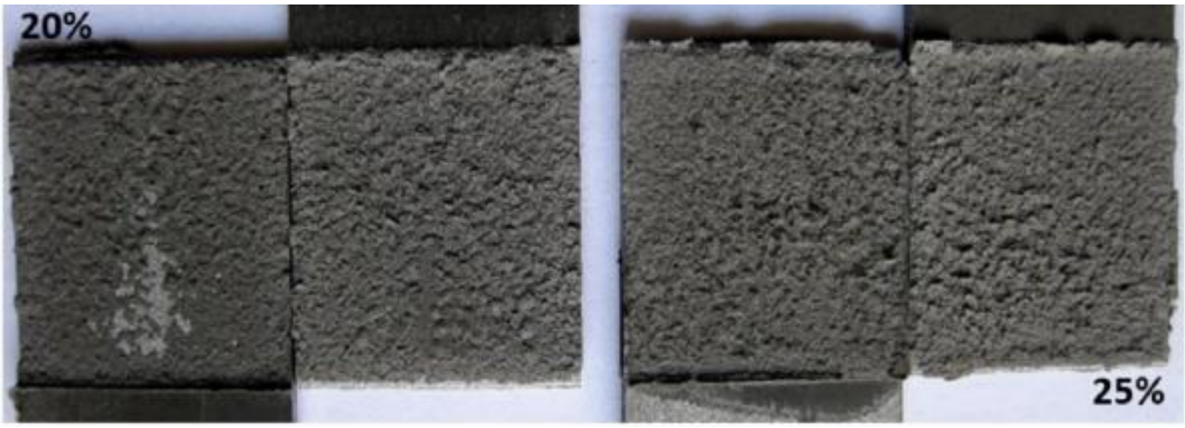

Figure 41 - SikaForce 7888 with a debonding temperature of 140ºC

For Betamate 2098 we can see that a mixed failure was also observed. On the 0 wt% the degradation of the adhesive was visible, due to the changed color (blue to green). The temperature for debonding was 250ºC for 0 wt% and 175ºC for 5 wt%, figure 44.

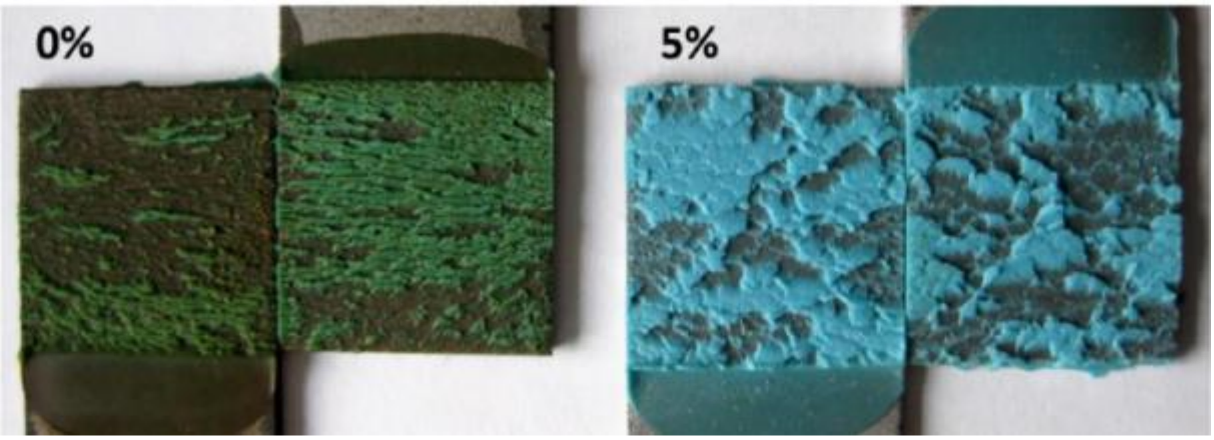

Figure 42 - Betamate 2098 0 wt% with debonding temperature of 250ºC and 175ºC for 5 wt%

5.2.2. DEBONDING TESTS

As can be seen in the following table, the specimens of SikaForce 7888 need different temperature and time for debonding, depending on the wt% TEPs of the specimens.

Table 12 – SikaForce 7888 debonding temperature and time needed for each wt%

SikaForce 7888	Temp. for debonding	Time[s]
0 wt%	230^0C	170
5 wt%	228^0C	170
10 wt%	226^0C	170
15 wt%	168.3^0C	100
20 wt%	143.3^0C	80
25 wt%	142.3^0C	75

The variation on 0 wt%, 5 wt% and 10 wt% is insignificant, both in temperature and time (T~230ºC; ~170secs). In all of them, the debonding occurred due to the degradation of the adhesive.

For 15 wt% the decrease was significant and dropped to ~170ºC.

For 20 wt% and 25 wt% the debonding occurred almost at the same temperature, ~140 ºC, and around 80 secs.

To sum up, for SikaForce 7888, we can assume that the easy conditions for debonding are with TEPs equal to or higher than 20 wt% and a temperature equal to or higher than 140ºC.

The SLJs that did not fail were submitted to strength test so the residual mechanical properties of the joint could be evaluated.

For the 0 wt%, the residual failure load increased approximately 30%. For 5 wt% a 20% increase was observed. This increase is due to the post-curing effect.

For the 10 wt% specimen, the residual failure load remained unchanged. For 15 wt% the failure load decreased by approximately 50%. This decrease indicates that with the increase of TEPs the joint weakens but maintains the cohesion, without debonding.

To conclude, the necessary temperature to debond the adhesive dropped over 40% of the initial value when 25 wt% TEPs were added.

Now, evaluating the debonding of the Betamate 2098, table 13 represents the temperature and time needed for debonding, depending on each wt%TEPs modified specimens.

Table 13 - Betamate 2098 debonding temperature for each wt%

Betamate 2098	Temp. for debonding	Time[s]
0 wt%	248.7^{0}C	200
5 wt%	174.3^{0}C	100
10 wt%	161.7^{0}C	90
15 wt%	145^{0}C	80
20 wt%	129.3^{0}C	70
25 wt%	121.3^{0}C	60

As can be seen, Betamate 2098 had a very different behavior. Comparing the unmodified specimens, SikaForce 7888 and Betamate 2098, the temperature and time needed for debonding is related to the different glass transition temperatures of the adhesives.

For the 0 wt% the temperature for debonding was around 250ºC.

For the 5 wt% the temperature and time decreased substantially to 175ºC and 100secs.

For 10 wt% the temperature for debonding decreased to 160 ºC and the time to 90secs.

For 15 wt% the debonding occurred at 145ºC, while for 20 wt% it occurred at 130ºC.

Finally, for 25 wt% the debonding happened at a temperature of 120ºC in 60secs.

So, the conclusion was that the conditions for easy debonding are a temperature equal to or higher than 120ºC and TEPs equal to or higher than 15wt%.

The temperature at which debonding occurs suffered a very significant decrease with a small percentage of TEPs, and at 25 wt% is under 50% of the necessary temperature to debond the adhesive without TEPs.

5.2.3. RESULTS OVERVIEW

From the analysis of table 14, one can gather that there is a relevant loss of mechanical properties with the necessary TEPs content for easy debonding, but SikaForce 7888 lap shear strength suffers a more pronounced loss, due in part to the higher initial value (0 wt%). If the same wt% (15%) of TEPs were applied to both adhesives, the resulting mechanical properties would be very similar but SikaForce would require approximately 170ºC and 100 seconds to debond, 30ºC higher and 20 seconds longer than Betamate.

Both adhesives lose part of their ductility, but again SikaForce 7888 is more affected as it loses over 50% of its displacement.

Table 14 – Results overview

Adhesive	**TEPs ideal debonding %wt**	**Debond. Temp. [ºC] 0 % wt TEPs**	**Debond. Temp. [ºC] ideal % wt TEPs**	**Time to debond [s]**	**Displacement [mm] 0% wt TEPs**	**Displacement [mm] ideal % wt TEPs**	**Displacement Loss[%]**	**L. Shear Strength [MPa] 0% wt TEPs**	**L. Shear Strength [MPa] ideal % wt TEPs**	**Av. Loss in L.Shear Strength ideal %wt TEPs [%]**
SikaForce 7888	>20%	230	>140	80	1.08	<0.53	51	24.16	<14.44	40
Betamate 2098	>15%	248.7	>120	60	0.99	<0.64	35	21.50	<15.64	27

6. CONCLUSION

In this study, the behavior of the debonding on command of adhesive joints with TEPs was investigated. The following conclusions could be drawn:

- The debonding of commercial automotive adhesives is possible. The wt% of TEPs and the temperature are the major factors in determining the debondability of the joints.
- With the increase of wt% TEPs in the adhesive structure, the lap shear strength reduces drastically because of the volume occupied by the particles.
- For the debonding to be easier, the induction temperature value should be above the expansion temperature of TEPs, which is from 80ºC to 135ºC, but closer to this last value as it coincides with the TEPs maximum expansion.
- By adding TEPs, the debonding temperature can be lowered by as much as 52% for Betamate 2098 and 40% for SikaForce 7888.
- Debonding is easier with Betamate2098 than with SikaForce 7888, this is probably due to SikaForce being stiffer (higher cross-density and therefore less available free volume for the expansion of TEPs).
- The mechanical properties (tensile lap-shear strength) depend on the TEPs content, decreasing with increasing the TEPs content. However, the joints retain an adequate amount of strength (i.e. more than 70% of strength (approximately 15 MPa) for Betamate 2098 and 60% of strength (approximately 14.5 MPa) for SikaForce 7888 adhesive), which can meet, depending on the application, the tensile lap-shear strength requirements of the automotive industry.
- The debonding takes place within a few seconds (60s for Betamate 2098 and 80s for Sikaforce).

7. FUTURE WORK

There are multiple study possibilities in this area, as it is far from developed at this point. Just to name a few possibilities:

- Study the compatibility of TEP’s with different adherents and repeat the test, trying to emulate possible applications for the intended industries.
- Carefully observe if the required temperature for debonding induce any alteration on the adherends, either cosmetic or structural.
- Broaden the adhesive pool to test with TEPs, to ascertain if other types might have a better behaviour.
- Study the effect of TEPs on bonding durability (submit the joints to humidity and temperature).
- Study the effect of TEPs to impact resistance, fatigue and tenacity.

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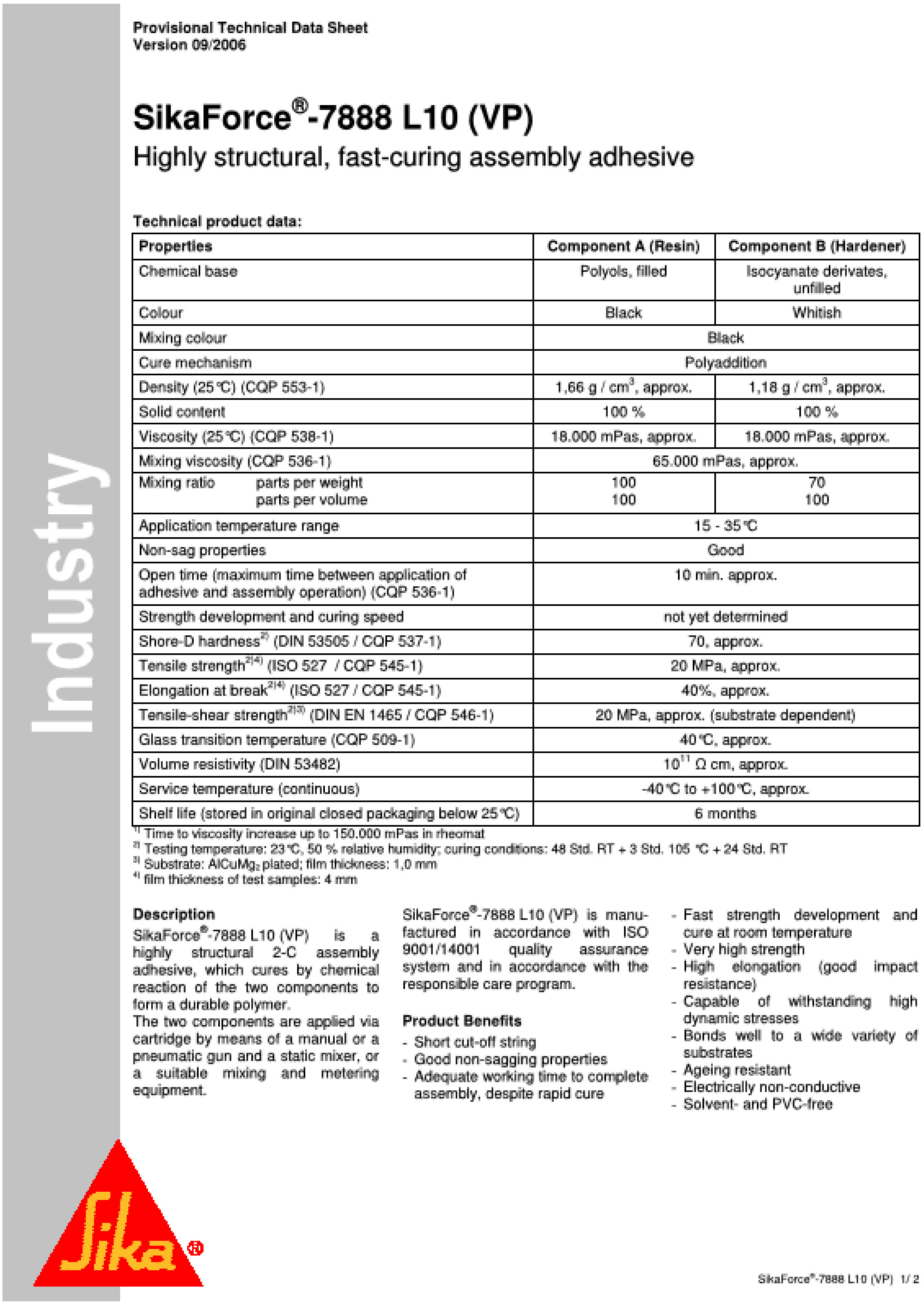
APPENDIX



Industry

Provisional Technical Data Sheet
Version 09/2006

SikaForce®-7888 L10 (VP)

Highly structural, fast-curing assembly adhesive

Technical product data:

Properties	Component A (Resin)	Component B (Hardener)
Chemical base	Polyols, filled	Isocyanate derivates, unfilled
Colour	Black	Whitish
Mixing colour	Black	
Cure mechanism	Polyaddition	
Density (25 °C) (CQP 553-1)	1,66 g / cm^3, approx.	1,18 g / cm^3, approx.
Solid content	100 %	100 %
Viscosity (25 °C) (CQP 538-1)	18.000 mPas, approx.	18.000 mPas, approx.
Mixing viscosity (CQP 536-1)	65.000 mPas, approx.	
Mixing ratio parts per weight	100	70
Mixing ratio parts per volume	100	100
Application temperature range	15 - 35 °C	
Non-sag properties	Good	
Open time (maximum time between application of adhesive and assembly operation) (CQP 536-1)	10 min. approx.	
Strength development and curing speed	not yet determined	
Shore-D hardness[2] (DIN 53505 / CQP 537-1)	70, approx.	
Tensile strength[2][4] (ISO 527 / CQP 545-1)	20 MPa, approx.	
Elongation at break[2][4] (ISO 527 / CQP 545-1)	40%, approx.	
Tensile-shear strength[2][3] (DIN EN 1465 / CQP 546-1)	20 MPa, approx. (substrate dependent)	
Glass transition temperature (CQP 509-1)	40 °C, approx.	
Volume resistivity (DIN 53482)	10^{11} Ω cm, approx.	
Service temperature (continuous)	-40 °C to +100 °C, approx.	
Shelf life (stored in original closed packaging below 25 °C)	6 months	

[1] Time to viscosity increase up to 150.000 mPas in rheomat
[2] Testing temperature: 23 °C, 50 % relative humidity; curing conditions: 48 Std. RT + 3 Std. 105 °C + 24 Std. RT
[3] Substrate: $AlCuMg_2$ plated; film thickness: 1,0 mm
[4] film thickness of test samples: 4 mm

Description

SikaForce®-7888 L10 (VP) is a highly structural 2-C assembly adhesive, which cures by chemical reaction of the two components to form a durable polymer.
The two components are applied via cartridge by means of a manual or a pneumatic gun and a static mixer, or a suitable mixing and metering equipment.

SikaForce®-7888 L10 (VP) is manufactured in accordance with ISO 9001/14001 quality assurance system and in accordance with the responsible care program.

Product Benefits

- Short cut-off string
- Good non-sagging properties
- Adequate working time to complete assembly, despite rapid cure
- Fast strength development and cure at room temperature
- Very high strength
- High elongation (good impact resistance)
- Capable of withstanding high dynamic stresses
- Bonds well to a wide variety of substrates
- Ageing resistant
- Electrically non-conductive
- Solvent- and PVC-free

SikaForce®-7888 L10 (VP) 1/ 2

Areas of Application

SikaForce®-7888 L10 (VP) is suitable for structural joints that will be subjected to dynamic stresses, and where the attainment of rapid strength development and fast cure is an essential requirement. SikaForce®-7888 L10 (VP) is ideal for the adhesive bonding of large components and assemblies. Suitable substrate materials are plastics and metals, particularly aluminium (including anodized components), steel (including phosphated, chromated and zinc-plated components), metal primers and paint coatings (2-C systems), SMC and other GRP materials, wood and ceramic materials. Seek manufacturers advice before using on transparent plastics that are prone to stress cracking.

Cure Mechanism

The curing of SikaForce®-7888 L10 (VP) takes place by chemical reaction of the two components.
Higher temperatures fasten, lower temperatures extend the curing process.

Chemical Resistance

SikaForce®-7888 L10 (VP) has an excellent resistance against hydrolysis. As the chemical resistance depends on type and condition of the substrate, chemical concentration, exposure duration and temperature, a project adapted adhesive performance test is strongly recommended. The same is valid for the temperature resistance. Without exposure to chemicals the adhesive is permanent resistant to temperatures up to 100°C. For short time exposure it resists even to higher temperatures.
In case of expected chemical or thermal exposure, we recommend a project related testing.

Method of Application

Surface preparation
Surfaces must be clean, dry and free from all traces of grease, oil and dust.
Advice on specific applications is available from the Technical Service Department of Sika Industry.

Application
2-c cartridges:
We recommend the use of a suitable manual or a compressed air piston-type cartridge gun.
Use a static-mixer Sulzer Quadro 8,7z. Before application on original substrates it is absolutely necessary to apply at least a bead of 30 cm to have a good mixing quality.

Hobbocks:
SikaForce®-7888 L10 (VP) is dispensed straight from hobbocks by means of a pneumatic or hydraulic metering and mixing pump system with dynamic or static mixers.
Do not apply at temperatures below 15°C or above 30°C. The optimum temperature for substrate is between 15°C and 30°C.
For advice on selecting and setting up a suitable pump system, as well as on the techniques of pump operated application, please contact the System Engineering Department of Sika Industry.

Removal
SikaForce®-7550 L03 in uncured state may be removed from tools and equipment with Sika® Remover-208, isopropanol, acetone, etc. Once cured, the material can only be removed mechanically.
Hands and exposed skin should be washed immediately using Sika® Handclean Towels or a suitable industrial hand cleaner and water. Do not use solvents!

Storage conditions
Resin and Hardener are sensitive to moisture. Therefore they have to be stored in tightly closed containers. After product take-out the containers have to be closed immediately.
The resin must be stored between 5-30°C. It has to be stirred before use.
The hardener must be stored between 15 - 30°C.
During delivery both components can be exposed to temperatures down to 0°C for a maximum of 3 days. Do not use crystallized or inhomogeneous components.

Further Information

The following publications are available on request:
- Material Safety Data Sheets

Packaging Information

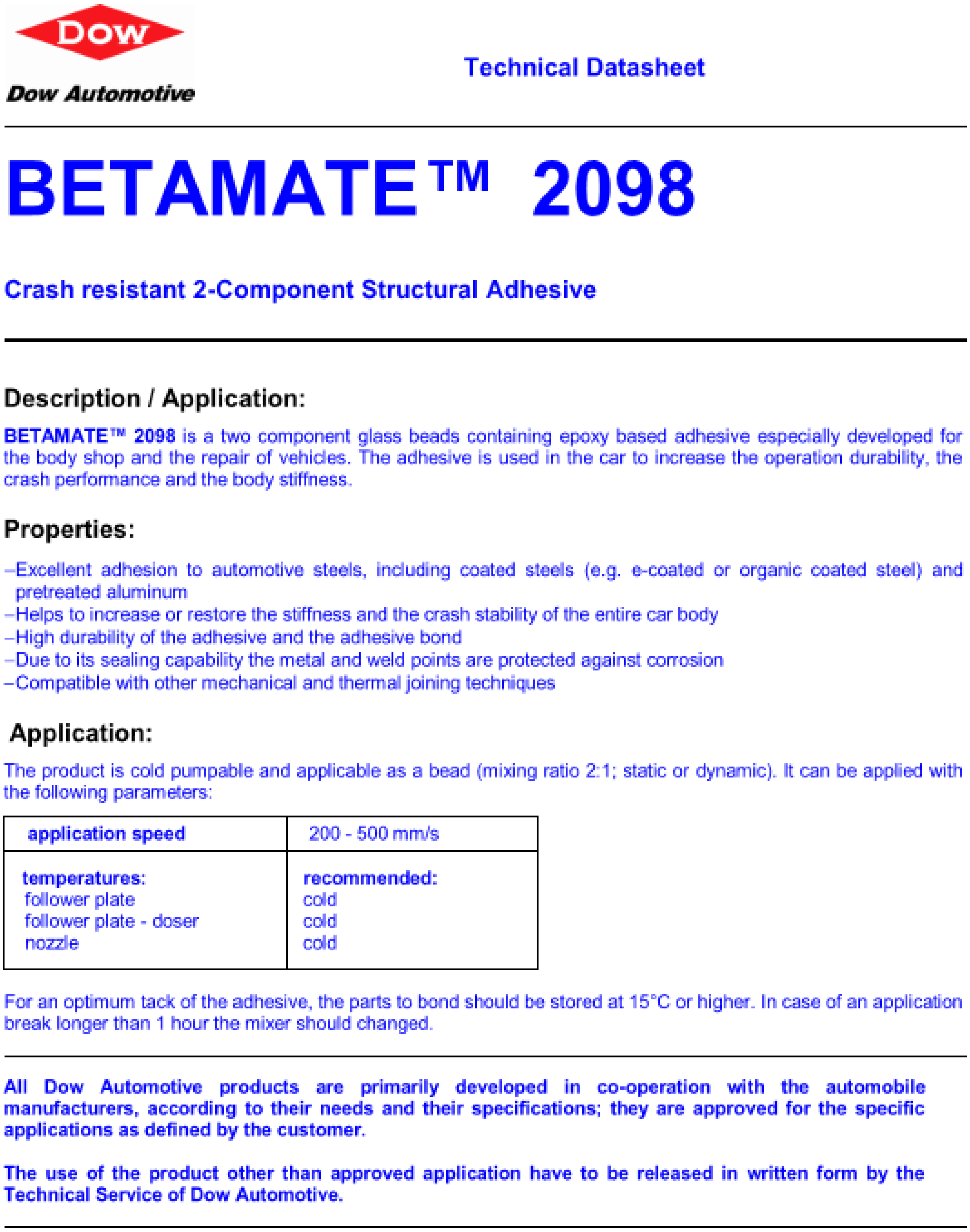
Component A (Resin)	Hobbock 25 kg
Component B (Hardener)	Hobbock 25 kg
2c-cartridge + static mixer Sulzer 8,7z	600 ml (component A+B)

Important

For information and advice regarding transportation, handling, storage and disposal of chemical products, users should refer to the actual Material Safety Data Sheets containing physical, ecological, toxicological and other safety-related data.

Note

The information, and, in particular, the recommendations relating to the application and end-use of Sika products, are given in good faith based on Sika's current knowledge and experience of the products when properly stored, handled and applied under normal conditions. In practice, the differences in materials, substrates and actual site conditions are such that no warranty in respect of merchantability or of fitness for a particular purpose, nor any liability arising out of any legal relationship whatsoever, can be inferred either from this information, or from any written recommendations, or from any other advice offered. The proprietary rights of third parties must be observed. All orders are accepted subject to our current terms of sale and delivery. Users should always refer to the most recent issue of the Technical Data Sheet for the product concerned, copies of which will be supplied on request.
For specific advice concerning preparation of the substrates or the choice of appropriate application devices, please contact our Technical Service.



Dow Automotive

Technical Datasheet

BETAMATE™ 2098

Crash resistant 2-Component Structural Adhesive

Description / Application:

BETAMATE™ 2098 is a two component glass beads containing epoxy based adhesive especially developed for the body shop and the repair of vehicles. The adhesive is used in the car to increase the operation durability, the crash performance and the body stiffness.

Properties:

- Excellent adhesion to automotive steels, including coated steels (e.g. e-coated or organic coated steel) and pretreated aluminum
- Helps to increase or restore the stiffness and the crash stability of the entire car body
- High durability of the adhesive and the adhesive bond
- Due to its sealing capability the metal and weld points are protected against corrosion
- Compatible with other mechanical and thermal joining techniques

Application:

The product is cold pumpable and applicable as a bead (mixing ratio 2:1; static or dynamic). It can be applied with the following parameters:

application speed	200 - 500 mm/s
temperatures:	**recommended:**
follower plate	cold
follower plate - doser	cold
nozzle	cold

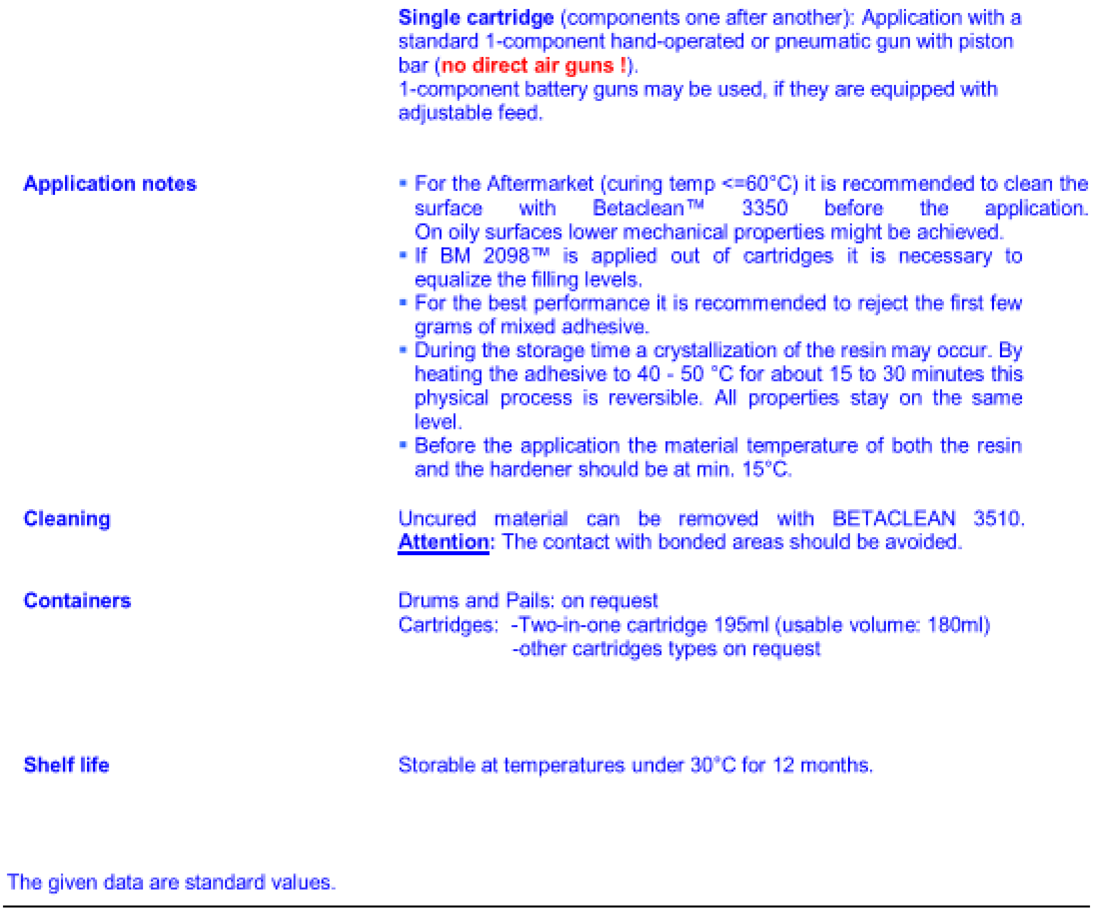
For an optimum tack of the adhesive, the parts to bond should be stored at 15°C or higher. In case of an application break longer than 1 hour the mixer should changed.

All Dow Automotive products are primarily developed in co-operation with the automobile manufacturers, according to their needs and their specifications; they are approved for the specific applications as defined by the customer.

The use of the product other than approved application have to be released in written form by the Technical Service of Dow Automotive.

Technical Data:

Basis	component A: epoxy resin / component B: polymeric amines
Colour	A: blue / B: white
Density (23°C)	1.12 g/ml
Mixing Ratio	A:B = 2:1
Viscosity/Yield Point (23°C, Bohlin, Casson)	component A: 120 Pas / 15Pa component B: 8 Pas / 500 Pa
Time to Handle	approx. 1 hour
Curing Condition	ambient temperature: after 2 days 90% of end toughness temperatures up to 180 °C feasible
Standard Curing	60°C / 2 hours, 2 or 7 days at room temperature (Drive away strength after approx. 10 hours)
Tensile Strength (DIN EN ISO 527-1)	22 MPa
Elongation at Break (DIN EN ISO 527-1)	approx. 20 %
E-Modulus (DIN EN ISO 527-1	1100 MPa
Lap Shear Strength (DIN EN 1465) (CRS 14O3, 0.75 mm) (Adhesive layer thickness: 0.2 mm Bonded area: 25x10 mm)	
7d RT	23 MPa
2h 60°C	23 MPa
(AA6016, pretreated, 1.3 mm) (Adhesive layer thickness: 0.2 mm Bonded area: 25x10 mm)	
7d RT	17 MPa
2h 60°C	17 MPa
T-Peel Strength (DIN EN ISO 11339) (H340 LAD + Z Daimler 0.8 mm) (Adhesive layer thickness: 0.2 mm Bonded area: 25x100 mm	9 N/mm
Impact Peel Strength (ISO 11343) (CRS 14O3, 1.0mm, 23°C, 2m/s) (Adhesive layer thickness: 0.2 mm	
7d RT	30 N/mm
2h 60°C	30 N/mm



	Single cartridge (components one after another): Application with a standard 1-component hand-operated or pneumatic gun with piston bar (**no direct air guns !**). 1-component battery guns may be used, if they are equipped with adjustable feed.
Application notes	▪ For the Aftermarket (curing temp <=60°C) it is recommended to clean the surface with Betaclean™ 3350 before the application. On oily surfaces lower mechanical properties might be achieved. ▪ If BM 2098™ is applied out of cartridges it is necessary to equalize the filling levels. ▪ For the best performance it is recommended to reject the first few grams of mixed adhesive. ▪ During the storage time a crystallization of the resin may occur. By heating the adhesive to 40 - 50 °C for about 15 to 30 minutes this physical process is reversible. All properties stay on the same level. ▪ Before the application the material temperature of both the resin and the hardener should be at min. 15°C.
Cleaning	Uncured material can be removed with BETACLEAN 3510. **Attention:** The contact with bonded areas should be avoided.
Containers	Drums and Pails: on request Cartridges: -Two-in-one cartridge 195ml (usable volume: 180ml) -other cartridges types on request
Shelf life	Storable at temperatures under 30°C for 12 months.

The given data are standard values.

Health and Safety:

- **Bulk Exothermic Reaction**
  The material curing reaction is exothermic. If the material is held in bulk the reaction is accompanied by a rapid build-up of exothermic heat. To avoid the risk of this bulk exothermy, containers of the material should in no circumstances be heated by e.g. hot plates or simple drum heaters. If heating a bulk quantity of the material is considered necessary, advice should be sought.

- **Caution**
  The adhesive resins are generally quite harmless to handle provided that certain precautions normally taken when handling chemicals are observed. The uncured materials must not, for instance, be allowed to come into contact with foodstuffs or food utensils, and measures should also be taken to prevent the uncured materials, from coming into contact with skin, since people with particularly sensitive skins may be affected. The wearing of impervious rubber or plastic gloves will normally be necessary; likewise the use of eye protection. The skin should be thoroughly cleaned at the end of each working period by washing with soap and warm water. The use of solvents is to be avoided. Disposable paper - not cloth towels - should be used to dry the skin. Adequate ventilation of the working area is recommended. For further and more detailed precaution measures see the Health and Safety Data Sheet.

Notice:

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All sites of Dow Automotive are certified according to ISO 14001.

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