FLANDERS MAKE
DRIVING INNOVATION IN MANUFACTURING

Circular bonding COOCK project

Report on reversible adhesive bonding technologies

Contents

Summary

This document summarizes the results of the research activities performed in the framework of WP2 in the Circular bonding COOCK project. In this WP, an extensive knowledge database of possible debonding technologies was created, focusing on thermal debonding technologies which are applicable for common and commercially available structural adhesives. These debonding technologies were evaluated and compared in the scope of the considered use cases. The technologies with the highest market potential were selected for further experimental validation on small scale (i.e., lap shear) samples. These technologies are namely; induction debonding, convection debonding, and debonding using thermally expandable particles. Experimental validation tests were performed using a wide range of structural adhesives (epoxy, polyurethane, and acrylics) and a wide range of substrate materials (aluminium, steel, thermoplastics, glass, composites) to study the feasibility of these debonding technologies over a wide range of material combinations. Hybrid debonding technologies were also considered. The results of this study are presented and discussed in detail.

1. Introduction

1.1. Objectives of the work package

The objective of work package 2 “Reversibele verlijmingstechnologie” is to create a knowledge database of suitable debonding techniques for multi-material constructions, with applications to various sectors such as automotive, construction, and machine building. These debonding techniques should allow easy and complete separation of bonded parts with minimum applicable force and debonding time (i.e., an on-demand option). In addition, a special attention is paid to technologies with high market and scalability potential. The most suitable debonding methods are identified and selected for further experimental validation using commercial adhesives and substrates. The selected and validated debonding methods will be used in WP5 to demonstrate their industrial feasibility using large scale demonstrators for a selected number of use cases.

1.2. Definition of debonding

In the framework of the circular bonding project, debonding can be defined as the complete separation of adhesively bonded substrates, without damaging the substrates themselves. This allows for the reuse, recycling, or repurposing of the substrates after debonding. Based on this definition, the desired separation of the substrates can occur either in the adhesive layer or at the interface between the adhesive and the substrate, as shown in
Figure 1. Debonding at the interface is generally difficult to achieve, since the adhesion process is inherently designed for surface bonding. However, interface debonding can allow for clean separation of the substrates without adhesive residue. Separation of the substrates by cutting the adhesive layer off the substrates can damage the substrates, which, according to the debonding definition, should be avoided. In addition, and despite the Dutch name of the work package “reversibele verlijmingstechnologie”, a clear distinction should be made between debonding and reversible bonding. On the one hand, reversible adhesive process can include a rebonding process, in which the substrates with adhesive residues can be bonded again with or without external stimulus (e.g., ultraviolet radiation, compressive force, heat, etc.). Such a process is applicable only to hotmelt adhesives or to adhesives having self healing capabilities. On the other hand, debonding alone does not necessarily include an option of rebonding after separation. Therefore, in the context of the circular bonding project and WP2, the Dutch term reversibele verlijmingstechnologie will be analogous to debonding without a rebonding option, since the title of the work package cannot be changed at the execution phase of the project.

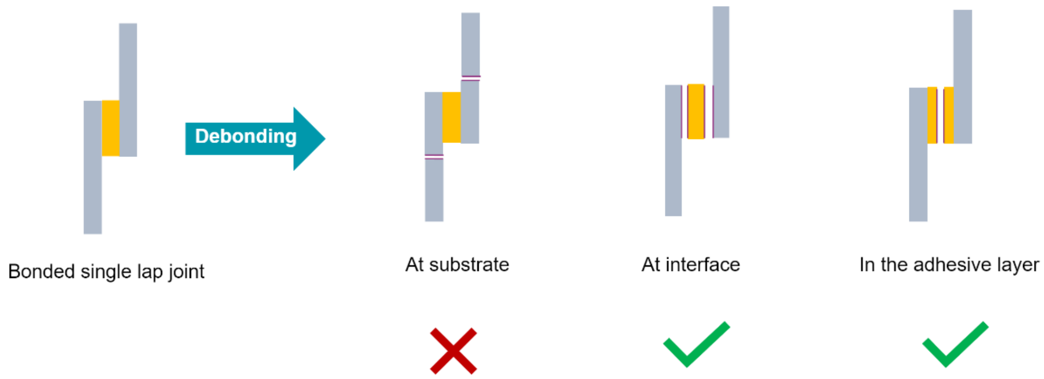


Figure 1. Definition of debonding

1.3. Classification of debonding mechanisms

In general, debonding can be divided into 3 main mechanisms, as illustrated in Figure 2:

a. Mechanical debonding
b. Electrochemical debonding
c. Thermal debonding

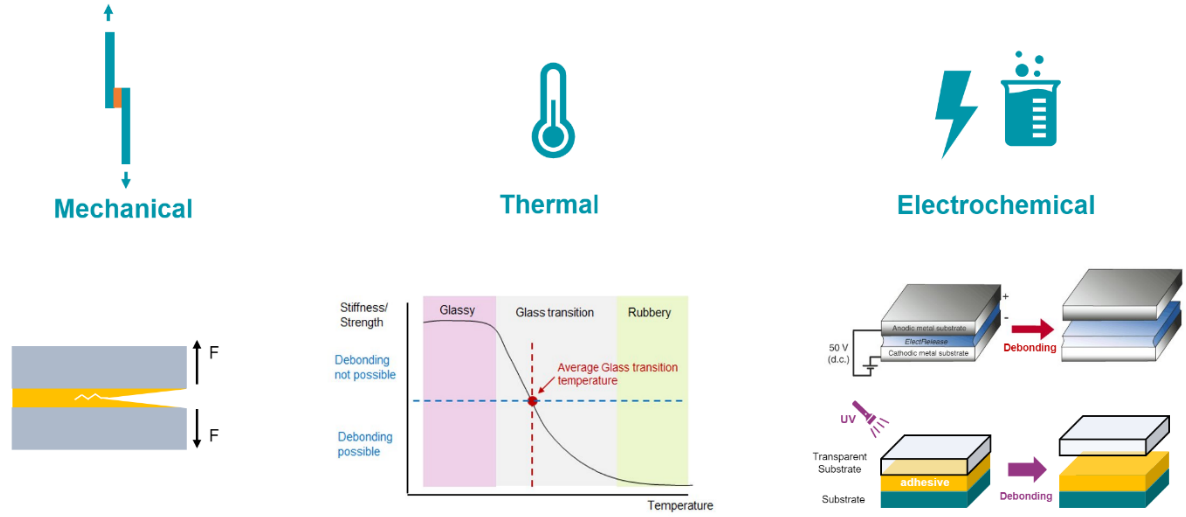


Figure 2. illustration of the different debonding mechanisms

Mechanical debonding mechanism can be performed by applying mechanical forces to separate the substrates, or by introducing cracks inside the adhesive layer which can propagate by the application of mechanical force to cause separation of the substrates. Despite the simplicity of this approach, mechanical separation can occur only when mechanical forces, which exceed the design limit of the joint, are applied. This, in turn, can be impractical when used with large joints or with high strength adhesives.

Electromechanical debonding mechanism includes the use of chemical agents or solvents to attack the adhesive layer, or the use of external triggers such as ultraviolet (UV) radiation or electrical current to degrade the adhesive layer and cause full separation of the substrates. This approach typically requires especially formulated adhesives which can respond to these external stimuli, in addition to specialized equipment to induce the stimulus such as electric battery or a UV lamp.

Thermal debonding mechanism is performed by heating the adhesive to a temperature above the glass transition temperature, where the adhesive changes from a solid glassy state to a rubbery state with low mechanical performance. Upon the application of a relatively low mechanical force, the adhesive fractures, causing full separation of the substrates. Heating equipment can include conduction ovens, microwave ovens, infrared, laser, etc. It is worth mentioning that while this approach works best with glassy adhesives such as epoxy or acrylics, it can still be used with flexible and rubbery adhesives, since they are also affected by elevated temperatures. Other methods include debonding by cooling, which turns the adhesives into a brittle state which easy debonding by shattering. However, this requires conditioning the adhesive at extremely low temperatures (<-70 °C) which is not practical given the complexity of the equipment used in such process (cryogenic chambers, injection of liquid nitrogen, etc.) As such, debonding by cooling can be considered out of the scope of this project.

1.4. Scope of the research work

As mentioned in the previous section, mechanical debonding is impractical, especially when used in large joints. Thermal debonding, however, is considered the closest debonding mechanism for industrial applicability, since the equipment used are commercially available and can be upscaled, and the mechanism can be applied to existing commercial adhesive formulations. In addition, some special adhesives which are debondable by electric potential or UV radiation are commercially available. Therefore, within the scope of this research, thermal and electrochemical debonding mechanisms will be considered. A detailed review of the literature including the possible debonding technologies within these mechanisms will be summarized. In this detailed review, the following aspects will be covered:

a. The working principle of each debonding technology.
b. The various infrastructure and equipment used per debonding technology.
c. The suitable materials which can be used with each debonding technology, including special adhesives and substrates.
d. The debonding performance (i.e., debonding strength, debonding time, etc.) of each technology based on scientific literature.
e. A market study including the commercial availability and scalability of each debonding technology.

Based on this extensive literature review, a systematic evaluation of each debonding technology and a consequent ranking of the technologies will be performed. Final selected debonding technologies will be further validated experimentally, as will be detailed in section 4.

2. Overview of debonding technologies

2.1. Debonding using convection heating

Convection heating is the simplest form of thermal debonding. It involves heating the adhesive beyond the glass transition temperature using convection heat transfer method such as hot air, then applying mechanical force to completely separate the bonded parts. Standard industrial heating ovens can be used to globally heat bonded joints of various sizes. **Error! Reference source not found.** (a) shows an examples of a large scale industrial oven at the joining and materials lab at Flanders Make, Lommel. Precise and calibrated temperature controls are often supplied for these types of industrial ovens. For a more localized convection heating, handheld heat guns are used, as shown in **Error! Reference source not found.** (b). Heat guns are usually used by repair personnel to debond sealants of water tight bonded structures such as mobile phones and watches, and also laminated bonded structures such as laminated screens.

(a) (b)

Figure 3. Convection heating equipment: (a) large scale heating over, (b) handheld heat gun

In general, this simple debonding method is suitable for most adhesives, since they cannot retain their strength at high temperatures. In addition, this debonding method does not require any special adhesive formulations, thus, it can be directly implemented to any commercially available structural adhesive. Moreover, the substrates do not require any special pretreatment or coating to be used with convection debonding. However, the substrates should be thermally conductive to allow the conductive heat transfer to the adhesive layer.

In terms of commercial availability and scalability, the industrial heating ovens and hot guns are widely available. Industrial ovens can be large enough to accommodate entire cars and trucks. Hot guns, however, are more used at a small scale, and therefore, strictly used for less demanding small scale heating applications. Depending on the thermal conductivity of the substrate material, the glass transition temperature of the adhesive, and the heating rate of the oven, various debonding forces can reached. Figure 4 shows an example of the variation of the average lap shear strength as a function of temperature for Araldite 2011 2 component epoxy adhesive. It can be seen that a debonding strength below 5 MPa can be achieved at approx. 100 °C.

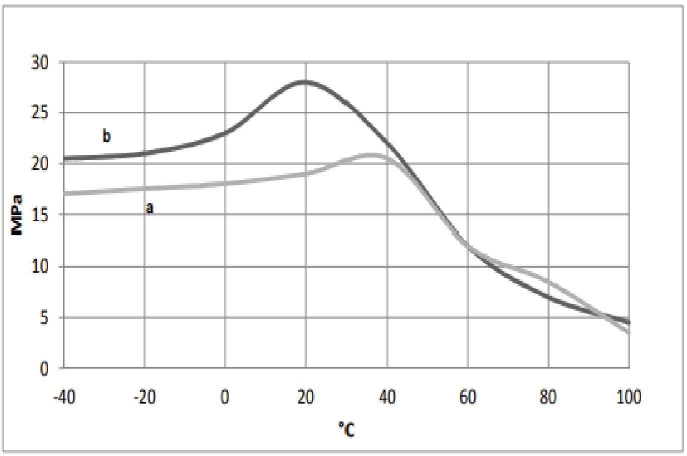


Figure 4. Average lap shear strength as a function of temperature for 2 different curing cycles (a: 7 days/23 °C, b: 24hours/23 °C + 30 minutes/80 °C) [1]

2.2. Debonding using induction heating

Debonding by induction heating occurs by exposing the adhesive joint to a high intensity alternating magnetic field, as shown in Figure 5. Heating can be done either by the joule effect, or by hysteresis losses, or by a combination of both. Debonding can be achieved by inductively heating the adhesive to temperatures above the glass transition temperature, then applying mechanical forces to separate the substrates. Induction heating can achieve very high heating rates compared to conventional convection heating (more than 100 °C/min).

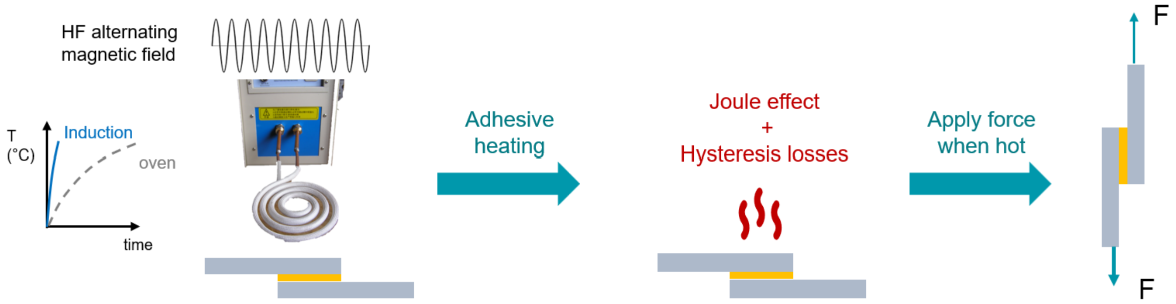


Figure 5. Illustration of heating by induction

In principle, adhesives by themselves cannot be heated by induction, since they are naturally electrically insulating materials. Therefore, there are 2 ways with which adhesives can be inductively heated. One way to heat the substrates if they are made of conductive or magnetic materials such as steel, aluminum, titanium, etc. In this case, the heat is transferred from the substrates to the adhesives by thermal conduction. The other way is to mix conductive particles to the adhesive at micro or nanoscales, and heat these particles by induction. In this case, heat is also transferred conductively to the adhesives from inwards to outwards direction. However, the addition of particles to the adhesive could influence the mechanical performance of the adhesive. Figure 6 shows the effect of adding metallic particles to epoxy adhesives. A reduction in lap shear strength can be seen in case of adding ferrite microparticles to brittle 2k Araldite epoxy, whereas this effect is not significant for flexible 2k Jowat epoxy adhesive.

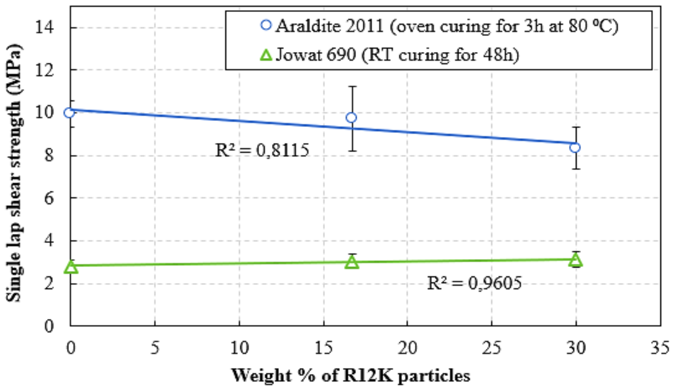
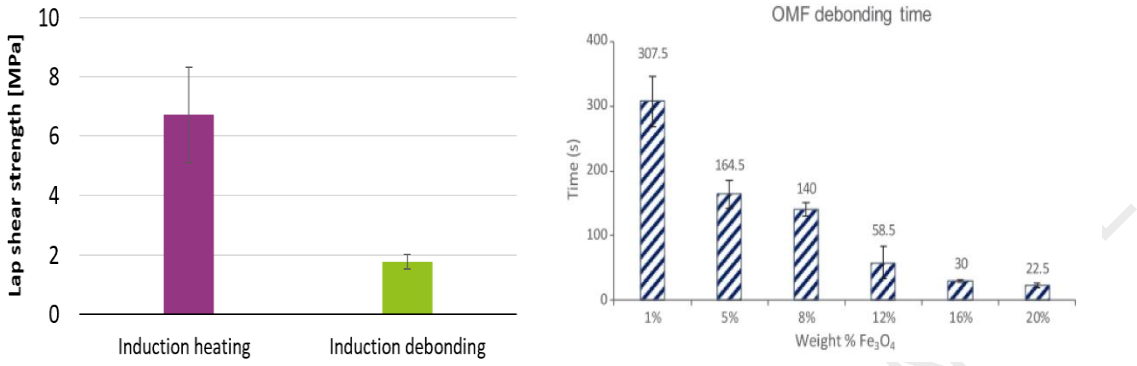


Figure 6. Influence of the addition of metallic particles on epoxy adhesives

Induction technology is well established and is extensively used in steel manufacturing and casting refineries [2]. As such, induction equipment are widely available on a commercial scale. Custom designed coils can be manufactured for heating complex geometries and contours. Additionally, large scale and continuous induction lines can be found commercially.

Since the heating rates achieved by induction heating are very high, debonding can be achieved in a significantly short time, ranging to 20 seconds to 5 minutes. Indeed, it was reported in ref. [3] that for PU adhesives, induction can be achieved in 22 seconds, while for epoxy adhesives, a debonding strength of approx. 2 MPa can be reached in 2 minutes, see **Error! Reference source not found.**.



(a) (b)

Figure 7. Debonding performance of induction technique: (a) debonding of epoxy adhesives, (b) debonding of PU adhesives [3]

2.3. Debonding using microwave heating

Microwave heating involves heating the adhesive with dielectric heating. Polar molecules heat up due to the alternating movement to align wish high frequency alternating electromagnetic fields. Only the microwave range of the electromagnetic spectrum is used in microwave heating, with frequencies ranging from 915 MHz to 2.5 GHz. Similar to induction heating, microwave heating can also achieve very high heating rates. Adhesives can be heated by microwave since they are dipolar in nature. However, microwave heating only works microwave transparent materials. Metallic substrates, for instance, can have microwave shielding effect, and as such, cannot be effectively heated. In addition, thin metallic substrates with sharp edges can induce electric arc, which can lead to fire hazards.

Microwave heating equipment are widely available for both commercial and domestic use. Additionally, a large variety of industrial microwave ovens are used in several industries, as shown in Figure 8.

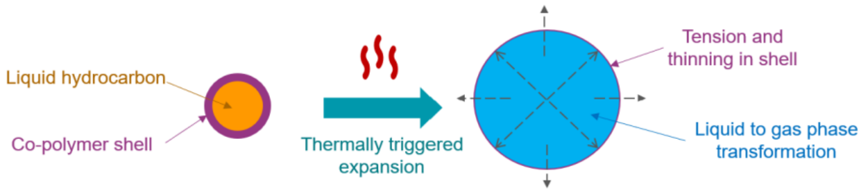
Figure 8. Large-scale microwave oven [4]

However, the use of microwave heating is strictly regulated in terms of safety and human exposure to microwaves. Short term exposure of the human body to microware is strictly limited according to the EU directive 2004/40/EC, which limits the exposure time to 6 minutes and 50W/m^2 power density [5]. The long term exposure to microwaves, however, are not regulated. Any microware leakage much be contained and limited, and correct safety actions must be taken. Over exposure to microwaves can lead to a series of hazards such as heat strokes, heating and burning of tissues and organs. For domestic microwave applications, it is obligatory to have fully closed and sealed enclosures, in addition to a fail safe mechanism to stop microwave generation upon leakage.

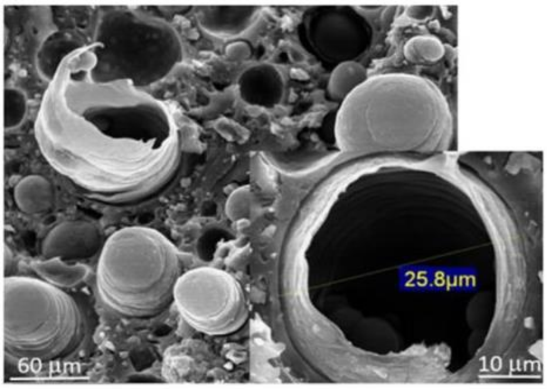
In terms of debonding performance, it is possible to debond PU adhesives within 3 to 4 minutes [6]. However, few literature articles are available in microwave debonding.

2.4. Debonding by thermally expandable particles

Thermally expandable particles (TEPs) are small micro-sized particles which consist of liquid hydrocarbon encapsulated in a polymer shell. When these particles are heated to a certain temperature, the liquid hydrocarbon changes from liquid state to gaseous state, building pressure on the polymer shell which expands and stretches. Such an expansion can be more than 5 times the original size. The particles are generally used in the manufacturing of foams, hence, they are also known as foaming agents. By mixing these particles into structural adhesives and heating the adhesive to a temperature to allow the triggering of the particles expansion, the adhesive will turn into a foam, see Figure 9 (a). The foamy adhesive generally have lower mechanical performance compared to the non-foamed state. By applying small mechanical forces after the expansion of the particles, debonding and full separation of the substrates can occur. Figure 9 (b) shows an illustration of the expansion of the TEPs and a scanning electron microscopy image of the TEPs (unburst and burst) mixing in a structural adhesive.



(a)



(b)

Figure 9. Thermally expandable particles: (a) Illustration of the expansion, (b) a SEM image of the burst particles mixed in an adhesive [7]

Since these particles needs to be heated to a certain temperature, any method of heating can be suitable to trigger their expansion. However, the particles needs to be homogeneously mixed in the adhesive. This can be done using a planetary speed mixer. Furthermore, care must be taken to ensure that the curing temperature of the adhesive is well below the expansion triggering temperature of the particle, otherwise, the adhesive will turn into a foam while being cured. Therefore, these particles are mainly limited to the use with 2 component systems, were the curing is achieved at room temperature and with limited exothermic reactions. Adhesive with 1 component systems that needs high temperature curing (e.g., 1 component epoxies) can be used provided that the curing temperature is lower than the expansion triggering temperature of the particles.

The addition of the TEPs can also influence the mechanical performance of the adhesive. As demonstrated in Figure 10, the addition of TEPs up to weight percentage of 25% can significantly reduce the average lap shear strength. In terms of debonding performance, depending on the heating rate, the TEP type, the thermal conductivity of the joint, and the particle content, debonding can be achieved within 1 to 2 minutes. As seen in Figure 11, increasing the particle content can significantly reduce the debonding time.

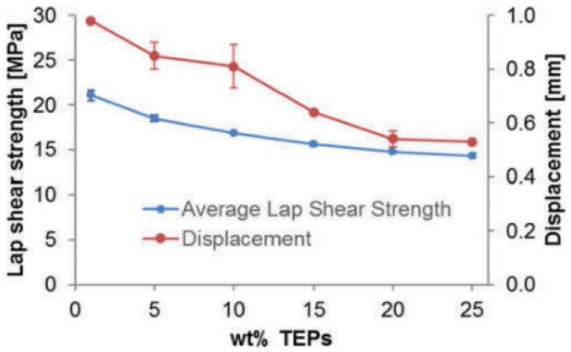


Figure 10. Influence of the TEPs on the mechanical performance of adhesive joints [8]

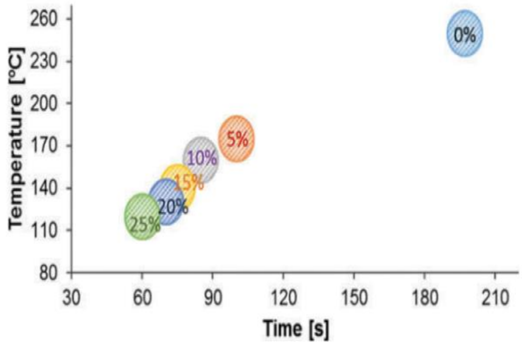


Figure 11. Influence of the particle content on the debonding time [9]

2.5. Electrically debondable adhesives

Electrically debonding adhesives are especially designed adhesives which allow interfacial debonding of bonded joints upon the application of electric potential across two conductive substrates, as shown in . The interfacial debonding takes places at the anode side, therefore, debonding at both interfaces of a joint can be achieved by reversing the polarity of the electric potential. EIC laboratories in the US developed the only commercial version of electrically debondable adhesives, under the commercial brand ElectRelease. Two different grades of 2 component epoxy formulations of ElectRelease are available: M4 and E4 (see . However, despite their commercial availability, very few data about these adhesives are available in literature. In addition, the ElectRelease brand does not have any supplier or representative in the European Union.

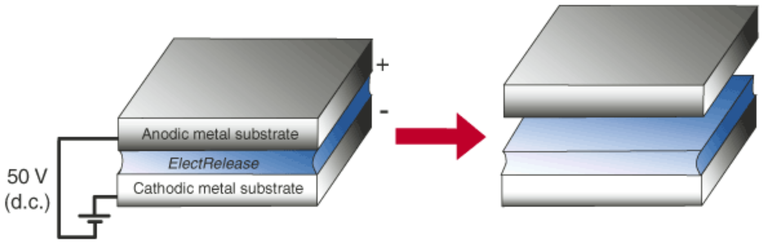


Figure 12. Illustration of debonding using electrically debondable adhesives [10]

Electrically debondable adhesives work only with conductive substrates. If non-conductive substrates are used, a special patch made of conductive substrates bonded with electrically debondable adhesives needs to be bonded between the non-conductive substrates. In terms of debonding performance, depending on the applied electric potential, the debonding can be achieved in the range of 10 seconds to 20 minutes after the application of the electric potential. In addition, debonding is primarily achieved without the application of mechanical forces. This means that large bonded areas can be easily debonded. Moreover, electrically debondable adhesives do not leave residues on the substrates, which means clean debonding can be achieved, provided some basic cleaning is achieved.
This method of debonding, however, cannot work with very think bond lines, or when the thickness of the bondline cannot be maintained uniform. This is due to the risk of short circuit during the application of the electric potential, and hence the inability of the adhesive to be debonded.

Figure 13. Electrelease adhesives [10]

2.6. Ultraviolet induced debondable adhesives

Ultraviolet (UV) induced debondable adhesievs incorporate light induced agents to cause debonding by several mechanisms, such as photoliquification, selective depolymerization or UV curable cross linkers, as shown in Figure 14. For the UV to reach the adhesive, transparent substrates must be used. The UV debondable adhesives are available for limited commercial use, such as silicon wafer bonding and debonding in chip manufacturing, and in medical applications. However, the efforts to develop a structural adhesive which is debondable by UV are currently at low technology readiness levels, and most of the efforts are concentrated in research laboratories of universities.

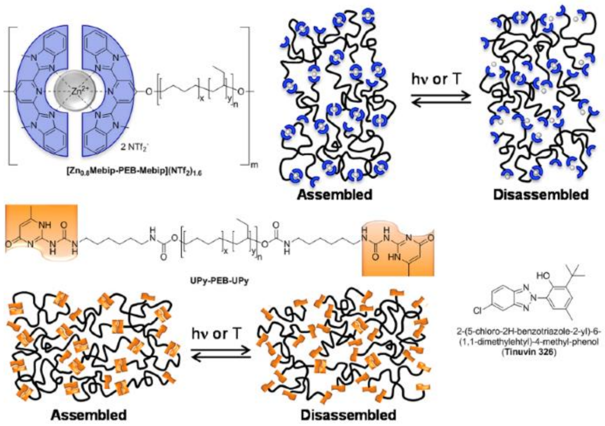


Figure 14. Illustration of UV debondable adhesives [11]

UV radiation can be generated from UV lamps. Several UV lamps are commercially used at various scales and powers. However, care must be taken to limit extended exposure to UV light. Extended exposure to UV light can result in severe hazards for the eyes and skin of the human body. Among these hazards are erythema (sun burn), photokeratitis (a feeling of sand in the eyes), skin cancer, increased skin pigmentation (tanning), cataracts, and retinal burns.

Several UV induced adhesives have been developed in literature which enables debonding by potoliquification and rebonding using blue light in 5 seconds [12]. Other formulations can achieve debonding from 5 minutes to 60 minutes when combined with additional convection heating [13]. It is worth mentioning that clean debonding can also be achieved with UV debondable adhesives.

3. Evaluation and ranking of the debonding technologies

In order to evaluate and rank the previously discussed debonding techniques for the best market and applicability potential, several evaluation criteria were defined as follows:

1. **Debonding time.** The time required to achieve full separation of the substrates. Fast debonding is considered a fulfillment condition for this criterion.
2. **Initial joint strength.** This criterion defines whether there is any effect on the initial joint strength due to the use of a certain debonding technique. For example, if particles need to be used, the joint performance will be negatively impacted. No effect on the initial joining strength is considered a fulfillment condition for this criterion.
3. **Scalability**. The degree of upscaling the debonding equipment to be used with large components. Easiness of upscaling using commercial availability of equipment with minimum costs is considered a fulfillment condition for this criterion.
4. **Commercial availability.** This criterion covers the commercial availability of the special adhesives, additives, particles, etc., in addition to adhesives premixed with particles. Full commercial availability is considered a fulfillment for this criterion.
5. **Safety.** This criterion defines how safe it is to apply the debonding technique for human operators, workers, and environment. A completely safe technique is considered a fulfilment condition for this criterion.
6. **Substrate materials.** This criterion covers which substrate materials can be used with each debonding technique. A technique which can work with all substrate materials is considered a fulfillment condition for this criterion.
7. **Complexity**. The degree of complexity (technical, financial, infrastructure, etc.) in applying this debonding technique. Easiness of using and applying the technique is considered a fulfillment condition for this criterion.

To give a final overall score for each debonding technology based on the abovementioned criteria, all criteria were given an equal weight. A basic ranking from 1 to 5 was given for each criteria and an overall score was given to each technology as the summation of each individual score of each criteria. The interpretation of each score, along with a partial quantification of the percentage of fulfillment of the evaluation criteria, can be listed as follows:

- Score of 1: The criteria is not fully fulfilled (20%).
- Score of 2: The criteria is somewhat fulfilled (40%).
- Score of 3: The criteria is partially fulfilled (60%).
- Score of 4: The criteria is fulfilled to a large extent (80%).
- Score of 5: The criteria is fully fulfilled (100%).

For example, the UV debonding technology scores and average score of 4 in commercial availability, which can be broken down to the following sub scores:

- Score of 5 for additives, since this technology does not require additives to be used with the adhesive.
- Score of 5 for the mixed adhesive, since the adhesive does not need to be mixed with particles before application.
- Score of 1 for adhesives, since the adhesives based on UV debonding are not commercially available.
- Average score is calculated based on the scores of the previous criteria (additives, adhesives, mixed adhesives) according to the following equation: Average score =(score of additives + score of adhesives + score of mixed adhesives)/3

It should be noted that the ranking and evaluation of these technologies is largely qualitative. This is due to the large disparities in literature, and the lack of a common framework to test and evaluate these techniques. Despite the largely qualitative nature of this ranking, it still gives a good indication of which debonding technologies have the biggest market potential.

Table 1 shows the overall evaluation and ranking table for each debonding technology based on the previously mentioned individual criteria. In terms of debonding time, induction, microwave, UV and electrical debonding achieved the fastest debonding time, therefore, receiving a score of 5 each. Whereas the thermally expandable particles scored 4 each due to the extra time taken to thermally trigger the particles. Convection heating was the slowest debonding technique, thus scoring 2.

Initial debonding strength with the microware and convection heating scored 5, since they do not involve adding any additives to the substate. The UV debonding has the least score due to the fact that the available adhesives do not achieve high initial strength for structural applications, despite the lack of additives. Induction and TEPs requires mixing of additives which influence the initial bonding strength, and therefore, receiving each the score of 3.

In terms of scalability, only the microwave debonding technique achieved a score of 3, due to the inability to upscale the microwave ovens for controlled debonding applications beyond the mid-size applications (such as chemicals, food, paper, etc.).

The commercial availability of premixed adhesives containing micro/nanoparticles for induction or thermal expansion is non-existent, therefore, the given score was 1. On the other hand, and despite the commercial availability of the electrically debondable adhesives, it was not possible to contact the producing company or to receive a small quantity for feasibility study. Therefore, the given score is 1.

Except for induction (which works with conductive substrates and non-conductive ones if the adhesive is mixed with conductive particles) and TEPs, all other debonding methods have constrains in terms of suitable substrate materials. UV debonding, for instance, works only with transparent substrates to let in UV rays. Electrically debondable adhesives work only with conductive substrates, microwave debonding works only with non-polar materials, while convection debonding works only with thermally conductive substrates. As such, a score of 2 in the substrate materials criterion is given to all debonding techniques except for induction and TEPs. Finally with respect to complexity, the easiest debonding method is convection, followed by UV and electrical debonding since they require very basic setups (UV lamp in a closed environment, or electric supply, respectively). Induction debonding requires optimized induction coil, in addition to an extensive optimization of the induction parameters (frequency, current, coupling distance, particle content) in order to achieve effective debonding. TEPs as well require optimizing the particle content inside the adhesive and monitoring the triggering temperature of the particles to achieve debonding. Therefore, each of these methods receive a score of 3. The most complex debonding technique is the microwave debonding, since it not only require special equipment, but also proper protection from microwave leakage and prolonged exposure to microwaves. Therefore, a score of 2 is given to the microwave debonding in the complexity criterion.

Based on the awarded scores for each debonding technique in each criterion, the overall scores indicate that induction, TEPs and convection are the only debonding technologies with the highest market potential. Therefore, these debonding technologies were selected for further validation and testing for lab scale demo and later in the upscaled demonstrators in WP5.

Table 1. Evaluation and ranking of the debonding technologies

Method	**Debonding time**	**Initial bond strength**	**Scalability**	**Commercial availability**				**Safety**	**Substrate Materials**	**Complexity**	**Overall score**	**Ranking**
				Additives	Adhesives	Mixed adhesive	Average score					
Induction	5	3	5	5	5	1	4	4	5	3	29	1
TEP	4	3	5	5	5	1	4	5	5	3	29	2
UV	5	2	5	5	1	5	4	3	2	4	25	5
Electric	5	4	5	5	1	5	4	4	2	4	28	4
Convection	2	5	5	5	5	5	5	5	2	5	29	3
Microwave	5	5	3	5	5	5	5	2	2	2	24	6

4. Testing and validation framework for selected debonding technologies

4.1. Testing framework

Lab scale validation tests were performed on the selected debonding technologies (i.e., induction, convection, and TEPs) on two phases. The first phase focused on testing the debonding technologies on joints made of steel, aluminium, and thermoplastic substrates which are bonded using epoxy adhesives (one- and two-component). Induction debonding was validated on steel and aluminium joints without the addition of ferritic microparticles, whereas for thermoplastic substrates, ferritic microparticles were added to enable debonding by induction. TEPs were mixed to all adhesives for all joint types to test the debonding with TEPs, whereas for convection debonding, no additives were mixed to the adhesives regardless of the type of the substrate. In this phase, the induction parameters including current, frequency and bond line temperature were studied. In addition, the expansion of the TEPs in two component epoxy adhesives was characterized. The second phase focused on testing the debonding technologies on joints made of composites and aluminium substrates, which are bonded using polyurethane adhesives (one- and two-component). In this second phase, hybrid debonding methods combining induction and TEPs are implemented. In this way, the selected debonding methods can be validated on a wide range of structural adhesives and substrate materials. A comparison between all debonding methods was also performed on thermoplastic samples. For both phases, benchmarking experiments were performed to determine the average lap shear strength of the joint before debonding.

4.2. Materials

4.2.1. Adhesives

Commercially available adhesives were used for all debonding tests. The epoxy adhesives used were SPE1539 (1k epoxy) and Araldite 2011 (2k epoxy), whereas the polyurethane adhesives were MS930 (1k polyurethane) and Araldite 2018 (2k polyurethane). The 2k epoxy adhesive used for thermoplastic joints was mixed with R12k ferromagnetic particles to allow for induction debonding. These particles are made from Fe-Mn-Zn sintered alloy, and have an average size of 20 microns. Thermally expandable particles Expancel 031 DU 40 of size 40 microns were mixed with all adhesives to allow for debonding with TEPs. All particles were mixed with the adhesives using a speed mixed at speed of 3000 rpm for a mixing time of 1 to 2 minutes. Both types of particles were mixed to the adhesives with the following percentages by weight: 10%, 30%, and 50%. In the context of this research, the triggering temperature of the TEPs was fixed at 100 °C.

4.2.2. Substrates

Standard aluminium and steel substrates of thickenss 1,5 mm each were used for metallic substrates, whereas Ryton® polypropylene sulfide (PPS) reinforced with 40% glass fibers and glass fiber reinforced epoxy GFRE substrates of thickness 2 mm each were used for non-metallic substrates. Samples were provided pre-cut to a length of 100 mm and a width of 25 mm. The surface of each sample were pre-treated prior to bonding to increase bonding quality. Aluminum, steel, and composite substrates were manually ground in cross 45° directions using sanding with grit no. 80. The surface of the PPS samples was treated with atmospheric plasma with the following parameters: 10 mm coupling distance, 40 mm/s velocity, and 500 w power. Table 2 summarise the joint material combinations and the corresponding adhesives used for each debonding test type.

Table 2. Joint material combinations and corresponding adhesives used for each debonding test type

Debonding test type	Joint material combination	Adhesives used
Convection	Aluminum/aluminum, PPS/PPS	1k and 2k epoxy
Induction	Aluminum/aluminum, PPS/PPS	1k and 2k epoxy
TEPs	Aluminum/aluminum, PPS/PPS	1k and 2k epoxy
Hybrid debonding (induction and TEPs)	Aluminum/composite	1k and 2k PU

4.2.3. Lap shear joints

Lap shear samples were prepared in special PTFE molds to maintain a bond line thickness of 0.1 mm, and an overlap distance of 12.5 mm, according to the ASTM D3163 standard. Joints with 2 component adhesives were cured at room temperature and relative humidity for at least 24 hours. Joints with SPE 1539 1k epoxy were cured in the oven at 70°C for 16 hours, while joints with 1k PU adhesives were cured for at least 7 days.

4.3. Methods

4.3.1. Induction setup

Induction debonding experiments were performed on the TruHeat HF 1005-5010 induction machine (manufactured by TRUMPF Hüttinger GmbH) available at the Joining and Materials Lab at Flanders Make. It consists of 3 main units: a water cooling unit, a generator unit, and an inductance-capacitance circuit unit with the induction coil. The coil was continuously cooled by the cooling unit and kept at a temperature range of 18 to 23 ºC. The power generator is capable of supplying a maximum induction power of 11.2 kW and a maximum current of 35 A. Figure 15 shows the induction setup used.

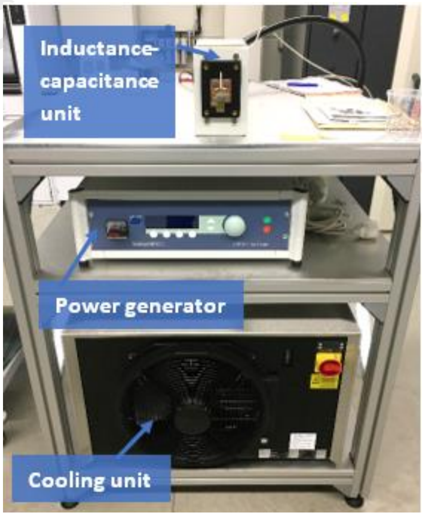


Figure 15. Induction machine at Flanders Make JML

Two coil geometries were used in the induction debonding tests, namely a two-turn rectangular coil with flux concentrator (for the thermoplastic substrates), and a four-turn flat spiral or pancake coil (for the aluminum and steel substrates). Figure 16 shows the coils used. The frequency ranges were 243 – 325 kHz and 400-600 kHz for the pancake and the rectangular coils, respectively. The coupling distance between the substrate and the coil was adjusted using polyamide height spacers. The temperature at the edge of the bondline was measured using an infrared pyrometer (Metis M323 from Sensortherm) with a temperature measurement range of 50 ºC to 800 ºC, spectral range of 2 to 2.6 μm, a response time of less than 1 ms, and a minimum measuring spot size of 0.6 mm. Since there was no closed feedback loop system to control the induction current and frequency based on the bondline temperature, separate optimization tests were performed to determine the suitable induction parameters required to have a bond line temperature either higher than the glass transition temperature of the adhesive or equals to the triggering temperature of the TEPs. The same induction setup was used to perform hybrid debonding tests with TEPs on aluminum/GFRE composite joints.

(a) (b)

Figure 16. Different induction coils used: (a) Rectangular coil with flux concentrator, (b) flat spiral (pancake) coils

4.3.2. Convection setup

Convection and TEP debonding tests were performed using a climate chamber having a range of -20 °C to 220 °C, as shown in Figure 17. Temperature inside the climate chamber was measured using a thermocouple fixed inside the heating cavity of the chamber. In addition, temperature in the bondline was measured using a thermocouple embedded inside the bondline between the substrates. Temperature measurements were continuously logged using Picolog data logger.

Figure 17. Climate chamber used in convection debonding tests

4.3.3. Lap shear tests

Benchmark and debonding single lap shear tests were performed using a Shimadzu AGS-50NX universal testing machine shown in
Figure 18. The load was measured using a 20 kN load cell. Special attention was paid to ensure the alignment of the lap shear samples with the grips in order to eliminate any bending moments. Lap shear samples were tested at cross head speeds of 2 mm/min according to the recommendations of the ASTM D3163 standard. For the determination of the debonding strength, samples were transferred to the testing machine after the application of the thermal debonding (induction or convection) within a time frame of 20 seconds.

Figure 18. Single lap shear testing setup

5. Results and discussion

5.1. Debonding by induction heating

5.1.1. Process parameters design and optimization

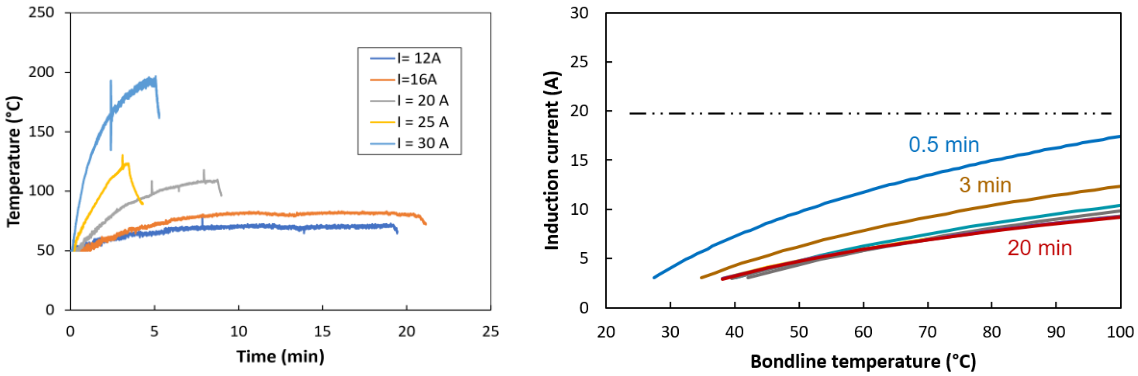
The induction debonding process parameters include: the induction current, the induction heating time and the debonding temperature. In general, the induction current needs to be optimized in order to achieve the desired debonding temperature at the shortest possible induction heating time. The addition of ferromagnetic particles adds another complexity to the optimization since the bond line temperature and the current needed will vary depending on the amount of particles in the adhesive. In this regard, several experiments were performed to measure the temperature of the bond line at different induction currents and different weight percentages of R12K particles for PPS joints, for at least 20 minutes of induction heating time. Figure 19 (a) shows an example of the temperature profiles measured for PPS joints with araldite 2011 mixed with 10% R12K ferromagnetic particles at different induction currents. It can be seen that the increase in induction current leads to a significant increase in bondline temperature, while also reduce the induction time required. In the context of the project, a maximum temperature of 100 °C was selected for all debonding experiments.

Figure 19 (b) shows an example of the induction current required to reach bondline temperatures of up to 100 °C at differnet induction times for PPS joints with araldite 2011 mixed with 30% R12K ferromagnetic particles. It can be seen that for all induction times, an induction of less than 20 A is requried to reach 100 °C.

The required induction current (I) to reach a certain debonding temperature (T) can be expressed by the following relation:

$$I = \mathrm{A} \cdot \ln T - B \tag{1}$$

Where A and B are empirical constant depending on the induction time and particle content in the adhesive.



(a) (b)

Figure 19. (a) Bondline temperature profiles at different induction currents for at least 20 minutes induction time, (b) variation of induction current with bondline temperatures at different induction times

5.1.2. Effect of magnetic particle content on the performance of the adhesive joints

Figure 20 shows the effect of the addition of R12K ferromagnetic microparticles on the average lap shear strength of PPS joints bonded with Araldite 2011 2k epoxy adhesive. It can be seen that the addition of the particles reduces the bond strength of the joint. The sharp decrease in the strength of the joint at 10% could be related to the agglomeration of the particles in the adhesive.

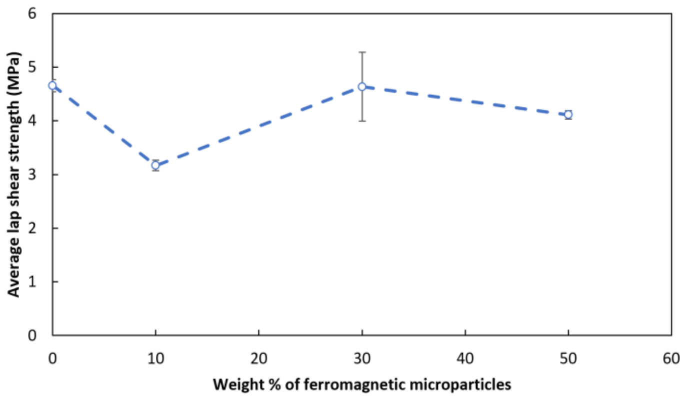


Figure 20. Effect of ferromagnetic particles weight percentage on the average lap shear strength of PPS joints with araldite 2011 2k epoxy adhesive

5.1.3. Debonding performance

Figure 21 shows a comparison between the lap shear strength before and after induction debonding at different weight percentages of R12K microparticles for PPS joints bonded with Araldite 2011 2k epoxy adhesive. It is clearly seen that rapid induction heating significantly reduced the strength of the joints by approx. 35% (for 30% particle content by weight) to 85% (for 10% particle content by weight). This significant decrease enabled debonding with the application of external mechanical separation force.

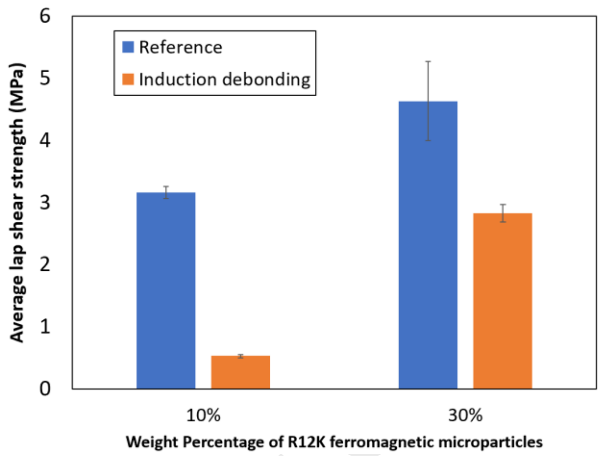


Figure 21. Debonding performance at different R12k particle weight percentages

5.2. Debonding by thermally expandable particles

5.2.1. Characterization of the expansion of the thermally expandable particles

The triggering temperature of the TEPs was fixed to 100 °C as mentioned earlier. However, the time required to trigger the expansion of the particles and the magnitude of the expansion at 100 °C are not predetermined. Therefore, small cuboid samples of Araldite 2011 2k epoxy mixed with different weight percentages of TEPs were heated in the climate chamber at 100 °C for 50 minutes. The volume of the samples was measured using Keyence 3D digital microscope prior to heating. At certain time intervals, heated samples were removed out of the oven and conditioned to room temperature to allow for remeasuring their volume after expansion using the microscope.

Figure 22 shows the volumetric expansion percentage of the Araldite 2011 samples mixed with TEPs at different heating times, along with the temperature profile of the climate chamber. It can be seen that the climate chamber requires at least 5 minutes to reach a steady state temperature of 100 °C, while triggering the expansion of the particles (which theoretically starts at 80 °C) can start after 10 minutes. The largest volumetric expansion can be seen with particles of 50% weight, while weigh percentages of 30% and 10% show similar expansion behaviour.

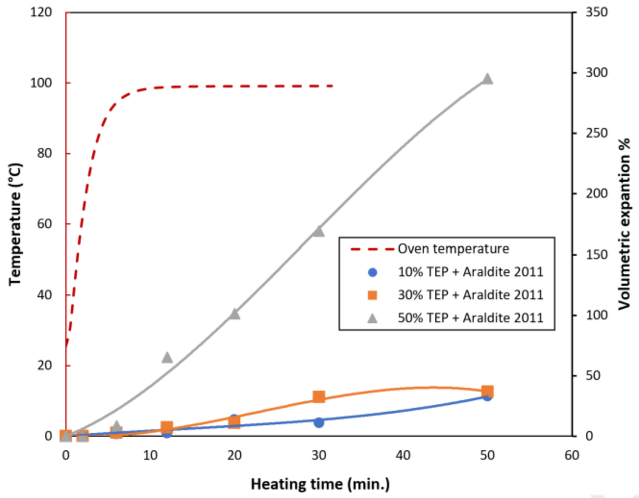


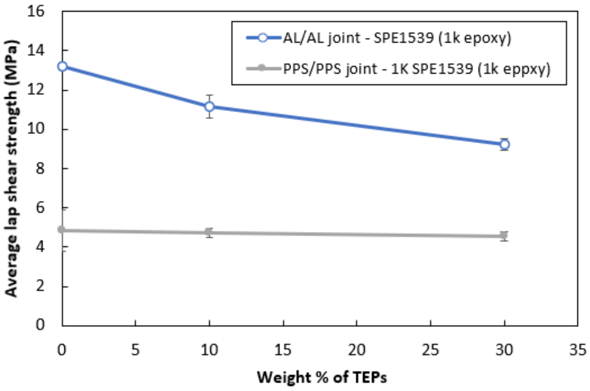
Figure 22. Time history of the volumetric expansion percentage of Adhesive/TEP mix at 100 °C at different TEPs weight percentages (right axis) and the temperature profile of the climate chamber (left axis)

5.2.2. Effect of TEPs particle content on the performance of the adhesive joints

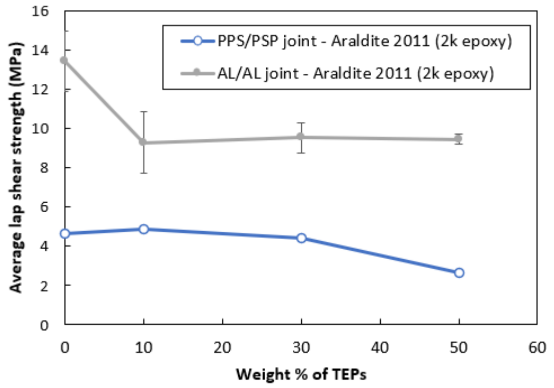
Shows the effect of adding TEPs on the average lap shear strength of PPS, AL, and AL/composite joints with diferent adhesive types. The addition of TEPs to adheisves generally reduces the la shear stength of the joints, which becomes more significant in brittle adhesives compared to flexible adhesies. The highed reduction percentages can be seen in aluminum joints with 1k epoxy adhesives and PPs joints with 2k epoxy adheisves, with percentage reduction down to approx. 24% at 30% particle content by weight for the 1k epoxy and approx. 37% for 2k epoxy. For the polyurethane adhesievs (one and 2 components), hardly any reduction in lap shear strength was observed. This could be attributed to the flexible nature of the adhesive, and the good adhesion between the outer polymer shell of the particles and the adhesive.

5.2.3. Debonding performance

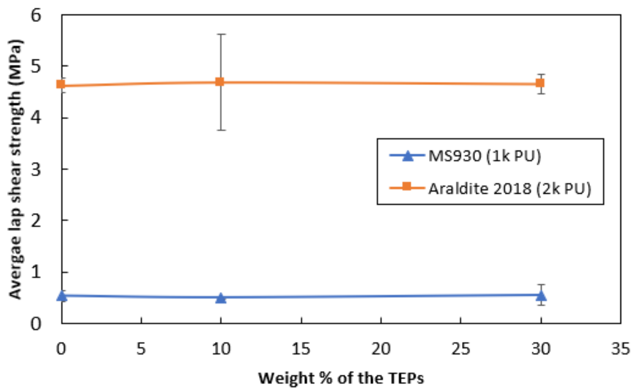
Figure 24 shows examples of the debonding performance of aluminum joints with epoxy adhesives mixed with TEPs. It can be seen that triggering the expansion of the TEPs within the adhesive reduced the joint's strength significantly. The largest decrease in strength was seen with Araldite 2k epoxy mixed with 50% TEPs by weight, followed by a the mixture with 10% TEPs by weight, at strength levels roughly below 2 MPa. This corresponds to very low force levels (less than 600 N) to separate the substrates. Whereas in the 1K epoxy adhesive, the addition of 30% TEPs by weight significantly reduced the strength of the joint to less than 0.5 MPa, which corresponds to force levels of 150 N to separate the substrates. This indicates the overall effectiveness of the TEPs to achieve on-demand debonding in 10 minutes with minimum use of additional force to separate the substrates. It should be noted, however, that since the triggering of the expansion of the TEPs is achieved at 100 °C which exceeds the glass transition temperature of the 2k Epoxy of 45 °C, the absolute effect of the TEPs in the debonding is overshadowed by the transition of the adhesive to the low strength rubbery state. This was also observed in the fracture pattern of the 2k epoxy samples, where the expansion foaming effect of the particles was not observed. On the other hand, since the 1k epoxy adhesive has a higher glass transition temperature, the foaming effect was clearly seen in the fractured samples, see Figure 25.



(a)

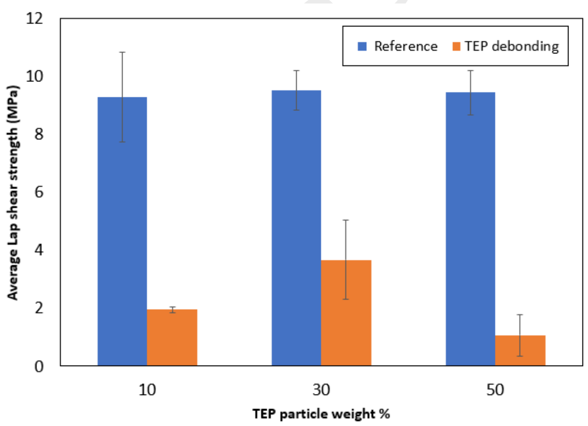


(b)

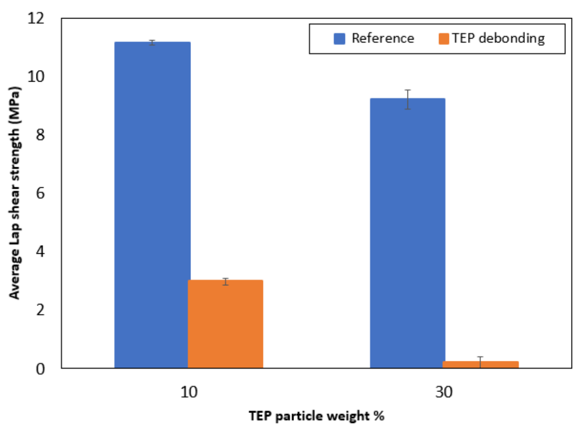


(c)

Figure 23. Effect of adding TEPs on the average lap shear strength of adhesive joints: (a) 1k epoxy with AL and PPS joints, (b) 2k epoxy with AL and PPS joints, (C) 1 and 2k Polyurethane adhesives with AL/Composite joints



(a)



(b)

Figure 24. Debonding performance of aluminum joints with TEPs: (a) Araldite 2011 2k epoxy, (b) SPE 1539 1k epoxy

(a) (b)

Figure 25. Fracture patten of aluminum joints with 30% TEPs by weight: (a) 1k epoxy, (b) 2k epoxy

5.3. Debonding by Convection

To determine the time required to reach the debonding temperature for convection (i.e., 100 °C), samples fitted with thermocouples embedded inside the bondline were heated in the climate chamber for at least 100 minutes. Shows the time required for aluminum and PPS joints with different epoxy adhesives to reach 100 °C in the climate chamber. The climate chamber was kept at a steady state temperature of 100 °C, which was measured using a thermocouple at the center of the chamber. It can be seen aluminium joints with 1k and 1k epoxy adhesives required at least 6 minutes to reach 100 °C in the bondline, whereas the PPS joints required at least 10 minutes to reach the same temperature levels. This could be attributed to the complex heat transfer nature of the joints, despite the fact that polymers, in general, are natural insulators with very low coefficient of thermal conductivity. Further research is required to understand the cause of this phenomenon. Due to the long time required to heat the aluminum samples by convection and consequently debond them using the testing machine, it was decided to focus on convection debonding of PPS joints which takes considerably less time to heat and debonding.

Figure 27 shows the debonding performance of PPS joints with 2k epoxy adhesive using convection. Similar to the TEPs, it can be seen that convection debonding reduced the average lap shear strength of the joint by approx. 84%. This corresponds to a debonding strength and force of approx. 0.8 MPa and 250 N, respectively.

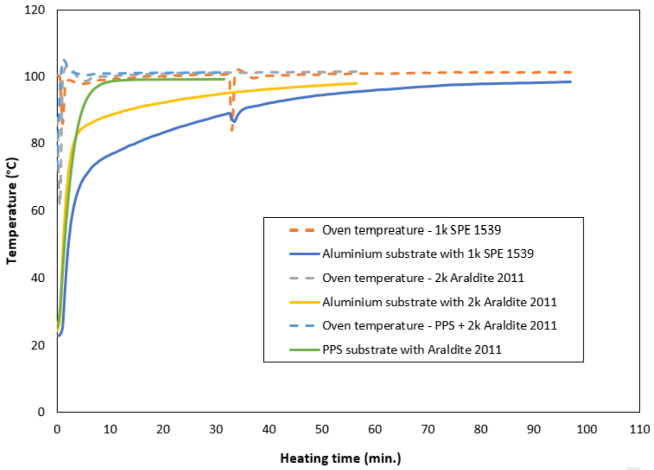


Figure 26. Time required to reach 100 °C for convection debonding

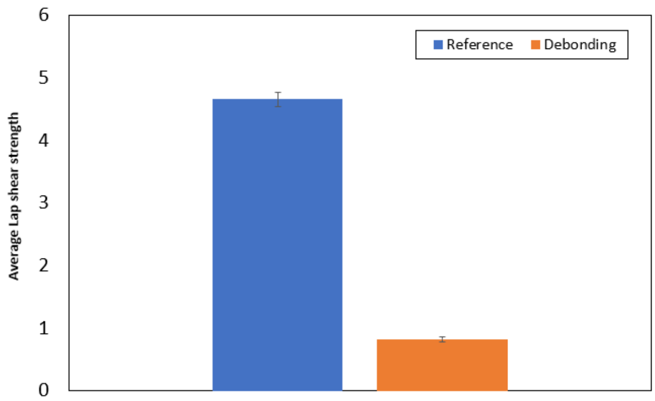


Figure 27. Debonding performance of PPS joints with 2k epoxy adhesive using convection

5.4. Comparison between debonding methods

Figure 28 shows a comparison between debonding performance of the 3 debonding methods (i.e., convection, induction with R12k particles, and TEPs) using PPS joints with Araldite 2011 2k epoxy, at a debonding temperature of 100 °C for all debonding methods. It can be seen that all debonding methods were effective in reducing the strength of the joint by ranges of approx. 38% to approx. 83% compared to reference joint strength before debonding. Induction debonding managed to reduce the bond strength by only 38%, however, it remains the fastest debonding method compared to the other methods. Both TEPs and convection achieved the same debonding strength levels with araldite 2011 2k epoxy. This could be attributed to the overshadowing effect of convection heating on the foaming effect of the TEPs, as mentioned previously in section 5.2.3.

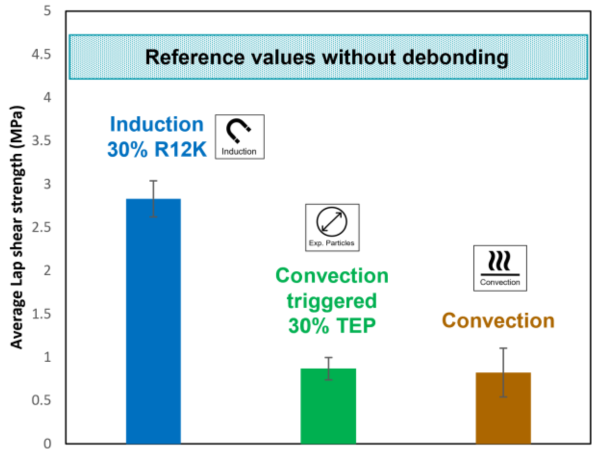


Figure 28. Comparison between debonding methods using 2k epoxy adhesives with PPS joints

5.5.Hybrid debonding methods (Induction and TEPs)

Figure 29 shows the debonding performance of induction and TEPs hybrid debonding method with 1k and 2k polyurethane adhesives on aluminum/GFRE joints. In this case, the induction heating is used to heat the aluminum substrate which consequently triggers the expansion of the TEPs at 100 °C by the effect of conduction heating to the adhesive layer. It can be seen that the addition of the TEPs significantly contributed to the reduction of the joint's strength by almost 93%. The largest reduction in strength can be seen with TEPs weight percentage of 30%. This indicates that the hybrid debonding method achieves the fasted heating times with virtually no additional debonding forces.

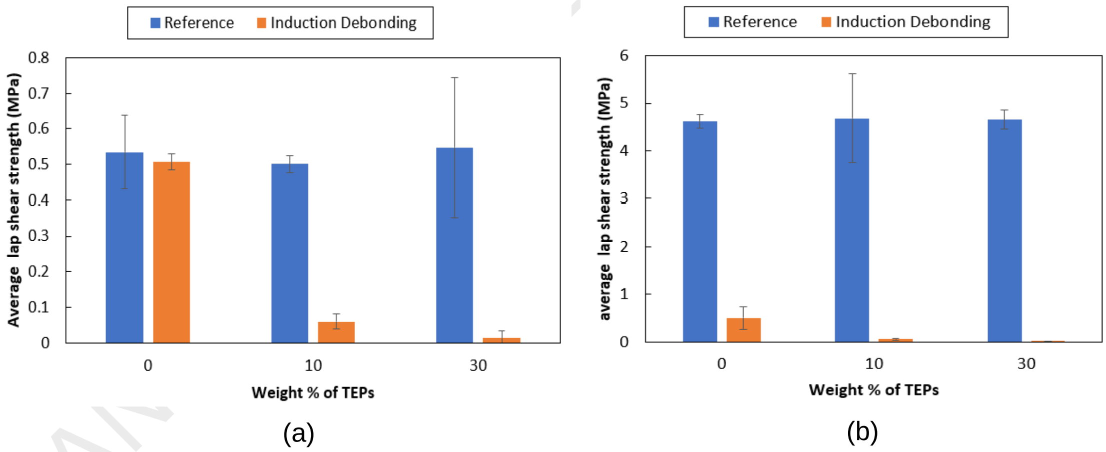


Figure 29. Debonding performance of induction/TEP hybrid debonding method with aluminum/GFRE composte joints: (a) using MS930 1k PU adhesive, (b) using Araldite 2018 2k PU adhesive

6. Conclusions

Within the framework of WP2 of the circular bonding project, this research focused on identifying possible debonding technologies which have a high market potential and validating these technologies on a lab scale. Following an extensive review of the literature, several debonding technologies were identified, namely induction, convection, thermally expandable particles, electrically debondable adhesive, microwave debonding and debonding using ultraviolet radiations. Each debonding technology was studied and reviewed with respect to several aspects, such as the working principle, the suitable materials and adhesives, the required infrastructure and equipment, the debonding performance, and their commercial availability and scalability. Based on this review, several criteria were defined to evaluate and rank these technologies, including the debonding time, the effect of the debonding method on the joint strength before debonding, the type of materials used with each technology, the safety, scalability and the commercial availability aspects. The ranking of the technologies revealed that induction, convection, and debonding with TEPs were the best candidate debonding technologies with the highest market potential compared to their debonding performance. Based on this ranking, these 3 methods were further validated experimentally. Several tests were performed to study the process parameters of each debonding technology, the effect of the addition of particles to the performance of the joints, and the final debonding performance for each technology. A comparison between all the technologies using the same substrate material and adhesive was performed, in addition to testing hybrid debonding concepts with induction and TEPs on several flexible adhesives. Based on the experimental conditions of this research, the materials and debonding methods used, the following can be concluded:

- Induction technology achieved the least debonding performance with respect to the reduction of the joint's strength by heating. This means that induction debonding requires additional mechanical force to separate the substrates. However, it remains the fastest and most efficient debonding method compared to convection and TEPs.
- Convection technology achieved a reasonable debonding performance compared to the other methods, however, with certain types of substrates, it requires long heating time in climate chambers.
- The use of TEPs as a debonding technology significantly reduced the strength of the joint after debonding, however, at the expense of the performance of the joint before debonding.
- The combination of induction and TEPs as a hybrid debonding technology shows a great potential as an on-demand debonding method.

References

[1] Hunstman Advanced Materials Corp., Araldite 2011 data sheet, August 2014.
[2] Rudnev, V.; Loveless, D.; Cook, R.L. *Handbook of Induction Heating, Second Edition*; 2018; ISBN 9781466553972.
[3] Salimi, S.; Babra, T.S.; Dines, G.S.; Baskerville, S.W.; Hayes, W.; Greenland, B.W. Composite polyurethane adhesives that debond-on-demand by hysteresis heating in an oscillating magnetic field. *Eur. Polym. J.* **2019**, *121*, 109264, doi:10.1016/j.eurpolymj.2019.109264.
[4] Sairem large scale microwave, https://www.sairem.com/test-center-and-equipment-rental/
[5] Gilbert, D., The European Directive 2004/40/EC related to microwave exposure in the workplace: a case study International Workshop on industrial microwave ovens November 16, 2006, Mol, Belgium, https://www.gd-emf-consulting.be/rapporten/INDUSTRIELE_MICROGOLFPOVENS.pdf
[6] Kim, D.; Chung, I.; Kim, G. Dismantlement studies of dismantlable polyurethane adhesive by controlling thermal property. *J. Adhes. Sci. Technol.* **2012**, *26*, 2571–2589, doi:10.1080/OI694243.2012.690213.
[7] Banea, M.D.; da Silva, L.F.M.; Carbas, R.J..; Campilho, R.D.S.G. Mechanical and thermal characterization of a structural polyurethane adhesive modified with thermally expandable particles. *Int. J. Adhes. Adhes.* **2014**, *54*, 191–199, doi:10.1016/j.ijadhadh.2014.06.008.
[8] Banea, M.D.; da Silva, L.F.M.; Carbas, R.J.C.; de Barros, S. Debonding on command of multi-material adhesive joints. *J. Adhes.* **2017**, *93*, 756–770, doi:10.1080/00218464.2016.1199963.
[9] Banea, M.D.; da Silva, L.F.M.; Carbas, R.J.C.; de Barros, S. Debonding on command of multi-material adhesive joints. *J. Adhes.* **2017**, *93*, 756–770, doi:10.1080/00218464.2016.1199963.
[10] EIC labs, Electrically debondable adhesive, http://www.eiclabs.com/ERtech.htm
[11] Heinzmann, C.; Coulibaly, S.; Roulin, A.; Fiore, G.L.; Weder, C. Light-Induced Bonding and Debonding with Supramolecular Adhesives. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4713–4719, doi:10.1021/am405302z.
[12] Zha, R.H.; Vantomme, G.; Berrocal, J.A.; Gosens, R.; de Waal, B.; Meskers, S.; Meijer, E.W. Photoswitchable Nanomaterials Based on Hierarchically Organized Siloxane Oligomers. *Adv. Funct. Mater.* **2018**, *28*, 1–8, doi:10.1002/adfm.201703952.
[13] Sasaki, T.; Hashimoto, S.; Nogami, N.; Sugiyama, Y.; Mori, M.; Naka, Y.; Le, K. V Dismantlable Thermosetting Adhesives Composed of a Cross- Linkable Poly(ole fi n sulfone) with a Photobase Generator. **2016**, doi:10.1021/acsami.5b10110.