Dismantlable Adhesive Joints For Decommissioning, Repair And Upgrade

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ABSTRACT

Adhesive bonding is well established as one the most successful means of joining advanced composite materials, which are increasingly employed to reduce weight and extend service life. It is also well known that adhesives used to sustain structural loads tend to be permanent, cross-linked and irreversible, which raises particular challenges when equipment becomes obsolete or when there is a need for upgrade or repair. This paper reviews the latest published work on dismantlable adhesive technologies, and highlights the criteria needed to evaluate potential disbondable systems. Whilst tailored formulations, originally developed as self-healing polymers, demonstrate considerable promise for self-repair, re-adjustment and disbonding, it concludes that additives, in the form of expandable reactive agents, offer demonstrable performance and relatively simple adaptation to bonding technology currently employed. These, in conjunction with appropriate design strategies in order to aid design for disassembly, should offer potential solutions for innovation in temporary repair and upgrade scenarios, including adaptive armour or the development of new modular design platforms using advanced composites.

1.0 INTRODUCTION

For reasons of economy, light-weighting increased payloads, adaptability, extended service life or simply a reduction in environmental impact (energy consumption and Green House Gas emissions) advanced composite materials are increasingly being adopted. The major sectors driving their uptake are aerospace, defence, transportation and wind energy. In total, this has led to global CAGR predictions of 8.13% for composites (10.8% for carbon fibre) between 2016 and 2022[1]. The current demand for advanced composites in the military is due to their increased application in body armour, helmets, holsters, space shuttles, radomes, rocket motor casing, fairings, satellites, antenna dishes, and missiles[1]. In the UK, composites are deployed in various ways in air (A400M, Typhoon, Agusta Westland), land (Mastiff, Ridgeback, Foxhound) and sea (Type 45, 26, Astute, MUFC) platforms. As a result, current UK defence spend on advanced composites is estimated to be £380m and is forecast to be £920m by 2020, with an expectation to grow to £1,150m by 2030[2].

As and when equipment becomes obsolete or irreparable, the increasing use of advanced composites will bring about new challenges in the re-use and reclamation of equipment and materials. This is already evident in civilian industry with the adoption of new regulations, such as the EU Directive introduced in 2015[1]. This sets targets for automobiles on emissions (130gCO_2/km) and material reclamation (95% by weight) that have forced an uptake of new light-weighting technologies, including advanced composites. Likewise, the aerospace sector is predicted to double between now and 2030[3]. The new generation of aircraft structures

have significant carbon composite content and strategies for dealing with obsolete aircraft are now underway[4], since abandoning them in a dessert is no longer deemed acceptable.

As advanced composites are increasingly and rapidly adopted there is an urgent need for an effective means by which obsolete equipment can be disassembled and materials reclaimed for further use or repair. Adhesive bonding is well established as one the most successful joining technologies for connecting advanced composites. Indeed, in many cases adhesives offer the only effective means of joining these materials in order to maximise their performance, especially for light-weighting purposes, in a way that traditional joining methods cannot compete[5]. In most cases, a permanent (cross-linked) and highly durable polymer network is developed. Whilst this is a major challenge for dismantlablility, a solution would also offer substantial potential for innovation in temporary repair and upgrade scenarios, including adaptive armour or the development of new modular design platforms using advanced composites.

2.0 GENREIC DISBONDING ADHESIVE SYSTEMS

Since the 1970's there have been a number of adhesive systems developed to disbond on-demand[6], but few have resulted in practical application. The least technical of these includes softening of the adhesive and mechanical separation of the bonded joint, typically using a heated wedge, knife or wire. This approach tends to be inefficient and labour intensive but has been found to be of practical use for the removal of damaged automotive windscreens[7]. Notably, the efficiency of debonding relies upon the adhesive exhibiting a relatively low stiffness, i.e. elastomeric adhesive, sealant or pre-heated above the glass transition temperature, as well as pre-designed features and sizable bondline thicknesses to aid accessibility, otherwise substrate damage is inevitable. Certain chemical degrading agents [8], solvent or acid immersion techniques, can also assist the adhesive disassembly process. Thermal softening, by exceeding the adhesive's glass transition temperature, has been exploited by the electronics industry over several decades in order to enable rapid removal of bonded chips at end of life [9,10], but thermal decomposition, by exceeding the temperature of flammability-in-air or auto-ignition point, raises major concerns regarding the release of toxins and irritants as a result of chemical decomposition [11].

2.1 Tailored Adhesive Formulations

This approach generally involves the inclusion of labile-chemical structures that on heating induce reversible chemical reaction(s) that re-establishes polymer flow. The Battelle Memorial Institute [12] developed a thermally reversible isocyanate-based polymer formulation, which was based on the dissociation of the isocyanate-labile hydrogen-based linkage to the isocyanate and labile-hydrogen starter groups. Upon disassociation, this polymer was found to become a free flowing melt, which was soluble in acids. Lap shear strengths up to 13MPa were recorded, before softening at 60degC and separation was possible above 130degC. A similar approach was developed for different chemistries by Atochem [13] and Yokohama [14].

Sandia National Laboratories [15] developed a removable elastomeric adhesive by incorporating thermally reversible furan-maleimide Diels-Alder (DA) adducts, which form below 60°C and dissociate above 90°C in a low modulus epoxy adhesive formulation. The relatively low dissociation temperature and weak mechanical properties exhibited by lap shear joints (4MPa) would rule out its use for structural applications. Nevertheless, this chemistry is currently the focus of significant research for the development of self-healing polymers (thermosets, thermoplastics, and elastomers) [16] and composites[17], thus potentially eliminating the need for certain repair scenarios. The majority of these systems require high thermal temperatures, typically ranging between 120degC to 180degC for complete disassociation[16]. They pose many technical challenges and their performance under long-term environmental exposure remains an open question[17]. Recent advances have,

however, demonstrated substantial improvements, reporting lap shear strengths as high as 23MPa[18] by introducing alternating rigid - flexible segments in the dynamic quaternization cross-links of ploy(1,2,3-triazolium) vitrimer (VPTA) adhesives. These systems have also demonstrated repeated fracture and self-healing over 20 times whilst maintaining lap shear strengths above 10MPa.

DC Polymers [19] adopted electrochemically active cross-linkers, which can be incorporated into the polymer structure. The system requires electrically conducting substrates, combined with an epoxy adhesive made ionically conductive with an addition of a salt (1-Ethyl-3-methylimidazoliumehtylsulfate (EMIM-ES) ionic liquid), forming an electrochemical cell. Electrochemical reduction is triggered by applying an electric current. This leads to scission of the polymer backbone at cross-link sites and thereby polymer degradation. Polarizing charge densities of 0.05mA/cm2 were applied, although this was dependent upon water content and mechanical bending of aluminium laminates was required for complete separation. Since cross-linking is quite common to all types of polymers, this technology can theoretically be applied to a wide range of polymeric materials. The proposed mechanism of debonding of the laminates was due to the formation of aluminium complexes as a result of the electrochemical reaction products on the anode. These aluminium complexes were thought to penetrate the adhesive phase, likely causing an increase in volume which in turn induces stresses at the adhesive/aluminium interface.

A variation on reworkable adhesive systems is the ability to change the polymer cross-link density through UV irradiation and modest temperatures. Sato et al [20] developed an acrylic polymer for use in pressure-sensitive (non structural) adhesives that respond to these energetic stimuli, resulting in a small modulus increase of the adhesive. When subjected to peel forces, the bonded joints failed rapidly at the adhesive/substrate interface. Akiyama et al [21] also used UV induced reversible isothermal phase changes with hot-melt adhesion of polyamide blends for disbonding glass substrates. Heinzmann et al [22] demonstrated lap shear strengths between glass substrates of 0.9 to 1.2 MPa. Though low strength these are fully reworkable adhesives that can be rebonded through exposure to light or heat (for non visible bondlines, e.g. stainless steel), regaining the original properties of the adhesive.

2.2 Active Substrates and Tapes

A series of electrically-reversible amine-cured epoxy adhesives were developed by EIC Laboratories under the trade name of ElectRelease™ [23]. Disbonding is achieved when a potential difference of 10-50V, and a current of 1-5mAcm-2, is applied between electrically conductive substrates. The disbonding mechanism is achieved through ion conduction along the resin-metal interface. Pseudo-micelles are formed by incorporating a nanoscaled backbone blocks of polydimethylsiloxane (PDMS) into a two-part amine-cured epoxy resin structure. The backbone structure is also attached to the arms of polyethylene glycol (PEG) which creates a comb-type polymer and pseudo-micelles structure in the uncured epoxy resin. Upon curing, the PEG micelle phase separates from the epoxy around the immiscible PDMS cores and forms a nanoscaled co-continuous network. Cure can be achieved at room temperature (24hours) or at 80degC (35mins). Lap shear strengths from 3MPa (100degC) up to 20MPa (room temperature) have been reported. The disbond mechanism requires a metal, acting as the positive substrate, and another suitable material acting as the negative substrate. When two metal substrates are bonded using ElectRelease™, disbonding at both interfaces can be achieved by reversing the polarity of the voltage. For non-conductive materials, an ElectRelease™ foil patch (EFP), which is essentially two sheets of metal foil, is applied onto the surface to facilitate electric conductivity [24]. Leijonmarck et al. [25] provided further understanding of the disbonding mechanisms involved with the ElectRelease™ system. They observed a delamination process at the interface between the aluminium anode and the adhesive layer, detected changes in polymer chemistry using Raman spectroscopy and also analysed the emission of volatile species using mass spectrometry. Possible applications are seen in the packaging[26], laminating [27] and manufacture of safety helmets[28]. The latter providing a means to separate the helmet from the head after an accident without further risk of endangering the patient.

Evonik developed MagSilica(R), a type of adhesive tape [29]. MagSilica(R) is used as a nano susceptor, which is essentially iron oxide wrapped in silicon dioxide. These particles begin to oscillate when subjected to a rapidly alternating magnetic field, which heat up for the purpose of both curing and disassembly. A major concern is that conductive or magnetic components can cause electromagnetic shielding, which deactivates the heating mechanism[30].

2.3 Chemical Additive Disbonding Technologies

Early work on shoe re-soling [31] included the incorporation of metallic particles into the adhesive to efficiently absorb and emit heat energy when subjected to alternating electro-magnetic field, thereby activating the release of micro-encapsulated solvents, which would further degrade the polymeric structure. Daimler-Chrysler and partners [32] patented similar work and specified examples of encapsulated solvents as organic amines or acids which can cleave an epoxide backbone. Microcapsules were recommended to be made of amino resin or metal halide. Obediat [33] reviewed recent patented works of different microcapsule preparation methods used in the pharmaceutical industry. The Nissan Motor Company [34] mixed oxidising agents (ammonium perchlorate, potassium permanganate, etc.) into the adhesive matrix which produced a self-burning reaction at elevated temperatures. The decomposition process generated abundant oxygen and caused failures in the bondline. Henkel [35], IBM [36], the US Army Research Laboratory [37] and Rescoll investigated a series of CFAs including Azo compounds, and hydrazides. The technology developed and patented by Rescoll is called INDAR Inside(R) [38]. Several debonding temperatures are possible, depending on the additive. A margin of 50°C between maximal service temperature and debonding temperature was suggested in order to avoid premature activation. In the case of INDAR Inside(R), the additive activates around 200°C. The decomposition temperature was chosen far beyond the curing temperature of the adhesive to avoid anticipated activation of the process. After 10 minutes at 200°C samples with INDAR Inside(R) exhibited a drastic loss of lap shear strengths from 45MPa to residual strengths around 2MPa, with adhesive failure on the adhesive/Invar interface.

Different types of foaming agents were incorporated into adhesive systems to promote disbonding at elevated temperatures[39,40,41]. It was noted that CFAs would become mobilised at higher temperatures when the adhesive bondline softened and melted. The CFAs would then migrate to and finally decompose at the joint interface. Functional additives, incorporated into adhesive bondlines, have been investigated by a number of other researchers [42,43,44]. McCurdy et al [42] investigated the effect of the incorporation of functional additives on the dismantling characteristics of three adhesives: two toughened epoxies and a semi-structural polyurethane. The functional additives selected were four types of CFAs: p-toluenesulfonyl hydrazide (pTSH), benzenesulfonyl hydrazide (BSH), azodicarboxamide (ADC) and 5-phenyl-1H-tetrazole (5P1HT). No discernible benefit was observed from the experimental data of CFA incorporated into the more compliant semi structural adhesive. Although these systems were promising they still showed problems of additive/adhesive incompatibility, which was also found to significantly affect long-term durability.

2.4 Physical Additive Disbonding Technologies

Physical additive mechanisms developed for dismantling cross-linked adhesive joints include, thermally expanding microspheres (TEM) and acid modified expandable graphite (EG). External heat energy is applied, which triggers the expansion of the additives that are mixed into the adhesive (or primer layer) in quantities from 1% up to 20% by weight.

Early work patented by 3M [45] used an expandable additive content of 10 to 50wt% with an initiation temperature between 250degC and 500degC. The challenge of automotive glazing replacement using non-

destructive means was addressed by Manfre and Vitkala [46], who investigated the incorporation of thermally-expandable microspheres in the primer layer on the metal. Elements of the system were later patented and developed commercially by Autoglass, a commercial windscreen replacement organisation.

Expandable additives have been used for disbonding in orthodontic applications[47,48]. Conventional techniques for the removal of orthodontic attachments carry risks of tooth enamel damage. The use of electrothermal, laser or ultrasonic methods may incur other problems such as expensive equipment cost, potential pulpal damage and mucosal burns. Tsuruoka et al [49] incorporated thermally expandable microspheres (TEMs) into 4-META/MMA-TBB (4-methacryloxyethyl trimellitate anhydride in methyl methacrylate initiated by tri-n-butyl borane) resin adhesive, which is widely used for bonding orthodontic brackets. The microspheres used in this study were Matsumoto F-36D, which starts to expand at 80degC. 40wt% TEMs were needed to reduce the bond strength by a third within 8s of heating.

Generally, TEMs consist of a thermoplastic polymer shell encapsulating a hydrocarbon blowing agent with a low boiling temperature. These microspheres are typically 10-50μm diameter, expanding to 40-60 times greater than their initial volume (Figure 2-1). TEMs were first developed by Dow Chemical Co. and are currently manufactured by many companies such as Polychem Alloy, Sekisui Chemical, Matsumoto Yushi Seiyaku, Akzo Nobel and Sigma Aldrich. Expansion temperatures are generally in the order of 115degC to 160degC with maximum expansion being attained between 160degC and 220degC. The Tokyo Institute of Technology [50, 51] conducted research on disbonding using expandable microspheres manufactured by Matsumoto. These studies additionally looked at its application for construction materials. The weight fraction of microspheres used and the roughness of substrate surfaces were found to be two major factors in determining the dismantlability of the bonded joints.

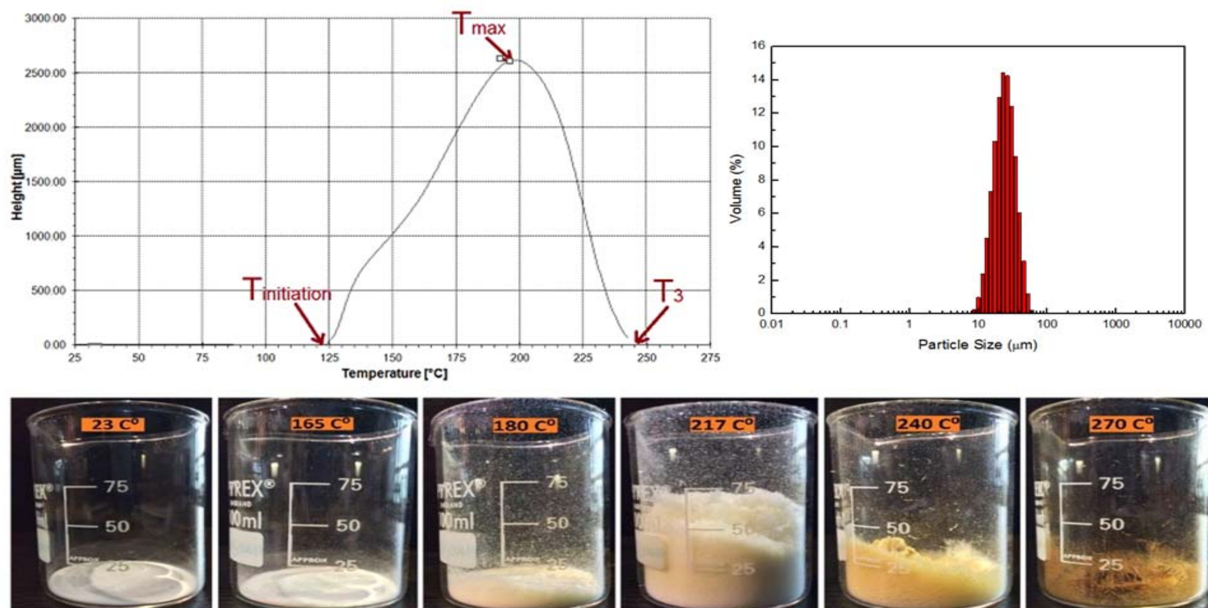

Figure 2.1 Expansion of TEMs as a function of temperature and particle size distribution (pre-heating)

De-Bonding Ltd and Evonik focused on thermally-activated disbonding of automotive glazing by incorporating TEMs in the primer layer of the sealant [46, 52]. An infra-red lamp was adopted as the heating source. Their research [53] successfully synthesised polypyrrole-coated TEMs; polypyrrole has a broad

absorption peak (900-1500 nm) in the infra-red. This provides the polypyrrole-coated TEMs with a very efficient thermal energy absorbance. Experimental results showed great potential for disbonding of automotive glazing and other vehicle panels. Disbonding can be also be achieved by adding expandable additives in adhesive system primer layers, if present. This is a very effective location for separation. The modified primer expands and separates the adherends upon heated, leaving a clean surface [54].

The incorporation of additives has been found to affect mechanical properties and, in particular, the durability of the adhesive system, by acting as weak links in the matrix or, in some cases, reacting with the matrix. Based on earlier work by Jonsson et al [55], Lu et al [44] successfully modified TEMs by grafting glycidyl methacrylate (GMA) on the surface of Acid treated TEMs by atom transfer radical polymerization, using activators regenerated by electron transfer (ARGET ATRP), see Figure 2-2.

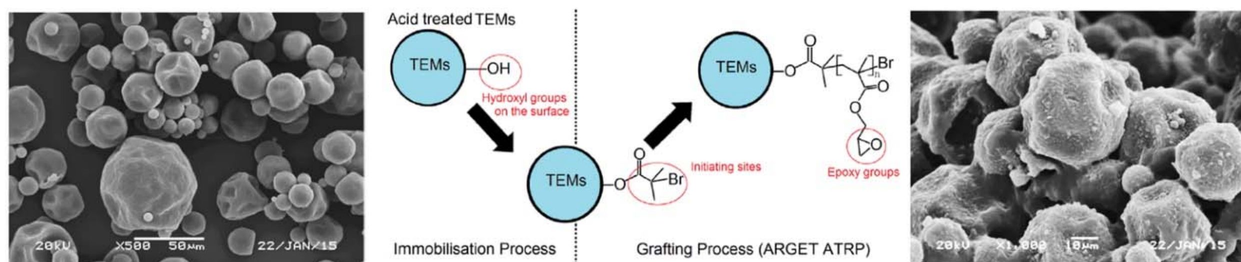

Figure 2-2: ARGET ATRP process and images for modification of TEMs.

The ARGET ATRP surface modification treatment promoted covalent bonding between the adhesive matrix and the thermoplastic surface and, whilst not optimised, significantly improved dry strength (by 25%) and enhanced environmental resistance to moisture for bulk epoxy/TEM tensile specimens with 20% wt TEMs (Figure 2-3). Lap shear strengths of 19MPa were maintained even in wet conditions after soaking for 6 months in DI water. Bulk tensile tests demonstrated a 25% drop in dry strength due to the inclusion of the modified TEMs, but wet trials demonstrated only 12% drop thereafter but still produced higher strength than the adhesive containing untreated dry TEMs.

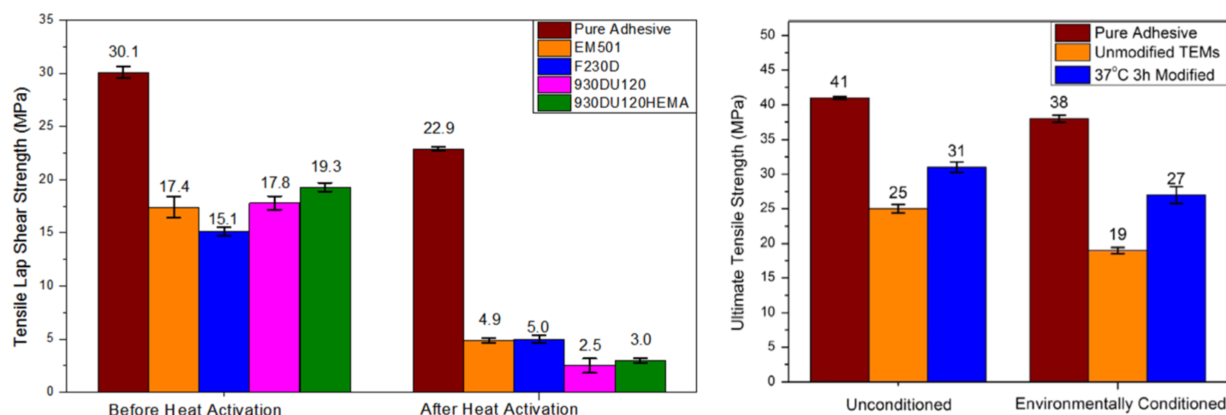

Figure 2-3: Strength retention post heat activation (left) and conditioned pre-activation performance (right)

Expandable graphite (EG), or intumescent flake graphite, represents an interesting type of inert, layered particle that can be triggered by heat, investigated by Kishi et al [56, 57], Sato [58] and Pausan et al [59].

Graphite also exhibits high thermal and electrical conductivity, which lends itself to rapid heating. An acid is intercalated into the crystal layers of the graphite and vaporization triggers exfoliation of the flake, at temperatures initiating from 150degC with increasing expansion experienced up to 950degC. The more rapid the heating rate is, the better the expansion. The flake planar dimensions are quite large (~200 - 600µm) and determine the resulting expansion. Smaller radii reduce expansion. That said, this material has the potential to expand many times more than typical TEMs, which permits lower concentration levels (3%) to be used and which also appear to be more effective in tough polymeric matrices, Figure 2-4. Moreover, recent preliminary work by Pausan et al [59] has also indicated excellent toughness and resistance to moisture attack, reflecting the inert properties of the graphite. Lap shear strengths of 26MPa were achieved with only 3%wt EG, achieving 83% of the unfilled bulk adhesive strength.

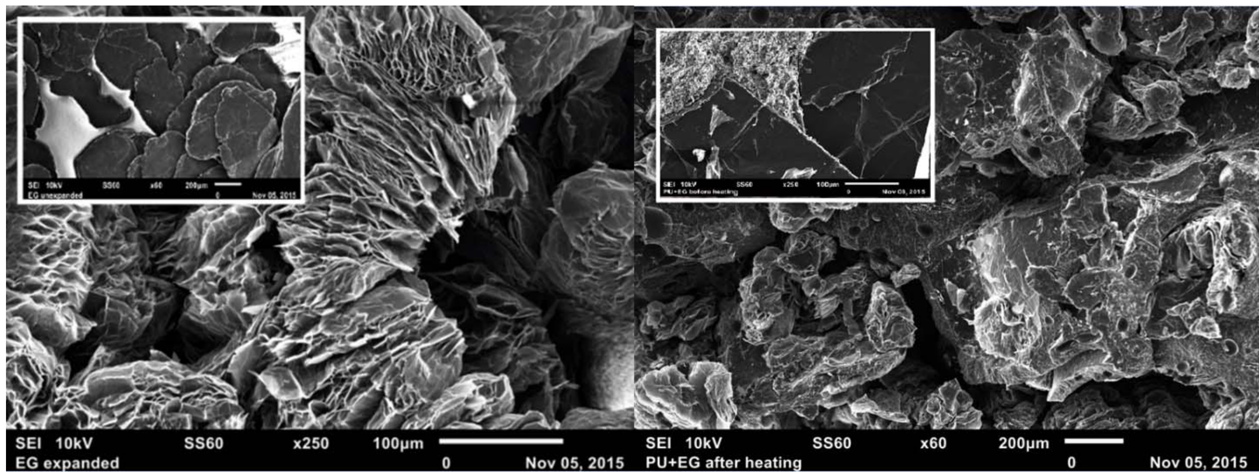

Figure 2-4: Graphite bisulphate before and after activation (left) and again in PU structural adhesive joint (right)

3.0 DESIGN FOR DISASSEMBLY

To date, the vast majority of multi-material structures have neither been designed nor built with disassembly in mind. The practicalities of separating materials dictate the efficacy of the chosen dismantling technology, which must include disassembly-enabling design features. The types of approach currently being adopted are increasingly informed by life cycle analysis [60], recent standards covering design for manufacture, assembly, disassembly and end-of-life processing (BS 8887-220:2010) [61], and an increasing awareness for circular design strategies including dis- and re-assembly[62]. As circular material models are adopted in new design, the more prevalent disassembly technologies and design for disassembly will become.

The fundamental considerations for a practical dismantlable adhesive system were categorised by Rodrigues [63], shown in Figure 3.1. More generally, these include (1) the mechanism for dismantling the joint must be an inherent part of the initial design stage, (2) the joint must survive pre-service requirements (i.e. adhesive pre- and post-cure conditions during manufacture, assembly and storage), (3) the joint must survive the service requirements (i.e. remain dormant whilst providing a durable connection), and (4) be cost effective and plausible for high volume and/or potentially large structures. With respect to repair and up-grade, the ease of separation and resulting substrate and surface condition once separated will also be important.

From the literature, heat is predominantly used as the trigger mechanism and typically some form of induction heating, infra-red lamp or oven has been employed. The effectiveness of the disbonding for those systems evaluating structural adhesives is often attained from single lap joints subject to a predefined load (20N). Some studies have demonstrated complete separation after triggering the disbonding within a short period of time (1s to 20mins), whilst others have reported residual strengths as high as 4MPa.

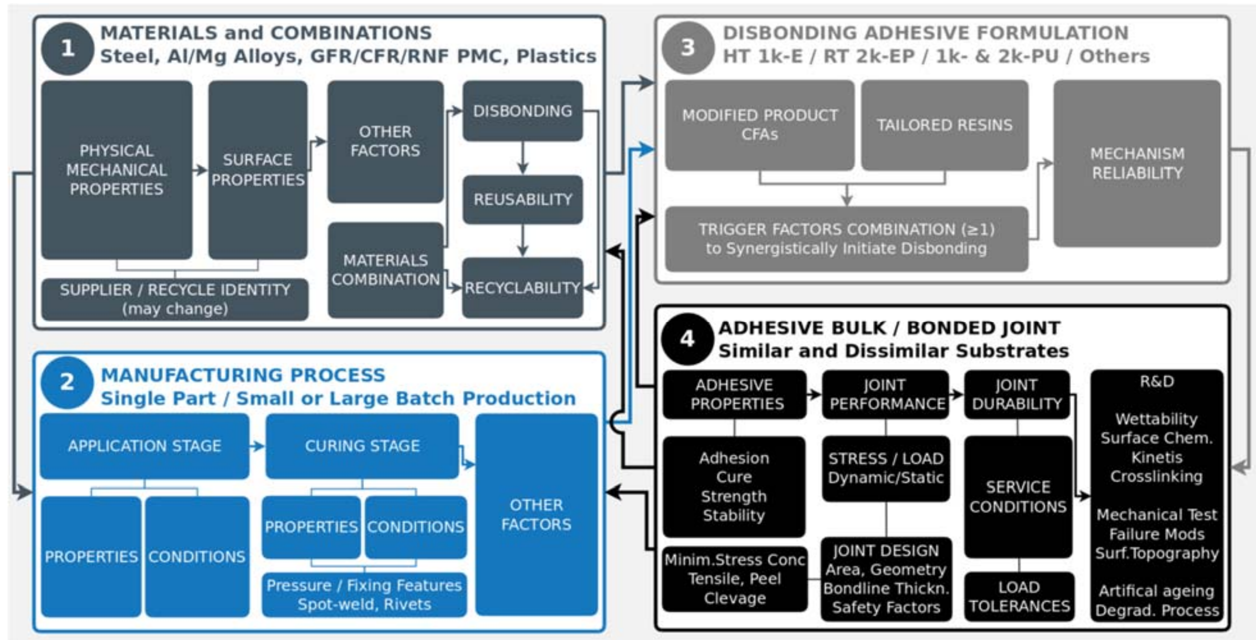

Figure 3-1: Factors to consider in a disbond-on demand adhesive solution [for the automotive industry]

4.0 DISCUSSION

It is clear that advanced composites will play a major role in future transport applications, which will predominately be joined using structural adhesives in order to maximise their potential. The inability for current adhesive systems to disbond is therefore a significant limitation to effective future recycling and reuse of equipment containing these materials. It also hinders potential for innovation in new platform builds as well as novel repair and upgrade scenarios, such as temporary patch repairs to aircraft and land vehicles, and increased modularity for future land vehicle concepts and designs.

There have been several approaches to developing disbond technologies for a variety of applications, though none are yet fully developed to perform in applications that support structural loads. Tailored adhesive formulations generally require high cure and disassociation temperatures, which can have implications when highly mismatched substrate thermal expansion properties are present. Generally, these do not yet support sufficient stress levels (1 to 13MPa) for structural applications, although recent developments with self-healing adhesives have even demonstrated lap shear strengths as high as 24MPa.

Concepts that use so-called active substrates include electrically-reversible adhesives, which are limited to metallic substrates or MagSilica(R) tapes. The former is curable at room temperatures up to 80degC. It exhibits medium strength at room temperature (20MPa) but falls off quickly at 100degC. The MagSilica(R) adhesive tape allows clean separation from one substrate but ultimately relies upon softening and mechanical separation by (rapidly) heating the adhesive above its glass transition temperature.

Where chemical additives have been developed, incompatibility with the adhesive can affect performance and durability, and so is not an approach that easily translates to a wide range of generic adhesive types.

Physical additives have demonstrated good performance as well as disbonding efficacy, and are potentially more versatile with respect to their incorporation into the many different generic types of adhesive. Some systems have reported susceptibility to moisture attack, which has been addressed to some extent with surface modification to promote covalent bonds between the additives and the adhesive hardener.

It is also evident that disbonding mechanisms need to be developed as part of a system to suit particular requirements. This includes forethought in order to design-in disassembly features to assist the disbonding process if the mechanism is to be both cost efficient and effective. The majority of mechanisms reporting semi-structural or structural performance require thermal energy to trigger the disbonding mechanism (typically at temperatures above 120degC), in some cases aided with additional additives (coatings) to speed up induction. Many mechanisms demonstrated residual strengths in laboratory tests, suggesting mechanical force will still be needed to aid separation. Considering multi-material applications, high activation temperatures combined with substrate thermal expansion mismatches could be exploited to assist separation where high residual strengths remain high. Those systems that act at the surface, either through electrochemical means or by migration of mobile species, typically exhibited the lowest residual strengths and cleaner surfaces once separated, but are ultimately limited by low structural performance.

Finally, whatever approach is taken the system needs to survive both pre- and post-assembly exposure to environmental and structural requirements. To date, very little has been reported on the durability of these systems and in all cases, where reported, performance is somewhat poorer.

5.0 CONCLUSION

This paper has discussed various disbonding mechanisms reported in the available public literature. Though not exhaustive, it has attempted to focus on the practical aspects of the various generic approaches. Whilst tailored formulations, originally developed as self-healing polymers, demonstrate considerable promise for self-repair, re-adjustment and disbonding it concludes that additives, in the form of expandable reactive agents, offer both demonstrable performance and relatively simple adaptation to bonding strategies currently employed. In order to aid separation there is also a need to incorporate appropriate practical aspects at the initial design stage. This includes strategies to enable the trigger mechanism (typically thermal) to be efficient, and also incorporation of some physical means that aids separation in order to overcome any residual strength remaining in the bondline. Finally, there remains a critical need to assess the durability of these systems to ensure that, whilst they meet the requirements of any in-service conditions, they remain effective when needed.

6.0 REFERENCES

[1] Composites Market: Global Forecast to 2022, www.marketsandmarkets.com , 2017
[2] UK Composites Market Study (2015) http://www.compositesleadershipforum.com/
[3] The Boeing Company: Current Market Outlook 2011-2030. Seattle, 2011. Company publication.
[4] Ribeiro[a], Oliveira Gomes[b], 12th Global Conference on Sustainable Manufacturing, Proposed framework for End-Of-Life aircraft recycling, CIRP 26 (2015) 311 – 316
[5] Lutz A., DOW Structural Adhesives The key to making lightweight cars, www.dowautomotive.com
[6] Lu, Y., Broughton, J.G. and Winfield, P.H., Int. J. Adhes. Adhes. 50,119- 127 (2014).
[7] BMW, (http://www.bmwblog.com/2014/07/11/learn-bmw-i3-repairprocess/). (Accessed 8 June 2016).
[8] Flegel, H. et al., Patent number DE 198 32 629 A1 (2000).
[9] Licari, J.J. and Bakhit, G. G., Patent number US 5002818 (1989).

[10] Afzali-Ardakani, A., Buchwalter, S., Gelorme, J., Kosbar, L., Newman, B. and Pompeo, F., Patent number US 5560934 (1996).
[11] Vigano, F. Consonni, S., Grosso, M. and Rigamonti, L., Waste Manag. 30,145-153 (2010).
[12] Maekle, R., Brusky, P., Cremeans, G., Elhard, J., Bigg,D. and Sowell, S., Patent number US 5470945 (1995).
[13] Patent number US 4744852 (1988).
[14] Patent number US 6746562 (2004).
[15] Aubert J.H., J Adhes 79, 609–616 (2003).
[16] Blaiszik, Kramer, Olugebefola, Moore, Sottos, S.R.White, Self-Healing Polymers and Composites, Annual Rev. Mater. Res. 2010.40:179-211 (2010)
[17] Yang, Ding, Urban, Chemical and physical aspects of self-healing materials , Progress in Polymer Science 49–50 (2015) 34–59
[18] Tang, Wan, Zhou, Pan, Huang, Strong and efficient self-healing adhesives based on dynamic quaternization cross-links, Journal of Materials Chemistry A, Issue 40 (2017)
[19] Leijonmarck, S., Cornell, A., Danielsson, C-O. and Lindbergh, G., J Electrochem Soc 158, 109-114 (2011).
[20] Sato, E., Iki, S., Yamanishi, K., Horibe, H. and Matsumoto, A., Ibid.
[21] Akiyama, H. and Yoshida, M., Adv Mater. 24, 2353-2356 (2012).
[22] Heinzmann
[23] Markle, R., Patent number US 5470945 (1995).
[24] Haydon D., Assem Autom. 22, 326–329 (2002).
[25] Leijonmarck, S., Cornell, A., Danielsson, C., Akermark, T. And Brandner,B.D., Int J Adhes Adhes. 32, 39-45 (2012).
[26] Patent number US 0070023382 (2007).
[27] Patent number US 0070023929 (2007).
[28] Patent number US 0070271686 (2007).
[29] https://www.nanowerk.com/products/product.php?id=5.
[30] Kolbe, J., Patent number US 20040249037 (2004).
[31] Cook, M., Patent number US 3938266 (1976).
[32] Becher, P., Patent number US 6764569B1 (2004).
[33] Obeidat , W.M., Recent Pat Drug Deliv Formul. 178–192 (2009).
[34] Nissan Motor Co., Patent number US 3993524 (1976).
[35] Henkel, Patent number DE 19961940 (2001).
[36] IBM, Patent number US 0014924 (2006).
[37] Minnicino, M. and Sands, J.M., US Army Research Laboratory 2011.
[38] Rescoll, INDAR inside.(https://rescoll.fr/la-technologie-indar-de-rescoll-sur-le-satellite-gaia__trashed/). (Accessed October 2017).
[39] Alcorta, J., Olive, M., Papon, E., JEC Compos Mag 40, 65-66 (2008).
[40] Alcorta, J., Patent number WO 2006/048585 A1 (2006).
[41] Foulc, M-P., Bergara, T. and Olive, M. Patent number US 20120258315A1 (2012).
[42] McCurdy, R.H., Hutchinson, A.R., Winfield, P.H., Int. J. Adhes. Adhes. 46, 100-113 (2013).
[43] Banea, M.D., da Silva, L.F.M., and Carbas, R.J.C., Int. J. Adhes. Adhes. 59,14-20 (2015).
[44] Lu, Y., Broughton J.G., and Winfield, P.H., Int. J. Adhes. Adhes. 66, 33- 40 (2016).
[45] Kawate, K. and Kanki, T., Patent number WO 0040648A1 (2000).
[46] Manfre, G. and Vitkala, J., 8th Int. conf. on architectural and automotive glass, Tampere, Finland (2003)
[47] Naini, F.B. and Gill, D.S., World J Orthod. 9, 78–82 (2008).
[48] Oztoprak, MO., Nalbantgi, lD., Erdem, AS., Tozlu, M. and Arun, T., Am J Orthod Dentofacial Orthop. 13, 195-200 (2010).
[49] Tsuruoka, T.Namura,Y and Shimizu, N.,Dent Mater J. 26, 78–83 (2007).
[50] Nishiyama. Y., Uto, N., Sato, C. and Sakurai, H., Int. J. Adhes. Adhes. 23, 377–382 (2003).
[51] Ishikawa, H., Seto, K., Shimotuma, S., Kishi, N. and Sato, C., Int. J. Adhes Adhes. 25, 193–199 (2005).

[52] Carter, S., Preparation and analysis of polypyrrole-coated TEM particles. (Classified report by De Bonding Ltd, 2008).
[53] Schmid, A., Sutton, L.R., Armes, S.P., Bain, P.S. and Manfre, G., J Soft Matter. 5, 407-412 (2009)
[54] Jose. A., Jacques, P., Patent number FR 2852965 (2003).
[55] Jonsson, M., Nyström, D., Nordin, O. and Malmström, E., Eur Polym J. 45, 2374–2382 (2009).
[56] Kishi, H., Imade, J., Inada, Y., Sato, C., Matsuda, S.A.M., ICCM16, Kyoto, Japan (2007).
[57] Kishi H., Inada, Y., Imade, J., Uesawa, K., Matsuda, S., Sato, C., J Adhes Soc Jpn. 42, 356–363 (2006).
[58] Sato, C et al., Ibid
[59] Pausan, N., Liu, Y., Lu, Y. and Hutchinson, A.R., Ibid.
[60] LCA guidelines, ISO 14040 (2006).
[61] C.A. Bakker , M.C. den Hollander, E. van Hinte, Y. Zijlstra (2014), Products That Last: product design for circular business models, Nov, TUdelft
[62] Boosting Circular Design for a Circular Economy, November 2015, A joint report by De Groene Zaak and Ethica
[63] Rodrigues, Winfield and Morrey, Mat Sc Forum (765), 766-770 (2013).