

Reversible cross-linking in composite binders - In-situ repair options and recyclability

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Abstract

Internal microscopic damage is ubiquitous in composites, whether this was caused or introduced during the manufacturing process (i.e. via thermal stresses), from machining (i.e. drilling holes for bolted joints), during component assembly or ultimately from in-service loading. Incorporating an in-situ repair solution that can be activated after each of these individual processes could have a significant impact on reducing composite component scrappage rates, post-manufacture and other repairs and increase the time-period for non-destructive testing (NDT) inspection. By utilizing specific self-healing chemistries (i.e. via epoxy-amine polymers containing Diels-Alder based thermo-reversible bonds and/or epoxy resin healing agents) that can achieve multiple repair/healing cycles, damage generated throughout a components life cycle can be repaired and service life extended as well as complete recycling of fibers and resins can be possible. Materials of optimized composition form densely crosslinked networks at room temperature while repeatedly regaining the ability to flow at elevated temperature. Mechanical testing of bulk epoxy and reinforced polymer composite films demonstrated that the thermo-reversible effect is strong enough to achieve repetitive full self-healing of a severely cracked and delaminated test specimens without significantly affecting the mechanics of the resin. The resin has been integrated in prepreg based test specimen and the self-healing efficiency remained around 40% with 5 subsequent healing cycles. The embedded self-healing agents are thermally activated post-damage to repair the internal structure, akin to the healing functionality in animals and plants. This approach represents a truly positive benefit to industry to aid in the optimization of composite manufacture, by reducing post-manufacture inspection time and material wastage costs, and also to maximize the longevity of composite components in service as well as to introduce a true recycling possibility by recovery of the binder material system and of the reinforcing fibers. Copyright © 2018 VBRI Press.

Keywords: Self-healing composites, retro-diels alder reaction, repair and recycling.

Introduction

The result of the combination of two or more different materials is called *composite*. First uses of composites go back to about 1500 B.C. when early Egyptians and Mesopotamians used a mixture of mud and straw to create strong and durable buildings. Straw provided also reinforcement to other ancient composite products like pottery and boats.

The modern era of composites began with the development of plastics and/or other artificial and synthetic constructive materials. In the early 1900s, synthetic polymers – plastics - such as condensates of phenol and formaldehyde (Bakelite), vinyl, polystyrol and polyester were developed. These new synthetic materials were an interesting alternative to single resins derived from nature.

However, these materials alone were not strong enough or much too brittle for some structural applications. Reinforcement was the solution to provide additional strength and rigidity.

With the introduction of the first glass fiber by Owens Corning in 1935 and the combination of these fiberglass with a polymer matrix or binder, incredibly strong structure that are also lightweight could be created. This was the birth of the Fiber Reinforced Polymers (FRP) material systems. The beginning of the use of lightweight constructions is especially connected with the development of aviation, with the application of synthetic or semi-synthetic polymer adhesives (such as the urea-formaldehyde 'Aerolite') to bond early wooden-framed aircraft e.g. structures of the de Havilland DH91 (1937) and DH98 (1940) as early composite materials. Following the proven performance of these synthetic polymer based adhesives, the first use of thermoset polymers in an aerospace structural composite was in one of the most iconic aircrafts ever produced, the Spitfire, a logical step "catalyzed" at the time by fear of aluminum shortages [1].

The main driver for the adoption of advanced structural composite materials in e.g. modern aerospace

applications is the impressive weight saving that may be achieved, without loss of specific strength.

Within the 30 - 40 years that thermoset composites have been used as construction material system, epoxy resins have come to dominate the market as a result of their design versatility, ease of cure with a large variety of initiators and curing agents, and modest cure temperatures. Owing to their relatively well-understood and familiar structure-property relationships, engineers are employing considerable efforts to design, build and test critical structures from these materials.

The main drawbacks of thermoset polymers are their inherent brittleness and poor impact properties, which limit their use as homo-polymers in engineering applications which is inherently an issue in the area of composite materials as well. Fatigue damage and especially impact damage often results in a large area of weakened material due to fiber-matrix delamination. Repair is often impossible or needs replacement of whole structural sections (**Fig. 1**).

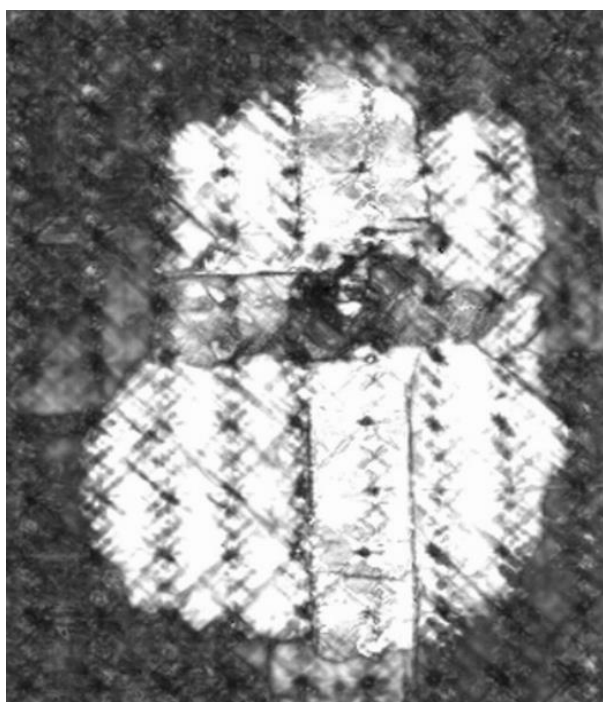


Fig. 1. Scanning acoustic microscopy of the damage dimensions after an impact in a Carbon fiber composite sheet showing large areas of delamination as consequence of the impact.

In general, internal microscopic damage is ubiquitous in composites, whether this occurred during the manufacturing process (i.e. via thermal stresses), by machining (i.e. drilling holes for bolted joints), during component assembly or ultimately from in-service loading.

On the other side repair is often very expensive in terms of time, labor and cost and in some cases difficult if impossible to realize since the damage is not directly visible and large areas need to be involved in the process. Additionally, and different to thermoplastics and metals, the repair patches need to adhere well to the basis and will add weight to the construction.

Also, recycling of thermoset composites is mainly and often restricted to either to mechanical recycling (milling), to thermal recycling meaning combustion with an energy recovery or pyrolysis for partial matrix recovery in terms of valuable low molecular weight building units (fuel, monomers) or as better alternative, chemical recycling by dissolution of matrix (only possible at limited systems). At present there are very limited commercial recycling operations for main stream composites due to technical and economic constraints, mainly the difficulty to liberate homogeneous particles hindered by the presence of both, the fibers and the matrix binders.

Reversible chemistry in binder systems

An incorporating of an in-situ repair solution that can be activated after each of the individual above mentioned and damage causing processes could have a significant impact on reducing composite component scrappage rates, post-manufacture and other repairs and increase the time-period for non-destructive testing (NDT) inspection and hence would be of high added value. For the instruction of self-healing, one can follow either of the two general strategies: 1. The introduction of external self-healing agents to be activated in case of mechanical damage [2] or 2. The built in of self-healing functionality by introduction of reversible bond in the resin and to be activated on demand externally e.g. be heat [3]. The first strategy has however severe drawbacks while applied in composites. Most of the self-healing agents display difficulties during the curing of the composites at high temperatures and capsules containing such agents are mostly in sizes comparable to the fiber diameters of the fabric. Consequently a homogeneous incorporation remains difficult.

So, following the second strategy may be more successful. **Fig. 2** shows a schematic presentation of the formation and function of such a system.

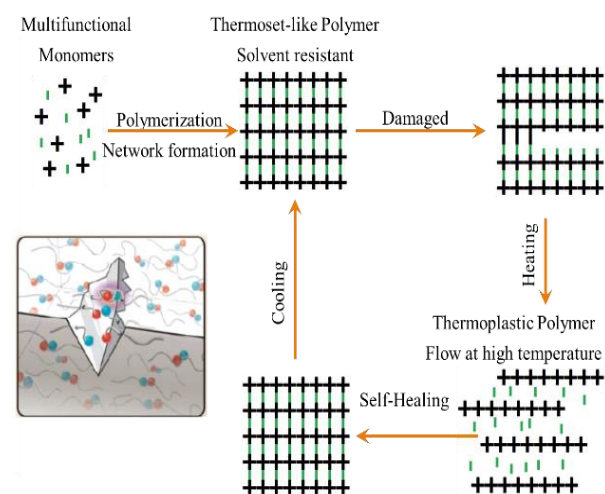


Fig. 2. Schematic overview of manufacturing and damage/healing processes. Between the monomers both permanent and thermo-reversible bounds are established. At high temperature the latter open and enable the system to flow thereby allowing cracks to heal and restore adhesion on sites of delamination.

Strongly **thermo-reversible** Diels-Alder reaction between furfuryl and maleimide group

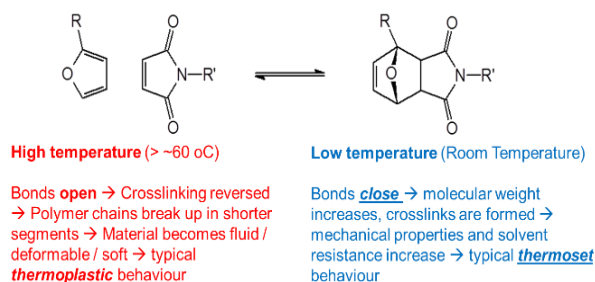


Fig. 3. Thermo-reversible Diels-Alder reaction as linkage bond resulting in case of a thermoset at higher temperatures in a low viscous material with thermoplastic behavior and at low temperatures in a highly cross-linked solvent resistant and mechanically strong thermoset.

Different systems are available for this purpose, based on reversible non-covalent interactions e.g. H-bonds as connecting elements resulting in softer systems or alternatively on reversible covalent bond linking units like remendable disulfide bridges or as mostly used reversible cross links based on the formation and splitting of a Diels-Alder linkage between furfuryl and maleimide units (**Fig. 3**) [3].

Such systems should be preferentially part or at least compatible with the currently existing and used rein binder systems.

Example: Thermoset epoxy amine systems with incorporated reversible covalent bonds

Thermoset epoxy amine systems are commonly used because of their excellent mechanical properties, compatibility with carbon fibers and chemical inertness. Once the composites are cured, however, there is not much that can be done about defects (micro-cracks and fiber-resin delamination).

Therefore, we developed a process that allows to combine Diels-Alder functional components with a conventional epoxy amine (**Fig. 4**) [4, 5].

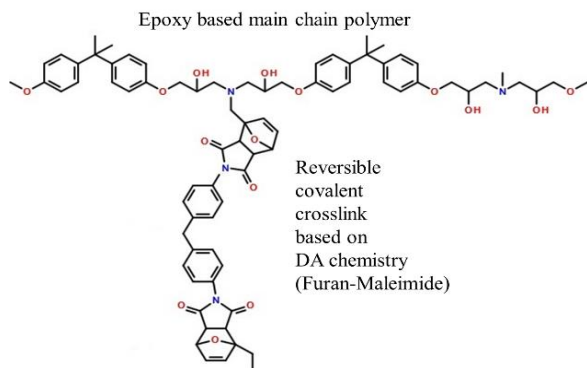


Fig. 4. Schematic overview of the manufactured composite binder resin based on epoxy amine polymers connected with thermo-reversible crosslinks based on furfuryl-maleimide Diels-Alder chemistry.

The synthetic route does not require complex equipment or process conditions and the starting materials are cost effective (no solvent or catalyst is needed), available on a large scale and commonly used

by the composite (aerospace) industry. A detailed description can be found in [5].

In brief, furfuryl amine has been reacted in a bulk reaction with diglycidyl ether of bisphenol A resulting in a polymeric yellow transparent glassy material. By choosing the ratio between the main epoxy building units, the size of the pre-polymer can be adjusted, which is of importance for the usability for the envisaged repair and recycling functionality. The chains should on the one side contain enough furfuryl groups for participation in a substantial cross-linking and on the other side they should be short enough to keep the viscosity of the system in the melt low enough to guarantee good flow and (re)wetting of the reinforcing fibers.

Subsequently, this pre-polymer was used without further purification for the synthesis of the self-healing Diels-Alder adduct (resin) via batch extrusion. For this 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BMI), the reversible crosslinker was added to the prepolymer powder, the crosslink densities can be tuned by variation of the ratios of both components. The obtained material displays an interesting mixture of properties some of which are typical for classical thermoset polymers, and some of which are typical for thermoplastics. The thermo-reversible nature of the Diels-Alder reaction allows the material to flow and self-repair at temperatures >120°C as is characterized using rheological studies. Self-healing of test specimens has been demonstrated. In analogy to epoxies, due to its rigidity, mechanics and thermoset behavior (high crosslink density proven by solvent resistance) the developed material could be used to construct fiber reinforced polymer (FRP) composites.

The obtained materials exhibit characteristics of both traditional thermoset epoxies having a high crosslink density as well as typical behavior of thermoplastics that soften and flow at elevated temperatures. The crosslink density, which is of importance for the chemical inertness and mechanical behavior of composites, was studied by solvent exposure tests. In a typical solvent test, non-crosslinked material dissolves, loosely cross-linked materials swells with solvent and densely cross-linked material remains inert. The un-crosslinked prepolymer was found to dissolve well in commonly used solvents although the required exposure time is different for each solvent.

Rheological measurements were executed to quantify the flow properties of the materials at elevated temperatures. The ability to flow, restore cracks and resin fiber delamination sites at elevated temperatures is of key importance to the self-healing effect and does not apply to conventional epoxy composites. In these experiments, a multiple healing was mimicked while subjecting systems with various BMI loading to five subsequent heat-cycles. In all measurements no significant hysteresis is found between heating and cooling curves, meaning that the reactions take place much faster than the heating / cooling rate of 2.5 K/min. The complex viscosity of the prepolymer without the presence of BMI gradually decreases over three orders

of magnitude when increasing the temperature from 60°C to 120°C (Fig. 5).

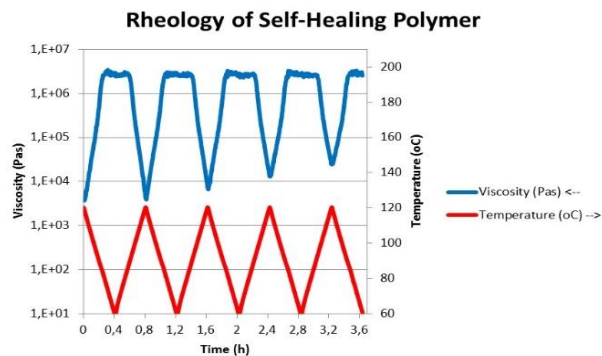


Fig. 5. Viscosity (left axis) with respect to a cyclic temperature profile (right axis) of glass fiber reinforced Diels-Alder functionalised epoxy composite after fabrication.

The flow properties of the crosslinked prepolymers are dramatically changed and two regimes can be discriminated within each heat cycle of the combined systems: the temperature independent plateaus at low temperature indicating the presence of a solid, and a liquid state at temperatures above the retro-Diels-Alder temperature (ca. 100°C) where viscosity scales inversely with temperature. The high temperature regime is dominated by the reverse Diels-Alder reaction. Reversible crosslinks are broken and the material behaves as a thermoplastic polymer melt in which free BMI is dissolved. BMI, having a rigid molecular structure and a high melting point (158°C), acts effectively as a thickener explaining the higher viscosity in the liquid state with respect to the curve of the prepolymer itself.

Comparing the subsequent heat cycles of the BMI prepolymer systems, some drift of the minima of the complex viscosity curves is observed, which is attributed to irreversible side-reactions and a consequently increased irreversible network formation. Although switchable behavior could well be identified for at least five subsequent heat cycles, irreversible side-reactions may eventually undermine the flow behavior. Additional crosslinking, may however also be of benefit to add some extra mechanical strength with each healing event.

The repair functionality / self-healing performance of the binder system was explored using a modified tapered double cantilever beam (TDCB) test specimen geometry. TDCB test specimens were tested at a displacement rate of 5 $\mu\text{m/s}$ until the inserted binder Diels-Alder polymer system film had fractured along the entire length (~30 mm) of the embedded film. Subsequently, test specimens were healed and retested for a further two healing cycles. A healing cycle of 150°C for 5 minutes was prescribed. Testing of a complete dataset (5 test specimens) resulted in average healing values (in terms of first failure load, $P \propto KIC$) of >100% for three repeated healing cycles, representing full recovery of mechanical performance. The first, second and third healing cycles resulted in healing efficiency percentages of 117 ± 23 , 123 ± 24 and 107 ± 15 , respectively.

For the manufacturing of composites, different strategies can be used. Either, long glass fibers can be added in a subsequent extrusion process to obtain directly a composite system. Alternatively, for composite film fabrication grains of the BMI crosslinked prepolymer are embedded within two woven glass fiber fabric sheets and heated in a hot press to 150 °C with a contact pressure of ~15 bar for 3 minutes (Fig. 6).



Fig. 6. Glass fiber reinforced Diels-Alder functionalised epoxy composite after fabrication.

The resulting composite sheet (similar as a prepreg) is optically transparent as demonstrated by the clarity of the text on the paper behind the sample, indicating that the surface of the fibers wets well with the polymer resin and that the viscosity of the resin becomes low enough to impregnate the fibers well thereby expelling air from the system. To further evaluate the repair/self-healing capability of such binder system for FRP composites, half of the sample artificially damaged by manual separating (delaminating) the material stack between the layers of glass fiber fabric. The damaged area is opaque due to the reflections from air-fiber and air-resin interfaces occurring at resin cracks and fiber-resin delamination sites. In the following, the damaged substrate was rotated 90° and inserted halfway into the hot press again (the other half sticking out of the press). Pressing at elevated temperature restores the fiber resin delamination and heals the cracks thereby fully regaining transparency of the sample. Three quarters of the sample (pristine, pristine-pressed, pristine-cleaved-pressed) have the same optical appearance and show a distinct contrast with the pristine-cleaved quarter, from which we conclude that self-healing can be established successfully without major side-effects (Fig. 7).

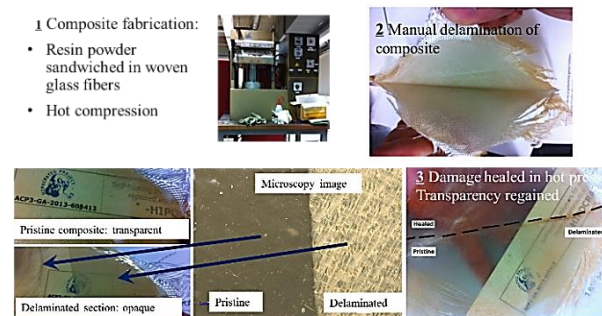


Fig. 7. Glass fiber reinforced Diels-Alder functionalized epoxy composite after fabrication (top left). Both woven glass fiber fabrics are pulled apart until halfway into the specimen (bottom left and microscopic image). Half of damaged area is healed using a hot press (right).

Herewith the ability of the reversible covalent cross-linked thermoset to repair large area delamination damage while enabling good re-flow of the resin and re-wetting of the fibers in the delaminated areas in the high temperature regime was demonstrated. This property is fundamentally different from an ordinary traditional thermoset and enables not only repair within the composite system but ensures also an intimate and homogenous integration of repair patches while re-forming a crosslinked network without the presence of interfaces between different separately cured layers.

There are different options to provide the heat for stimulation of the repair action. The generation of the heat can either be internally e. g. by eddy currents or currents applied to the system or by microwave activation, in this case possibly supported via the incorporation of active nanoparticle fillers. An external application of heat by heating blankets or by induction heating coils is also possible and may be more practical (Fig. 8).

Curing / Healing Strategies

METHOD	STIMULUS	HEATING
Induction heater	EXTERNAL	EXTERNAL
Current/eddy current	EXTERNAL	INTERNAL
Microwaves	EXTERNAL	INTERNAL
Oven	EXTERNAL	EXTERNAL
Electric Blanket	EXTERNAL	EXTERNAL

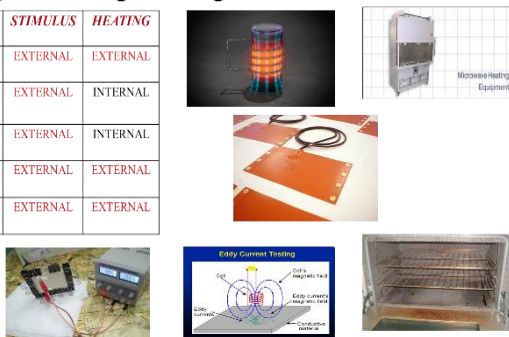
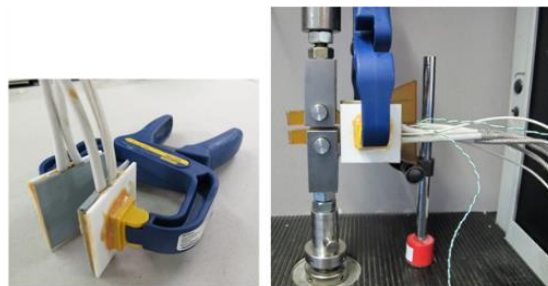


Fig. 8. Overview of Curing/Healing strategies for thermally stimulated repair of reversible covalent cross-linked composites

Although the relatively high healing temperature (ca. 150°C) may be an issue for commercial implementation, the short healing time (of 5 minutes) is certainly favorable in the scope of maintenance, repair and overhaul (MRO) systems and processes. It is envisioned that an externally mounted controlled heating pad configuration could provide the requirements for this self-healing system once incorporated into FRP composites.

Such installations can be easily realized for special areas of damage of composites, which appear frequently during manufacturing, machining and handling before the actual use of composite parts (Fig. 9).

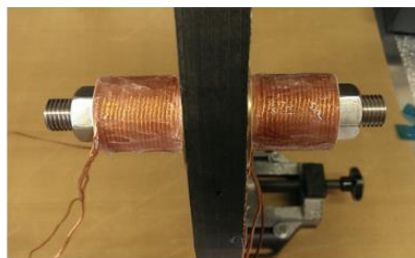
Recycling [6] and re-use of the components of such composites can be realized via the same process; heating of the system above the temperatures where the retro-Diels-Alder occurs results in a low viscous resin, which can be either directly or solvent assistant separated from the comparatively un-damaged reinforcing fibers and both may be re-used in closed cycles [7].



In-situ healing device via heating using ceramic heating elements with temperature control via K-type thermocouple attached to the specimen



The magnetic coil configuration, (a) pancake coil, (b) classic cylindrical Coilrack deflection



Induction coils fitted over a heating bolt for healing of damage on holes in composite panels

Fig. 9. Possible options and configurations for heat supply/activation technologies for reversible chemistry based thermoset composite systems.

Conclusions and further perspective

The introduction of reversible chemistry incorporated in polymeric materials and especially in binder systems as part of composite materials opens a whole new world of possibilities in terms of either repair on the one side and finally at the end-of-life of parts and constructions of complete recycling in close loops.

The principle chemistry has been demonstrated on an epoxy based system, which is possibly most familiar to the state-of-the-art composite industry. In the meantime a number of alternative systems based on the same principles were realized including polyesters, polyurethanes and acrylates also helping to overcome the difficulties in processing and recycling of thermoplastic binder composite systems [8, 9]. This includes even polymers based nearly completely on bio-based origin [10].

Acknowledgements

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