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Diels-Alder Chemistry to Develop Self-Healing Epoxy Resins and Composites Thereof

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Abstract

Self-healing polymers are a class of smart materials able to recover after sustaining damage. A family of thermosetting epoxy resins, containing Diels-Alder (DA) adducts in the epoxy precursor backbone, has been prepared and characterized. The DA adducts can be reversibly cleaved and reformed under the appropriate thermal conditions, and this feature has been exploited to produce intrinsically self-repairing materials. This chapter focuses on the effects of different structural features, such as average number of cross-linking functionality and molecular mobility of epoxy precursors, on the efficiency of healing process. High cross-linking density and molecular stiffness improve mechanical performances, such as elastic modulus and glass transition temperature, and allow fabrication of self-healing fiber-reinforced composites by conventional manufacturing technologies. Within this chapter, the molecular design, the preparation, and the evaluation of properties of self-healing epoxy and its composites have been discussed.

Keywords: thermo-reversible network, fracture toughness, self-healing, intrinsic healing, sustainable materials

1. Introduction

High-performance polymeric materials used in the automotive, aerospace, and space industries are progressively replacing metals as structural materials. However, their performances, such as mechanical properties, fatigue life, and esthetic features are usually deteriorated by severe in-service loads and/or environmental conditions. Therefore, the integration of recovery damage capability represents a major challenge for the next generation of technopolymers. [1]

Soon after the landmark work by White and Sottos [2] demonstrating the concept of self-healing features in a man-made material, the academic and industrial scientists recognized the ability of this new class of polymers to mitigate the effects of local damages in order to restore mechanical or functional properties and to postpone catastrophic failure of the whole structure. Two primary healing methodologies in polymers focus either on the incorporation of encapsulated healing agents in the polymer bulk or on the introduction of dynamic bonds in the macromolecular backbone. The former mechanism is referred to as extrinsic healing [2–4]: it is autonomic and is limited to a single, or to very few, healing events occurring in the same site. While the latter is referred to as intrinsic healing [5, 6]: it requires an external stimulus for its activation and can be applied multiple times on the same damaged spot. A thermal process is convenient and effective for treatment of polymers with a wide range of sample sizes and treatment durations. As a result, temperature-dependent reversible covalent cross-linking of polymers or block copolymers, such as DA-based materials, represents an effective method for the implementation of intrinsic self-healing into functional materials [5–8].

Self-healing thermosets potentially offer increased safety and durability of artifacts produced thereof, and remendable materials are particularly desirable for severe load-bearing applications in which repair and maintenance are costly and safety is concerned.

In addition, costs for material development and production would greatly benefit from the possibility to combine new self-healing materials with conventional resin and from the compatibility with current processing techniques. Nevertheless, the heterogeneity of people involved led to many strategies for improving the durability of existing materials or the synthesis of brand-new polymeric systems. [1] The layout of an efficient strategy to achieve healing efficiency and balance it with mechanical performances exhibited by this new class of materials is a complex task.

This chapter will describe the results we achieved in developing a self-healing epoxy system based on DA reaction. At first, design parameters of an epoxy adduct able to induce mendability will be discussed. Following, techniques to assess the healing capability of a polymeric material are described. Finally, the effort to fabricate composite structural material made by Diels-Alder (DA) thermoset will be discussed [8–10].

2. Molecular design for self-healing

Intrinsic healing mechanism relies on complex chemistry, and its development affords several combined advantages. Therefore, following recent interest of scientific community on this topic, development of chemical pathways leading to self-healing strategy will be discussed.

Several reversible bonds have been used to achieve self-mending functionality. Hydrogen bonds, Van der Waals forces, and electrostatic interactions in polymeric ionomers [11] are claimed to explain self-repair features in supramolecular structures, while covalent disulfide bridges [12], ester linkages [13], alkoxyamine moieties [14], and Diels-Alder bonds [15, 16] account for damage recovery in cross-linked structures. Among them, Diels-Alder chemistry has been widely adopted because of its simplicity, high efficiency, and repeatability through only the application of heat.

Diels-Alder chemistry was first described by Otto Diels and Kurt Alder in 1928 [17] and is particularly useful in synthetic organic chemistry as a reliable and clean method for introducing a six-membered DA adducts on a wide range of organic substrates which can be end-capped by reactive functional groups, such as epoxies, acrylates, amines, isocyanates, and hydroxyls. The DA reaction is a thermally reversible cycloaddition between a conjugated diene and a dienophile resulting in a cyclohexene derivative. The cross-linked DA adducts can undergo a cleavage reverse reaction at higher temperatures (rDA) [18, 19]. While several diene-dienophile couples are available for DA reaction, to date, the most investigated precursors are furan/maleimide derivatives. The bond energy of the new C-C σ bonds in DA adducts was evaluated to account to 96.2 kJ/mol [20], while other covalent bond energies are 348 kJ/mol for C-C bonding and 293 kJ/mol for C-N [21]. Since covalent bonds are three to four times stronger than C-C σ bonds formed in DA adducts, cracks are more likely to form and propagate between the new formed bonds in DA adducts. Consequently, available diene and dienophile on the freshly generated surface increase the efficiency of the self-healing method, through the DA recombination. Another notable implication, resulting for the diene-dienophile choice, is the temperature where the self-recovery can be achieved. The range for the rDA reaction of furan/maleimide derivatives is approximately at temperatures higher than 115–120°C, while at lower temperatures the DA recombination is favored.

When considering self-healing thermosets with the DA reaction, the local molecular mobility, displayed during mending cycles, is a key parameter affecting the healing efficiency. Fast and efficient damage recovery and DA bond recombination are achieved via a local and temporary increase of mobility occurring at temperatures higher than polymer glass transition temperature but lower than rDA cleavage temperature. In the case of DA adducts based on the furan/maleimide couple, the processing window can be identified between the polymer's T_g and rDA temperature.

Epoxy resins have been widely used due to their excellent heat resistance, outstanding corrosion protection, high electrical resistivity, and superior mechanical properties. However, cracks might occur as a result of thermal stress and mechanical fatigues during processing and service conditions. Many papers already described epoxy resins containing DA adducts in their backbone [22, 23].

Following a related concept, bifunctional epoxy precursors cross-linked with amines [24] will be described in the present work. The choice to locate the reversible DA bond on the epoxy or on the amine moieties results in structurally equivalent networks, as far as the self-healing phenomena are concerned. Nevertheless, the synthetic path to produce epoxy DA adducts is easier with respect to the preparation of DA amines, due to the added complexity of amine protection/deprotection. For the sake of simplicity, tetrafunctional amines were used as cross-linkers in the following, while the epoxy functionality was varied between two and four, to investigate about the effect of different cross-linking density.

Cross-linking density and conformational stiffness of molecular fragments between adjacent cross-links are the main parameters, which affect properties, such as T_g , mechanical stiffness, and overall molecular mobility. However, accurate experimental evaluation of cross-linking density is often difficult, especially for glassy and rigid polymers. Therefore, the use of an easily defined marker as a measure of cross-linking density is strongly envisaged. In this respect,

the average functionality of a mixture of monomers can be defined as the average number of functional groups per monomer molecule for all types of monomer molecules. It is defined by

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} \quad (1)$$

where N_i is the number of molecules of monomer i with functionality f_i and the summations are over all the monomers present in the system. As a rule of thumb, reactive mixture with f_{avg} strictly equal to 2 can lead to high molecular weight linear polymer and f_{avg} smaller than 2 results in low molar mass oligomers, while f_{avg} greater than 2 produces branched and cross-linked networks. In our specific case, for a system consisting of 2 mol of di-epoxy and 1 mol of tetrafunctional amine, f_{avg} is 2.67; for a system consisting of 1 mol of tetrafunctional epoxy and 1 mol of tetrafunctional amine, f_{avg} is 4.00. All the intermediate values are achievable by proper adjustment of the ratio between bifunctional versus tetrafunctional epoxy, stoichiometrically balanced by the amine.

In the case of conventional cross-linked networks, f_{avg} is invariant with respect to temperature, and the network cannot flow upon heating. If the network precursors include reversible bonds, such as DA, f_{avg} decreases at high temperatures, after triggering the rDA cleavage reaction. Referring to the bi- and tetrafunctional DA epoxy cross-linked with conventional tetrafunctional amine, the f_{avg} drops to 1.60 in the former case, while the value is 2.67 for the latter one. Obviously, a high cross-linking density hinders molecular mobility: a value of f_{avg} higher than 2 prevents the healing phenomenon, if the condition holds true also in the cleavage state at high temperature.

The ability to adjust the molecular mobility during the healing cycle at a desired preset value is an important molecular design tool, which is helpful in addressing specific application requirements. For example, if the thermosetting DA resin is intended for restoration of small impact damages or micro-delaminations, which are often encountered in the case of barely visible impact damages (BVID) of composite materials, a moderate molecular mobility is required. The sample has to retain its geometry and fiber placement, and long-range viscous flows are detrimental. This target can be achieved tailoring the cleaved state f_{avg} so as its value is close to 2. On the contrary, if thermal recycling of thermoset is sought after, a high extent of molecular mobility is required in the cleaved state to allow materials to flow. While in the first case the overall material properties closely resemble the conventional thermosets, in the latter case, a dynamic thermoplastic-like state is achieved during self-healing. The epoxy mixture formulation can be properly adjusted to suit one of the previous conditions to achieve bespoke molecular mobility, measured by f_{avg} . For this purpose, cross-linking density of the cleaved stage can be preset to different levels, corresponding to reduced molecular mobility, by mixing bifunctional Diels-Alder epoxy with conventional epoxy or mixing a bi- and a tetrafunctional Diels-Alder epoxy. The introduction of conventional epoxy brings the added benefits of overall reduced costs because of the use of a cheaper precursor, while the introduction of tetrafunctional Diels-Alder epoxy benefits the healing efficiency increasing the overall concentration of DA functional groups.

Further degree of freedom can be introduced in the molecular design if detailed precursor structure is considered. In fact, according to **Figure 1(a)**, a symmetrical Diels-Alder precursor, bearing a pair of cleavable dienophile groups, can be considered. But the same structural features can be achieved using a smaller molecule, as shown in **Figure 1(b)**. In the former case, the formation of an unbound dienophile allows higher molecular mobility, increasing therefore the healing efficiency.

The coexistence of a stable and a thermo-reversible polymeric network, required for the development of robust self-healing ability [8, 25], is depicted in **Figure 2**. The hybrid polymer architecture is guaranteed by irreversible cross-links of conventional epoxy (green oval) with tetrafunctional amines (green rectangle) and reversible covalent bonds between

Figure 1. Examples of Diels-Alder adducts: a) symmetric molecules, b) asymmetric molecules.

Figure 2. Hybrid network scheme.

furan derivative diene (red pincer) and bismaleimide derivative dienophile (yellow square) of a DA adduct.

The left-hand side of **Figure 2** is representative of the cross-linked structure which prevents viscous flows. At low temperatures, the material behaves like a thermoset. As the temperature is increased above the rDA threshold trigger, the cleavage of epoxy DA activates a higher molecular mobility. Small molecular fragments, depicted in the right-hand side schematic of **Figure 2** as result of retro Diels-Alder reaction, symbolize distinguishing mobile state and viscous flow of thermoplastic material. Therefore, the presence of thermo-reversible chemical bonds switches the material state between thermoset-like behavior at low temperature and thermoplastic-like flow at high temperature.

3. Chemical-physical assessment on self-healing features

The presence of mechanical, thermal, or electrochemical damages results in regions with reduced performances with respect to the surrounding materials and deteriorates the overall response of the component.

The evaluation of self-healing efficiency is a complex task, which is not extensively disciplined yet in test standards or experimental procedures. It can be performed at different dimensional scales, starting from visual inspection or optical microscopy (OM) observation, up to spectroscopic techniques based on molecular interaction, comprising mechanical and dynamical-mechanical characterization [26].

The self-healing mechanism of thermo-reversible epoxy resins relies on the direct and reverse cycloaddition Diels-Alder reaction, which could be monitored by FTIR through the investigation of the spectral band of the C-O-C peak around 1180 cm^{-1} [8, 27]. Similarly, stretching vibrations in Raman spectra of C=C at 1501 , 1575 , 1585 , and 1600 cm^{-1} bands, related to furan/maleimide-based DA adduct, could be used to monitor the progress of the reactions [28]. Due to the system complexity, only the signal at 1501 cm^{-1} , ascribable to C=C stretching vibration of the furan ring [28, 29], is a useful marker.

Since reversible epoxy thermosets exhibit properties of both highly cross-linked epoxy thermosets as well as typical behavior of thermoplastics that soften and flow at elevated temperatures, the study of thermomechanical behavior of self-healing DA system allows the identification of macroscopic behavior related to low-temperature highly cross-linked status or the high-temperature viscous thermoplastic-like condition.

Figure 3 depicts the healing and reshaping cycles of a composite coupon based on self-healing resin. Thermo-reversible bonds affect the molecular mobility [30]; therefore, the investigation of linear viscoelastic behavior is a suitable procedure to assess the self-healing feature of the material.

Rheological tests can be used to discriminate between the solid like behavior and the semi-viscous state of degenerated networks, by measuring storage and loss moduli as a function of temperature [8, 31, 32].

Figure 3. Schematic of the transition between thermoset state and thermoplastic state triggered by temperature.

On the other hand, rheological experiments can effectively complement the mechanical and dynamical-mechanical characterization. Thermo-reversible epoxy resins, similar to conventional ones, exhibit little elongation at break. This characteristic depends on the degree of cross-linking of the polymer chains, and then failure of such systems could be described in terms of linear fracture mechanics [6].

The experimental assessment of the fracture properties relies on the study of short-term monotonical loading.

The failures in polymeric materials are a result of chain scission and structural breakup. Self-healing recovery of damaged polymeric structure prevents or reduces the fracture propagation. When the applied load exceeds the critical fracture stress, the crack grows. If the healing cycles preserve the initial shape and dimensions, the healing efficiency, η , may be calculated as expressed in Eq. (2):

$$\eta = \frac{\sigma_{crit}^{healed}}{\sigma_{crit}^{virgin}} \approx \frac{K_{crit}^{healed}}{K_{crit}^{virgin}} \quad (2)$$

where σ_{crit}^{healed} is the stress required to propagate the crack to a given length in the healed material and where σ_{crit}^{virgin} is the stress required to propagate the crack to approximately the same length in the virgin one. Analogously, K_{crit}^{healed} and K_{crit}^{virgin} are the stress-intensity factors for the healed and the virgin materials, respectively.

However, while the efficiency defined in terms of the applied stress represents an actual measured quantity, the same quantity expressed in terms of the stress-intensity factor represents an estimate using a fracture model. The lack of control inherent in the fracture process precludes a direct comparison.

Generally, the efficiency of the healing process is evaluated by the experimental comparison between the performance of intact and healed material [2]:

$$\eta = \frac{P_{healed}}{P_{initial}} \cdot 100 \tag{3}$$

The subscripts refer to whether the property is measured after healing (*healed*) or before damage occurs (*initial*). In many cases, healing efficiency is defined in terms of the fracture toughness [33] or in terms of material strength [34, 35] or material stiffness [10, 12].

4. Self-healing Diels-Alder epoxy systems

Self-healing feature increases the durability of thermosets by reducing the service costs for high-end applications. Unfortunately, the use of smart polymeric materials raises the issue of a compromise between material performance and integration of self-healing properties. Rigid materials have specific properties, which should remain unchanged by the self-healing chemistry both during use and later to a healing treatment. Such surfaces are usually made of highly cross-linked thermoset polymers; the incorporation of self-healing functionalities into their formulations can be problematic and needs to be investigated.

4.1. Synthesis of epoxy Diels-Alder adducts

Based on the hierarchical criteria developed on Section 2, a family of epoxy precursors was prepared integrating Diels-Alder precursors 2Ph2Epo and 2Ph4Epo cross-linked with tetra-functional amines (Table 1).

The two precursors differ in number of epoxy groups, keeping central furan/maleimide DA adduct fixed. Structural formulae of epoxy precursors are shown in Table 1. The 2Ph2Epo is characterized by the presence of two oxirane rings and two Diels-Alder adducts. The introduction of two additional functional groups results in 2Ph4Epo.

Acronym	Molecular structure	Mw (gmol ⁻¹)
2Ph2Epo		666.68
2Ph4Epo		776.84

Table 1. Diels-Alder epoxy precursors.

To induce the self-healing capability, two identical dienes (furfural derivatives) were capped on a bismaleimide dienophiles, resulting in a symmetrical epoxy compound containing two Diels-Alder adducts. The synthesis of 2Ph2Epo has already been described by the authors in [24]. $^1\text{H-NMR}$ spectrum, recorded in d_6 -DMSO with Bruker Avance 400, points out the appearance of characteristic peak of DA adduct ($\delta \sim 5.5$), because two carbon atoms change from sp^2 to sp^3 hybridization (double peak slightly split for the formation of the two stereoisomers, endo and exo, with the former overwhelming the latter).

Analogously, the use of furan derivative with a pair of oxirane rings results in the preparation of 2Ph4Epo adduct. Also in this case, the $^1\text{H-NMR}$ spectrum confirmed the accuracy of structure reported in **Table 1**.

4.2. Cross-linked sample preparation

The Diels-Alder epoxies 2Ph2Epo and 2Ph4Epo and their mixture with DGEBA were cross-linked using stoichiometrically balanced DDM and Jeff500 as curing agents (**Figure 4**) at 90°C for 24 hours.

Suitable samples of self-healing epoxy resin have been developed by application of the criteria shown in Section 2. To vouch for a complete physical-chemical and technological compatibility with conventional epoxy system and production technology used in the field of epoxy resin and composites thereof, a mixture of commercial tetrafunctional amines was used as curing agent. The mixture of two different amines was used to finely tune the glass transition temperature of the self-healing resin in the range of 90°C and achieve full cure at temperatures below rDA reaction without incurring the temporary scission of epoxy precursor. The cross-linking density and f_{avg} during the healing process were controlled by the proper ratio between the functional DA epoxy and a commercial epoxy resin.

Composition of all samples is reported in **Table 2**.

Samples reported in **Table 2** were cured at 90°C for 24 hours. DSC confirmed the complete conversion of cross-linking reaction by the absence of residual reactivity.

4.3. Self-healing properties

As already discussed, the self-healing capability of small fractures and BVID is related to local molecular mobility, temporarily activated by temperature increase. The observation of superficial scratches and their recovery is a generally accepted technique for the assessment of self-healing features. For this task, a controlled mark has been produced by sharp scalpel

Figure 4. Molecular structures of DGEBA, DDM, and Jeff500.

Acronym	DA epoxy (mol)	DGEBA (mol)	DDM (mol)	Jeff500 (mol)
DGEBA100	—	1.00	0.30	0.20
2Ph2Epo100	1.00	—	0.30	0.20
2Ph2Epo65	0.65	0.35	0.30	0.20
2Ph4Epo100	1.00	—	0.60	0.40
DGEBA100	—	1.00	0.30	0.20

Table 2. Cross-linked sample composition.

and observed by optical microscopy (Olympus BX 51 M), applying suitable thermal stimulus by means of Linkam THM600 hot stage.

As expected, microscopy observation performed on cross-linked DGEBA resin cured with a mixture of 60/40 mol/mol of DDM and Jeff500 amines (DGEBA100, $T_g = 90^{\circ}\text{C}$) evidenced the lack of scratch recovery even at 140°C (Figure 5), well above sample T_g .

Only a minor modification of scratch width can be detected as a result of stress relaxation at temperature higher than resin T_g . Nevertheless, self-healing is hindered by cross-links.

On the other hand, thermal treatment at 120°C for 5 min completely restored the damaged surface of 2Ph2Epo100 sample, as depicted in Figure 6. Unfortunately, the high molecular mobility achieved in the activated stage produced sample deformation and viscous flow. In fact, due to the high concentration of reversible bonds, the cross-linking density in the cleaved stage dropped, and materials transformed into viscous thermoplastic.

The occurrence of this phenomenon is not desirable if self-healing materials have to be used for structural application and the molecular mobility has to be reduced, either by introducing a thermally stable epoxy precursor such as DGEBA or by using a tetrafunctional DA precursor.

In the first case, the 2Ph2Epo65 system, containing 65% of DA epoxy and 35% of DGEBA (Table 2), was prepared, with T_g of 90°C . Self-healing capability of 2Ph2Epo65 was confirmed even after reduction of thermo-reversible bond concentration. The increased network stability preserved the sample shape and dimension still allowing self-healing phenomenon, as

Figure 5. Scratch recovery for DGEBA100, $10\times$ magnification. From left to right: at room temperature, at 140°C , after additional annealing for 20 min at 140°C .

Figure 6. Scratch recovery for 2Ph2Epo100, 10 × magnification. From left to right: at room temperature, at 120°C, after additional annealing for 5 min at 120°C.

reported in **Figure 7**. The scratch completely disappeared after 30 min at 120°C, restoring the pristine surface.

The second approach to prevent viscous flow of materials during the high-temperature stage is to use Diels-Alder epoxy adduct with functionality higher than 2. The presence of four reacting epoxy groups for each precursor molecule (2Ph4Epo) increases the cross-linking density. 2Ph4Epo100 was prepared according to **Table 2** and fully cured at 90°C for 24 hours, reaching a T_g of 95°C. The occurrence of rDA reaction reduces the cross-linking density at high temperature. But the f_{avg} calculated in the cleaved state for tetrafunctional DA epoxy is 2.67 and suggests hindered molecular mobility, as already discussed in Paragraph 2. As a consequence, morphological damages were not recovered for 2Ph4Epo100 (**Figure 8**).

Figure 7. Scratch recovery for 2Ph2Epo65, 10 × magnification. From left to right: at room temperature, at 120°C, after additional annealing for 30 min at 120°C.

Figure 8. Scratch recovery for DGEBA2Ph4Epo100, 10 × magnification. From left to right: at room temperature, at 120°C, after additional annealing for 20 min at 120°C.

Upon sample breakage, Diels-Alder bonds are preferentially cleaved because they are weaker than other covalent bonds building up the cross-linked network. Therefore, the occurrence of mechanical damage makes diene and dienophile groups available for self-healing on the fracture surface. But molecular backbone in the close proximity of damage remains unaffected, and the overall material stiffness prevents an efficient fracture healing. For this reason, further thermal treatment at 120°C is applied to complete cleavage of DA bonds and to maximize molecular mobility. Physical healing, due to diffusion of molecular fragments in the activated stage, allows the fracture edges recombination. After the first step, a further annealing at 90°C is required to restore the pristine cross-linking density and mechanical properties by direct Diels-Alder reaction.

The proposed healing mechanism is validated by analysis of micro-mechanical tests, performed by Micro Materials NanoTest™ Platform. 2Ph2Epo65 properties have been evaluated and compared between the pristine as prepared and after incremental treatments, including morphological healing and structural annealing.

The reduced elastic modulus, E_r , was calculated based on Eq. (4), taking into account the effect of nonrigid indenter column:

$$E_r = \frac{\sqrt{\pi} S}{2 \beta \sqrt{A}} = \left[\frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu_s^2)}{E_s} \right]^{-1} \tag{4}$$

where A is the contact area, β the geometric constant (1.034 for a Berkovich indenter), and S the unloading stiffness at maximum load. E and ν are the elastic modulus and the Poisson ratio; and the subscripts “i” and “s” refer to the diamond indenter and the specimen, respectively. The E_i is 1140 GPa, the ν_i is 0.07, and the ν_s is 0.35.

All data were corrected for thermal drift and instrument compliance and subsequently analyzed with the Oliver and Pharr method [36]. According to Zheng [37], elastic modulus measured by depth indentation technique overrates the elastic modulus by a factor of 5–20%. Reduced modulus is reported in **Table 3**. After heating at 120°C, required to promote the morphological recombination of scratch edges, the modulus drops down by a factor of 2. In fact, the occurrence of rDA reaction induces the cleavage of specific covalent bonds and reduces the cross-linking density. However, the effect is not permanent. The pristine properties can be recovered by prolonged annealing at 90°C, when DA reaction can lead to network restoration.

Specimen type	Reduced modulus, E_r (GPa)
As prepared	4.80 ± 0.03
Morphological healing: 20' @ 120°C	2.54 ± 0.05
Structural healing: 20' @ 120°C + 12h @ 90°C	4.56 ± 0.05

Table 3. Reduced modulus (GPa) of self-healing 2Ph2Epo65 epoxy resin.

5. Crack healing in long fiber composites

The self-healing epoxy 2Ph2Epo65 has been considered for manufacturing a composite plate with the aim to investigate the fracture behavior and to assess the healing efficiency of the system. Interlaminar behavior of the CFRP (composite fiber-reinforced plastic) has been studied by means of shear strength of the laminate.

Shear tests can be conducted on composite laminates following different experimental approaches, depending on the mode of fracture that needs to be assessed. The ability to recover damages after a cohesive failure has been investigated by interlaminar shear strength (ILSS), and mode II fracture loading has been studied by performing the End Notch Failure (ENF).

A composite plate has been manufactured by liquid molding process under vacuum bag; 12 unidirectional layers were laminated to reach a nominal thickness of 3 mm. The presence of a Kapton layer in a bending test (in the case of ENF tests) leads to the mutual sliding of separated parts promoting a mode II failure (shear mode) [38], according to ASTM D7905.

Load versus displacement curves during ENF tests is reported in **Figure 9** and show an initial linear behaviour up to the critical load (nonlinearity load, NL). Above this point, delaminations start and steadily propagate until the maximum load is achieved. Afterwards, unstable delamination growth leads to load decrease.

The first healing treatment allowed to recover the pristine stiffness, with a sample strength decrease. However, during the third load cycle (i.e., after the second healing), a significant stiffness loss is experienced. Different behaviors between neat polymer and laminate should

Figure 9. End Notched Failure test.

Cycle	ILSS (MPa)	η (%)	G_{IIc} (J/m ²)	η (%)
0	54.1 ± 1.1	100	650 ± 20	100
1	51.4 ± 5.1	95.1	583 ± 13	89.7
2	44.2 ± 4.9	81.7	341 ± 32	52.4

Table 4. Strength recovery after failures.

be related to specific composite features. Delaminations could occur both as effect of a matrix failure and as interface debonding. Moreover, any damage incurring to the reinforcing fibers would reduce material stiffness without chance of recovery.

The critical strain energy release rate should be evaluated as function of the NL load:

$$G_{IIc} = \frac{3 m P^2 a^2}{2 B} \tag{5}$$

Fracture toughness was determined using Eq. (5), where m is the calibration compliance, P is the critical load, a is the critical length, and B is the specimen width.

Table 4 reports the recovery efficiencies measured as interlaminar critical strength and as critical energy for mode II delaminations. Fracture toughness showed a less effective recovery ability of 52.4% compared to static interlaminar strength recovery of 81.7%.

6. Conclusions

The development of self-healing materials is a very attractive approach to provide long-lasting and efficient protection against micro damages. Great attention from numerous research groups has been paid to polymers, composites, and coatings, which exhibit self-healing behavior at different dimensional scales. Through the chapter, the overall design flow for achieving hybrid epoxy systems containing covalent thermo-reversible bonds and the preparation and evaluation of selected examples were detailed. This paper underlines that the concurring presence of thermo-reversible covalent bonds and high molecular mobility are essential requirements to develop self-healing systems. The most effective structural modification has been pursued by adjustment of the several features: average functionality of reacting precursor mixture and cross-linking density and thermosetting network and concentration of self-healing reversible bonds. Also, the requirements of easy and efficient self-healing were compromised with development of material properties compliant with structural and semi-structural applications.

In particular, possibility to tailor the properties of “dynamic” epoxy resins containing Diels-Alder bonds would allow the development of novel materials, such as reengineered FRP combining the ease of processability typical of thermosets with reworking/recycling capability at the end of life typical of thermoplastics, as an effort to improve environmental sustainability of advanced materials.

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Conflict of interest

The authors declare no conflict.

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