INTERLAMINAR FRACTURE OF COMPOSITES MADE BY THERMO-REVERSIBLE EPOXY

A. Martone, S. Dello Iacono, M. Zarrelli, M. Giordano and E. Amendola

CNR-IPCB Institute for Polymers Composites and Biomaterial, National Research Council
P.le E Fermi 1 80055 Portici (NA), Italy
Email: alfonso.martone@cnr.it, Web Page: http://www.ipcb.cnr.it

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Abstract
Composite materials are ideal candidates for structural applications due to high specific stiffness and strength and their excellent fatigue resistance. However, there are still concerns regarding their fracture toughness performance. In this paper, an epoxy based system has been synthetized containing D-A adducts. The recovery capability has been proved by morphological study on damaged samples. Mechanical tests performed on virgin and self-healed system revealed the ability to recover efficiently the pristine stiffness, triggering from ductile to fragile the failure of the epoxy matrix. The synthesised system (2Ph2Epo65 D-A epoxy) lead to the fabrication of carbon fiber reinforced polymer that exhibits repeatable healing. Furthermore the self-healing polymer was processed through typical commercial resin infusion processes thus allowing them to be applied in the manufacture of composites with both shape and strength recovery.

1. Introduction

Composite materials are ideal candidates for structural applications due to high specific stiffness and strength and their excellent fatigue resistance. However, there are still concerns regarding their fracture toughness performance. Integration of self-healing features within the hosting matrix would lead to a new vision in damage tolerant design and in the maintenance strategies of composite structures during operative life.
Healing feature should be pursued by different strategies such as the release of an healing agent or reversible cross-links [1]-[2]. Several concepts have been developed to induce healing property into the matrix material, a well establish approach provide distributed, nanosized, reservoirs (i.e. capsules or a vascular system) which release the healing agent when the material is damaged [3]-[4]. Drawbacks of such approach are that irreversible systems can heal only once and that the presence of weak point within the material should negatively affects the manufacturing processes and the structural performances. Therefore, reversible systems able to break and heal repeatedly are becoming extremely appealing. Reversible cross-links firstly introduced to improve processability and recyclability showed also self healing capability [5]. Stimuli responsive polymers should recover their pristine status after destructive events, thanks to the interaction of chemical functionalities with various forms of energy such as thermal, electrical, pressure, mechanical.
Reversible systems based on covalent interactions, such as Diels–Alder (DA) and retro Diels–Alder (rDA) processes are ideal for the synthesis of crosslinkable epoxy precursors amenable to self-mending through thermal stimulus [6]–[9].
Most representative damage scenarios for composite materials is delamination in which the bonding between plies is compromised; this leads to an abrupt decrease in properties[10], [11]. The chance to mend interlaminar failure is of great interest, short beam tests has been considered by many authors as representative of the interlaminar strength of the composite, therefore the healing feature of the matrix

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have been evaluated by the recovery of this property[12]–[14]. Polyurethane hosting matrices modified by D-A adducts showed recovery between 70-85 % after many failure and healing cycles.
In this work, an epoxy mendable system has been synthesised to achieve mechanical performances suitable for structural applications. The coexistence of a stable polymeric network and a thermo-reversible one allows coupling the stiffness required for structural applications and the mendability properties. Due to complete compatibility and miscibility of D-A adduct previously developed by authors [15] with DGEBA, both contributions to the network are simultaneously present in the homogeneous resin. Self-healing epoxy synthesised has been considered for manufacturing a composite plate with the aim of 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 short beam strength features of the laminate, the composite verified the capability to recover its interlaminar strength in further tests after healing stages.

2. Experimental section

2.1. D-A epoxy synthesis

In this work, D-A adduct (2Ph2Epo) has been synthesised and added to dgeba. the mixture has been subsequently cured using 4,4′-diaminodiphenylmethane (DDM) and o,o′-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeff 500) as curing agents.

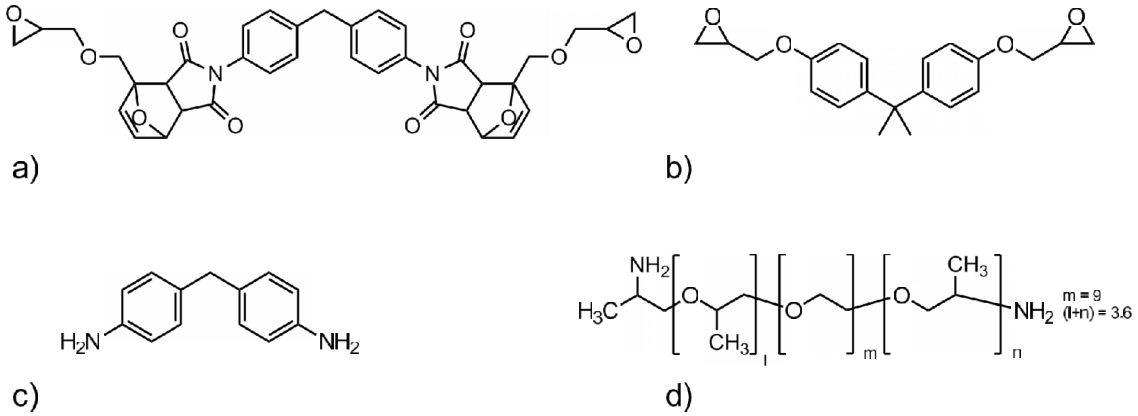

Figura 1. Resin components: a) 2Ph2Epo, b) DGEBA, c) DDM, d) Jeff 500

An epoxy system, 2Ph2Epo65, was prepared blending the adduct 2Ph2Epo with DGEBA in the epoxy stoichiometric ratio 65/35, and curing, at 90°C for 24 hours, using DDM and Jeff 500 as curing agents in the 60/40 amine stoichiometric ratio.

2.3. Characterization methods

Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer FTIR Frontier spectrometer using a single reflection ATR accessory.
Mechanical tests on the D-A epoxy were performed with a TA Instruments DMA Q800 equipped with three point bending clamp, nominal sample size is 20 x 5.0 x 0.90 mm3 and span is 15 mm.
The healing capability of the composite samples was preliminary evaluated by short beam shear strength, according to ASTM D2344. According to the standard for plate with nominal thickness of 3.5 mm the SBS (Short Beam Strenght) specimens has got a width of 7.0 mm and a length of 21.0 mm. At least 5 samples were initially tested at room temperature at the rate of 1 mm/min. This process was performed three times more on each specimen to obtain first, second and third healing cycle efficiencies. After each test optical microscopy was carried out with the aim of evaluate the effective delamination extension. Optical microscopy was performed by Olympus BX 51M, equipped with

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Linkam THM600 hot stage. Mechanical tests were performed on a Lonos TensoTest equipped with 5kN load cell and three point bending fixture with tunable nose size and distances.

3. Results and Discussion

3.1. Mendabilty of the epoxy system

Covalent bonds are exposed to intense stress during mechanical loading, which eventually results in mechanical failure. Diels-Alder covalent bonds are weaker than other bonds in the polymer backbone, so that when loaded excessively they may break preferentially.

Regarding the healing procedure, after testing, the composite specimens were placed in an oven under a compaction pressure (less than 2 bar). The specimens were heated up to 120°C for 20 minutes and then cooled at kept at 90°C for 24 hours. The temperature profile was determinated in order to allow the reverse D-A and direct D-A reactions to proceed. Specific experimental conditions have been confirmed by FT-IR analysis [16]. Rationale for the healing temperature profile is to heat the samples above the cleaving point in order to break the crosslinked DA molecules to enhance the healing ability due to the presence of additional D-A reactions. Heating the sample above the rD-A threshold opens the Diels-Alder bonds resulting in high molecular mobility. This step is beneficial in promoting fracture rejoining and allowing molecular diffusion across the fracture rims. Thereafter, the last annealing at temperature corresponding to D-A reaction allows to regain the pristine mechanical properties due to restoration of network crosslinking density.

Figure 2 reports FTIR spectra of 2Ph2Epo65 crosslinked resin, in the healed or broken configuration as a consequence of different thermal treatments. As an invariant reference, the peak at 1700 cm^{-1} associated to C=O stretching of imide was chosen.

The IR absorbance signals at 688, 832 and 1146 cm^{-1} were selected to monitor the progress of D-A and rD-A reactions. The peak at 688 cm^{-1} is related to C=C stretching vibration in the maleimide ring, while the peak at 832 cm^{-1} is related to the asymmetric C–N–C stretch in 1,1'methylene di-4,1-phenylene-bismaleimmide and C–O–C stretch in furan ring, the peak at 1146 cm^{-1} is associated to C-H bond attached to C=C.

The FTIR spectra were recorded on the cross-linked epoxy system after three different thermal treatments:

(a) after heating at 120°C and cooling to 90°C at 0.1 °C/min rate, (b) after heating at 120°C for 20 minutes and quenching to room temperature, (c) as prepared sample.

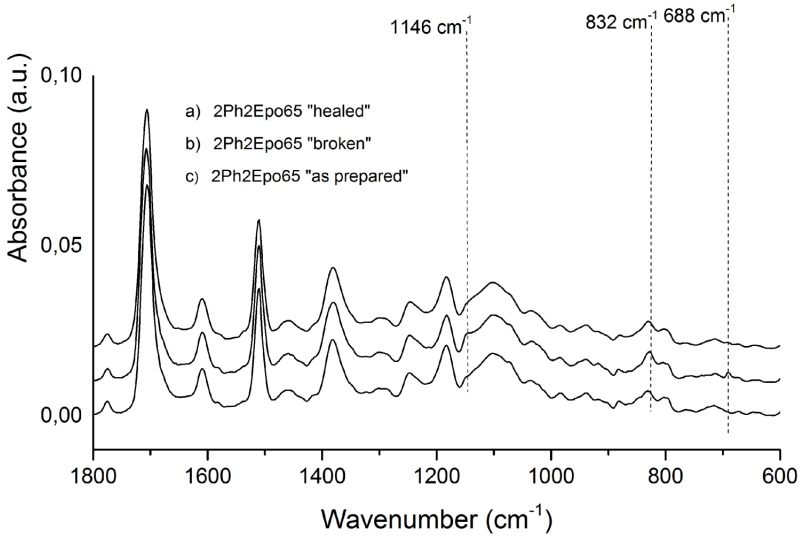

Figura 2. FTIR spectra

The most accurate information can be gained observing the trend of 688 cm^{-1} peak. It can be found in the b) sample, after thermal treatment at 120°C. Its absence can be verified in the pristine

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crosslinked resin (c), and it disappears again after healing cycle (a). A similar trend can be identified for the 1146 cm^{-1} band, although its observation is hindered by the presence of other complex spectrum features. The band at 832 cm^{-1} cannot be used for the characterization of D-A reaction extent in the crosslinked sample.
After the treatment at 120°C, promoting the rD-A reaction, the intensities of these three absorption peaks increased due to D-A adduct rupture, as can be observed from figure 2. A further annealing at 90°C following the heat treatment at 120°C, strongly reduced the aforementioned peaks, resulting in a FTIR spectrum similar to the "as prepared" sample. This is a strong evidence that annealing at reduced temperature (90°C) promoted again the formation of D-A adduct, depleting the maleimide and furan groups during the D-A reaction.

Quasi-static mechanical tests were carried out on specimens in order to evaluate the mechanical performances of the hybrid system. Figure 3 reports stress strain curve for 2Ph2Epo65 system. The broken samples were thermally treated at 120 and 90°C in order to restore mechanical properties and improve the healing fracture surface were brought closer together by polyamide adhesive film. Multiple healing was studied by repeating the test three times.
The virgin sample experienced elastic behaviour until 2% strain after that a plastic deformation occurred until the sample breaked at 3.5%. Healed sample exhibited the same stiffness (slope of the stress-strain curve) while them had a fragile fracture in the elastic region. The first healing led to a final strain of 1.8%, the second thermal treatment lead to 0.7 % strain at break. Since the sample were able to recover all their original stiffness, probably further thermal treatment could affect the DGEBA network, modifying the failure mechanism of the sample.

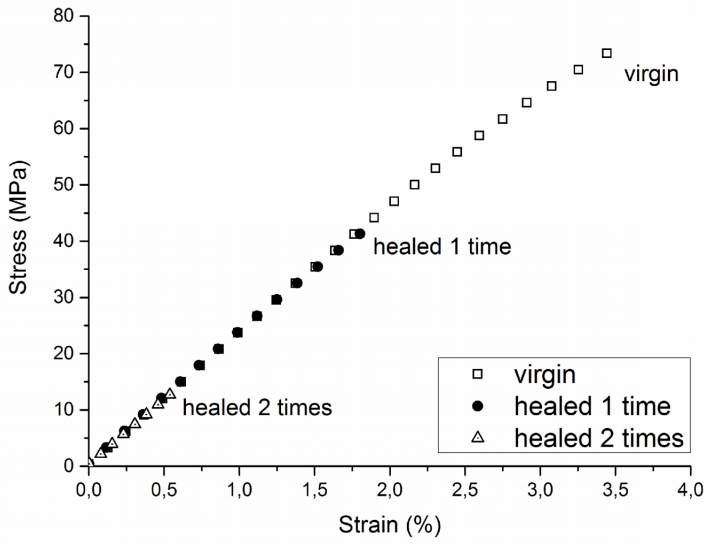

Figure 3. Three point bending on as prepared and healed samples

The healing treatment allows a complete recover of mechanical stiffness (mean value 2.750 GPa) while the failure at break decreases.

3.2. Non conventional composites enabling the healing capability

A Composite plate has been manufactured by liquid moulding process under vacuum bag, a total of 12 unidirectional plies were laminated to reach a nominal thickness of 4 mm final coupon size is 170 x170 mm^2. Composite healing efficiencies were determined by conducting short beam shear (SBS) testing on unidirectional samples. Each sample after the test was treated according to the healing cycle previously described and then tested again.
Figure 4 and 5 show micrographs carried out on broken sample and after the healing treatment. Figure 4 reports the behaviour of a sample which failed as result of a delamination during the test (picture 4a), such failure mode involves only the matrix of the composite as results of a slippage load between

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layers and could be completely restored by the thermal treatment. Pictures 4c and 4d report micrographs taken after the further testing and related healing stage.

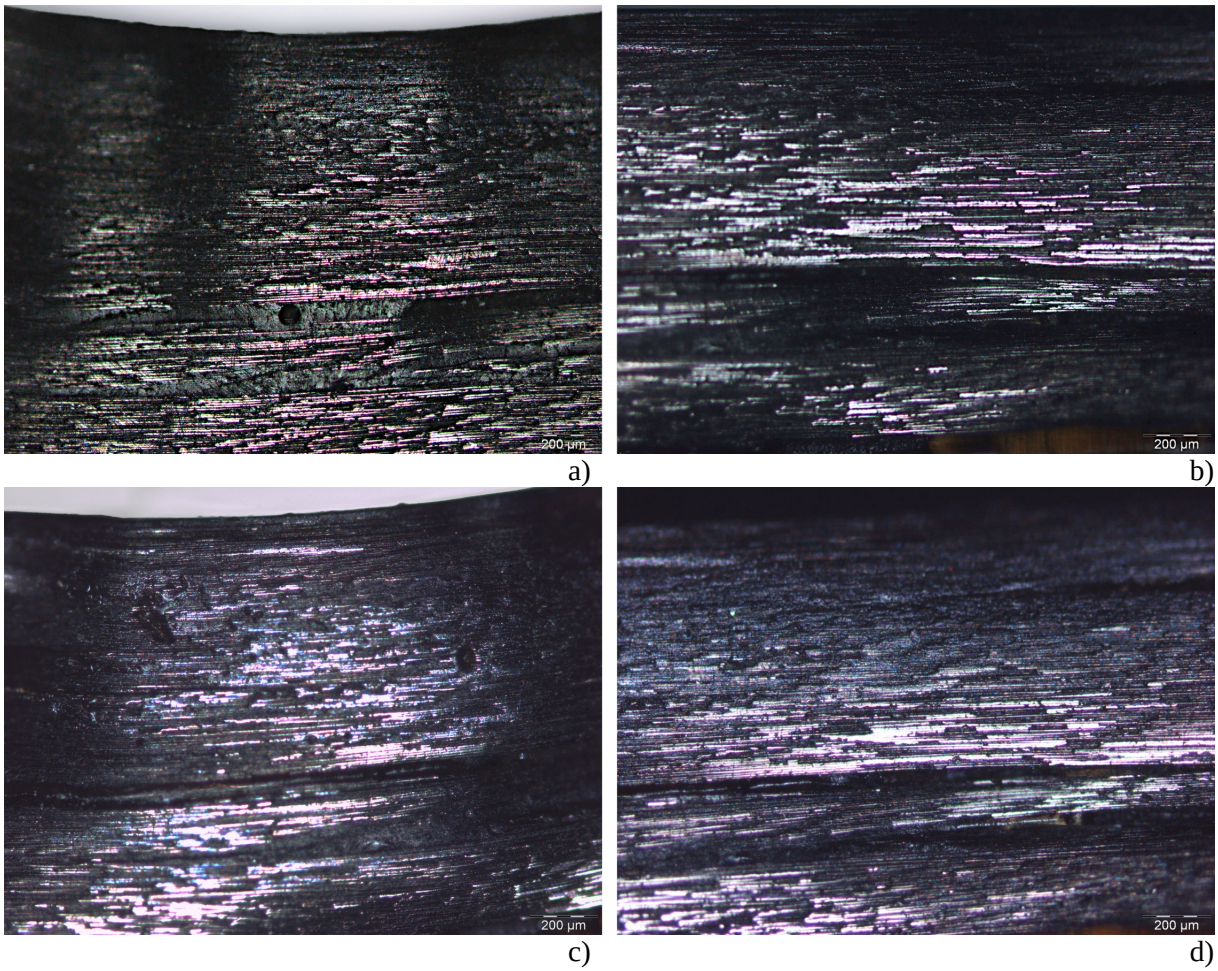

Figure 4. Optical micrographs on a delaminated sample.

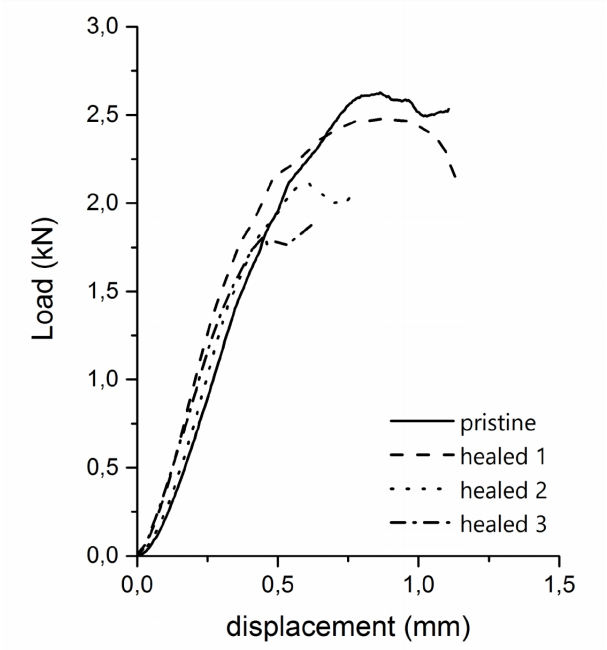

Figure 5. Short Beam test on composite sample

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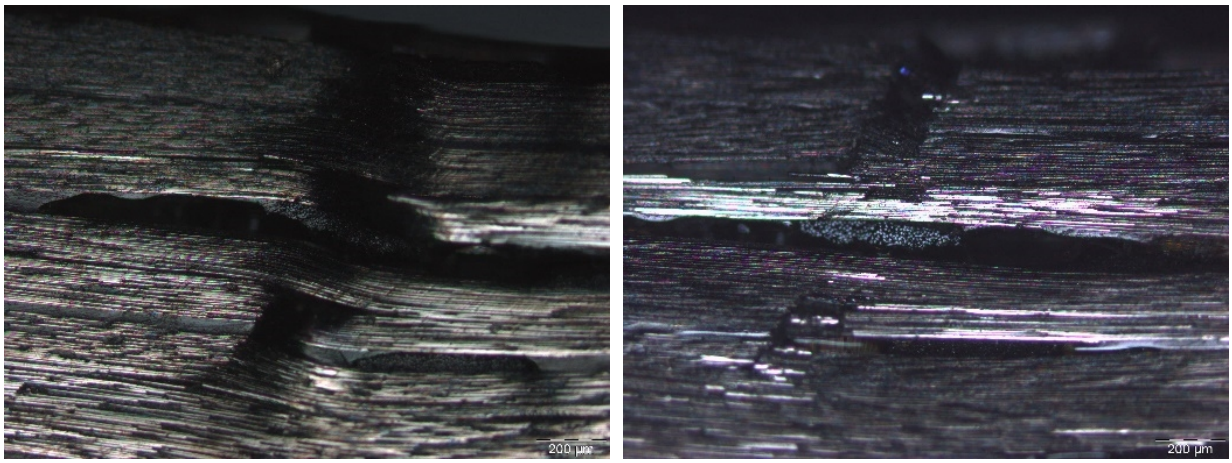
Figure 5 reports typical load displacement curve for short beam test. The composite reproduced the behavior observed on the neat D-A epoxy system. The sample stiffness was restored during each healing cycle, while a depression in the maximum load (strength) achieved at the specimen failure was observed during mechanical tests.



a) b)

Figure 6. Optical micrographs on a delaminated sample with fibre breakage.

Some of samples experienced failure involving fiber breaks; figure 6 shows the case of a combined scenario with delamination and fibers breakage in the compression area. In the latter case, after the healing stage samples exhibited a reduced stiffness up to the failure, which affects the actual shear strength. Obviously, such strong depression is related to fibre failure, which could not be recovered by the system. Table 1 reports the interlaminar shear strength measured on the composite sample. It is worth to notice that the increased standard deviation is affected by the fibre break observed in some sample.

The experimental comparison between the loading capacity of intact and healed material indicated healing efficiency. In this perspective, the polymer healing evaluation methodology has originated from fracture models and classical mechanics. In the present work, the ability of sample to recover the initial interlaminar strength (equation 1) is considered as recovery parameter.

$$\text{¦}(\%) = \frac{ILSS^{healed}}{ILSS^{pristine}} \cdot 100 \quad (1)$$

Differences between polymers and composite healing should be related to specific behavior of composite. In fact, delaminations could occur both as effect of a matrix failure, both as interface debonding.

Cracks created between the polymers were healed by the D-A reaction since the healing properties are only associated with the polymer matrix moieties. In addition, fracture of the reinforcing fiber cannot be healed and thus any damage to the carbon fiber would lead to reduced strength upon reloading.

Table 1. Interlaminar shear strength evolution.

Healing Cycle	*ILSS (MPa)*	*Recovery* (%)
0	54.1±1.1	100
1	51.4±5.1	95.1
2	44.2±4.9	81.7
3	37.0±5.2	68.4

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4. Conclusions

In this work, a hybrid epoxy system integrating thermo-reversible D-A adducts have been employed to manufacture advanced composites by conventional liquid moulding techniques. Fracture behaviour of coupons made by such system has been studied across multiple healing treatments in order to assess the effectiveness of the material recovery. The synthesised system (2Ph2Epo65 D-A epoxy) lead to the fabrication of carbon fiber reinforced polymer that exhibits repeatable healing. Furthermore the self-healing polymer was processed through typical commercial resin infusion processes thus allowing them to be applied in the manufacture of composites with both shape and strength recovery.

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