IMPACT AND CAI TESTS ON DOPED CARBON FIBER REINFORCED PLASTICS WITH BIS-MALEIMIDE BASED POLYMERS. THERMAL CHARACTERIZATION AND HEALING EFFICIENCY VALUE

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Abstract
Bis-maleimide (BMI) polymers exhibit healing functionalities on polymer level. Two unidirectional (UD) pre-pregs containing self-healing materials BMI polymers, based on Diels-Alder (DA) reaction were symmetrically and successfully incorporated into quasi isotropic carbon fibre-reinforced polymers (CFRPs). The assessment of potential knock down effects and the healing capability of the modified samples were investigated under low velocity impact and compression after impact (CAI) tests. According to C-scan inspections, it was shown that the BMI-modified samples exhibited higher damaged area compared to the reference one samples without BMI material. Additionally C-scan inspections showed that after the healing cycle the modified samples were entirely healed as the damage disappeared. After the healing cycle damaged and healed samples were tested under CAI tests and the healing efficiency (HE) value was calculated to be approximately 120% and 110% for the compressive modulus (E_{comp}) and the maximum compressive stress value (σ_{max}) respectively. Thermal conductivity experiments were also conducted for both the reference and modified samples in which was shown that the modified samples exhibited a decrease at the level of 17%. Finally optical microscopy examination of the cross-sections and acoustic emission activity of the samples was monitored and led to qualitative conclusions regarding the involved failure and healing mechanisms.

1. Introduction

Last decades the use of carbon fibre reinforced polymers (CFRPs) has been rapidly increased. Their enhanced specific properties make them attractive for structural applications (aerospace, automotive etc). However, the efficient use of these properties requires in depth knowledge of the processes that lead to composite failure. In its turn, the failure of composite materials is a complex phenomenon that may include matrix cracking, delamination and fibre breakage. During the service life of these types of materials delaminations can occur resulted either from fatigue loading or from low velocity impact events due to the bridging of matrix cracks. These delaminations are particularly dangerous because they are not visible and may lead to localized buckling phenomena. A variety of mechanisms take place during an impact event [1], in which the incident energy is absorbed. Conventional repair techniques of composites are – among their other weak points – not appropriate for the repair of micro-defects deep inside the material. Self-healing polymers [2] is an approach which has not yet been incorporated to commercial composites but promises to face some principal weak points. This smart technology aims to in-situ repair matrix cracks and matrix/reinforcement debonding and thus to

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extend the effective life-span of the composites, to reduce the maintenance needs and costs and to improve the damage tolerance and reliability of composite structures.
Lately, on the focus of various researchers has been the enhancement of the fracture and fatigue behaviour of high performance structural composites. A variety of methods are proposed in the literature which includes interleaving, hybridization, stitching, short-fibres, and z-pinning [3-8]. Kostopoulos et al. [9] investigated the influence of multi-wall carbon nano tubes (MWCNTs) on the impact and after impact behavior of CFRPs. It was shown that by the incorporation of MWCNTs at the rate of 0.5% by weight, the impact performance was enhanced at higher energy levels while the after impact performance was also improved by extending the fatigue life. In a recent work, Papanicolaou et al. [10] investigated the post impact behavior of the epoxy matrix-woven flax fabric composites which were subjected to low energy impact tests. The degradation of the mechanical properties was determined under three-point bending tests, using samples sectioned from the damaged composite plates. Self-healing composites have previously been developed by embedding healing agents into the matrix using microcapsules or vascular networks, [11-12] that will release the healing agent upon crack damage. A different approach towards self-healing composites, are matrices that comprise thermoplastic polymers, [13-14] but all these healable materials are not suitable for applications that need higher mechanical properties and stiffness, due to their poor mechanical properties. A new technology that could be beneficial for self-healing in composites has been built on DA and retro-DA (R-DA) reaction. The DA and R-DA reaction is widely used in constructing such healable polymeric materials, as a result of high yield, mild reaction condition and good thermal reversibility [15, 16]. The exploration of the DA and R-DA reaction for self-healing application has been pioneered by Chen et al. [17]. Healing in the thermally reversible crosslinked polymers depends upon the failure and re-establishment of specific reversible bonds. At elevated temperatures, the DA adduct undergoes R-DA reaction to generate the original diene and dienophile. Zhang et al. [18] utilized thermo-reversible DA bonds to generate an interphase between carbon fibres and an epoxy matrix leading to the ability of interfacial self-healing in CFRPs. It was shown that all the interphases designed with reversible DA bonds have a repeatable self-healing ability. Morgan and Jurek [19] reported toughening procedures, processing optimization and performance evaluation of BMI-CFRPs. The effects of toughening procedures in terms of G_{IC}, impact penetration, compression after impact and open hole compression as a function of temperature were discussed. Finally, in a more recent paper, GFRPs comprising DA based thermo-reversible crosslinks, showed good self-healing behavior combined with good compatibility with the glass fibres [20].
The current work investigated the influence of the incorporation of BMI reversible polymer based on DA reaction on the impact, CAI behavior and healing capability of quasi-isotropic CFRPs. It is complementing and extended the work of study [21] where mode I fracture was investigated. The BMI reversible polymer was incorporated into the CFRPs in the form of two UD pre-pregs and placed symmetrically. After the manufacturing process reference and modified CFRPs were tested under impact tests and compared. It was shown that the damage area was higher for the modified CFRPs. After the impact events damaged modified samples were subjected to heating under controlled loading using a thermo-press machine in order to activate the R-DA reaction and the damage to be healed. It was shown that the damage was entirely healed according to C-scan inspections. Subsequently CAI tests were conducted for reference, modified damaged and modified healed samples. Additionally, it was shown that the damaged reference CFRPs exhibited better CAI properties compare to the unhealed modified ones. On the other hand the healed modified CFRPs exhibited better CAI properties compared to the damaged reference and unhealed modified CFRPs. Thermal conductivity experiments were conducted in through the thickness direction and it was shown a reduction at the rate of 17%. Finally optical microscopy examination of the cross-sections and acoustic emission activity of the samples was monitored and led to qualitative conclusions regarding the involved failure and healing mechanisms.

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2. Materials and methods

2.1. Materials

The composite materials which were used in this study were fabricated by using commercial UD carbon fibre-epoxy pre-preg CE-1007 150-38 as well as in-house developed pre-preg by impregnating carbon fabric in a blend of BMI polymer. The commercial pre-preg tape was supplied by SGL Group, Germany. The in-house developed BMI polymer blend was used to impregnate UD carbon fabrics, and play the role of the toughening and healing agent in the current work. The fabrics that were impregnated by the BMI reversible polymer were supplied by Torayca, Japan. The homemade BMI polymer blend was synthesized according to the following process: a trifurane monomer (TF) was prepared by reacting furfuryl glycidylether with furfuryl amine and was allowed to react with commercially available BMI oligomers (BMI-1700), that were supplied by Designer Molecules Inc., San Diego, USA. The TF and BMI were mixed in stoichiometric analogy and the resulting polymer was used to impregnate the carbon fabrics.

2.2. Preparation of the BMI pre-preg plies and composite manufacturing

The preparation process of the BMI pre-preg plies is illustrated in Fig. 1. The homemade BMI polymer (Fig. 1(a)) was poured in the centre of the UD carbon fabric, with dimensions of 150 mm x 100 mm and the system was vacuum bagged. Using a spatula the polymer was spread from the centre to the edges of the fabric and then vacuum was applied to the system. Due to the large viscosity of the BMI resin the impregnation was carried out by medium temperature heating at 110 °C, using a heating gun (Fig. 1(b)). The melting temperature (T_m) of the BMI polymer was measured to be approximately 110 °C, using a Perkin-Elmer DSC 8500 differential scanning calorimeter. The DSC samples were heated from 30 °C to 150 °C at a rate of 5 °C/min. Above this temperature, the R-DA reaction takes place as the DA reactions start to decrease significantly and thereby the interactions between adjacent polymer chains of the material. After the impregnation of the fabrics, the volume fraction of the fibres of the BMI pre-pregs was calculated to be close to 55% (Fig. 1(c)).
Two quasi-isotropic laminated plates with 16-layers with the following stacking sequence $[45/0/-45/90]_{2S}$, each were manufactured for the needs of the current study; the reference laminate and the modified laminate with two BMI pre-pregs, both intended to low velocity impact and CAI tests. Fig. 2 shows schematically the plate's configuration and the positions in which the two BMI pre-pregs were placed (6th and 11th UD 0^{O} layers). The dimensions of the final plates were 150 mm x 100 mm x 2±0.1 mm. Following the lay-up, the laminates were vacuum bagged and cured in an autoclave for 2 h at 130 °C under 6 bars applied pressure, according to the pre-preg manufacturer guidelines. C-scan inspection of the manufactured plates, using a Physical Acoustics Corporation (PAC) UT C-Scan system with a 5 MHz transducer secures the high quality of the manufactured plates. Thickness measurements were also performed. Five and ten impact samples were manufactured for the reference and the modified plates respectively. Five of the modified samples are intended for CAI tests after the impact tests while the other five samples are intended for CAI tests after the healing cycle.

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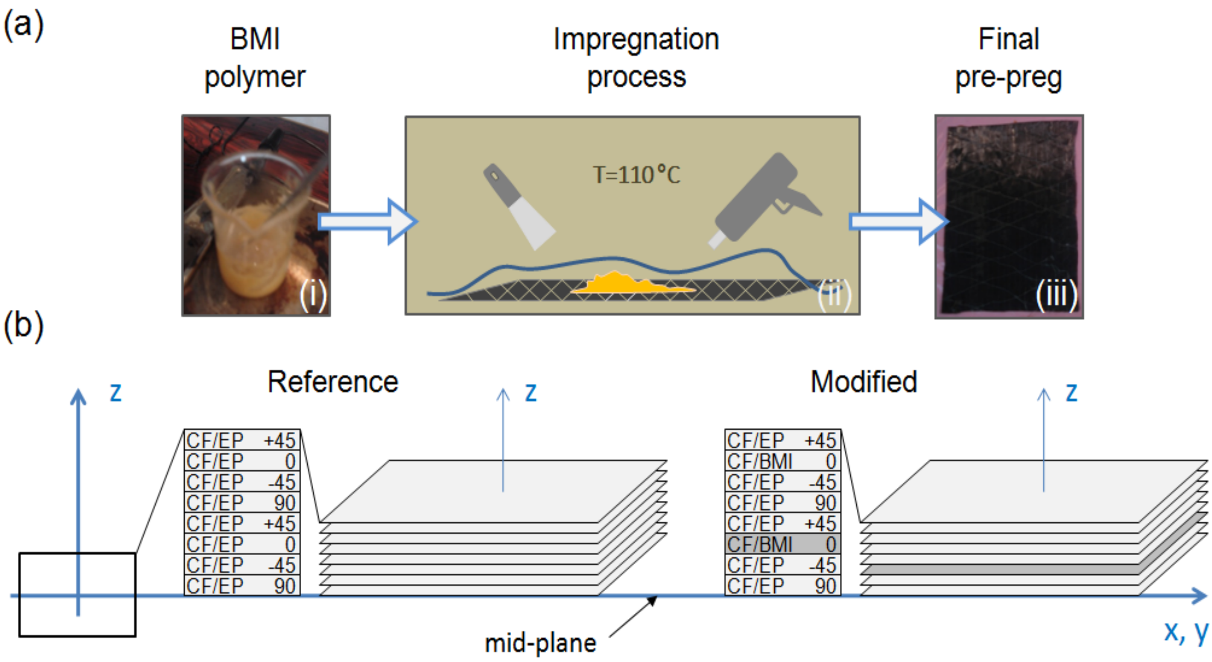

Figure 1. (a) Preparation process of the modified pre-preg plies. (i) The "homemade" BMI polymer in high viscosity liquid form. (ii) Impregnation process of the carbon fabric with BMI polymer at 110 °C. (iii) Photograph of the final modified pre-preg ply. (b) Design of the reference and the modified composite plates.

2.3. Low velocity impact CAI tests and AE recordings

The impact tests were performed according to AITM1-0010: 2015 of Airbus using a homemade impact machine. A drop tower equipped with 2.5 kg hemispherical alumium impactor having a diameter of 16 mm was employed (Fig. 2a). The selected impact energy was that of 25 J and was delivered by adjusting the initial height of the impactor. After the impact tests, the induced damage was measured and evaluated using non-destructive testing including ultrasonics (C-scan). After the C-scan process, five of ten modified samples were subjected to healing procedure described bellow in subsection 2.4. Subsequently, damaged reference, damaged modified and healed modified samples were subjected to CAI tests according to AITM1-0010: 2015 standard of Airbus (Fig. 2b). In-situ with the mechanical testing, the AE activity of the samples during the CAI tests was monitored. AE is an ideally suited non-destructive technique for the on-line monitoring of the crack propagation and was utilized in order to contribute to the extraction of useful conclusions, regarding the damage mechanisms activated during the mechanical experiments. An AE transducer was mounted on the specimens' surface as shown in Fig. 2b. The transducer type is wideband WD 100-900 kHz manufactured by PAC, USA. The transducer was attached on the specimens' surface using a suitable glycerine-based coupling agent. AE signal acquisition was performed via a four channel 16-bit PCI/DSP-4 by PAC data acquisition system. Pre-amplification of 40 dB and band-bass filtering of 20-1200 kHz was performed using general purpose voltage pre-amplifiers with 0/20/40 dB variable gain (2/4/6-AST Auto Sensor Testing Pre-amplifiers by PAC). A threshold of 40 dB was chosen and the timing parameters were set at PDT (Peak Definition Time)=50 µs, HDT (Hit Definition Time)=100 µs and HLT (Hit Lockout Time)=300 µs.

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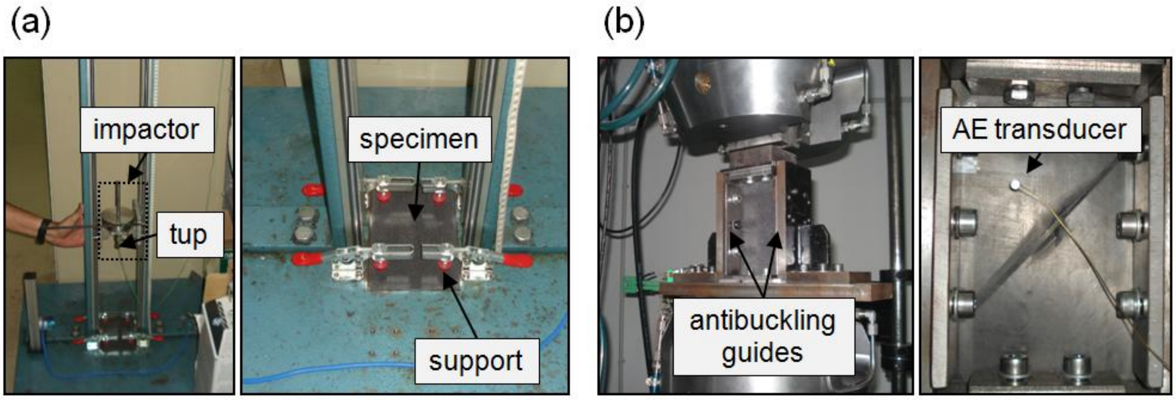

Figure 2. Photographs of the (a) impact and (b) compression after impact (CAI) testing configurations.

2.4. Healing procedure and healing efficiency calculations

After the impact tests, five modified composites were subjected to a simple healing cycle of 130 °C for 15 min under a loading of 5 kN using a heat pressing machine. Then, the samples were left to cool down to room temperature. After the healing process, the samples were tested under CAI tests. The calculations of the HE of the estimated system were based on equation (1):

$$HE=(a_{\mathrm{healed}}/a_{\mathrm{damaged}}).100\% \tag{1}$$

where, a is the property under examination, a_{healed} refers to the value of the property after healing and a_{damaged} refers to the value of the property before healing, after the impact tests.

3. Results and discussion

3.1. Low velocity impact, C-scans, optical microscopy, CAI tests and recovery

After the impact tests in which the procedure is described in subsection 2.3, C-scan measurements were performed in order to evaluate the impact induced delamination damage. Fig. 3a,b shows C-scan ultrasound inspection images for both the reference and modified plates before and after the impact tests as well as image for the modified sample after the healing cycle. The plate's images before the impact tests secure the good quality and show the absence of non-conformances (manufacturing induced porosity and delaminations). The fibre volume fraction of the plates was calculated to be close to 60%. After the impact testing a general qualitative note is that the reference sample exhibited more resistance to delamination compared to the modified sample with BMI reversible polymer. This behavior is attributed to the softening that causes the BMI polymer to the whole composite by the incorporation of the two BMI pre-pregs, which in it's turn resulted in making them more susceptible to damage. After the impact tests, the modified samples were subjected to heating under controlled loading in order the cracks to be healed. The healing process ensures that the healing agent will flow between the cracks and heal them. This behavior is confirmed by a previous work [20] in which the healing process was performed in DCB samples containing the same type of healing agent in the mid-plane. As it is shown in Fig. 3b for the modified sample's C-scan image after the healing cycle, the damage seems to have been entirely healed. The BMI polymer achieved to flow between the cracks and healed them during the healing process. The aforementioned behavior is in line with optical microscopy image of the healed modified plates after the impact event which is illustrated in Fig. 3c. In this image the healed transverse cracks and delaminations that were created during the impact tests are clearly visible. The healing agent has been released between the cracks and entirely healed them.

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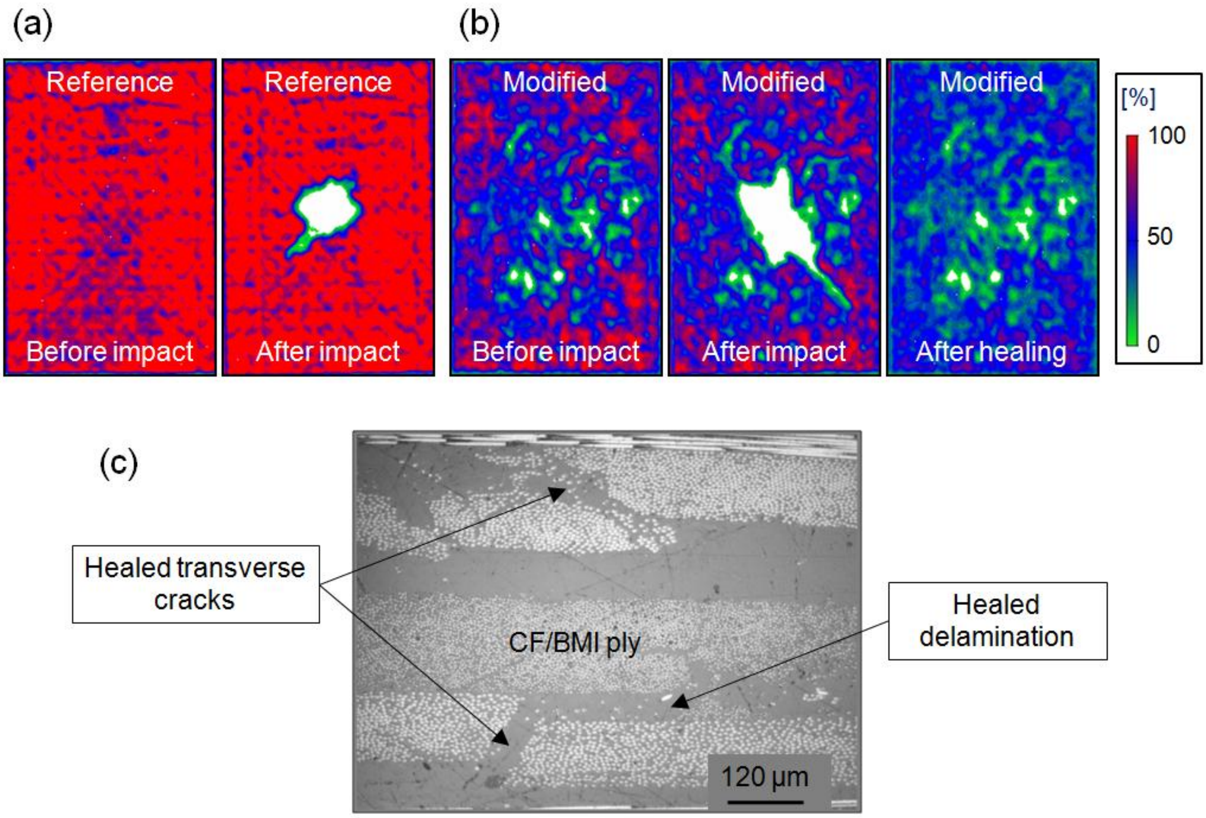

Figure 3. C-scan recording images of (a) the reference in the before impact and after impact situation and (b) the modified CFRP in the before impact, after impact and after healing situation. (c) optical microscopy photograph for the BMI-modified plate in the after healing situation.

Typical stress-strain curves for the reference, the unhealed and healed modified samples under CAI testing are shown in Fig. 4a. In Table 1 the CAI characteristics and the HE proportions of them are illustrated. More precisely as it is shown the E_{comp} of the reference and the unhealed modified sample does not differentiate significantly for both damaged samples is calculated to be approximately the same (~26 GPa). On the other hand the healed modified sample exhibited higher σ_{max} (~31 GPa).This behavior is attributed to the healing cycle that causes damage repair and recovery of the initial mechanical properties of the plate. The HE for the E_{comp} was calculated to be close to 120%. Additionally the σ_{max} value for the reference sample is slightly higher compare to the value for the unhealed modified sample (approx. 125 and 110 MPa respectively) while the σ_{max} value for the healed modified sample was calculated to be approximately the same as the value for the reference sample (approx. 125 MPa). According to AE recordings, the aforementioned behavior is validated. In the bar diagram of Fig. 4b the cumulative AE hits and energy at σ_{max} are illustrated. As it is shown the AE characteristics are higher for the healed modified samples. The healing process made the samples stiffer and resulted to higher AE characteristic values compare to the unhealed damaged samples. Finally in Table 1 the thermal conductivity values for both the reference and BMI-modified samples in through-the-thickness direction are illustrated. As it is shown the incorporation of the two BMI-layers symmetrically into the CFRP caused a decrease of the thermal conductivity at the rate of approximately 17%. This behavior is attributed to the lower thermal conductivity of the BMI material that resulted in lowering of the thermal conductivity value of the entire CFRP system.

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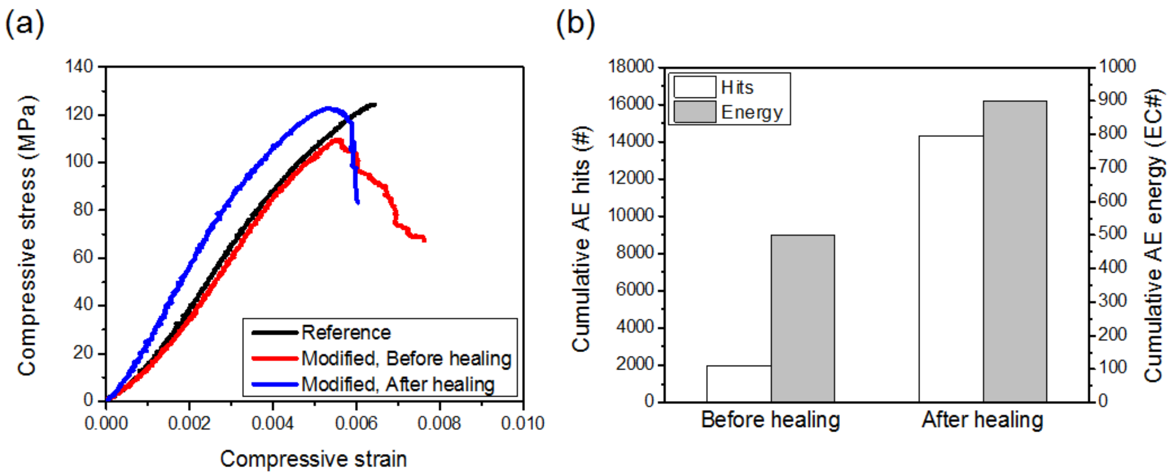

Figure 4. (a) Representative compressive stress vs. compressive strain resulted from the compression after impact (CAI) testing of the reference and of the modified CFRPs before and after healing. (b) Results from AE analysis of the reference and the modified CFRP at σ_{max} point.

Table 1. Compression after impact (CAI) characteristics and thermal conductivity measurements.

Specimen Type	E_{comp} (GPa)	σ_{max} (MPa)	Thermal Conductivity $(W(mK)^{-1})$
			22 °C
Reference	26.47	124.31	0.761
Modified (Unhealed)	25.64	109.48	
Modified (Healed)	31.06	123.20	0.632
HE (%)	121.13	112.53	

4. Conclusions

Reference and BMI-modified quasi-isotropic CFRP laminates were manufactured using the autoclave method. The produced composites were subjected to low velocity impact using a drop tower and examined non-destructively after the impact test. The modified samples were subjected to heating and loading, NDT examination after the healing process. Finally reference, unhealed and healed BMI-modified samples were tested under CAI tests. Additionally thermal conductivity tests were performed for both reference and BMI-modified samples. It was proven that the modified samples are more susceptible to damage as the reference samples exhibited more resistance to delamination. During the healing process, the BMI-modified damaged samples were entirely healed; this claim is confirmed by C-scan inspections, by the AE recordings during the tests and then by the optical microscopy photographs of the plates. The healed BMI-modified samples exhibited better CAI characteristics than the reference CFRP and the HE values were calculated to be approximately 120% and 110% for the E_{comp} and the σ_{max} values respectively. Finally the BMI-modified samples exhibited a decrease for the thermal conductivity value at the rate of 17%.

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