ASSESSMENT OF SELF-HEALING EFFICACY OF THERMOPLASTIC IONOMER FILMS INTERLEAVING CARBON-FIBRE REINFORCED EPOXY MATRIX LAMINATES

J. R. Tarpani[1], K. S. Morioka[2]

[1] São Carlos School of Engineering, Department of Materials Engineering, University of São Paulo, Avenida João Dagnone 1100 - Jardim Santa Angelina, 13563-120, São Carlos SP, Brazil
jrpan@sc.usp.br, http://www.smm.eesc.usp.br/

[2] São Carlos School of Engineering, Department of Materials Engineering, University of São Paulo, Avenida João Dagnone 1100 - Jardim Santa Angelina, 13563-120, São Carlos SP, Brazil
karen.morioka@sc.usp.br, http://www.smm.eesc.usp.br/

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Abstract

In recent years there has been a strong interest in thermoplastic polymers with self-healing behaviour, which after suffering mechanically-induced damage they self-repair via energy-activated macromolecular rearrangements. The use of film-shaped self-regenerating polymers in alternating layers with high-performance continuous fibre-reinforced thermosetting polymer matrix laminates is considered particularly attractive in the mitigation of impact damage in high-demanding components and structures, insofar as the self-healing films may at the same time toughen the base fibrous thermosetting matrix laminate composite while providing immediate or subsequent self-repairing according to the above mentioned mechanisms. In this work, mechanical flexural testing along with infrared thermography inspection are proposed for characterizing low temperature (typical of the altitudes in which modern civil and military aircrafts travel) transverse low-energy ballistic impact damage (commonly occurring under the above cited conditions) in thermoplastic ionomer films interleaving carbon-fibre reinforced epoxy matrix laminates, as well as to assess the degree of success of thermally-activated self-healing process of ionomeric phase by external heating sources. Preliminary mechanical results supported the self-healing hypothesis of impact damaged hybrid laminates, and exploratory thermography imaging of both the as-damaged and as-rejuvenated test coupons suggested that this nondestructive evaluation technique is sensitive enough to detect healing effects.

1. Introduction

1.1 Carbon fibre-reinforced polymer (CFRP) laminates

CFRP composite laminates are rationally conceived to exhibit, in a significant manner and proportionally to the respective volumetric fractions, the characteristics of both the matrix and reinforcing phases, thus giving rise to a final product presenting an optimized combination of their mechanical properties [1]. Since continuous fibres displays maximum performance along their main axis, the most valuable asset of this class of materials is that the designer has the possibility of disposing individual uni-directional tape, or bi/multi-directional fabric layers onto the laminate plane to match the principal in service loads hence simutaneously maximizing mechanical behavior and saving structural weight, thus leading to very high structural efficiency and enormous advantages when compared to more traditional structural materials, notably metallic alloys [2]. Nonetheless, termosetting matrices are widely recognized by their intrinsic brittlenes and low energy fracture, especially at low temperatures. In spite of inumerous attempts to toughnen them, specially the epoxy resin ones, there still exists a number of drawbacks to be overcome, the mainly ones associated to strength and stiffnnes loss [3].

1.2 Self-healing thermoplastic polymers

Thermoplastic polymers with self-healing behavior exhibit the ability to self-repair, thus avoiding or postponing failures, so that they are of tremendous interest to several structural engineering fields [4-

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10], which obviously include aerospace industry. In this regard, Ethylene-MethAcrylic Acid (E-MAA) copolymer ionomers have received increased attention and their heat activated self-healing potential has demonstrated [11-13]. Hence, one could envision their application to mitigate the so-called Barely Visible Impact Damage (BVID) in CFRP, which typically causes significant degradation of mechanical properties in a laminated aircraft composite structure (therefore compromising airworthiness), even though the only external indication of damage may be a very small surface indentation [14]. As an example, composite structural members of modern civilian and military aircrafts flying at altitudes from 5,000 to 15,000 m permanently face the possibility of BVID followed by instantaneous depletion of impact energy, since air temperature ranges from -30°C to -70°C in-between those heights in the sky. Common BVID sources include foreign object debris hits like volcanic particles and small size metal parts detached from the aircraft propulsion system, though fragmenting munitions of Man-Portable Air-Defense Systems (MAMPADS), which are shoulder-launched surface-to-air missiles (SAMs, typically guided weapons) has also become a worry threaten to flying civilian aircrafts [15]. So, the possibility of conceiving, designing and manufacturing a composite aircraft material prone to self-heal BVID when subsequently xposed to thermal activation sources (e.g., fuselage surface temperatures up to 100°C are predicted in grounded composite-made aircrafts due to solar heating: http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19810013888.pdf) would be of noteworthy interest.

1.3 Thermoplastic film interleaved CFRP laminates

The use of thermoplastic polymer films in extra alternate layers with continuous fiber (particularly carbon one)-reinforced thermosetting polymer matrix (especially epoxy resin) laminates is already a well-succeeded strategy to obtain hybrid composites with very high mechanical performance (tensile strength and stiffness), as provided by the CFRP skeleton, at the same time that they exhibit high transverse impact toughness, as granted by the interspersed thermoplastic films preventing or minimizing intralaminar, interlaminar and translaminar fractures [16-17].

1.4 Nondestructive InfraRed Thermography (IRT) inspection

InfraRed Thermography (IRT) is a nondestructive testing imaging technique that allows the visualization of heat patterns on an object or a scene. The basic equipment comprises an IR detector, a monitor to display images and a PC to record (and sometimes process) data. The passive approach is mainly qualitative, such as the diagnosis of the presence of a given abnormality with respect to the immediate surroundings. Active thermography finds a large number of applications in nondestructive testing techniques since practically any form of energy can be used to stimulate the inspected object, provided that the thermo-physical properties of the eventual defects are different enough to the non-defective areas in order to produce a measurable thermal contrast. Besides, the time of application of the external stimulus can be synchronized with the acquisition, providing the possibility of developing quantitative data analysis [18]. Pulsed phase thermography (PPT) is an very attractive modality of IRT insofar as it combines the high signal to noise ratio and depth resolution of lock-in thermography with the imaging speed of pulse thermography. In PPT, the material is heated with a single, square thermal pulse and the reflected thermal wave is measured as a function of time during the cooling transient. The square thermal pulse contains a range of input modulation frequencies, from which the information at each frequency is extracted through signal processing of the measured thermal wave. Therefore only a single imaging measurement must be performed and the imaging time is relatively short. Of great interest is the phase image which, being related to the propagation time delay, is independent of optical or infrared surface features, besides it can probe roughly twice the thickness probed by, for instace, pulse thermography images [19-20].

Considering the successful methodology of thermoplastic film interleaving of CFRP laminates towards fiber-reinforced composite toughening, as well as the high self-healing potential of some thermoplastic ionomers films, it seems to be extremely advantageous and relevant to build in innovative hybrid material with a broad range of applications in structural engineering making use of both the ready-to-use technologies and then put it to proof in conditions resembling those faced by in-service composite parts of modern aircrafts. In this regard, the present work proposes (i) the manufacture of such inventive engineered material in the form of small test coupons, (ii) to damage

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them by ballistic impact under low temperatures, (iii) to inspect them nondestructively via infrared thermography, (iv) to measure their residual stiffness under 4-point-bend loading, (v) to subject them to thermally-activated self-repair processes, and finally (vi) to evaluate the degree of success of the self-restoration processes by applying a new round of thermographic inspection followed by mechanical flexural testing to determine their after-healing rigidity.

2. Materials and Test Coupons

Test coupons were manufactured as flat tablets with in-plane dimensions of 100 x 50 mm^2 whose thickness depended upon the pille-up architecture of CFRP layers along with self-healing thermoplastic films. Individual 0.35 mm-thick solid layers of CFRP were obtained by vacuum infusing aeronautical grade liquid epoxy resin in a single blank of bidirectional [0/90°] carbon fiber fabric (areal weight of 200g/m^2) preform, followed by cure at ambient temperature. An advanced E-MAA ionomeric copolymer exhibiting self-healing behaviour, density of 0.95 g/cm^3, melting temperature around 100°C and glass-transition temperature close to -100°C, was hot-compressed as 0.5 mm-thick films which were interspersed with the CFRP rigid foils. The assembled hybrid laminate was finally hot-compressed at a temperature high enough (approximateely 150°C) to permit not only CFRP layers to be bonded together by melting the thermoplastic polymer, but also proper post-cure of the thermosseting epoxy resin. Two specimen configurations were fabricated, namely: (i) 6 CFRP : 5 E-MAA array exhibiting full-thickness of 3.8 mm, and (ii) 7 CFRP : 6 E-MAA architecture with full-thickness of 5.2 mm. In these work, results from one 6 CFRP : 5 E-MAA testpiece ("Testpiece 1", coded 3-6/5-3) and two 7 CFRP : 6 E-MAA testpieces ("Testpiece 2" and "Testpiece 3", coded respectively 1-7/6-2 and 1-7/6-4) are provided.

3. Test Procedures

3.1 Impact testing at low temperature

All the three test coupons were transversselly impacted for non-trespassing condition in ballistic regime by employing lead projectiles weighting 1.6 g. The 5.5 mm caliber projectiles were accelerated by an air gun device properly calibrated and assembled to ensure the repeatability of the impact events in terms of impact velocity (230 m/s), impact position at the center of the specimens (frontal) face, and impact angle (45°) in regard to the specimens' plane. Testpieces were cooled down to a temperature of order of -70°C during 10 minutes in gaseous nitrogen before impact in order to simulate critical in-flight low temperatures experienced by commercial aircrafts.

3.2 Self-healing process

Attempts to thermally activate the self-healing potential of the intermixed ionomeric films were carried out by heating up the pre-impact damaged test coupons by air convection in a resistance furnace (Testpiece 1, at 70ºC), or via radiation by incident infrared light (Testpiece 2, at 55ºC, and Testpiece 3, at 70ºC). Tipically, only few hours of thermal conditioning were impose to each test coupon.

3.3 Flexural testing

Four-point flexural testing as per ASTM-D7264 (2007) standard were carried out at ambient temperature to determine testpieces' stiffness in both the as-impacted and as-healed conditions. The crosshead displacement rate of the testing machine was fixed at 1 mm/min, and load divided by load line displacement ratios were obtained well within the linear elastic strain regimen of the test coupons. These numerical values were then taken as a measurement of the specimens' rigidity in both their tested conditions, so that a direct comparison between as-impacted and as-healed mechanical status could be made.

3.4 Pulsed Phase Thermography - PPT

IRT-PPT images were captured with a mid-wavelength (3-5 μm) infrared camera FLIR Phoenix with an InSb detector array exhibiting sensitivity of less than 20 mK at 25°C and producing images with a resolution of 640 x 512 pixels at a frame rate of 55 Hz. The specimens were heated up in reflection

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mode by two halogen lamps, each of 1000 W maximum capacity, by means of a function generator which sent a square wave pulse to the IRT power module to activate the heat lamps during periods of 7 s, at a frequency of 0.65 Hz, followed by cooling down cycles. The lamps were placed at an angle of 30° and a distance of 0.5 m in respect to the specimens' front plane to minimize non-uniformities in the applied heating, whereas the camera was positioned perpendicular to the specimen plane and at approximately 70 cm from the samples. The images were captured during cooling transients from the IRT camera using a computer and dedicated software. The image data files were then saved and imported into Matlab for further processing. The data from the cooling period was processed using the open access Matlab based IR VIEW to calculate the phase images.

4. Results and Discussion

4.1 Low temperature impact testing

Fig. 1 shows the front (impacted) faces of testpieces 1, 2 e 3, respectively, where a residual dent is clearly seen on the center region. BVID condition was warrantied for all the specimens tested, insofar as the criterion of maximum residual dent depth of 0.3 mm [21] was always fully satisfied.

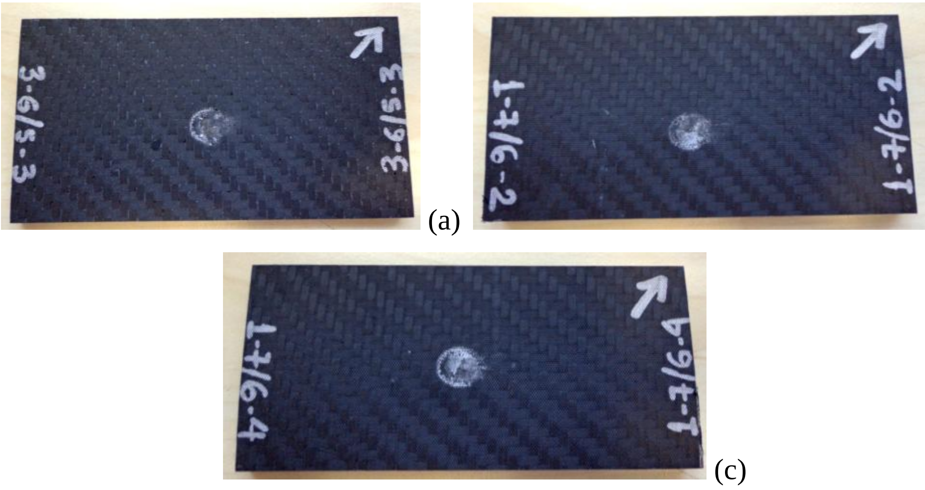

Figure 1. Front (impacted) face of test coupons after ballistic impact at approximately -70°C: (a) Testpiece 1, coded 3-6/5-3 (b) Testpiece 2, coded 1-7/6-2; (c) Testpiece 3, coded 1-7/6-4.

4.2 Infrared thermography

Fig. 2 displays phase thermograms and respectives color pallete referring to the Testpiece 1 (code 3-6/5-3), thus permiting the reader to differentiate typical features related to particular thermal responses of distinct regions in the test coupon, which are intrinsically associated to manufacturing defects, sub-zero impact damage and subsequent thermally-activated healing.

For instance, the peripherical magenta area of Fig. 2a much probably corresponds to delamination, as it is also the case in the central region of the test coupon subjected to the single sub-zero ballistic impact. Red central spots may refer to the first E-MAA layer to experience the impact loading and be exposed to the external environment. After thermal-healing at 70°C (Fig. 2b) there is a noticeable remission of delaminated areas, while regions corresponding to the uncoverd E-MAA film still persist to some extent, so corroborating earlier assumptions.

Fig. 3 exhibits phase thermograms of Testpiece 2 (code 1-7/6-2) in the as-impacted and as-healed conditions, respectively. Once again the peripherical magenta area of Fig. 3a is likely to be delaminated, and this also seems to happen with the central region directly subjected to the impacting contact of the metal projectile at very low temperature. Likewise observed in Testpiece 1, the red central spot may refer to the first layer of inner E-MAA film uncover due to the impact loading. Once more, after the thermal-healing carried out at 70°C (Fig. 3b) there was a noticeable reduction of delaminated areas, while regions corresponding to the uncovered E-MAA film still remains though as tiny remanecent red and light green spots, thus substantiating the premise of self rejuvenation potential of the hybrid laminate. Interestingly, some catching-attention features in Testpiece 2 did not change

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with the restoration thermal treatment, as for instance the red/yellow/green large blot (5 o'clock from the impact area), and the green blur with little red spots at the left (7 o'clock from the impact area). In this regard, it can be inferred that they are post-cured (≈ 150°C) epoxy resin-rich areas.

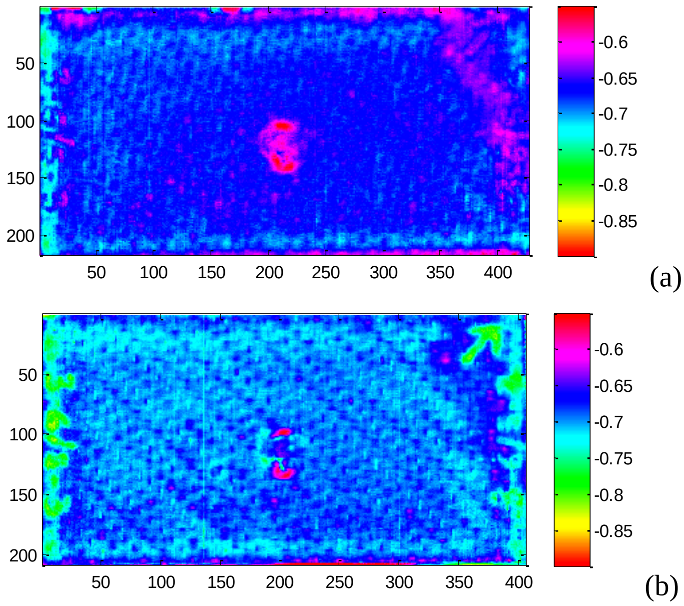

Figure 2. PPT phase termograms obtained from Testpiece 1 (code 3-6/5-3) in reflection mode: (a) As-impacted at -70ºC; (b) As-repaired at 70ºC in convective furnace.

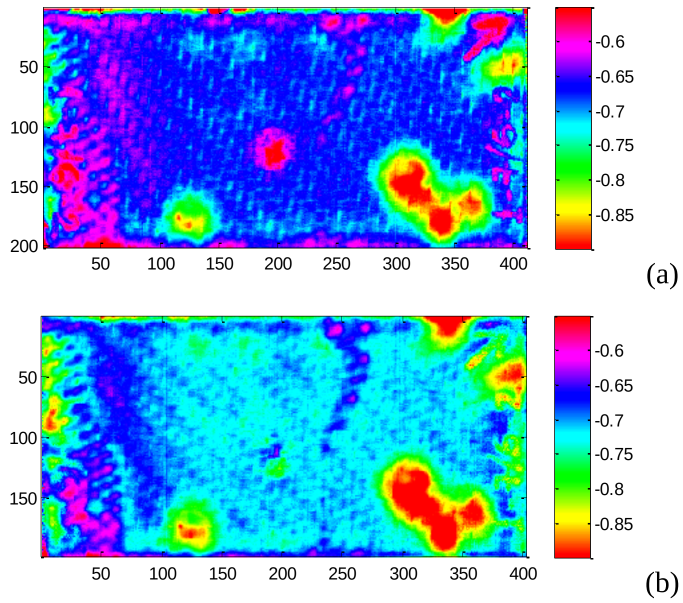

Figure 3. PPT phase termograms obtained from Testpiece 2 (code 1-7/6-2) in reflection mode: (a) As-impacted at -70ºC; (b) As-repaired at 55ºC under direct infrared light.

Fig. 4 portraits phase thermograms and respective color scale related to Testpiece 3 (code 1-7/6-4), where one can identify a mix of features already noticed in the latter coupons. These are the cases of red/yellow blots (4 and 8 o'clock respectively from the impact area), which do not suffer influence of healing thermal conditioning (and presumably refering to epoxy resin-rich regions), the lateral and central magenta areas in Fig. 4a, both of them much likely associated to delaminations, and the central red spot referring to the exposed E-MAA film. The features directly dependent on the thermal behaviour of E-MAA ionomer almost completely vanish after healing heating cyles so demonstrating once again the self-restoration achiavibility for the hybrid laminate herein porposed and tested.

It should be emphasized that the temperature of 70°C (Testpieces 1 e 3) is well below the melting temperature range of the E-MAA thermoplastic ionomer, as can be seen in Fig. 5 (melting temperature spectrum indicated by a dashed black circle), so that at this conditioning temperature of pre-impacted specimens crystalline structure annihilation by no means is the operating mechanism that can possibly lead to damage restoration in E-MAA thermoplastic ionomer.

Additionaly, and yet more surprisingly, is the clear indication that structural integrity recover of CFRP/E-MAA hybrid laminate can take place at temperatures as low as 55°C (Testpiece 2), as shown in Fig. 3 (whose data were collected in the presente work), which can be related to the so-called order-disorder transition of E-MAA ionomers [22]. According to the original proposal, this first order transition refers to the rearrangement (towards disordenation when temperature increases and pass through 55°C) of ions whithin clusters, which means polymer chain mobility and so the possibility of restauration or healing.

Since in this particular case healing was detected and characterized after direct infrared light irradiation of Testpiece 2, one could argue for its superiority over convection heating, and therefore recommend the former rejuvenation strategy in the space environment, where spacecrafts travel and vacuum prevents heat transfer by convection.

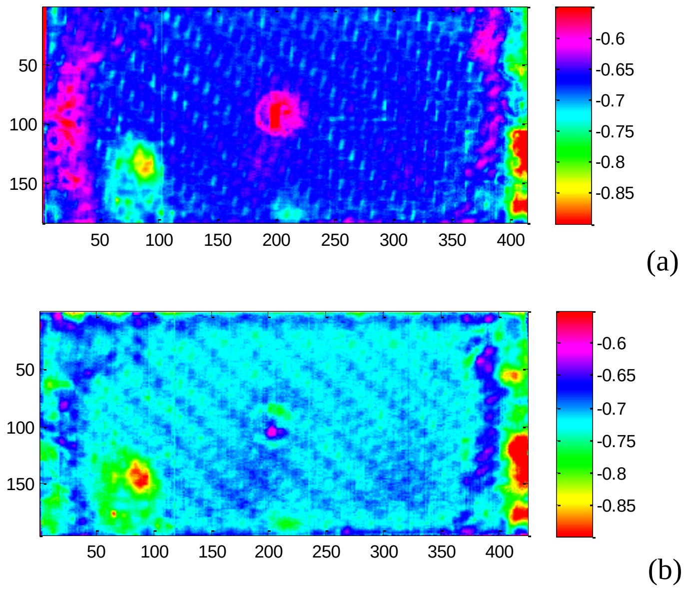

Figure 4. PPT phase termograms obtained from Testpiece 3 (code 1-7/6-4) in reflection mode: (a) As-impacted at -70ºC; (b) As-repaired at 70ºC under direct infrared light.

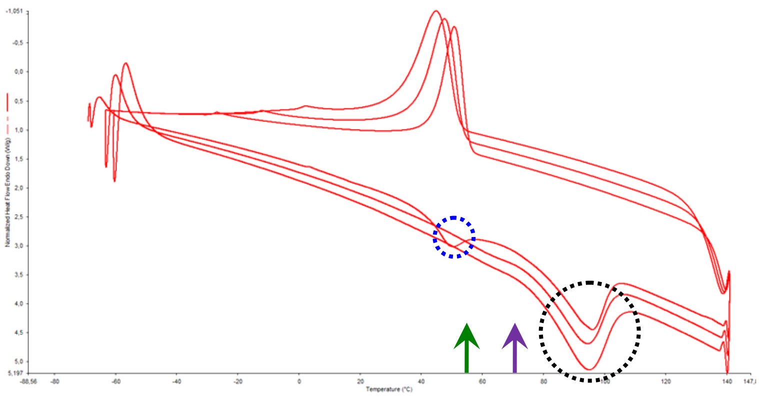

Figure 5. DSC curves for a 0.5 mm-thick E-MAA film ballistically impacted and autonomously recovered at ambient temperature. Order-disorder transition temperature [22] and melting temperature range of pre-damaged and immediatelly self-healed E-MAA film indicated by dashed blue and black circles, respectively. Minimum and maximum temperatures where thermally-activated healing was observed in hybrid laminate are indicated by green (55°C) and purple (70°C) arrows.

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4.3 Flexural testing

In order to confirm the degree of success of self-repair attained in this exploratory study, Fig. 6 plots representative straight lines (elastic strain regimen) of load vs. load line displacement (deflection) relationship as obtained for testpieces 1, 2 and 3 in both the as-impact and as-healed conditions. In this graph the slope of load-deflection straight lines should be understood as a measure of the "structural stiffness" of the tespiece at ambient temperature, in either one or another abovementioned condition. This way, data points represented by triangle symbols refer to the as-impacted condition, whereas circle symbols point out the as-healed situation.
It can be noted that stiffness was imparted in all the cases analysed, with the restoration index attaining values ranging from 45 to 50%. These seemingly high values should be evaluated in the light of the relative size of created impact damage when compared to the dimensions of the tested coupons. In this regard, the transverse central impact caused damage in the borders of the rectangular-shaped specimens (as confirmed by the thermograms provided in Figs 2a, 3a and 4a, respectively), so that test coupons' stiffness (in both the as-impacted and as-healed conditions) became expressivelly dependent upon the damage (essentially delamination) extent. This way, the results obtained so far in laboratory scale-testpieces could hardly be considered representative of full-size components and structures made with this very same hybrid CFRP/E-MAA laminate.

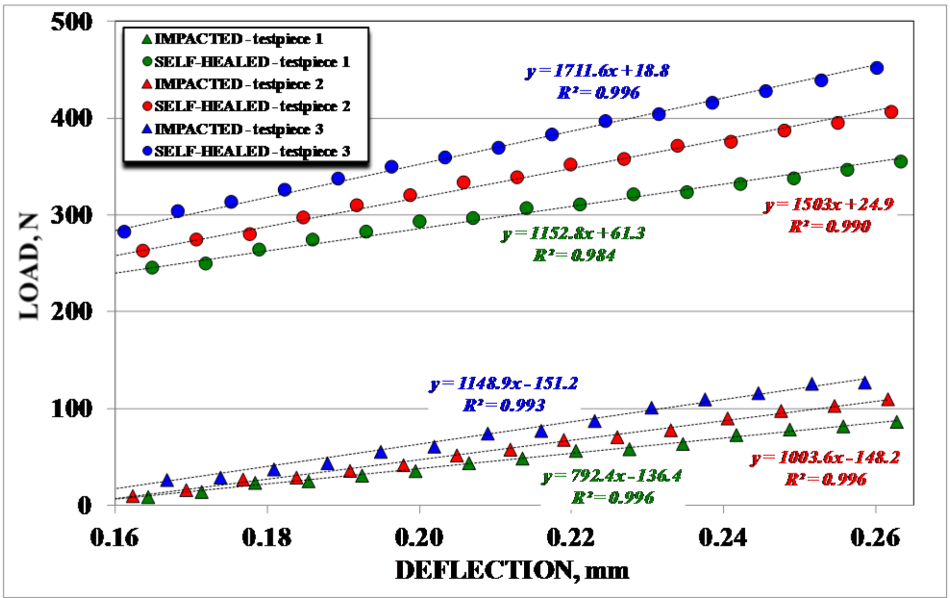

Figure 6. Load-load line deflection graph from 4-point flexural testing of as-impacted hybrid laminate and after thermally-activated self-healing of interleaved ionomeric thermoplastic E-MAA film.

5. Conclusions

i. Auspicious results were obtained in terms of clear and consistent mechanical and thermographical detection and characterization of non-autonomous self-healing potential of E-MAA thermoplastic ionomer films interspersed with CFRP solid layers, giving raise to hybrid laminate having compelling appeal to structural application;
ii. The maximum temperature where self-healing of E-MAA ionomer was attempted approached 70°C, which is well bellow the melting temperature range of the material, so denoting that other molecular mobility mechanism rather than melting caused self-restoration;
iii. The minimum temperature where self-healing of E-MAA was observed reached 55°C, which may well be related to the order-desorder transition of this ionomer class, when rearrangement of ions whithin clusters is the only one phenomenon reponsible for polymer chain mobility.
iv. Such relatively low temperature admits one to antecipate the possibility to engender self-rejuvenation in conditions compatible to solar radiation environments on earth surface, as well as in the space environment where vacuum precludes heat transfer by convection.

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