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# 1 **Monitoring of Self-Healing composites: a non-linear ultrasound** 2 **approach**

3  
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## 11 **Abstract**

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14  
15 Self-healing composites using a thermally mendable polymer based on Diels–Alder reaction were  
16 fabricated and subjected to various multiple damage loads. Unlike the traditional destructive  
17 methods, this work presents a nonlinear ultrasound technique to evaluate the efficiency of the  
18 structural recovery of the proposed self-healing laminate structures. The results were compared to  
19 Computer Tomography (CT) and linear ultrasound methods. The laminates were subjected to  
20 multiple loading/healing cycles and the extent of damage at each of these stages was evaluated using  
21 various NDT/E techniques. The results highlight the benefit and added advantage of the use of a  
22 nonlinear based methodology to monitor the structural recovery of self-healing composites.

23  
24 **Keywords**: Nonlinear Ultrasound, Phased Array, Self-Healing, Composite, Computer Tomography  
25 (CT)

## 26 **1. Introduction**

27  
28  
29 Over the last twenty years, the advancement of material technology and composite manufacturing  
30 techniques has expanded with the number of applications in which carbon fibres reinforced polymers  
31 (CFRP) can be employed. CFRP applications range from a very specific highly technological  
32 environment (aerospace, Formula 1 and nuclear) to mass market applications (sport equipment,  
33 automotive and energy applications). This is due to CFRPs very high specific properties and  
34 versatility which make them perfect for utilisation in those applications that require very good  
35 mechanical properties and low weight [1].

36 However, because of their intrinsic layered structure, composite laminates are characterised by weak  
37 resistance in the out-of-plane direction, which make them susceptible to damage growth and  
38 propagation when subjected to an impact event [2]. Indeed, due to the high stiffness and low strain  
39 given by the carbon fibres, composite materials cannot deform plastically, hence low impact in the  
40 out-of-plane direction will lead to the formation of barely visible impact damage (BVID) that if not  
41 immediately identified could cause critical failure of the entire structure.

42 Based on these premises, the possibility of recovering the integrity of a damaged composite  
43 component constitutes a fundamental breakthrough in the development of advanced composite  
44 systems and has attracted the attention of several researchers, leading to the development of a new  
45 class of smart systems called self-healing materials [3-5].

46 From the current literature it is possible to identify three different classes of self-healing materials  
47 that can be summarised as intrinsic, extrinsic and shape-memory assisted. Intrinsic or remediable  
48 self-healing systems are based on polymers that can repair themselves by exploiting the reversibility  
49 of specific reactions such as the Diels-Alder [6, 7] or the presence of thermoreversible functional  
50 groups, such as disulphide or ester [8-10]. Extrinsic self-healing materials are systems that  
51 incorporate capsules filled with a healing agent, such as dicyclopentadiene: when a damage occurs,

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1 the capsules are fractured and the healing agent fills the damaged area and solidifies due to the  
2 catalyst particles dispersed into the resin [11, 12]. Vascular self-healing materials are an  
3 improvement of capsule-based extrinsic materials inspired by biological systems and are based on  
4 the presence of a complex system of micro-channels (similar to blood vessels) incorporated within a  
5 polymer matrix that can deliver the reactive fluid in damaged areas in order to mend them [13, 14].  
6 As for the shape-memory assisted self-healing materials, they are based on the inclusion of shape  
7 memory materials such as shape memory alloys wires (SMA) [15] or shape memory polymer (SMP)  
8 both in form of fibres [16] or “bulk” [17] to partially or fully close cracks. Once activated these  
9 materials are able to exert a local contractual force that pulls the crack surfaces closer, healing the  
10 damaged material. All these systems have been proved to be very effective for the recovering of the  
11 mechanical properties of composite laminates subjected to impact damage under different destructive  
12 approaches, however very few works have been focused on the use of non-destructive techniques to  
13 monitor the healing process and to measure the recovery of the healed portion of the material.  
14 In particular, apart from Raman Spectroscopy which is probably the most common technique used  
15 for this kind of investigation [18, 19], the vast majority of literature in this subject is focused on the  
16 use of ultrasonics for the monitoring of healing processes in concrete systems. For instance, In et al  
17 [20] have used ultrasonic waves to measure the effectiveness of the healing process in fractured  
18 concrete samples. In particular, by analysing diffuse ultrasonic parameters such as effective  
19 ultrasonic diffusivity and Arrival Time of Maximum Energy (ATME) it is possible to monitor the  
20 self-healing process over time, although the proposed method shows some fluctuations due to partial  
21 crack closure. The decrease of the ultrasonic pulse velocity (UPV) was also used to measure the  
22 extent of the healing process in cracked concrete samples, as illustrated in the work by Zhong and  
23 Yao [21]. In their work they identify a relationship between the extent of a damaged area and the  
24 healing effect by correlating the UPV measures with the strength increment after the healing process  
25 for both normal and high strength concrete samples.  
26 In a different approach, non-destructive methods were used to assess the effect of the presence of an  
27 embedded vascular system in bioinspired self-healing composites, as illustrated in a study conducted  
28 by Coppola et al, in which they used acoustic emission to monitor in real-time the behaviour of  
29 vascular composite sample subjected to tensile tests [22]. The effectiveness of the healing processes  
30 was also monitored using a technique based on time reversal of acoustic waves as demonstrated by  
31 Granger et al, who correlated the drift of a signal emitted initially in high performance concrete  
32 samples with the presence of damaged areas. By analysing different signals collected during a  
33 bending/healing cycle and then time reversed on a sensor positioned near the expected crack path it  
34 is possible to observe a decrease in amplitude due to cracking and an increase as a result of the  
35 healing process [23].  
36 In this context, this paper is focused on the use of different non-destructive techniques to analyse the  
37 effectiveness of the healing process in composite laminates prepared using Diels-Alder epoxy  
38 adducts. The methods comprised of CT-Scans and various ultrasound pulse/echo techniques, with  
39 the focus on evaluating the potential of a nonlinear ultrasound phased array technique to assess  
40 damage recovery. The CT-Scan tests were used as the control to evaluate the performance of the  
41 other ultrasound techniques as they provide the highest definition and damage assessment  
42 capabilities. Thus, the focus has been on evaluating various ultrasound techniques due to their  
43 capability, flexibility and relative cost-effectiveness. The analysis was conducted by following both  
44 linear and non-linear approaches, investigating the behaviour of several composite samples subjected  
45 to a cycle consisting of multiple end-notch-failure tests followed by healing.

46

## 47 **2. Experimental procedure**

48

49 As previously illustrated, one of the most used chemical approaches to implement healing into  
50 polymeric matrices is the use of Diels Alder (D-A) chemistry, hence, this typology of self-healing  
51 materials was chosen to test the effectiveness of the different NDT techniques.

52 The resin used for the manufacturing of the samples is a self-healing epoxy system 2Ph2Epo65,  
53 manufactured by Amendola et al [7, 24], which is based on the introduction of diene and a dienophile  
54 moieties in the polymer precursors which are used as reversible crosslinkers. The use of furan-

1 maleimide Diels-Alder moieties allows for the synthesis of epoxy resins with reversible crosslinks  
 2 capable of multiple healing events upon thermal stimulus. The coexistence of a stable polymeric  
 3 network and a thermo-reversible one is one of the preferred paths to develop self-healing materials  
 4 with robust self-healing ability and good mechanical behaviour during healing [25].  
 5 In order to evaluate the effectiveness of the healing mechanism, different samples were manufactured  
 6 and subjected to shear tests over multiple healing processes. Table 1 illustrates the different phases  
 7 of the experimental procedure including the different NDT techniques, the mechanical tests and the  
 8 healing processes.

9  
 10

**Table 1 - Step-by-step experimental procedure**

| Step | Test Procedure         | Damage State                |
|------|------------------------|-----------------------------|
| 1    | Phased Array Testing 1 | Undamaged                   |
| 2    | Water Tank C-Scan 1    | Undamaged                   |
| 3    | CT-Scan 1              | Undamaged                   |
| 4    | <b>SHEAR TEST 1</b>    | <b>Induce Damage 1 (D1)</b> |
| 5    | Phased Array Testing 2 | D1                          |
| 6    | Water Tank C-Scan 2    | D1                          |
| 7    | CT-Scan 2              | D1                          |
| 8    | <b>Healing 1</b>       | D1/Heal 1 (H1)              |
| 9    | Phased Array Testing 3 | D1/H1                       |
| 10   | Water Tank C-Scan 3    | D1/H1                       |
| 11   | CT-Scan 3              | D1/H1                       |
| 12   | <b>SHEAR TEST 2</b>    | <b>Induce Damage 2 (D2)</b> |
| 13   | Phased Array Testing 4 | D1/H1/D2                    |
| 14   | Water Tank C-Scan 4    | D1/H1/D2                    |
| 15   | CT-Scan 4              | D1/H1/D2                    |
| 16   | <b>Healing 2</b>       | D1/H1/D2/ Heal 2 (H2)       |
| 17   | Phased Array Testing 5 | D1/H1/D2/H2                 |
| 18   | Water Tank C-Scan 5    | D1/H1/D2/H2                 |
| 19   | CT-Scan 5              | D1/H1/D2/H2                 |
| 20   | <b>SHEAR TEST 3</b>    | <b>Induce Damage 3 (D3)</b> |
| 21   | Phased Array Testing 4 | D1/H1/D2/H2/D3              |
| 22   | Water Tank C-Scan 4    | D1/H1/D2/H2/D3              |
| 23   | CT-Scan 6              | D1/H1/D2/H2/D3              |

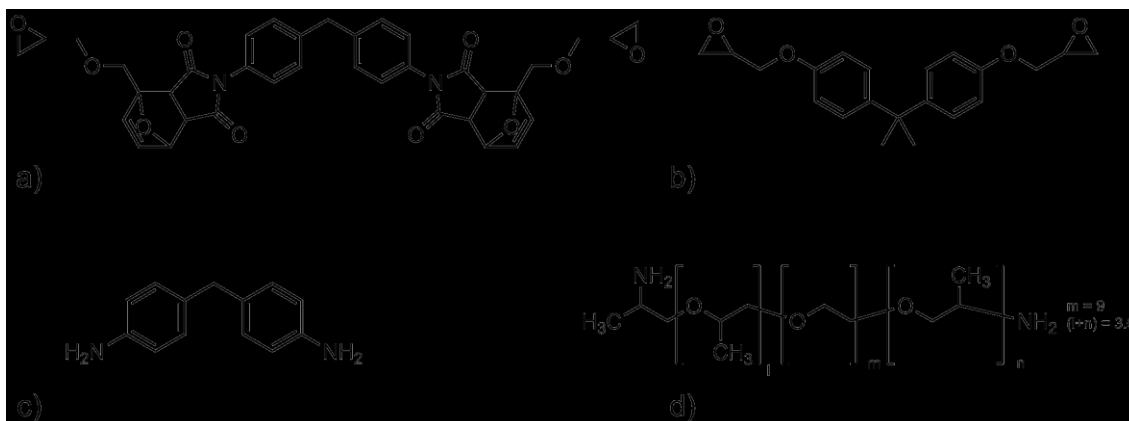
11  
 12 The selected healing cycle is a two-step thermal treatment:  
 13 - I step: heating 20 min at 120°C, to induce the rD-A reaction, to activate diene and dienophile  
 14 reacting pairs and increase molecular mobility required to let molecular segments diffuse across the  
 15 fracture surface;  
 16 - II step: annealing 12 hours at 90°C, to promote the direct D-A recombination and restore resin  
 17 crosslinked structure.

18  
 19

### 3. Self-Healing Information

Structural formulae of all components used in the preparation of self-healing epoxy 2Ph2Epo65 are described in Figure 1. The suffix -65 refers to the percentage of Diels-Alder epoxy (2Ph2Epo), with respect to the total epoxy used. 2Ph2Epo epoxy precursor is characterized by the presence of two oxirane rings and two Diels Alder adducts.

Its synthesis was already described elsewhere [24]. Diglycidyl ether of bisphenol A (DGEBA) with an Epoxy Equivalent Weight of 185-190 g/eq was kindly supplied by Elantas S.p.A. with commercial name of EC01.



**Figure 1 - Main chemical components of the 2Ph2Epo65 compound. a) 2Ph2Epo adduct, b) DGEBA, c) DDM, d) Jeff500 ammine**

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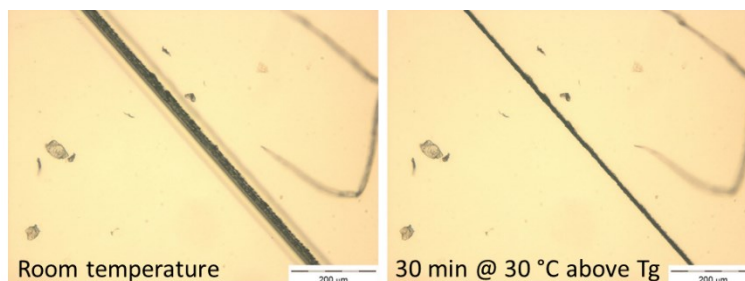
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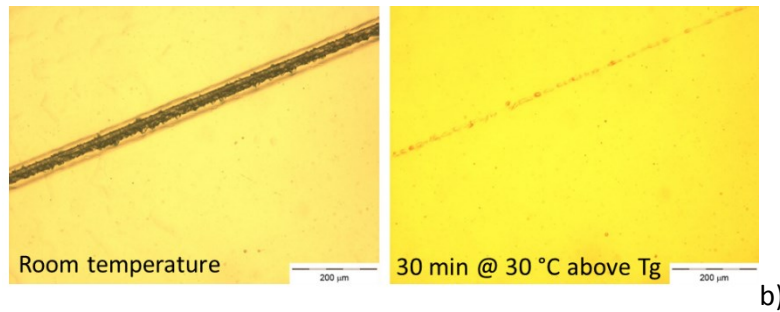
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DDM and Jeff 500 were purchased from Sigma and used without further purification in the stoichiometry ratio of DDM/Jeff500 = 60/40. The flexible amine Jeff500 was added to the formulation in order to limit the glass transition temperature of the completely crosslinked system to the value of about 90°C. In fact, a higher value of Tg would require high curing temperature potentially interfering with the Diels-Alder and rDiels-Alder reactions responsible for self-healing phenomena. Curing was performed at 90°C for 24 hours. The epoxy and amine groups were stoichiometrically balanced before curing.

Mechanical tests carried out on the formulated D-A epoxy showed its ability to recover stiffness after multiple testing cycles (bending failure and thermal healing). The 2Ph2Epo65 epoxy resin showed a progressive decrease of the strength in further cycles while the stiffness is restored (Figure 2). Since the samples were able to recover all their original stiffness, probably further thermal treatment could affect the DGEBA network, modifying the failure mechanism of the sample [7].



a)



1 **Figure 2 - Difference between the behaviour of a traditional resin system and the**  
 2 **remendable 2Ph2Epo65 epoxy when subjected to a damage-heating cycle.**  
 3

4 **4. Mechanical Testing**  
 5

6 Shear tests can be conducted on composite laminates following different experimental approaches,  
 7 depending on the mode of fracture that needs to be assessed. Due to the layered structure of composite  
 8 laminates, in this work the effect of the self-healing epoxy resin and its healing capability were  
 9 investigated under mode II fracture loading by performing End Notch Failure (ENF).

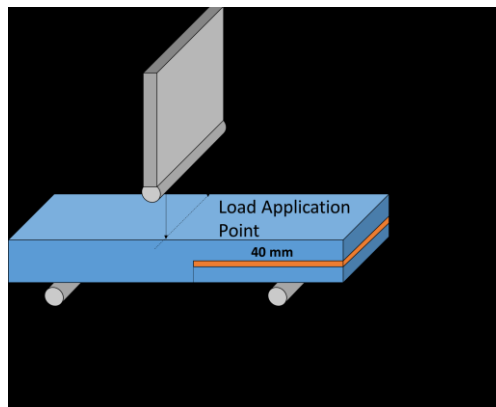
10 A Composite plate has been manufactured by liquid moulding process under vacuum bag, 12  
 11 unidirectional layers were laminated to reach a nominal thickness of 3 mm. A polyimide film  
 12 (Kapton) was lied down at the mid plane to induce an initial delamination. Table 2 reports geometry  
 13 of two samples (S1 and S2) cut from the plate. The presence of a Kapton layer in a bending test (End  
 14 Notched Failure, ENF) leads to the mutual sliding of separated parts promoting a Mode II failure  
 15 (shear mode) according to ASTM D7905.

16 ENF tests were carried out by positioning the different samples in an Instron 3369 Universal Testing  
 17 Machine using a three point bending setup. The crosshead was then lowered with a constant speed  
 18 of 4 mm/min in order to apply a load on the central portion of the sample and propagate the crack  
 19 from the edge of the embedded Kapton film towards the loading point through the length of the  
 20 specimen. Sample dimensions and the parameters of the ENF tests are illustrated in Table 2 and  
 21 Figure 3.  
 22

23 **Table 2 - Geometrical and experimental parameter of the End Notch Failure (ENF) tested**  
 24 **samples**

| Number of Plies | Length           | Width               | Thickness         | Position of the kapton film |
|-----------------|------------------|---------------------|-------------------|-----------------------------|
| 12              | 120 mm           | 25 mm               | 3 mm              | middle section              |
| Span Length     | Crosshead veloci | Initial crack lengt | Load Pin dimensic | Support Pins dimension      |
| 100 mm          | 4 mm/min         | 40 mm               | 6 mm              | 6 mm                        |

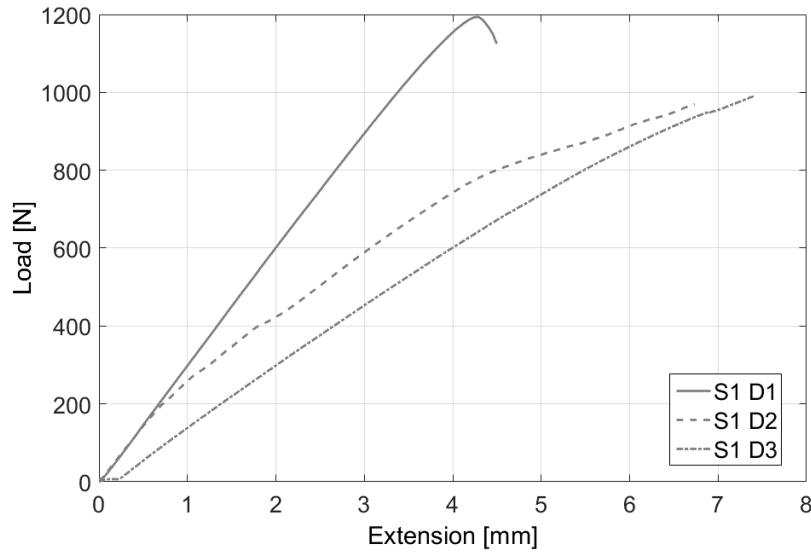
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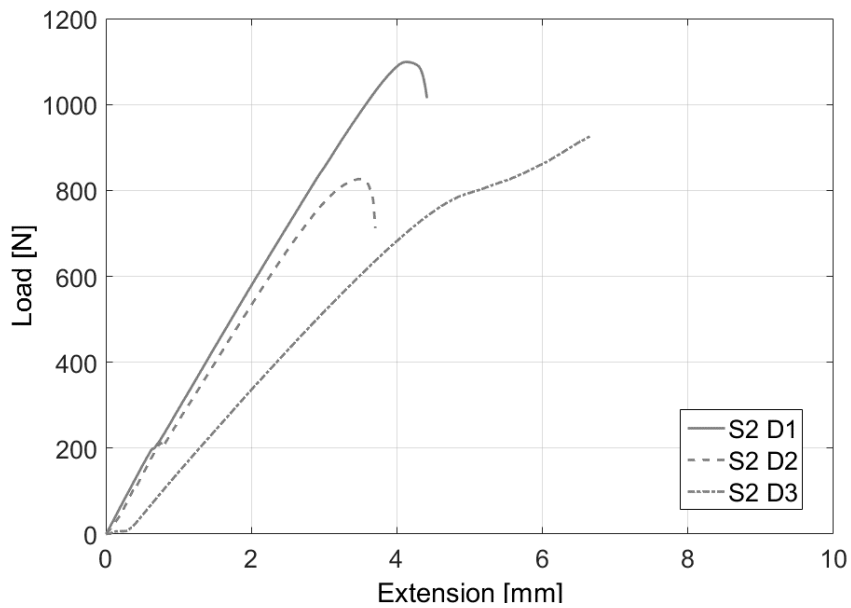
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 27

**Figure 3 - End Notch Failure (ENF) Test experimental setup**

1  
2 Figure 4 and Figure 5 show the load-extension curves collected for both Sample 1 and Sample 2  
3 during the entire experimental campaign (three loading cycles for each sample).



4  
5 **Figure 4 - Load - Displacement curves obtained for the Sample 1 during the entire**  
6 **experimental campaign**



7  
8 **Figure 5 - Load - Displacement curves obtained for the Sample 2 during the entire**  
9 **experimental campaign**

10  
11 Sample 1 and Sample 2 are representative of possible scenarios, a non-complete recovery due to poor  
12 compaction pressure during treatment and a proper healing procedure, respectively. Sample 2  
13 recovered its pristine stiffness after the first healing cycle, even if a slight decrease of the critical load  
14 is reported in further healing/loading cycles. Sample 1 showed quite different behaviour; the test  
15 after first healing cycle showed initially the same stiffness of pristine material, however, there was  
16 an abrupt deviation after 200 N. The effect of this “incomplete” healing and a comparison with a  
17 completely healed samples over different healing/damage cycles will be analysed in detail in the next  
18 paragraphs.

19  
20

## 5. Non-destructive testing (NDT) of recovery process

Ultrasound testing can be broken into many different groups and testing methods which vary depending on the various parameters used to evaluate damage/defects. In this piece of work the focus has been to evaluate various methods than focus on the evaluation of pulse/echo responses through the thickness of the tested medium to determine damage. The simplest of these methods is the Water Tank C-Scan, which uses a single element piezoelectric transducer to transmit and capture signal responses and has been already employed by several authors to evaluate crack self-healing performance [26, 27]. The next method used was a traditional ultrasound phased array system, which operates with the same basic principles as the Water Tank C-Scan method, although it relies on an array of piezoelectric transducers where the sequence of firing and capturing determines the accuracy. Traditionally, these two methods rely on evaluating the response signal in the time domain, by evaluating responses captured as peaks at the front and back wall of the testing medium (echoes), with damage being highlighted as a peak between these two surfaces of the structure.

Phased array techniques are arguably leading the field in ultrasonic testing, recent focus has been on the development of nonlinear ultrasound phased array [28, 29]. The primary focus of this work is to evaluate the effectiveness of a nonlinear based ultrasound phased array technique in imaging the recovery process of the testing self-healing structures. In order to evaluate nonlinear behaviour (the production of higher order harmonics), the presence of damage was correlated to higher harmonics.

Nonlinear ultrasound phased array and imaging techniques have been assessed by the following authors [30-34]; Ohara *et al* and Park *et al* have extensively developed, evaluated and improved the detection of open and closed cracks in metallic structures using a subharmonic phased array, while Potter *et al* has developed a nonlinear array based on the traditional total focusing method (TFM). These works have not focused on composite material or healing evaluation using these techniques.

### 5.1. CT-Scan

Figure 6 below shows the CT-Scan layout for the undamaged (green) and damaged (red) scanned areas. Initially the whole undamaged sample was scanned in order to evaluate whether damage was present in the samples. The red solid line on the sample indicates the end of the Kapton layer (40mm in length). After the first damage cycle the scanned area was reduced in order to increase the CT resolution, undamaged area resolution ~ 90 microns, damaged area resolution ~ 35 microns. CT resolution depends on the size of the area being inspected and the minimum resolution that can be obtained by the system.

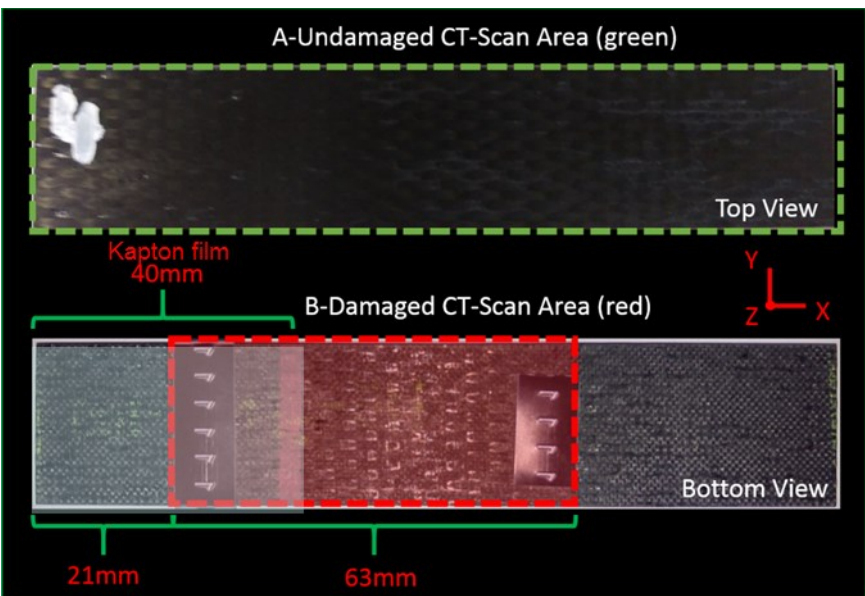
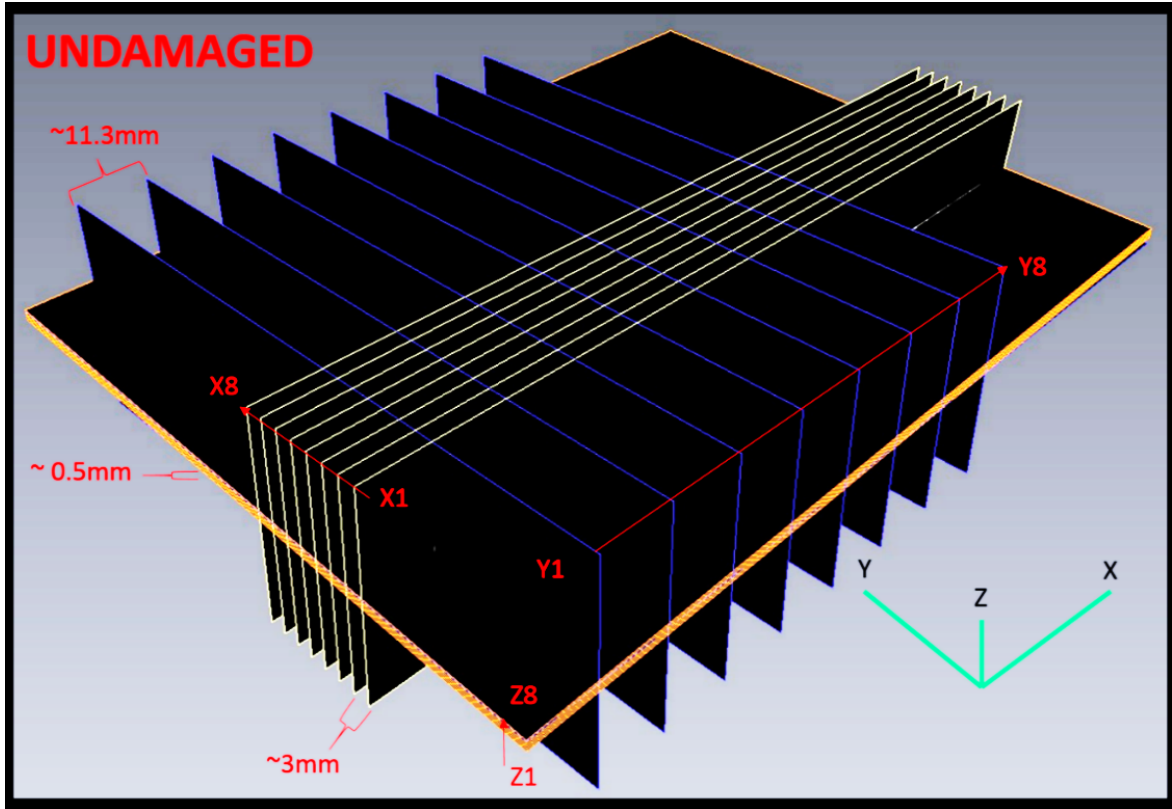


Figure 6: CT-Scan Scan Areas



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Assessment of the CT-Scan results was done by taking multiple planes; through the thickness (Z-Axis), along the breadth (Y-Axis) and along the length (X-Axis) of the samples (refer to Figure 7, Figure 8 and Figure 9 below). In the case of the undamaged sample 8 planes were used for each axis with the distances between these planes shown in Figure 7. It should be noted that each plane started on the edge of the relative surface, for example: the X1 plane starts on the edge of the length surface and then shifts 3mm for each further plane.



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15

**Figure 7: Undamaged CT-Scan Plane Allocation**

After damage a smaller area was evaluated near the expected damage regions. A similar plane setup was used, except nine planes were used for the Y-Axis. Y9 was used to evaluate an area where damage was not expected to occur, while planes Y1-Y8 were used to evaluate damage regions.

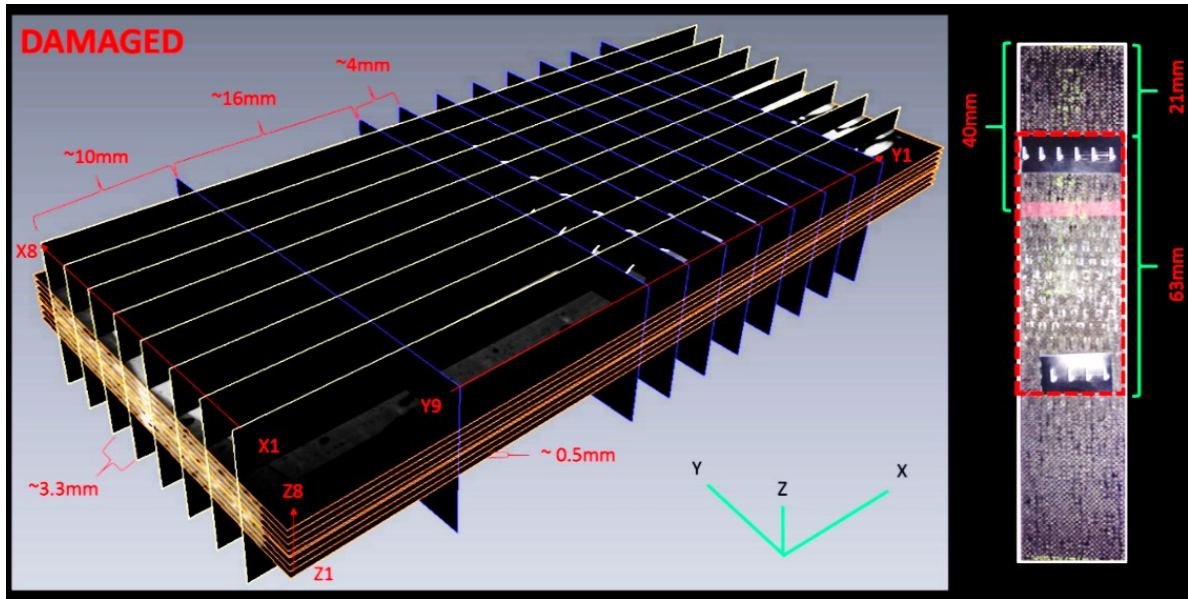


Figure 8: Damaged CT-Scan Plane Allocation

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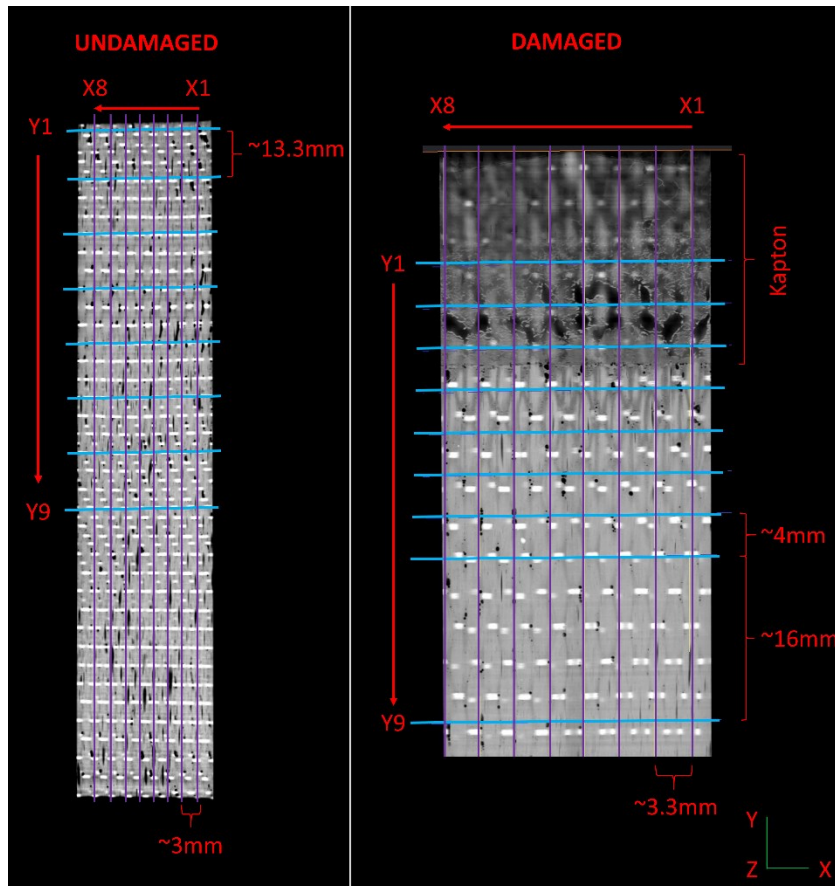


Figure 9: X and Y Axis Plane allocation

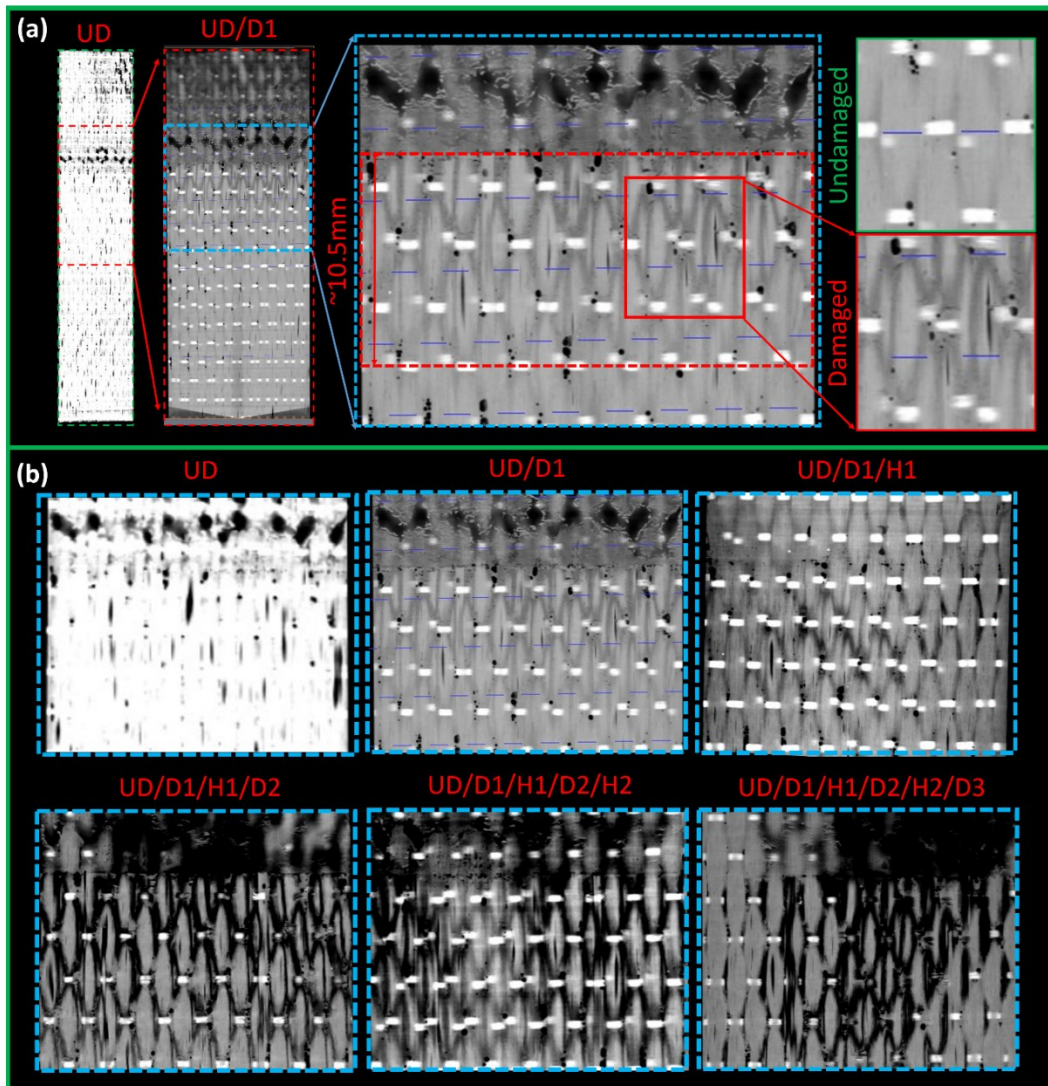
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### 5.1.1. CT-Scan Results

8

9 Figure 10, Figure 11 and Figure 13 below show the Z, X and Y-Axis planes for S1, respectively.  
10 Figure 10 focuses on the damage layer plane and shows the damage through the six damage and  
11 healing cycles. Figure 10 (a) shows the damage generated after the first damage cycle vs. an  
12 undamaged area, the areas between the weaved composite fibres becomes darker after the damage is

1 sustained during the mechanical tests. Due to the orientation and propagation of the damage along  
 2 the Z-Axis, it becomes difficult to visualise the damage, as one plane cannot sufficiently follow the  
 3 non-uniform nature of the crack propagation (refer to Figure 11, Figure 13 and Figure 14).  
 4



5  
 6 **Figure 10: Z-Axis Plane Results for S1 (Damage Layer)**  
 7

8 Figure 11 below shows the edge slice (X8), after the first mechanical test, there is clear evidence of  
 9 an extension in the Kapton layer between UD and D1 (crack propagation – black line extending down  
 10 from the top middle of the sample). After the first healing cycle (H1) the crack extension has reduced  
 11 back to the Kapton layer, although this is not clearly visible in the image, through analysis of the Y-  
 12 Axis Plane (Figure 13) this response was confirmed. While the first damage and healing cycle show  
 13 healing, the healing between D2 and H2 has reduced. After H2 there is a reduction in the damage  
 14 region but this reduction is not consistent over the whole length, leaving areas where damage persists  
 15 (again confirmed during Y-Axis Plane evaluation). The final damage phase shows that damage has  
 16 grown to the middle of the sample and is clearly evident along the section.  
 17

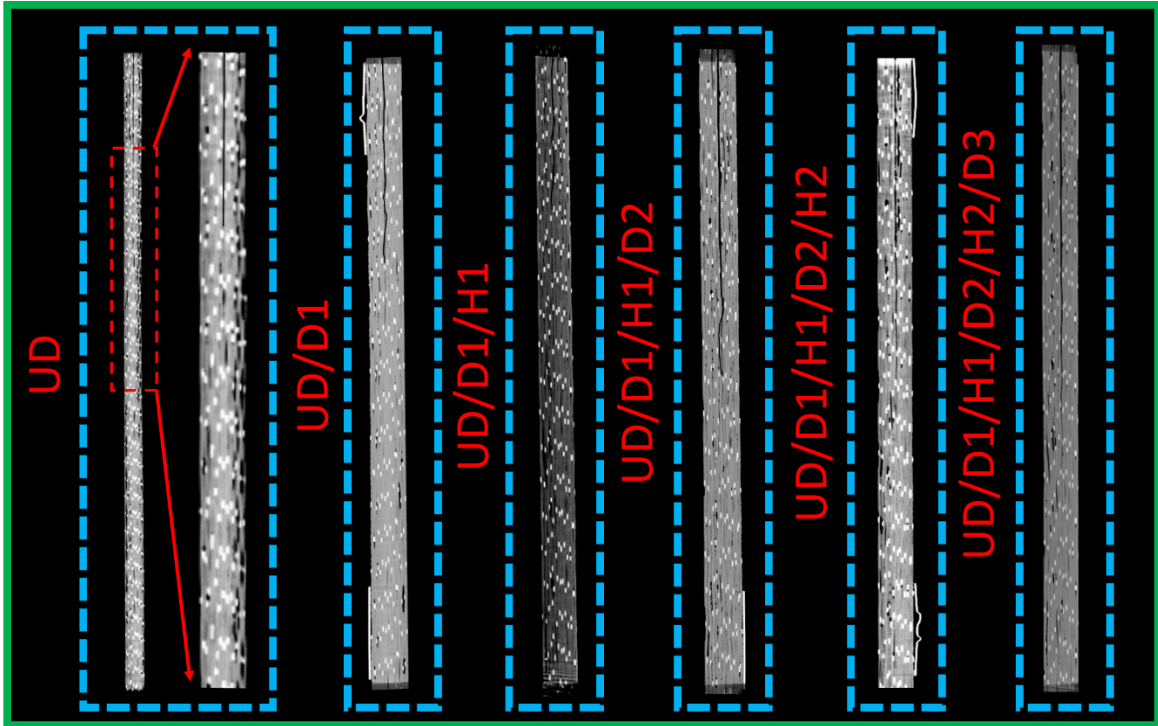


Figure 11: X-Axis Plane Results for S1 (X8)

Using the X-Axis CT-Scan information it is possible to evaluate the extent of damage and recovery for each damage state. Figure 12 below shows the total length of delamination starting from the undamaged state, which includes the 40mm Kapton layer. The diagram clearly shows the recovery of the delamination after each healing cycle, although recovery does occur, the structure weakens after each damage/recovery cycle.

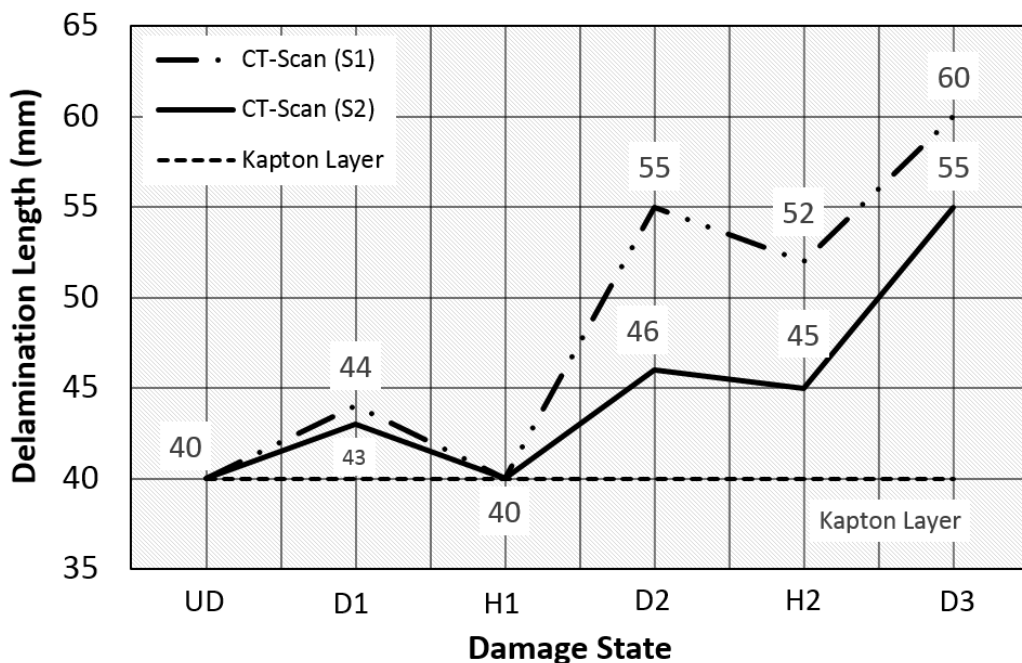
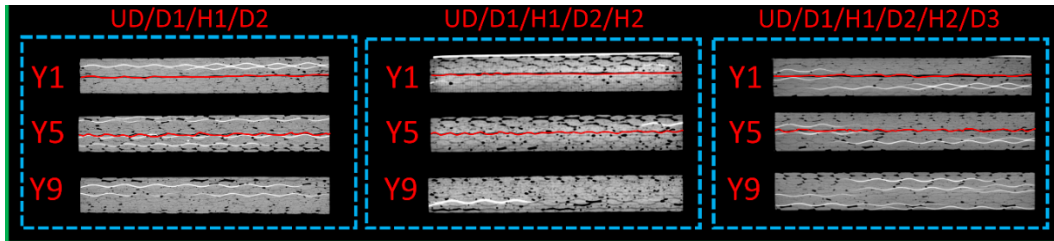


Figure 12: Damage progression and recession for each damage state S1 and S2

While Figure 10 and Figure 11 show the extent of the damage and healing process the results do not clearly show the damage interface with as much detail as the images obtained along the Y plane; which are highlighted in Figure 13 and Figure 14 below. These figures show three points along the

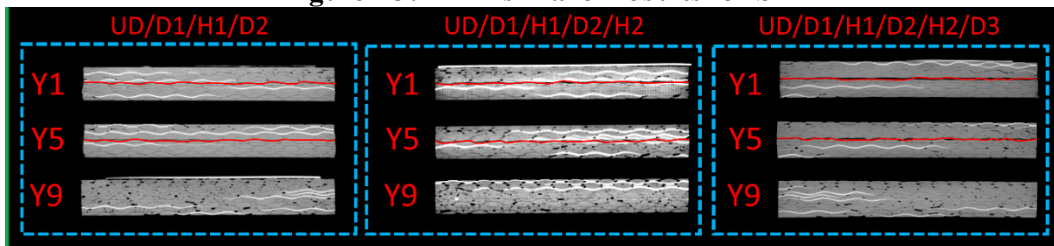
1 Y-Axis for the last three phases of testing, with Y1 being a cross-section of the Kapton layer, Y5 a  
 2 cross section of a potential damage region and Y9 being an undamage region (refer to Figure 8). The  
 3 red uniform line underlines a discontinuity within laminate cross section. A straight line is observed  
 4 at Y1 section, where kapton layer is laid, while no discontinuity is detected at Y9 section out of the  
 5 damaged area. In the intermediate location (Y5) a wavy discontinuity underlines a propagating  
 6 delamination. The material was not able to recover after the second damage/healing cycle (D2/H2),  
 7 because the crack line is still evident at section Y5 in both the samples.

8



9

10 **Figure 13: Y-Axis Plane Results for S1**



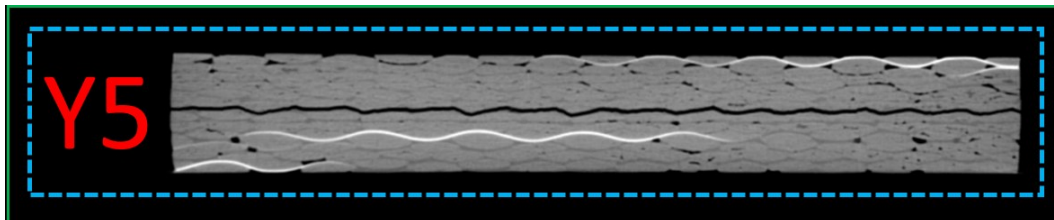
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12 **Figure 14: Y-Axis Plane Results for S2**

13

14 Figure 15 below shows a zoomed image of S2 position Y5 with the delamination visible as the black  
 15 wavy line through the middle of the sample.

16



17

18 **Figure 15: Y-Axis Plane Results for S2, D3 position Y5**

19

20 **5.2. NDT Testing**

21

22 **5.2.1. Standard phased array and water tank C-Scan Results**

23

24 Standard phased array testing was conducted using a 128 element array at 5MHz. While the water-  
 25 tank C-Scan was conducted using a single element 35MHz probe (with a step of 0.1mm). These  
 26 results are shown in Figure 16 and Figure 19 for the two samples tested. Results from the phased  
 27 array testing show the crack and Kapton layer as white (a large response) while results from the water  
 28 tank tests are shown as green. From the images, before damage was induced the Kapton layer is  
 29 visible, with the length being equal to the expected length of 40mm. The crack lengths were  
 30 calculated as the middle point between the shortest and longest crack point, this was done because  
 31 the propagation of the crack was not consistent along the width of the sample.

32 After D1 there is a clear evidence that the crack has propagated from the Kapton area for S1 and S2,  
 33 in both cases the phased array technique being more accurate and sensitive in detecting the occurred  
 34 damage. This confirms that damage has in fact occurred after the first damage cycle, this agrees with  
 35 the mechanical testing. It is evident after H1 that the delaminated area reduces back towards the end  
 36 of the Kapton layer suggesting healing, although in both cases this does not results in a return to the  
 37 original undamaged response. Once D2 has been conducted in both S1 and S2 the crack propagation

1 has exceeded that of the first damage state as the high amplitude responses move further out, this is  
 2 in line with the CT-Scans that showed a further extension of the crack after D2 (refer to Figure 11).  
 3 The mechanical testing also showed a weakening of the structure after D2, which would be expected  
 4 if the structure was not healed back to its undamaged state.  
 5 Up until D2 both S1 and S2 behaved in similar manners with respect to the extension of the damage  
 6 after the damage and healing cycles i.e. the crack extended after damage and receded after healing.  
 7 After H2, S1 does not appear to heal significantly per the phased array results, small discrepancies  
 8 are observed in the clamping area The C-scan results show that after H2, the structure seems to be  
 9 healed up to the cracked layer (which is not consistent with the CT-Scan results, Figure 12), further  
 10 adding to this inconsistency is the fact that after D3 the delamination does not seem to have  
 11 propagated further. In Figure 19, S2 shows a clear increase in delamination after D2, reduction after  
 12 H2 and a further increase after D3 for both the phased array and C-Scan results. It should be noted  
 13 that on the far right hand side for both samples for D2 and D3 there seems to be damage initiation. This  
 14 was visibly evident during the mechanical testing as splitting between the composite layers at both  
 15 ends of the sample was observed.  
 16



17 **Figure 16: Phased array (5MHz) vs. Water Tank C-Scan (35MHz) S1**

18  
 19  
 20 Figure 17 shows a comparison of the delamination lengths over the various damage states between  
 21 the CT-Scan results and the ultrasound testing for S1. S1 was used as the comparison because S2  
 22 behaved in a much more consistent manner between the healing and damage cycles. It is evident that  
 23 the results are consistent for S1 between the CT-Scan and Phased Array testing methods but after D2  
 24 for the C-Scan tests it becomes difficult to evaluate the damage extent. Whereas in Figure 18 the  
 25 different test results show more consistency throughout the whole testing procedure.

1

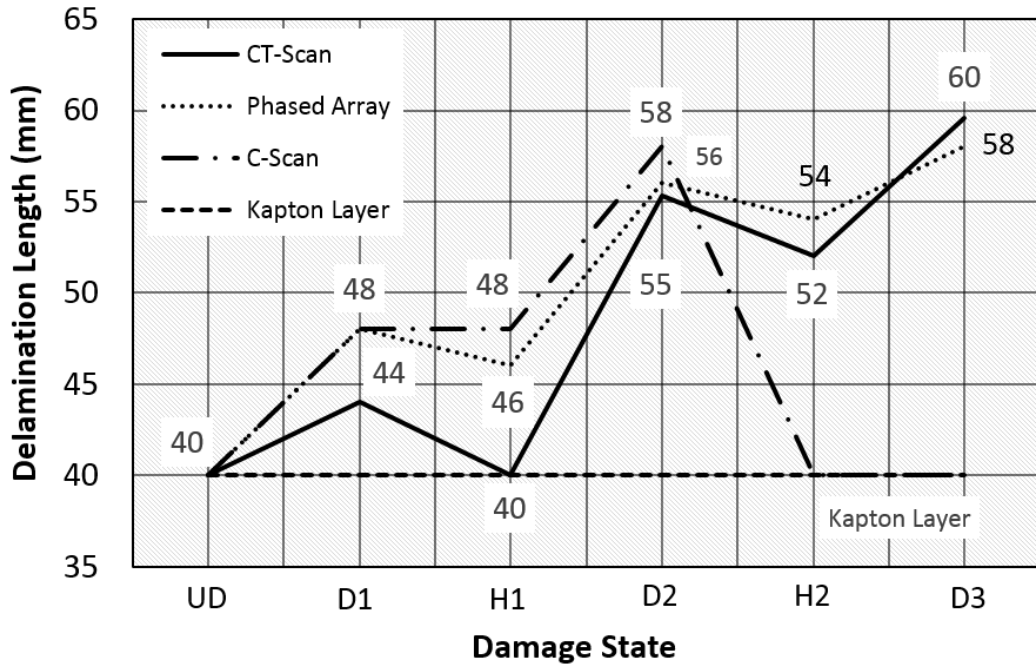


Figure 17: Phased Array and C-Scan results vs. CT-Scan S1

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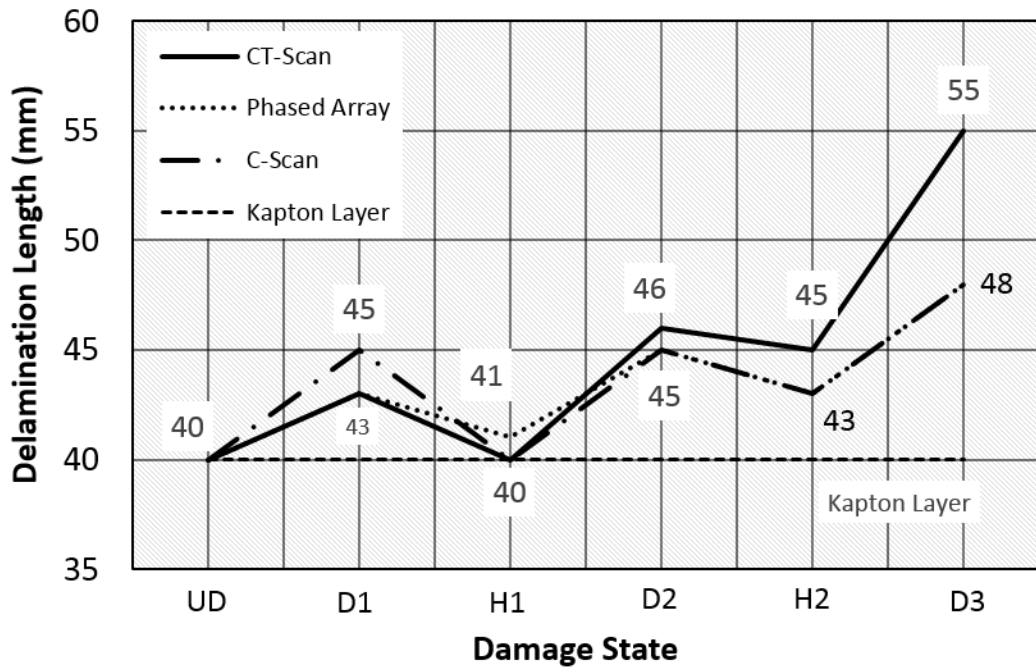


Figure 18: Phased Array and C-Scan results vs. CT-Scan S2

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Figure 19 shows the results for S2, unlike S1, there is a clear reduction in the damage area after H2, while D3 clearly shows a further extension of the delamination. The results for S2 are very consistent between the two methods used and show very similar damage propagation and reduction of each successive damage and healing cycle.

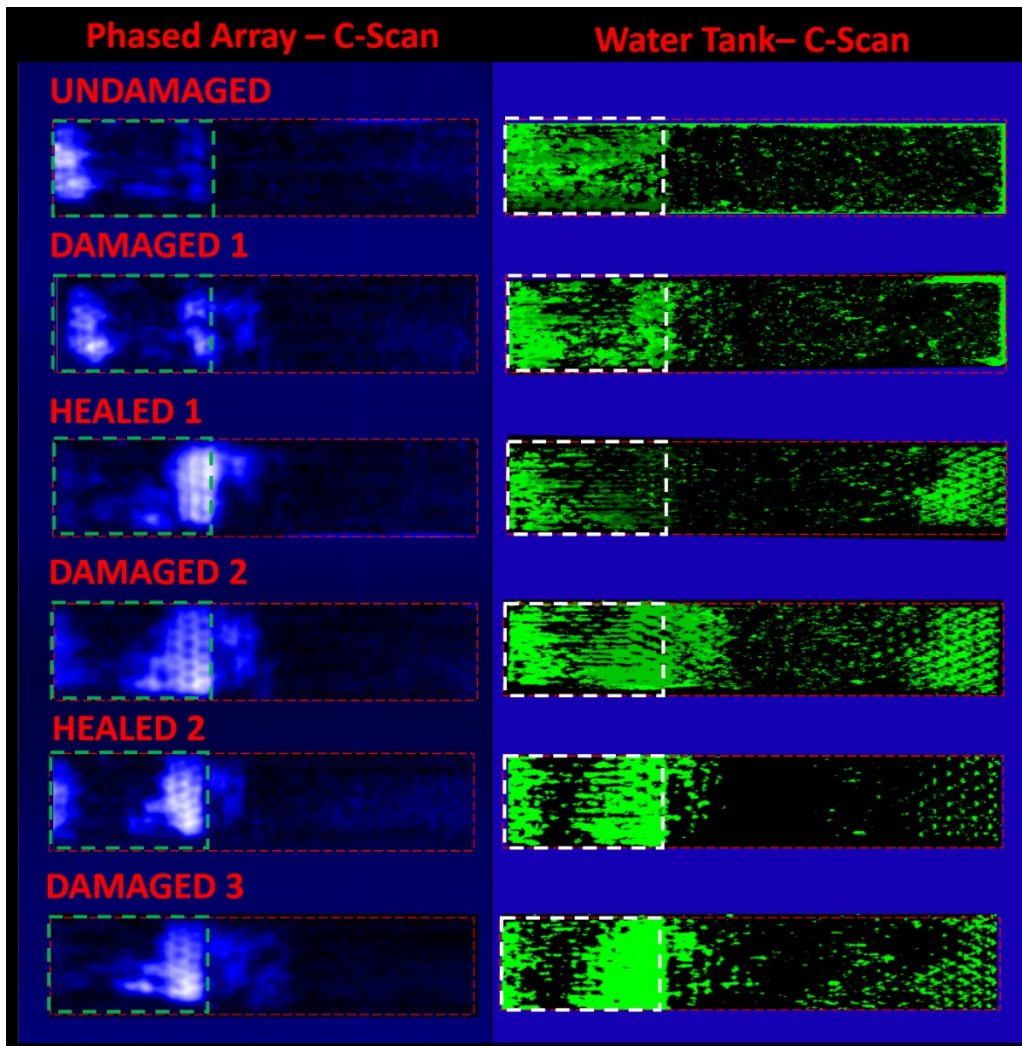


Figure 19: Phased array (5MHz) vs. Water Tank C-Scan (35MHz) S2

### 5.2.2. Nonlinear Phased array tests

Nonlinear elastic wave spectroscopy (NEWS) techniques are an innovative class of ultrasonic NDE and SHM inspection methods that measure nonlinear elastic effects in the kHz to MHz frequency range to reveal the presence of surface and sub-surface micro-flaws [34-40]. Generally, the interaction of an ultrasonic signal with material is ‘linear’, with the ultrasonic and material response being linear with respect to the amplitude of the excitation signal. However, linear/conventional ultrasonics are typically only sensitive to large defects and rely on large impedance mismatches caused by open cracks or delaminations, while nonlinear ultrasound relies on the interaction between the ultrasonic signal and discontinuities within the material, in this case related to damage, such as cracks, interfaces and voids. Nonlinear ultrasound relies on these interactions giving rise to higher order harmonics (second, third and fourth harmonics and so forth), sub-harmonics, shifts in the resonance frequencies as well as mixed frequency responses (modulation – two frequency excitation) [41]. The generation of higher order harmonics, which will be used in this piece of work, is attributed to the nonlinearity of the elastic behaviour of the material, with nonlinear Hooke’s law at the core of this phenomenon. These techniques have shown higher sensitivity in diagnosing material micro-defects such as porosity, hardening, thermal aging and corrosion when compared to linear ultrasound methods. For this work the second and third order nonlinearity parameters have been simplified in order to determine the nonlinear interaction of imbedded defects. The second ( $\beta$ ) and third ( $\gamma$ ) order nonlinearity parameter can be described by the equations below [37, 42]:



1 
$$\beta = \frac{8A_2}{A_1^2 k^2 a_1} \propto \frac{A_2}{A_1} \quad (1)$$

2 
$$\gamma \approx \frac{A_3}{A_1} \frac{48}{k^3 a_1} \propto \frac{A_3}{A_1} \quad (2)$$

3

4 where:  $A_1$ ,  $A_2$  and  $A_3$  are the respective frequency amplitudes of the first, second and third  
 5 harmonics of the recorded time domain waveforms,  $k$  is the wavenumber, and  $a_1$  is the propagation  
 6 distance.

7

8 Considering an array with transmitting elements  $j$  and receiving element  $k$  (Figure 20) the time  
 9 domain signal with a certain frequency ( $f$ ) can be represented as  $f_{j,k}(t)$ , thus the frequency  
 10 spectrum of a given time window can be expressed as:

11

12 
$$F(f) = FFT(f_{j,k}(t)) \quad (3)$$

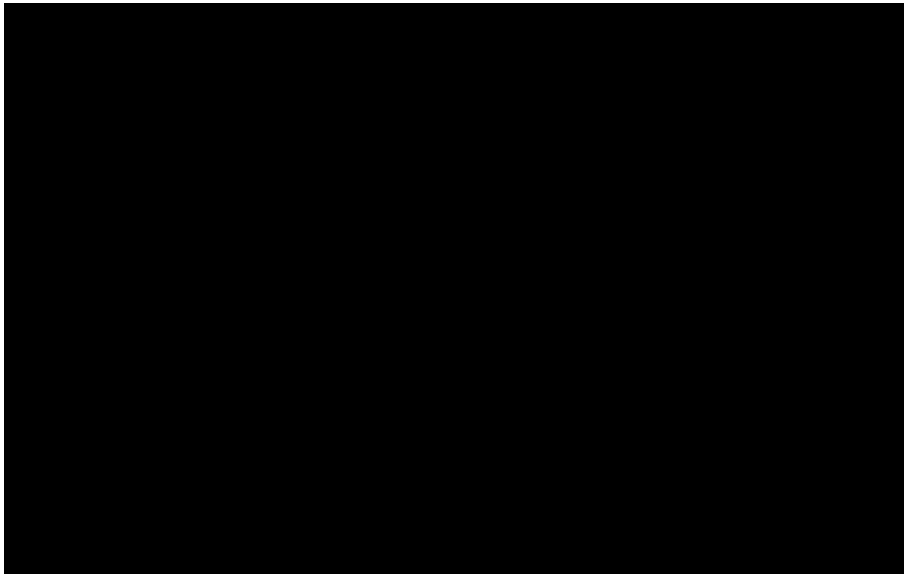
13

14 where:  $f$  represents the fundamental, second and third harmonic response of the system.

15

16 If an ultrasound array is considered and set up as in Figure 20 (a) and (b) below, multiple  $k$  transmit  
 17 and receive positions (pulse-echo testing) will result in multiple time domain response signals for  
 18 each point tested. The system comprised of a 128 element 5MHz probe half-stepped linear C-Scan  
 19 of the damage area using a set of 16 elements.

20



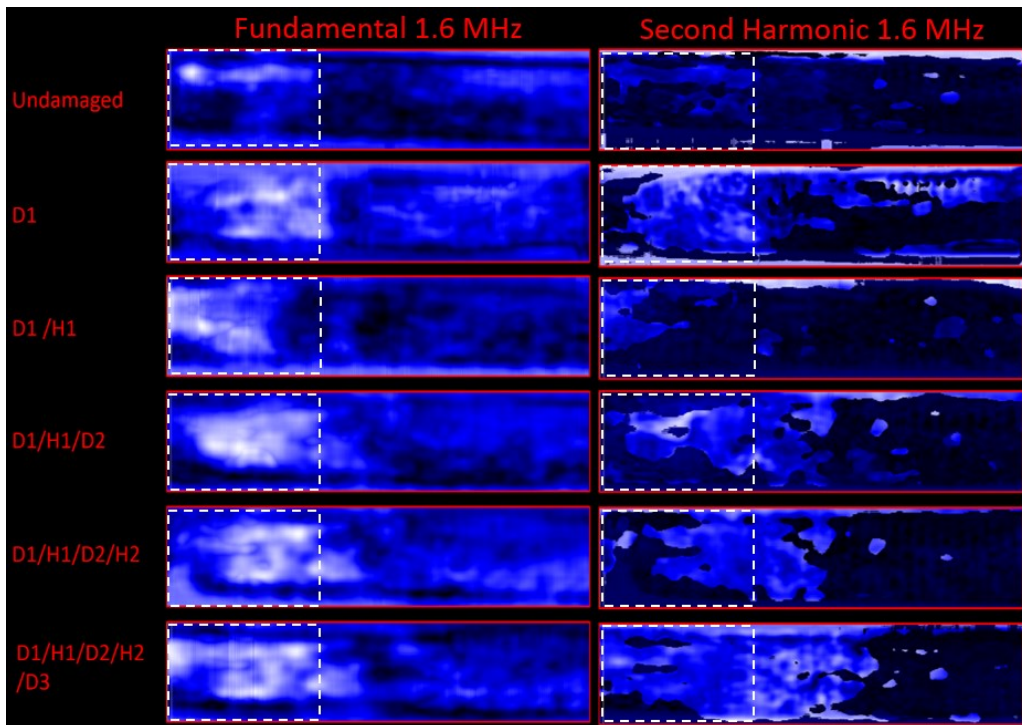
21

22 **Figure 20: Isometric (a) and cross section (b) view of scan points for an array setup**

23

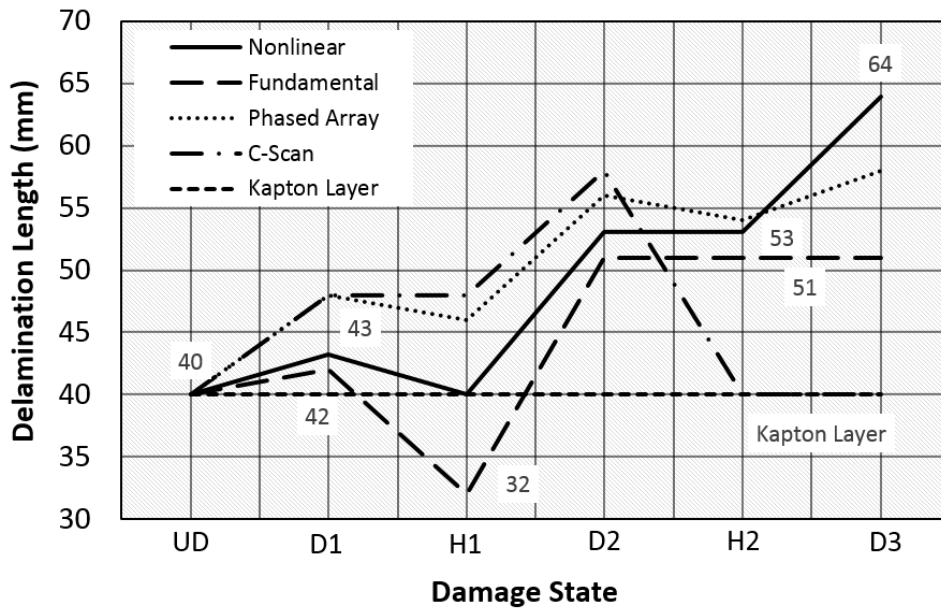
24 After considering the frequency spectrum of each captured element it is possible to determine the  
 25 responses of the higher order harmonics. The simplified nonlinearity parameters were also evaluated  
 26 (Equation 1 and 2), these results are show in Figure 21 to Figure 25 for S1. Figure 21 shows the  
 27 fundamental and second harmonic frequency responses for S1 at 1.6MHz. There is a clear increase  
 28 in the amplitude of responses between the undamaged and first damage cycle. The increase in  
 29 amplitude is a direct response to damage, as damage is induced in the sample the reflection of  
 30 ultrasonic waves will result in larger amplitude linear response, while damage will generate nonlinear  
 31 responses determined by the second harmonic. The results show a clear increase in the amplitude  
 32 after the first damage cycle. Once H1 had been completed there is a reduction in these areas in a  
 33 manner to that found with the traditional C-Scan methods. D2 shows a further extension in the

1 damage region and H2 a slight reduction that is mainly within the Kapton layer, again in line with  
 2 mechanical results, CT-Scans and C-Scans. D3 provides an even further extension of the damage  
 3 region, it should be noted that this region extends much further when evaluated using the higher order  
 4 harmonics and nonlinear parameters than when being evaluated with the fundamental frequency.  
 5



6  
 7 **Figure 21: Fundamental frequency response ( $A_1$ ) Second harmonic response ( $A_2$ ) S1**  
 8

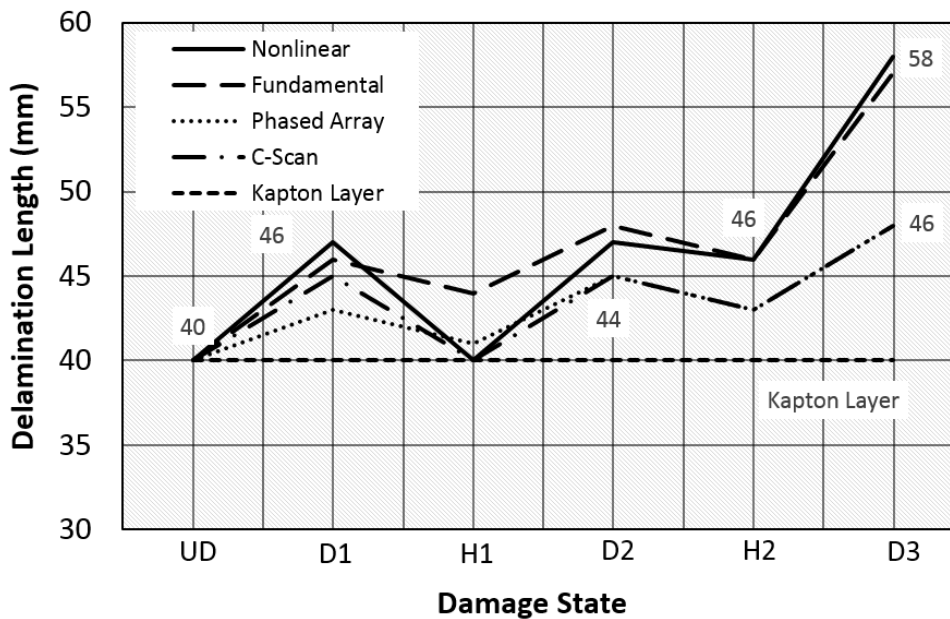
9 Figure 22 and Figure 23 show a comparison between the standard ultrasound results and the  
 10 fundamental (frequency domain) and nonlinear results. The nonlinear results have been grouped  
 11 together as they are consistent for all the parameters tested ( $A_2, A_3, \beta$  and  $\gamma$ ). The results for the  
 12 fundamental and nonlinear tests show an improved evaluation of damage at H2 and D3. Although  
 13 the damage state of S1 does not change between D2 and D3 for the fundamental results. While the  
 14 nonlinear results suggest no healing has occurred to the right of the Kapton layer between D2 and  
 15 H2. Healing is observed within the Kapton layer area after H2, as in Figure 16 earlier. The results  
 16 for S2 are more consistent between the various testing methods, except for the response of the  
 17 Fundamental, which suggests that very little healing has occurred at H1.  
 18



1  
2

**Figure 22: Nonlinear results vs. various ultrasound testing techniques S1**

3 While Figure 21, Figure 22 and Figure 26 indicate that there is healing within the Kapton region  
 4 according to the fundamental frequency response, this is not the case when reviewing the CT-  
 5 Scan results nor would this be reasonable to assume considering the presence of the Kapton  
 6 layer. The fundamental frequency response is calculated as the amplitude determined from  
 7 the FFT of the time signal through the thickness of the sample. The indicated healing up to  
 8 32mm suggests that the amplitude reflection from 32mm to the end of the Kapton layer  
 9 (40mm) is low relative to the area preceding 32mm (the evident damage area). A reason for  
 10 this apparent healing can be given by a shift of the Kapton film after the healing process as a  
 11 result of a non-uniform pressure distribution during the heating process. Thus, the layer does  
 12 not lie perpendicular to the array, resulting in lower reflections from the Kapton layer to the  
 13 array or, if at an angle great enough, no reflection at all, resulting in the low amplitude  
 14 response visualised in Figure 21 (D1/H1).



15  
16  
17

**Figure 23: Nonlinear results vs. various ultrasound testing techniques S2**

1

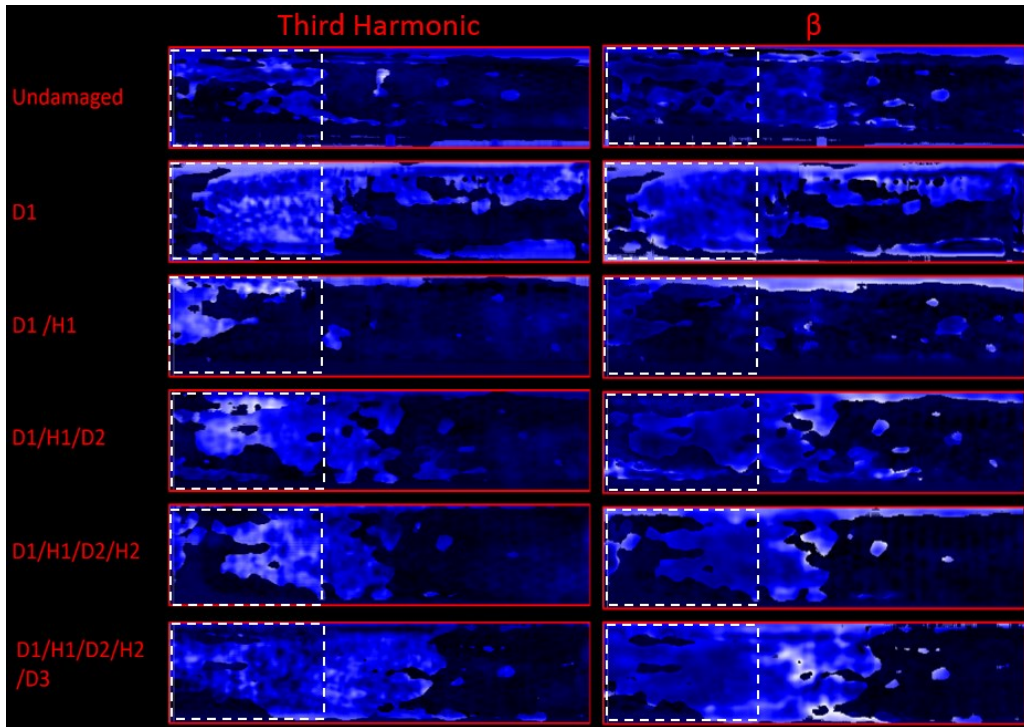


Figure 24: Third harmonic response ( $A_3$ ) Beta response ( $\beta$ ) S1

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3  
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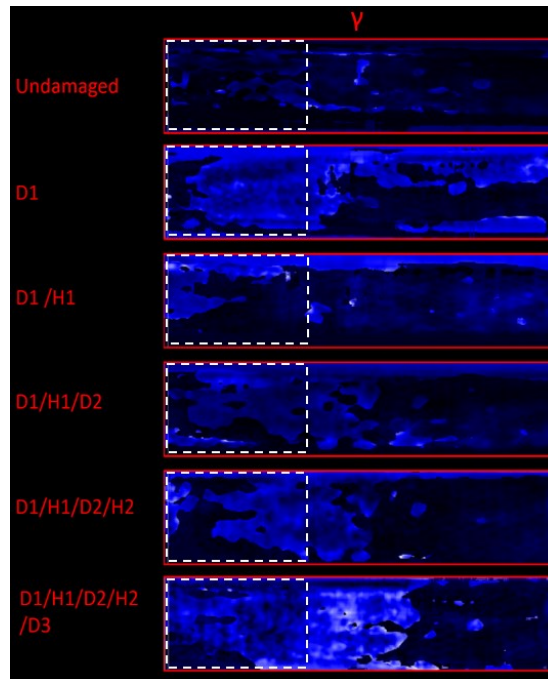
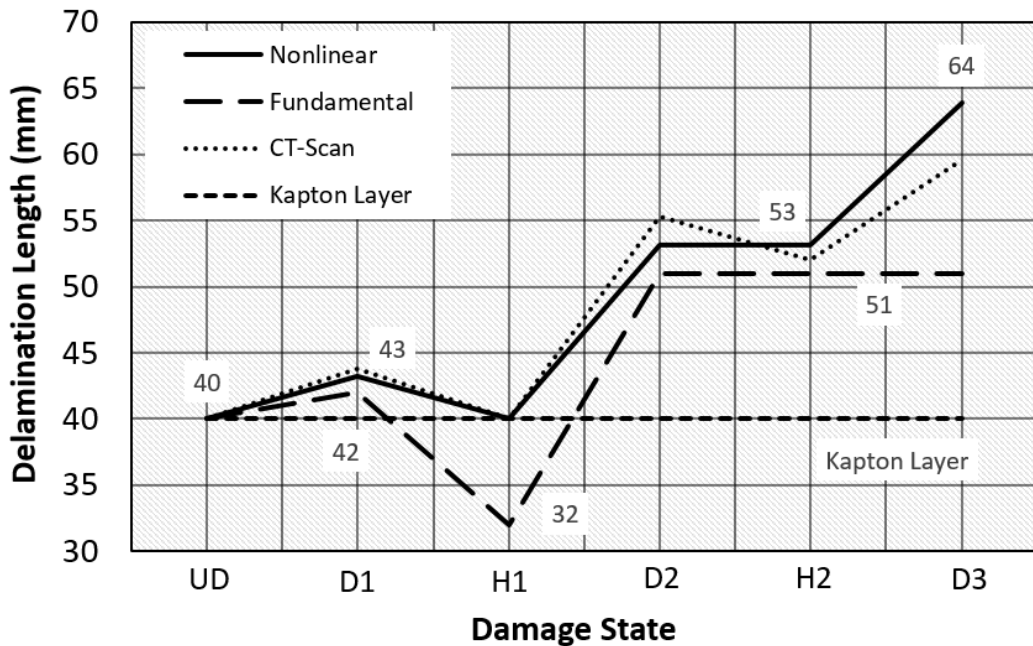


Figure 25: Gamma Response ( $\gamma$ ) S1

5  
6  
7

8 Figure 26 below compares the fundamental and nonlinear results to those determined by the CT-  
 9 Scan for S1. The nonlinear results follow the CT-Scan results very closely, and therefore provide  
 10 good information about the damage state of the sample throughout the investigated process.  
 11 Surprisingly the fundamental results do not change significantly after the second damage state,  
 12 suggesting that no healing or further damage was introduced into the sample. The fundamental results  
 13 although better than those achieved using the traditional methods, would still provide incorrect  
 14 information regarding the damage state of the structure between D2 and D3. While the nonlinear

1 method suggests that at H2 there was no reduction in the delamination from the right-hand side of  
 2 the sample, the images clearly show a reduction in damage within the Kapton area.  
 3



4 **Figure 26: Nonlinear and Fundamental responses vs. CT-Scan Results S1**

6 Multiple ultrasound techniques were evaluated in order to generate a clear understanding of  
 7 the effectiveness of each detection method to evaluate healing. From a theoretical  
 8 perspective the water tank C-Scan should be the least effective method due to the fact that it  
 9 only uses a single element (single transducer) while the phased array consisted of a 128  
 10 element transducer with 16 elements used for beam forming. The improved accuracy in the  
 11 phased array C-Scan is due to beam forming which focuses multiple signals through the  
 12 thickness of a sample, increasing the excitation energy focused at damage regions, which  
 13 increases the amplitude of the echo. Linear techniques including the water tank and phased  
 14 array system rely on impedance mismatches (i.e. changes in densities at interfaces – cracks),  
 15 which makes the detection of ‘closed’ cracks (small to no impedance mismatch) difficult using  
 16 these techniques. Crack propagation during shear testing is likely to generate areas where  
 17 closed cracks exist, making it difficult for linear techniques to evaluate these regions.  
 18 Nonlinear methods do not rely on impedance mismatches, but rather excitation  
 19 (clapping/rubbing) of damage interfaces which result in the generation of further harmonics  
 20 (second/third etc.). Thus nonlinear methods should be more sensitive to this type of damage  
 21 and, as it is shown in the results, they more accurately represent the fracture toughness  
 22 (which will be discussing in the following section) when compared to the CT-Scan (acting as  
 23 the baseline) than the linear results

## 24 6. Characterisation of healing performance

25  
 26 In order to test the effectiveness of the different NDT techniques illustrated in the previous  
 27 paragraphs, the values of the initial crack length evaluated with both the linear and non-linear phased  
 28 array for the three different healing/damage cycles were used to calculate the mode II fracture  
 29 toughness ( $G_{II}$ ) and the results were compared with the results obtained from the CT-Scan images.  
 30 Analysing the loading curves obtained during the ENF test, it is possible to observe that the first  
 31 portion is linear and it corresponds to the initial elastic response of the sample. Once a critical Load  
 32 ( $P_{NL}$ ) is reached, the samples show a more complex non-linear behaviour. This change in the response  
 33 of the sample is due to the ENF sample geometry. Indeed, because of the ductility of the resin and

1 due to the presence of the initial edge crack, the samples respond to a bending load by showing crack  
 2 growth and propagation prior to fast fracture. Table 3 illustrates the values of the critical load at the  
 3 onset of stable crack propagation that were identified for all the curves and the extent of the initial  
 4 delamination according to the CT-Scan, the linear phased array (LPA) and the non-linear phased  
 5 array (NLPA).

7 **Table 3: Critical Load values for each damage cycle and extension of the initial crack**  
 8 **evaluated by linear and non-linear phased array and compared with CT-Scan measurement**

|                                       | S1 D1 | S1 D2 | S1 D3 | S2 D1 | S2 D2 | S2 D3 |
|---------------------------------------|-------|-------|-------|-------|-------|-------|
| $P_{NL}$ [N]                          | 780   | 179   | 252   | 650   | 583   | 341   |
| initial crack length (a LPA) [mm]     | 30    | 36    | 44    | 30    | 31    | 33    |
| initial crack length (a NLPA) [mm]    | 30    | 33    | 43    | 30    | 30    | 36    |
| initial crack length (a CT Scan) [mm] | 30    | 30    | 42    | 30    | 30    | 35    |

11 From these data it is possible to evaluate the mode II fracture toughness by following the compliance  
 12 method demonstrated by Cairns et al [43] and using the equation:

$$G_{II} = \frac{9P^2 Ca^2}{2w(2L^3 + 3a^3)} \quad (4)$$

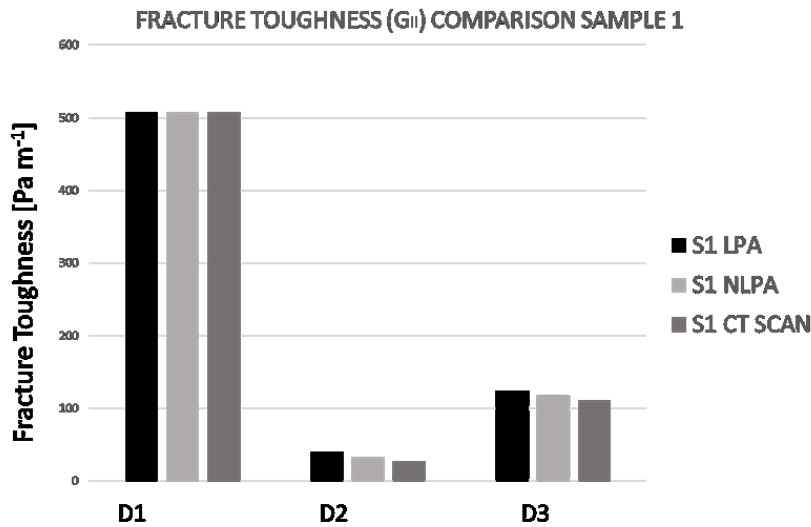
16 Where P represents the load at the onset of the delamination propagation, C is the compliance of a  
 17 simple supported beam with a crack extending from one ledge towards the middle section, a is the  
 18 length of the initial crack, w is the width of the sample and L the span length used during the test.

20 The value of the compliance can be calculated from the following equation:

$$C = \frac{2L^3 + 3a^3}{8Ewh^3} \quad (5)$$

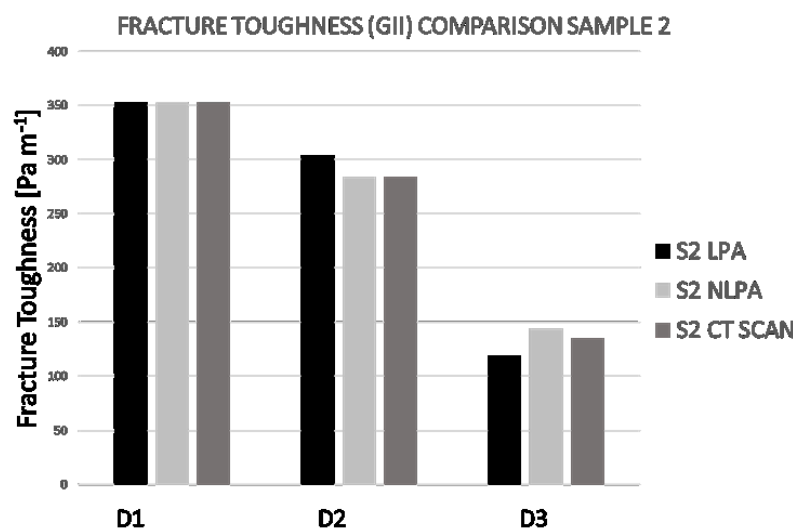
23 where E represents the elastic modulus of the material and h is half of the thickness of the sample.

25 The values of the fracture toughness calculated for both samples over the three healing/damage cycles  
 26 with linear and non-linear phased array and CT-Scan are represented in Figure 27 and Figure 28.



27 **Figure 27: Comparison between fracture toughness of S1 evaluated from linear and non-**  
 28 **linear phased array inspection and compared with CT-Scan analysis data.**

1 As it is possible to see from Figure 27, in case of S1 after the first damage cycle (which has the same  
 2 value because the initial crack length was given by the Kapton layer) the values of GII are strongly  
 3 affected by the different techniques used. It is important to remember that the CT-Scan results of the  
 4 crack length, in this case, are being used as the baseline as the CT-Scan is the most accurate method  
 5 available. By determining the fracture toughness (directly related to the crack length) of the linear  
 6 and NLPA methods and comparing them to the CT-Scan results, it is possible to measure which  
 7 method more accurately determines the damage state of the sample. Therefore, the calculated percent  
 8 error between the fracture toughness of the linear and NLPA against the CT-Scan provides a  
 9 quantitative method to determine which technique is more accurate. The error between the linear  
 10 phased array and the CT-Scan was +48.1% (vs +22.5% of the NLPA) for the second cycle and  
 11 +11.4% (vs +5.5% of the NLPA) for the third cycle, which showed an error of twice that determined  
 12 using the NLPA. Therefore it is clear that the non-linear phased array technique is more accurate  
 13 than the linear technique as it more accurately describes the damage state of the sample. Furthermore  
 14 it is important to underline that the NLPA is also more accurate in the case of the incomplete or  
 15 partial healing (D2).  
 16



17  
 18 **Figure 28: Comparison between fracture toughness of S2 evaluated from linear and non-**  
 19 **linear phased array inspection and compared with CT-Scan analysis data.**  
 20

21 Results from S2 are illustrated in Figure 28 and they are consistent with what observed in the previous  
 22 sample. Indeed, also in this case it is possible to clearly see that the increased accuracy of the non-  
 23 linear analysis reduces the error with the CT-Scan. In particular, during the second healing/damage  
 24 cycle (D2) it is possible to observe that while the LPA technique gives an error of +7.2%, the NLPA  
 25 method shows exactly the same reading of the CT-Scan measurement. As for the third cycle, results  
 26 in D3 show an error of the LPA of -11.97%, while NLPA data decreases this difference to +6.65%.  
 27 The samples studied showed a quite different sensibility to the healing treatment. The S1 sample  
 28 recovered its mode II strength with lower efficiency compared to the S2 sample. Even if the neat  
 29 resin proved its capability to recover severe damages after thermally activated healing, selection of  
 30 effective healing procedures and parameters are quite critical and are beyond the context of the  
 31 present paper.  
 32

### 33 7. Conclusions

34  
 35 The performance of different non-destructive techniques in assessing the effectiveness of thermally  
 36 activated self-healing polymers based on reversible Diels–Alder reaction was investigated during  
 37 multiple damage/healing cycles.  
 38 Five successive damaged and healed states were studied using nonlinear ultrasound techniques by  
 39 measuring the extent of damage propagation and healing recovery during each cycle. The results

1 were compared to standard linear ultrasound and benchmarked against CT-Scan results. While linear  
2 phased array techniques provide a good approximation of the extent and recover of damage in the  
3 structure, in some cases they fail to provide a clear and accurate image of damage evolution. The  
4 increased accuracy of the non-linear approach to detect bonded regions over the traditional linear  
5 phased array was shown by evaluating the values of mode II fracture toughness. Results from the  
6 experimental campaign showed that in the passage from a linear to a nonlinear approach, it is possible  
7 to increase the resolution of the analysis, reducing the difference with the CT-Scan readings up to  
8 50%. This work demonstrated the successful use of a nonlinear ultrasound phased array method for  
9 the assessment of the efficiency of recovery of self-healing samples.

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15 Agreement 314768”

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