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The Role of Semi-Curing in Liquid Composite Moulding

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ABSTRACT

This study investigates how Semi-Cured interfaces form and preform in Liquid Composite Moulding processes in order to support the drive towards low cost and high rate manufacture of complex composites. A two-step program was devised. Firstly, the effect on neat resin toughness properties arising from additional thermal cycling needed for Semi-Curing was explored. This confirmed that the Semi-Curing process had little effect on plane-strain fracture toughness values. Secondly, Semi-Cured laminates with elements initially cured to varying degrees of cure were manufactured and tested in Mode I and Mode II. The results of these tests indicated interfacial properties are fully retained in Mode II and a reduction in Mode I is seen after the resin enters the post-gel stage. These initial results demonstrate the usefulness of Semi-Curing to integrate preforms up until the gel point of the material.

INTRODUCTION

There is currently a move to explore higher rate and lower cost composite manufacturing processes for the production of primary aerospace parts [1,2]. This is enabling the production of larger more integrated structures produced through infusion processes. Creating more highly integrated structures reduces the need for post cure joining operations and secondary bonding. However, the creation of such large, complex, integrated structures is not without its challenges, not least of which are the risks surrounding the potential for preform misalignment and infusion. A potential solution to these problems is seen within the Semi-Curing process. The Semi-Curing processes is a manufacturing process whereby sub-elements of an integrated structure are taken and initially semi-cured. After this initial step the semi-cured sub-elements can be assessed for quality. This creates a set of pre-inspected, semi-cured elements which can be combined with dry preforms to manufacture the integrated structure in a final infusion and cure step. As a result, fewer or no additional post cure joining

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operations are needed. The key steps in the Semi-Curing process are outlined in Figure 1.

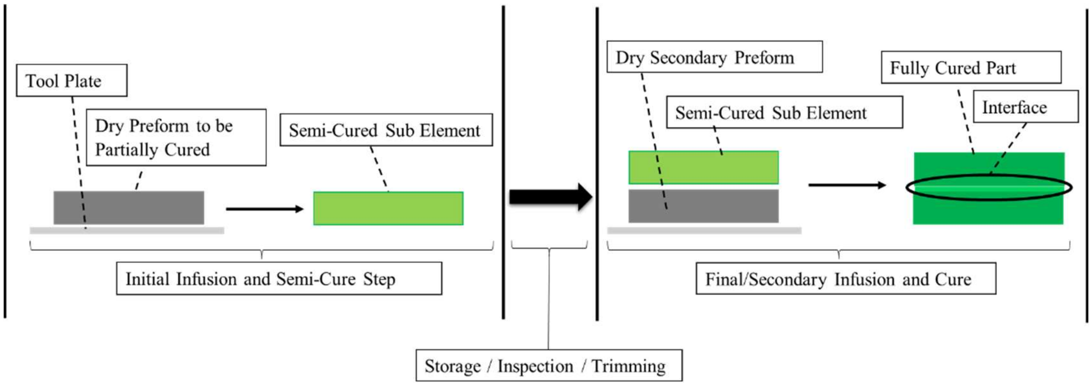

Figure 1. Schematic outlining the steps in the Semi-Curing Process.

The foundations of the Semi-Curing process are rooted in the work surrounding the staged curing of composites conducted by White and Kim [3]. Stage curing was originally proposed to reduce thermal spiking in thick composite parts by incrementally semi-curing stacks of prepreg together. As each stack of prepreg gets deposited and heated, the degree of cure (DoC) advances in the previously deposited layers. Following on from this, the concept of melding has been brough forward by Corbett and Griffiths [4]. This process involves the production of composite parts where small regions of a part remains partially cured while the wider structure is fully cured. These regions have chemically active surfaces available for reacting and forming new bonds, thus avoiding the need for secondary bonding when mated with a similarly partially cured surface.

Examples of a modified co-curing process on infused carbon composites similar to Semi-Curing have also been proposed [5–8].Within these works Moosburger-Will *et al.* have established that there is interdependence between the interfacial properties and the degree of cure of the semi-cured element [8].

Initial explorations on the effect on thermo-physical and mechanical properties of partially curing RTM6 resin prior to fully curing it have also been carried out [9]. However, limited work has been carried out to explore the effect of these modified co-curing processes on the toughness of neat resin when subjected to the additional thermal cycling required for Semi-Curing.

This work builds on the state-of-the-art in Semi-Curing in two ways. Firstly by exploring the performance of fully cured laminates that had initially semi-cured elements in both Mode I and Mode II. Secondly, by exploring the effect of the semi-curing process on the toughness of the neat resin.

To quantify the performance of the interface both Mode I, Double Cantilever (DCB), and Mode II, End Notch Flexure (ENF), tests were carried out. The inclusion of Mode II is important as laminates undergoing dynamic fracture events, such as those that occur during impact, are primarily loaded in shear. Understanding this is critical if Semi-Curing is to be employed on interfaces expected to fail under shear loads and this failure has yet to be characterized for composites made using this manufacturing approach. For this work, any form of surface treatment, contamination, or preparation (such as the use of peel-plies) has been avoided in the manufacture of the Semi-Cured interfaces. This was done with the aim of isolating the residual activity as the lone variable affecting the interfacial properties between the semi-cured elements. Post testing, DCB samples were sectioned and observed under scanning electron microscope (SEM).

To explore the effect of the Semi-Curing process on resin toughness, Single Edge Notched Bending (SENB) tests were preformed on cast resin specimens to determine the material's critical stress intensity factor and critical strain energy release rate. These metrics are measures of the plane strain fracture toughness of the materials. The SENB specimens were manufactured using representative cure cycles, typical of what could be seen in a Semi-Curing process. The samples were imaged under SEM to observe the fracture surfaces produced from fracture testing.

This paper will first give the materials used in this work before outlining the manufacturing processes employed. The manufacturing sections will cover both the laminates and the castings. Leading from this, the testing and imaging procedure is explained. This will then feed into a results and discussions section. Finally conclusions will be drawn around the feasibility of Semi-Curing for the material system used.

MATERIALS

At all points in this work a commercially available, single part epoxy infusion resin was used. The epoxy material is representative of the type of thermoset epoxies used for infusions within the aerospace industry. The fibre reinforcement used in the creation of the Semi-Cured laminates was a carbon fibre, biaxial, non-crimp fabric (NCF) with a 3mm tricot stitch in a 0°/90° orientation, with an areal weight of 480g/m^2 and had powder binder applied.

METHODS

Manufacture Of Single Edge Notch Bending Specimens

To explore the effect of the non-conventional cure paths resulting from the Semi-Curing process resin was cast into blocks before being machined into SENB specimens for mechanical testing. A total of six castings were completed. The purpose and cure path of each casting is outlined in Table I. Block 1 was cured using the recommended cure schedule provided by the manufacturer. Block 2 was cured using a lower curing temperature and was cured in a single step. Blocks 3-6 explore the effect of employing cure schedules mimicking the Semi-Curing process. Additionally, a lower and a higher initial cure temperature was used during the semi-curing stage to see what, if any effect this has on the fracture toughness of the resin. The Semi-Curing process happens in the pre-gelled state as the DoC at gelation is 0.71-0.77 for the material studied here.

To create the cast resin blocks resin was first degassed for 30 minutes before being poured between two parallel, release agent coated, glass plates, separated by a Polytetrafluoroethylene (PTFE) spacer containing a machined slot. The glass plates were then clamped together before being stood upright in an oven and cured with their prescribed cure schedule. The resulting cast blocks were then machined into SENB specimens using a CNC router fitted with a 1mm milling bit. The specimens met the plain strain dimensional requirements outlined in ASTM D5045 [10], measuring

48.9mm × 11.1mm × 5mm with a 1mm wide notch machined into them. Prior to testing each sample was pre-cracked using a fresh razor producing the required pre-crack length as outlined in the ASTM standard.

TABLE I. SINGLE EDGE NOTCH BENDING SPECIMEN DETAILS.

Block No.	Initial Doc	Initial Cure Temp. (°C)	Secondary Cure Temp. (°C)	Details
1	0	180	N/A	Baseline @180°C (recommended temperature)
2	0	140	N/A	Baseline @140°C (lower cure temperature than recommended)
3	0.3	180	180	Semi-cure below gel and with high temp
4	0.3	140	180	Semi-cure below gel and with lower temp
5	0.7	180	180	Semi-cure to gel and with high temp
6	0.7	140	180	Semi-cure to gel and with lower temp

Manufacture of Mode I and Mode II Samples

Using the Semi-Curing process outlined in Figure 1, flat panels consisting of two sub-elements stacked on top of each other with a horizonal interface between them were manufactured using the two-step cure process. In the initial stage, the semi-cured element was created by infusing and advancing the degree of cure of the resin by a set amount. This element was then placed on top of the secondary dry element before the secondary infusion and cure. Thus creating the interface of interest between the initially semi-cured sub element and the freshly infused lower element. A total of six panels were manufactured. The final layup of each of the laminates was $[(90/0)_4,(+95/+5),(-5/-95),(0/90)_4]$. The mid plane contains fibres at +/-5° to avoid nesting of the fibres, which can lead to bridging, which in turn can lead to artificially higher Mode I resistance curve being reported. The manufactured dimensions of each panels were 350mm × 350mm × 4.7mm. A 12 µm thick PTFE insert was included at the midplane to act as a crack initiator for testing.

Of the six panels, one was produced through a single infusion and cure step to act as a base-line for comparison against laminates produced through the Semi-Curing process. Table II outlines the manufacturing details of all six laminates. This table includes the partial degrees of cure investigated in each laminate and the reason for their selection.

Two types of test specimen were machined from the panels; 1) 148 mm × 20 mm Mode I DCB specimens with a 75 mm PTFE insert; 2) 170 mm × 20 mm Mode II ENF specimens with a 50 mm PTFE insert.

TABLE III. LAMINTE MANUFACTURING DETAILS.

Laminate ID.	Manufacturing Process	Initial Doc	Reason for DoC Chosen
BL0	Single Infusion	N/A	Baseline for comparison with traditional methods
SC0.2	Semi-Cure	0.2	DoC below gel and Tg below room temperature
SC0.3	Semi-Cure	0.3	DoC below gel and Tg around room temperature
SC0.5	Semi-Cure	0.5	DoC below gel and Tg above room temperature
SC0.7	Semi-Cure	0.7	DoC roughly at gel
SC0.9	Semi-Cure	0.9	Comparable to adhesive bonding

Testing Methodology

SINGLE EDGE NOTCH BENDING TESTING

Fracture toughness testing of the SENB specimens was undertaken in accordance with ASTM D5045 [10]. Testing was carried out on a Shimadzu AGS-X electro mechanical universal testing machines, the same test machine which was used for all testing in this work. For SENB testing the test machine was fitted with a 1kN load cell. Testing was carried out using a 3-point bend set-up with the test machine under displacement control with a constant cross head displacement of 10mm/min. During the test both cross head displacement and load were recorded.

To calculate the plane strain fracture toughness values, K_{Ic}, from the SENB tests Equation (1) was used. Where P_{Ic} is the peak load from the test, $B$is specimen thickness (5mm), W is specimen width (11.1mm) and *f(x)* is calculated using Equation (2) where $(0 < x < 1)$.

$$K_{Ic} = \left(\frac{P_{Ic}}{BW^{1/2}}\right) f(x) \tag{1}$$

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1 - x)(2.15 - 3.39x + 2.7x^2)]}{(1 + 2x)(1 - x)^{3/2}} \tag{2}$$

To calculate the plane strain energy release rate, G_{Ic}, from the SENB tests Equation (3) was used. Where a is the crack length (milled notch plus pre-crack), U is the energy released during the test and corrected to account for machine compliance, and η_e is a calibration factor found as a ratio of a/W.

$$G_{Ic} = \eta_e U/[B(W - a)] \tag{3}$$

MODE I TESTING

Mode I performance of the laminates made through the Semi-Curing process was assessed through DCB testing. This testing was carried out according to ASTM D5528-13 [11]. Prior to testing steel strap hinges were bonded to the top and bottom surfaces of the samples with Araldite paste adhesive. This was done to apply an opening load to the specimen arms. To observe crack growth in the specimens the sides were spray painted with a fine layer of white paint. On the white paint a ruler was painted to measure the crack growth.

The universal testing machine was fitted with a 500N load cell. It was used in conjunction with an iMetrum Video Gauge to record the tests so that that crack growth could be measured. Testing was preformed under displacement control with a constant cross head displacement of 2mm/min up until the crack growth exceeded 50mm. Crosshead displacement, applied load, and crack growth were all recorded.

To calculate Mode I critical strain energy release rate, G_{Ic}, Equation (4) was used. Where P is the applied load, δ is the load point displacement, b is the specimen width (20mm), and a is the delamination length. The $|\Delta|$ term is a correction factor determined by generating a least squares plot of the cubed root of the compliance versus delamination length. Where the compliance is defined as δ/P. The value of $|\Delta|$ is then found as the point on the x-axis where the least squares plot intersects.

$$G_{Ic} = \frac{3P\delta}{2b(a + |\Delta|)} \tag{4}$$

MODE II TESTING

Mode II performance of the laminates made through the Semi-Curing process was assessed through ENF testing. The ENF testing, carried out in a three-point-bend setup, was undertaken following ASTM D7905 [12]. Both non-pre-crack (NPC) and pre-crack (PC) tests were carried out, as outlined in the testing standard. The testing was again conducted with a Shimadzu AGS-X Series universal tester. For the ENF testing it was fitted with a 10kN load cell. Testing was carried out under displacement control with a constant crosshead displacement of 0.5mm/min. A video gauge was again used to record crack growth. As such the sides of the specimens were spray painted white to aid in the observation of crack growth. It also allowed for the marking of the specimens for compliance calibration tests as outlined in the standard [12]. Cross head displacement, load, and time were all recorded.

To determine the Mode II performance of the interfaces the Mode II critical strain energy release rate, G_{IIc}, was calculated. It was calculated using Equation (5). Where m is a calibration coefficient found through the compliance testing carried out prior to each test set. P_{max} is the max load from the fracture test, a_0 is the crack length caused by fracture, and b is the specimen width (20mm).

$$G_{IIc} = \frac{3mP_{max}^2 a_0^2}{2b} \tag{5}$$

Imaging

To image the fracture surfaces of the DCB and SENB samples a Hitachi TM3030Plus tabletop SEM was used. Prior to imaging SENB samples were sputter coated with a silver coating.

RESULTS AND DISCUSSION

Neat Resin Fracture Toughness Results and Discussion

Figure 2, outlines the results of the SENB testing to determine the effect of varying cure paths on the neat resin properties of the resin. Specifically, the plain strain facture toughness of the neat resin. Results indicate that the Semi-Curing process does not appear to affect the plane strain fracture toughness of the neat resin. Additionally the temperature at which semi-curing was taking place at does not affect the results. Nor does the extent to which the resin was partially cured prior its secondary ramp and cure. Figure 3 shows the surface topography of representative samples from each sample group. As can be seen in the figure, there is no significant difference between the fracture surfaces, bar the sample fully cured at 140°C which shows a slightly smoother surface. This may be the result of the resin never reaching the recommended curing temperature of 180°C.

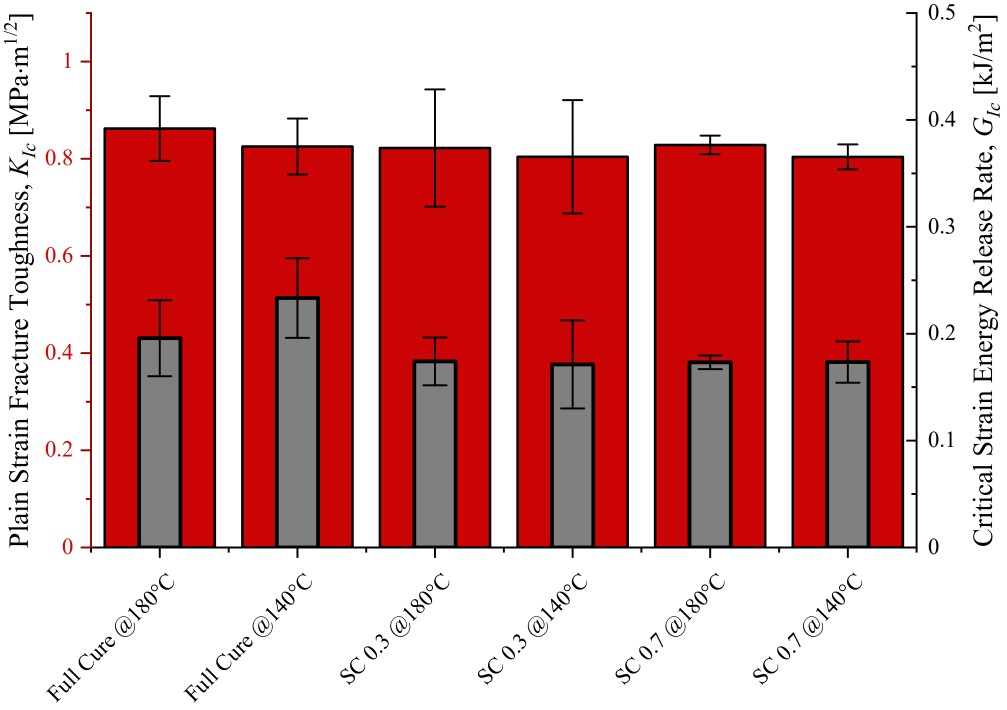

Figure 2. SENB test results. With SC denoting initial degree of semi-cure.

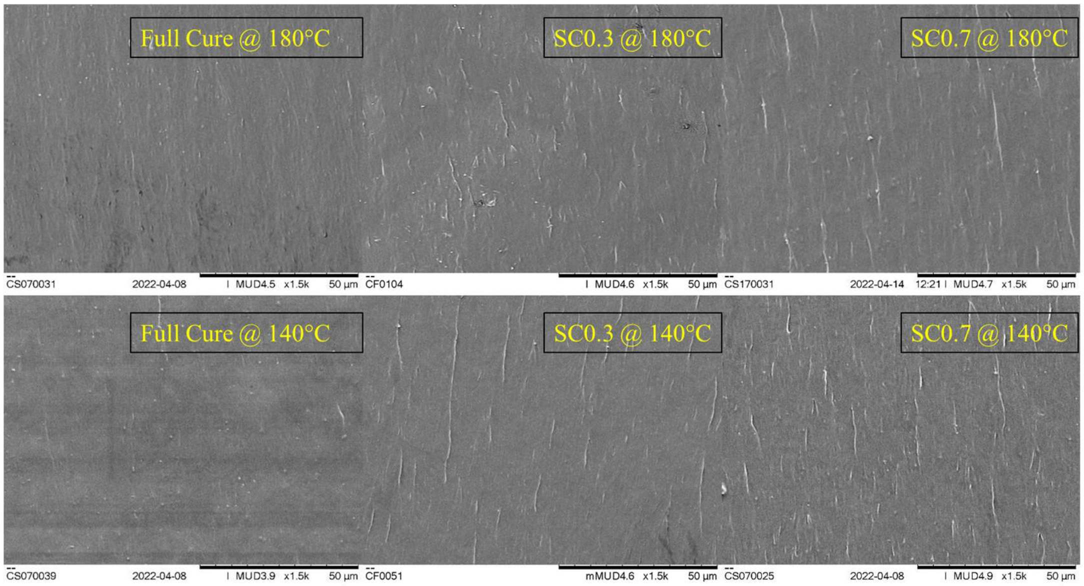

Figure 3. SEM of SENB fracture surfaces.

Mode I and Mode II Performance

Figure 4 shows the results from the DCB and ENF tests carried out on the samples machined from the laminates made through the Semi-Curing process. In the case of the ENF testing, only the NPC test results are shown. PC test results, when calculated, showed near identical results to those for the NPC tests.

The result for the Mode II tests indicate that the Semi-Curing process has no detrimental effect on interfacial properties when being loaded in shear. This result is very encouraging as load transfer between the NCF plies happens in shear in the interleaf between the plies. It is also the first time this load case has been applied to laminates made through this type of altered co-curing process.

Mode I performance was also promising as can be seen in Figure 4. Interfacial properties were broadly retained only falling off past the gel point of the resin. With the gel point of this resin system being between 0.7-0.79 DoC. This is when compared to the baseline panel which was produced through a single infusion and cure. Similar trends have been observed in literature. In these cases it was also surmised that Semi-Curing was not wholly detrimental to Mode I performance [7]. However, work which included the use of peel ply in the formation of the tested interface showed considerably different results [8]. This work determined that better interfacial properties were found at higher degrees of cure/ past gelation when peel ply was used. This has been attributed to the peel ply creating a surface which facilitates mechanical interlocking of the semi-cured resin with freshly infused resin. Below the gel point the resin was found to break away with the peel ply, hence reducing the degree of interlocking seen. Imaging of the fracture surface helps reinforce the findings from Figure 4. From Figure 5. it can be seen that the samples which had an initially semi-cured element below gel (0, 0.3, 0.5) have strikingly similar failure surfaces where as the sample taken above gel (0.9) shows a surface much more akin to what would be seen in an adhesive failure.

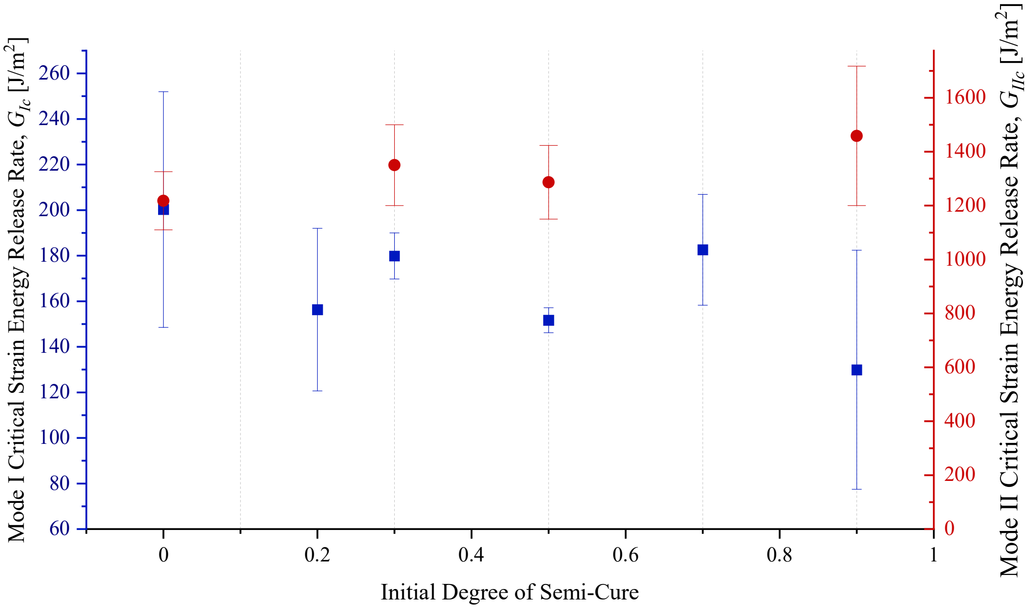

Figure 4. Mode I and Mode II results from DCN and ENF testing.

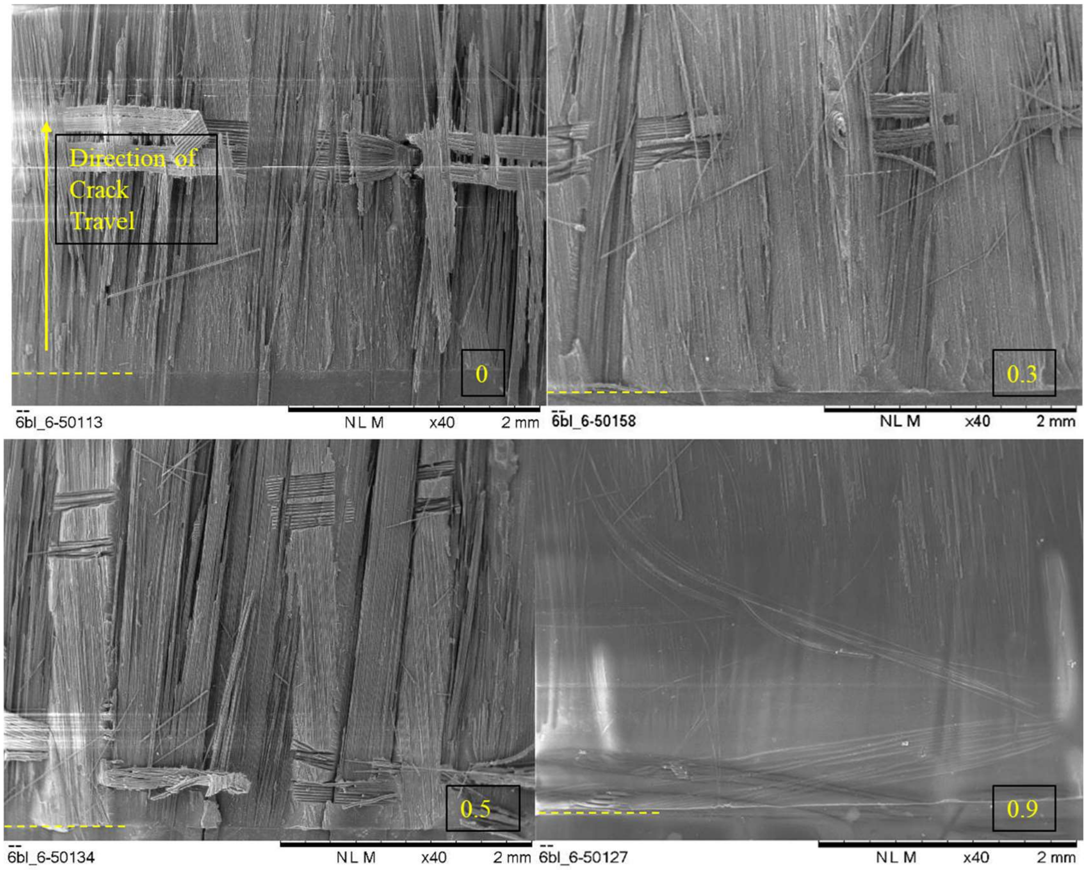

Figure 5. Fracture surfaces of tested DCB specimens where the provided number indicates the initial degree of cure if an initially semi-cured elements was present in the sample. Dashed yellow lines represent the end of the pre-crack and the start of the fracture surface.

CONCLUSIONS AND FUTURE WORK

The Semi-Curing process and its affect on both laminate interfacial and neat resin properties have been explored in this work.

Cast resin specimens showed that the Semi-Curing process had little to no negative effect on the plain strain fracture toughness or strain energy release rate of the base polymer material. There has been no sign of degradation of the material from the additional thermal cycling as a result of the manufacturing process being altered.

In terms of the mechanical performance of the composite laminate interfaces, Mode II performance was retained entirely when compared to the baseline samples. Meanwhile Mode I results were more sensitive to the DoC of the initially semi-cured laminate. There was approximately a 30% decrease in interfacial properties if the initial degree of cure advanced to the post-gel state, a drop which was not seen in Mode II. It is also clear that Mode I testing is far more sensitive for quantifying the affect of employing the Semi-Curing process on interfacial properties.

Overall, Semi-Curing appears to be a promising manufacturing technique which can be employed as a LCM process. It does have the potential to de-risk preform integration before infusion of complex composite parts.

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