

INITIAL STUDIES TO CHARACTERISE A POLYMER MATRIX FOR USE IN COMPOSITE WIND TURBINE BLADES

Bethany K. Russell ^{1a}, Carwyn Ward ^{1b}, Shinji Takeda ² and Ian Hamerton ^{1c}

¹ Bristol Composite Centre (ACCIS), Queens Building, University of Bristol, University Walk, Bristol, BS8 1TR, UK.

Email: ^a beth.russell@bristol.ac.uk, ^b C.ward@bristol.ac.uk, ^c ian.hamerton@bristol.ac.uk

² Hitachi Chemical Company Ltd, Tokyo, Japan. Email: shin-takeda@hitachi-chem.co.jp

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ABSTRACT

Hitachi Chemical Company Ltd. (HCCL) has developed a glass fibre reinforced polymer composite based on an anhydride-cured epoxy resin. Preliminary HCCL testing has suggested that it has improved interlaminar and mechanical properties compared to the amine-cured epoxy system which is currently used, making it an attractive alternative for use in wind turbine blades. In this work, extensive studies on the epoxy-anhydride system were conducted, allowing the determination of thermal properties, such as the glass transition temperature and modulus, along with cure kinetics. Processing parameters of rheological behaviour and *in-situ* resin shrinkage during cure were also studied. The apparent interlaminar shear strength was determined to be 62 MPa, verifying the improved interlaminar properties originally stated. The multifaceted nature of this research enabled the characterisation of a novel composite system, this will be pivotal in future research to develop an informed manufacturing process and has identified some mechanical properties which can be improved.

1 INTRODUCTION

The wind turbine industry has been using composite materials for their blades since the 1970s [1]. In recent decades epoxy glass fibre reinforced composite systems have been employed in the construction of 2 MW wind turbines, which offer the maximum power generation for on-shore turbines, where blades typically have rotor diameters of 80 m. Owing to the increased demand for renewable energy sources the desire to build larger and more efficient wind turbines the industry is growing. Consequently, HCCL has moved towards in-house production of the matrix resin systems, whereas previously the company would have used commercially available products from other manufactures. In-house production allows the systems to be tailored to meet specific requirements set by the turbine manufacturer, and this increased flexibility can facilitate further optimisation into the design and of the materials used in these applications [2].

The matrix system which has been developed by HCCL, is composed of three parts: a bisphenol A epoxy resin, an anhydride curing agent and a tertiary amine catalyst. The cure reaction to form the polymer network, occurs in two main steps: first, the amine is pre-reacted with the anhydride to initiate the reaction. Upon addition of the epoxy the resulting anion attacks the highly-strained epoxide ring, causing ring opening. The homopolymerisation reaction can then proceed leading to the development of the 3D highly crosslinked network during the cure cycle. HCCL have previously conducted some preliminary tests, showing this resin to have improved interlaminar properties compared to the commercially sourced, amine-cured epoxy resin system.

Wind turbine blades are typically manufactured using vacuum assisted resin infusion, a process which pulls uncured resin through a preform of dry fabric. The infusion process is affected by several factors including: the resin viscosity (ideally below 500 cps) [3], fabric permeability, and the infusion strategy (number and location of resin inlets) chosen. To determine whether the resin would be suitable for such a process, it is necessary to conduct a preliminary study of selected manufacturing considerations such as resin viscosity and resin shrinkage.

The present study aimed to conduct a preliminary investigation into the resin system developed by HCCL and how it performs in a glass fibre reinforced polymer (GFRP). The main aims were to characterise the resin system in terms of selected thermo-mechanical properties, to obtain benchmark results for the mechanical performance of the GFRP for several key tests to determine the interlaminar shear strength and interlaminar fracture toughness. To develop the resin system further, the response of the composite to impact damage will be important and thus some preliminary results will be discussed herein.

2 MATERIALS AND MANUFACTURE

2.1 Materials

The resin is a blend of three constituents mixed in a specified ratio: bisphenol A diglycidyl ether (DGEBA), methyltetrahydrophthalic anhydride (MTHPA) and Ancamine K54. Ancamine K54 is a blend of tris-2,4,6-(dimethylaminomethyl)phenol (90-95 wt%) and bis(dimethylaminomethyl)phenol (5-10 wt%). Chemicals were supplied by HCCL. Once blended the resin was degassed at room temperature until no more outgassing was observed. The cure cycle for the resin prescribed by HCCL, was 75 °C for 12 hours.

The H-glass fibre cloth was a biased non-crimp-fabric with two layers of fibres arranged in a 0/90° pattern with an areal weight of 1241 g/m², supplied by Owens Corning Technical Fabrics.

2.2 Processing

Vacuum assisted resin infusion was used to produce GFRP laminates. Preforms of the glass fabric were laid up with the same orientation of the fibres, the preform was placed between two layers of peel ply on a steel tool plate covered with release film, a resin distribution mesh was used on both the top and bottom of the preform stack. The preform was covered with a standard vacuum bag and sealed with tacky tape. The resin inlet and outlet tubes were connected to the fluid pot and a vacuum pump respectively. The resin was then infused in an oven heated to 50 °C, and once fully saturated, the laminate was cured at 75 °C for 12 hours. A fibre volume of 55% was determined from resin burn off tests conducted adhering to the ASTM standard D2584.

3 RESIN PERFORMANCE

To study the thermo-mechanical performance of the resin and cure cycle of the reaction, a series of experiments were conducted including differential scanning calorimetry, dynamic mechanical analysis and rheology on both cured and uncured resin samples.

3.1 Differential scanning calorimetry (DSC)

Both dynamic and isothermal DSC experiments were conducted using a TA Instrument Q2000 DSC, under nitrogen, 50 mL/min. All samples (both of cured and uncured resins) (10 mg) were enclosed in hermetically sealed aluminum pans.

Initially, dynamic scans were conducted, the uncured resin was heated at 10 K/min from 25 °C to 250 °C. The sample was then rescanned under the same experiment conditions. This showed the enthalpy of the polymerization to be 10.6 kJ/mol with peak exotherm at 135 °C. The rescan showed the ultimate glass transition temperature (T_g) for the system to be 102 °C.

Modulated DSC experiments were also conducted on samples cured in the oven as the residual cure peak overlapped the T_g . In this experiment, the temperature was swept from 25 °C to 220 °C with a ramp rate of 3 K/min, the modulation period selected was 60 s with a modulation temperature amplitude of +/- 1 K. This showed that following the prescribed cure cycle the final degree of cure was 86% and the resulting T_g was 100 °C.

An isothermal DSC was conducted to probe how the degree of cure changed with respect to time when the temperature was held at 75 °C for 12 hours (matching the oven cure cycle). Figure 1 shows a plot of how the degree of cure varies over time, the data suggests that the degree of cure reaches a plateau at 86% after 6 hours (320 minutes), which indicates the potential to optimise the cure cycle.

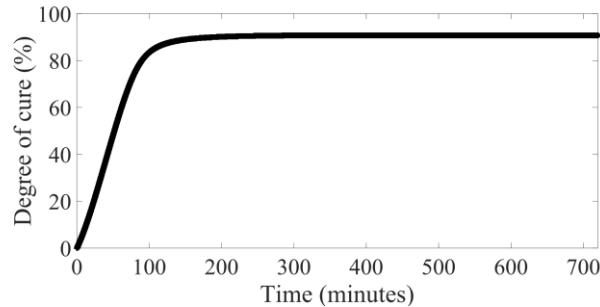


Figure 1: Isothermal DSC

A modulated DSC trace was obtained for a resin sample cured in an oven for 6 hours at 75 °C. The degree of cure was determined to be 84% and T_g of 97 °C. Which within the batch variability and error in the test setup shows the resin to be equivalent to that cured for 12 hours.

3.2 Rheological studies

An Anton Parr MCR 302 rheometer with oscillatory parallel plates was used for all rheological studies. To determine the rheological behaviour of the resin at both the cure (75 °C) and processing (50 °C) temperatures, oscillation-time experiments were conducted: frequency 1 Hz, normal force 0.05 N and strain 10% (determined to be within the linear viscoelastic regime of the resin).

Figure 2, shows how the loss modulus, storage modulus and complex viscosity of the resin vary with time when the temperature is maintained at 75 °C. It is observed that the resin gels after 52 minutes at elevated temperature, evidenced by the crossover of the loss and storage moduli. The resin was kept at elevated temperature for 4 hours, and it was observed that the complex viscosity seems to reach a plateau towards the end of the experiment, further indicating that the 12 hour cure cycle is excessive.

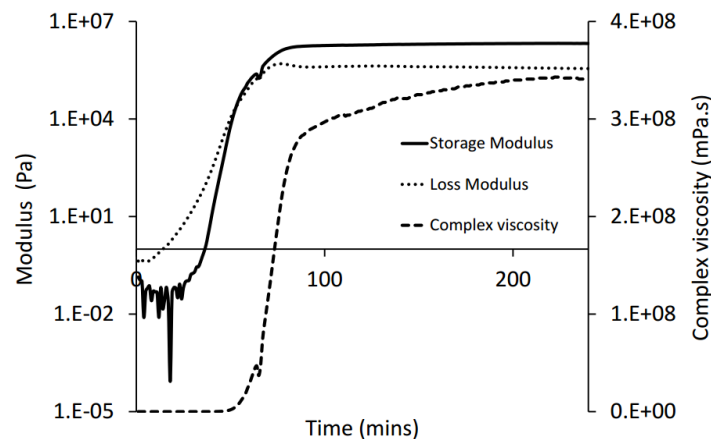


Figure 2: Rheological data of the uncured resin held at 75 °C for 4 hours.

3.3 Dynamic Mechanical Analysis (DMA)

A TA Q800 DMA instrument was used with the specimen (35 mm x 12 mm x 3 mm) using the single cantilever configuration test fixture. The temperature was swept from 25 °C to 250 °C at 5 K/min as the specimen was oscillated at a frequency of 1 Hz.

To examine if the resin thermo-mechanical properties were equivalent when cured at 75 °C for both 12 hours and 6 hours samples cured under both conditions were prepared and tested. Table 1 shows key data for both these samples including the $\tan \delta$ peak, onset of fall in storage modulus, peak of loss modulus.

Cure dwell time (hours)	Tan δ peak (°C)	Storage modulus below T_g (MPa)	Low modulus peak (°C)
12	115	2400	105
6	117	1800	103

Table 1: Thermo-mechanical properties of the resin as determined using DMA.

This data shows that although the thermal properties such as T_g are comparable the storage modulus is reduced when the resin is cured in 6 hours. Further studies to assess if this is within the limits expected from batch to batch variation will be conducted. If this is not the case, from the DSC data and the fact the $\tan \delta$ peaks of the DMA testing are comparable this would indicate that the cure cycle can be optimised. Hence assessing the resin after different lengths of cure between 6 and 12 hours can be studied.

3.4 Discussion

The thermo-mechanical properties of the cured resin have all been determined from resin mixed in the ratios prescribed. There could be the potential to assess the effects of changing the ratio of reactants has on the resulting resin properties such as T_g and degree of cure.

A study into the major costs associated with composite manufacture identified that the only real way to significantly reduce the cost per part is to reduce the cure cycle which in turn increases the manufacturing frequency. With higher turnover of parts, the labourers also have more practical experience and therefore issues become identified much earlier in the process, further reducing the manufacturing costs [4]. Both rheology and DSC experiments indicated that halving the cure cycle would produce a resin with the same thermal and rheological characteristics. However, the DMA data suggests that within 6 hours the mechanical properties, such as modulus, are not quite matched in a 6 hour cure. Further experiments with slightly longer cure times could allow for an improvement in the modulus of the resin and thus make thermo-mechanical properties of the resin system comparable whilst still optimising the cure cycle. Another consideration will be the thickness variation of a wind turbine blade from root to tip. The main load carrying member of a turbine blade is the spar cap, for a 40 m long turbine blade this is approximately 60 mm thick and tapers toward the tip to 15 mm [5]. It will be vital to assess if the degree of cure required to achieve the desired mechanical properties can still be attained in a shorter cure cycle in a thick laminate.

4 MANUFACTURING PERFORMANCE

Vacuum assisted resin transfer and composite manufacture in general has very niche issues which will impact the quality of the laminates produced and in turn its performance. Within this preliminary study two parameters were identified for study: the pot life of the resin at elevated processing temperature (50 °C) and the resin shrinkage.

4.1 Processing window

Through an isothermal study of the rheological behaviour of the resin at 50 °C conducted in an analogous manner as outlined in Section 3.2. It was shown that within 4 hours the resin did not gel (no intersection of the loss and storage moduli was observed). From in-house preparation of small laminates (250 mm x 150 mm x 5 mm) and long laminates (1 m x 10 mm x 5 mm), it was demonstrated that the whole process from resin mixing, degassing and infusion could be completed within 2 hours. Thus, there were no issues with the resin gelling within the required processing window. Looking to the

infusion over a wind turbine blade this becomes more critical and influences the infusion strategy in terms of location and number of resin inlet points.

4.2 *In-situ* resin shrinkage

Resin shrinkage was identified as another key parameter, as chemical shrinkage of the resin during cure leads to the development of residual stresses within thick laminates. Residual stresses can induce warpage, delamination and cracks to form in the laminate and therefore affect its mechanical performance [6,7].

A novel gravimetric method was developed by Li *et al.* [7] to enable the *in-situ* resin shrinkage during cure to be measured. The method works by measuring the buoyancy of the sample by observing the change in the apparent weight of the sample immersed in silicone oil. Thus, in accordance with Archimedes' principle the change in volume can be determined. Khoun *et al.* [8] developed an improved test setup based on that reported by Li *et al.*, and the later method was adopted in this study.

Two samples of very similar mass were sealed in Nylon 6 bagging film, using an impulse bag sealer, and immersed in silicone oil (Alfa Aesar, with density at 20 °C of 0.963 g/cm³). One specimen was suspended from a weighing scale and used for the weight measurement, the bag was suspended using a steel wire and nylon thread. The steel wire was used to prevent any influence of the surface tension effect affecting the results and the nylon thread was required to prevent the transfer of heat to the scale. The other enclosed sample had a K-type thermocouple in and was used to monitor the temperature of the resin. Another thermocouple was placed within the beaker of silicone oil. The setup is shown schematically in Figure 3.

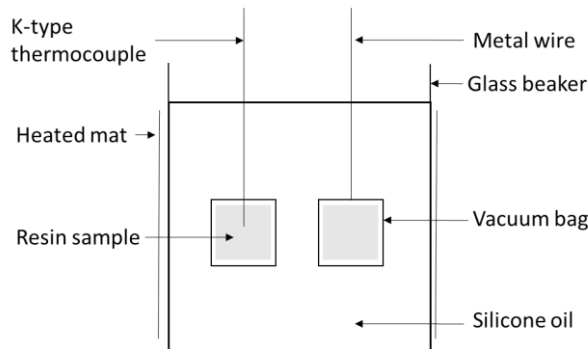


Figure 3: Schematic of resin shrinkage test setup.

The oil was kept at the cure temperature 75 °C throughout the duration of the experiment using a heat mat connected to a Watlow EZ temperature controller. Both samples were immersed in the oil at the same time, and weight and temperature were recorded. Every 60 seconds the data of the apparent weight and temperatures for the resin, silicone oil and thermal chamber were recorded using a data acquisition system, LabVIEW.

From the data recorded the chemical shrinkage was calculated using Equation 1:

$$\left(\frac{\Delta V}{V}\right)_{shrinkage, T_c} = \frac{\Delta G_{T_c}}{\rho_{f, T_f} \times V_{r, T_c}} \quad (1)$$

where, ΔG_{T_c} is the measured change in apparent weight of the resin weighed in the bath of silicone oil during cure at temperature, T_c . V_{r, T_c} is the volume of the uncured resin at T_c , ρ_{f, T_f} is the density of the silicone oil at T_c , calculated using Equations 2 and 3 respectively.

$$V_{r,T_c} = \frac{m_{r,T_0}}{\rho_{r,T_0}} \times [1 + 3 \times \alpha_1(T_c - T_0)] \quad (2)$$

$$\rho_{f,T_c} = \frac{\rho_{f,T_0}}{1 + \gamma_f(T_c - T_0)} \quad (3)$$

m_{r,T_0} and ρ_{r,T_0} represent the weight and density of the uncured resin at 20 °C respectively. α_1 is the CTE of the resin above T_g , which was determined from a DMA experiment; specimens (35 mm x 5 mm x 5 mm) of cured resin were prepared. The specimens were placed between the compression plates and the growth of the sample was measured as the temperature was swept from 25 to 200 °C. γ_f is the volumetric expansion of the silicone oil, which is $1040 \times 10^{-6} \text{ K}^{-1}$ as stated by the manufacturer. From the experiments conducted, the change in apparent weight following 12 hours at 75 °C was 0.125 g. Using Equation 1, this calculated the chemical shrinkage to be 7.3%, which is within the expected range for an epoxy resin which is typically between 6-8% [7].

4.3. Discussion

The preliminary testing of the manufacturing performance conducted has shown some promising results. The *in-situ* resin shrinkage is in-line with what is expected of a typical cured crosslinked epoxy resin. From rheology studies and infusion trials the resin has been shown not to gel within the time required for the infusion of small panels when held at the elevated processing temperature. The quality of the laminates produced seems to be consistent with V_f of 55% and all parts having a cured ply thickness of 0.82 mm.

5 PRELIMINARY MECHANICAL PERFORMANCE

5.1 Interlaminar shear strength (ILSS)

5.1.1 Experimental

Short beam shear tests were conducted following the D2344 ASTM standard. A Shimadzu Autograph AGSX test machine with a 10 kN load cell and fitted with a three-point bend test fixture was used. The fixture had a 6 mm diameter loading nose and 3 mm diameter supports. The span length of the fixture was 24 mm. The test specimens were cut from laminates using a diamond saw; the samples were cut oversized and polished to refine the size to the desired geometry of 33 mm x 9 mm. To account for biaxial nature of the reinforcement, specimens were cut with both the dominant fibre direction being along the length and width of the specimen. The specimens were loaded until failure (10% drop in load was detected).

5.1.2 Results and discussion

The ILSS of the laminate was determined using Equation 4, where P_m is the maximum load observed (N), b and h are the specimen width and thickness (mm) respectively.

$$F^{sbs} = \frac{3P_m}{4 \times b \times h} \quad (4)$$

Figure 4, shows the load displacement plots for specimens loaded transverse to the dominant fibre direction. The maximum load, P_m , for specimens loaded transverse to the dominant fibre direction was on average 3.2 kN. Using Equation 4, the ILSS for the composite system was determined to be 62 MPa (SD = 6). The specimens all failed in an approved interlaminar shear manner as observed by the crack formed from the centre to one side of the laminate section as shown in Figure 4 b(i). As the fibre was biased the test loading was also conducted parallel to the dominant fibre direction to give a resin dominated value which could be used as a benchmark to compare this baseline system to in the future, this gave a short beam shear value of 7.3 MPa with maximum loads observed being 370 N. This was also highlighted by the much more progressive failure observed in Figure 4 b(ii), here the specimen failed stepwise as the crack propagated through the matrix for the bottom ply of the laminate.

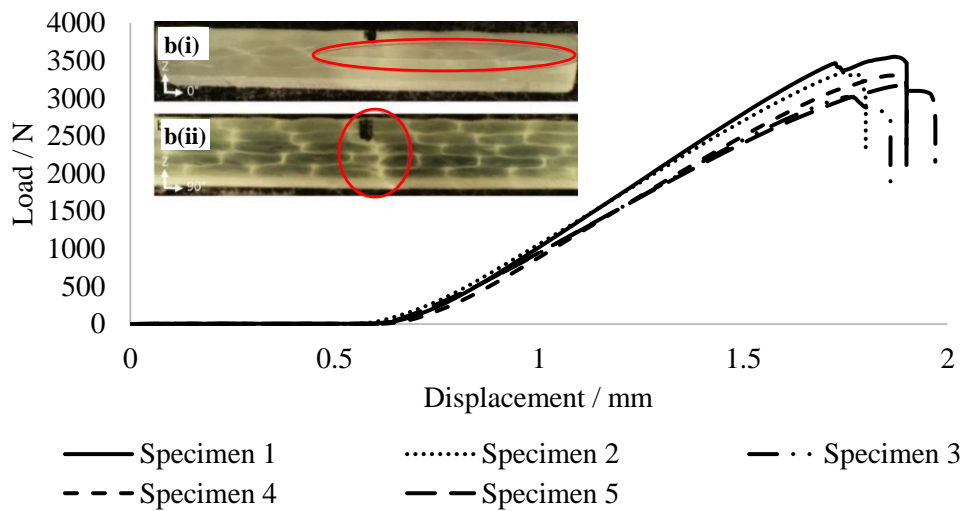


Figure 4: a) Plot of load versus displacement for several specimens. b) Failure observed from short beam shear tests: i) specimen loaded perpendicular to dominant fibre direction; ii) specimen loaded parallel to dominant fibre direction.

5.2 Impact resistance

Wind turbine blades must be able to withstand impacts in various forms from hail to bird strikes. The blades are also designed to have a working life of 20-30 years with minimal maintenance, and consequently the resistance of the composite to impacts is a key property. As part of this preliminary investigation the delamination pattern after an impact event was evaluated, where the main aim was to assess the feasibility of testing the laminate for central, near-edge and on-edge impact. Given the geometry of the wind turbine blade over the leading and trailing edges it is vital to understand the impact of the laminate in these three configurations. Hence these preliminary investigations focused upon development of the test setup and assessment of the clearly visible impact damage (CVID) mainly observing the delamination patterns created from the impact event.

5.2.1 Experimental

Centre, near-edge and on-edge impacts on the laminate were conducted in these experiments, shown schematically in Figure 5 (a-d). An Instron Dynatup 9250HV drop weight impact tester fitted with a 15 kN load cell and a hemi-spherical tup of radius 10 mm was used. As the impact mass of the tup remained constant, the impact height was varied to achieve impact velocities of 1.26 m s^{-1} and 1.49 m s^{-1} , leading to impact energies of 5 or 7 J respectively.

It was vital to assess both the near and on-edge impact resistance of the laminate, as composites are being used to greater extents in structural applications, hence impacts to laminate edges are more probable [9], but for these tests, a standard has not yet been developed. To assess the clearly visible impact damage (CVID) a high-resolution scanner was used to image the delamination pattern. Two different specimen sizes were required: for centre impact tests, square specimens of 60 mm x 60 mm, while for near-edge and on-edge tests specimens of 60 mm x 30 mm were machined from the laminate. For both the centre and near-edge impact the specimens were supported between two steel plates with a central circular opening (40 mm diameter), at the centre of which the impact event occurred. To support the specimens for on-edge impact a fixture was designed and built (shown in Figure 5 d). It was composed of four hinges mounted to the lower support of the original test fixture and the hinges were clamped to the specimen on either side using small toolmakers clamps. This configuration ensured that the specimen was held at the centre of the circular opening to ensure the impact was at the centre of the laminate.

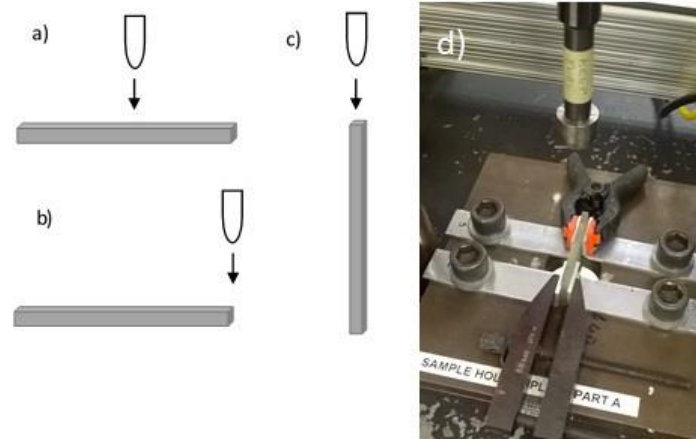


Figure 5: Schematic identifying the different test conditions used: a) centre impact, b) near-edge impact and c) on-edge impact. d) Photograph of the on-edge impact test rig.

5.2.2 Results and discussion

The site of impact was identified on all samples by a semi-spherical indentation on the upper surface of the laminate. For both the centre and near-edge impacted samples the delamination was shown to be more severe when observed from the back face, Figure 6. In the case of the centre impacted samples, cracks were noted on the bottom surface of the laminates in the dominant fibre direction. Work continues to quantify these impact data.

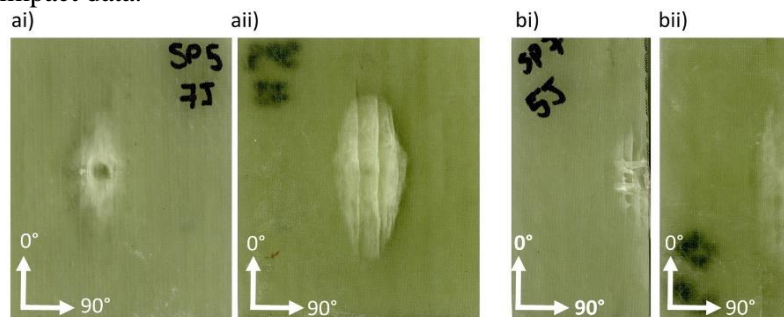


Figure 6: Photographs of impacted specimens, a) centre impact: i) front, ii) back; b) near-edge impact: i) front, ii) back.

The on-edge impact experiments were deemed to be of interest due to the nature of impact on wind turbine blades in operation. However, this approach has not been explored extensively in literature, and as a result a test standard, which can produce reliable and reproducible results will be developed in the future work of this project. Figure 7, depicts the images of the on-edge impact specimens, which show that the surface plies on either side were affected symmetrically. Also visible, was the high degree of delamination at the central plies, particularly for the specimen where the dominant fibre direction was perpendicular to the impact direction.

Owing to the low velocity impact, two failure modes were observed: intraply and interply. Intraply failure is characterised by fibre/matrix interfacial failure and matrix cracking, whereas during interply failure the plies delaminate from one another. Initially, owing to high transverse shear stress at the top ply, matrix cracking and debonding of fibres from the resin occurs; bending stress then causes the bottom laminate surface to crack. These cracks then propagate through the laminate and are either arrested or diverted along interlaminar regions leading to delamination. No fibre rupture or catastrophic failure was observed during the testing.

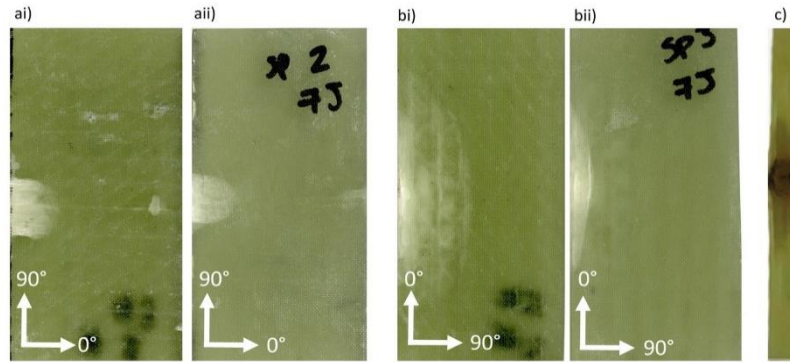


Figure 7: Images of the on-edge impact specimens: a) dominant fibre direction parallel to impact top; b) dominant fibre direction perpendicular to the impact top, where i) refers to left and ii) corresponds to right sides of the impact site. c) Impact site for the on-edge impacted sample b.

Increasing resin toughness has been widely studied, with many looking at the incorporation of a thermoplastic phase in the bulk matrix, this however increases the resin viscosity, and thus making manufacturing using vacuum assisted resin infusion difficult. One area which may be more applicable to the system discussed in this research, could potentially be the use of hyperbranched polymers (HBP) or electrospun nanofibers and dissolvable thermoplastic nanofibers. These would all be techniques to consider as they have been shown to improve damage tolerance without affecting the resin properties such as T_g or modulus. They have also been reported not to affect the infusion process as they undergo phase separation during cure [10]. Another approach could be the incorporation of thermoplastic veils. These are not added to the resin but are laid up in the fibre preform between layers of structural fibres. They have already been shown to enhance the impact resistance and moreover they can be used with the current manufacturing process adding little increase in production costs [11].

6 CONCLUSION

There are several key conclusions which can be drawn from this preliminary investigation. Firstly, the data from experiments conducted upon the resin system suggest that the cure cycle might be optimised by halving the cure time at which the part is at elevated temperature. If the mechanical properties of the composite parts are comparable with those cured using the original cycle, then this would offer a major cost saving in the part manufacture. Secondly, HCCL state that the new resin system offers improved interlaminar properties over the commercial amine-cured epoxy resin system. Through the present study a baseline value has been established for the anhydride-cured epoxy composite. It is possible to expand this work and look to improve the material further and optimise both its mechanical and manufacture performance. The overarching aim behind the project is to facilitate the low-cost insertion of a new material, much like the work conducted by Boeing in 2004 which led to the development of a methodology for the accelerated insertion of composite materials. This methodology allows for the development of materials which can be quickly progressed through the technology readiness levels (TRLs) to be qualified for use in their intended application much quicker than previously seen, by heavily reducing the risks at key stages and understanding the key features and test which must be conducted [12]. The development of this anhydride-cured epoxy for wind turbine blades essentially needs to follow a similar methodology to allow for its accelerated qualification and use in the turbines produced by Hitachi Ltd.

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