Reduced Dependence on Redundant Fasteners in Secondary-Bonded Composite Structures Using Modified Epoxy Matrix Resins

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Introduction

Polymer matrix composites are used in high performance aerospace structures because of their excellent specific strength, toughness and stiffness along the fiber. To realize the full performance advantages of composites, complex, built-up structures must be assembled using adhesives, but uncertainty in bond strength often requires manufacturers to install bolts or other crack-arrest features to ensure safety in critical applications and achieve certification.[1] The inherent uncertainty in adhesive bonds stems from the material discontinuity at the composite-to-adhesive interfaces, which are susceptible to contamination.[2] In contrast, co-cured composites, although limited in size and complexity, result in predictable structures that are certifiable for commercial aviation with reduced dependence on redundant load paths.[1] The proposed technology uses a stoichiometric offset of the hardener-to-epoxy ratio on the faying surfaces of laminates. Assembly of the components in a subsequent "secondary-co-cure" process results in a joint with no material discontinuities (Figure 1).

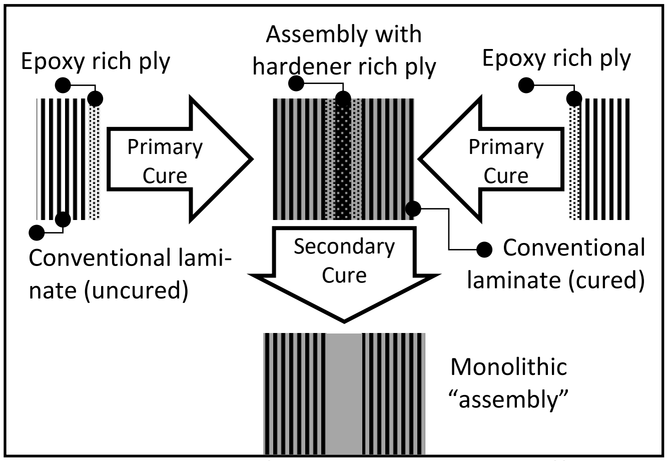

Figure 1: Schematic of assembly process using offset resin and reinforcing fiber.

In one embodiment of this technique, composite components are prepared with surfaces that are stoichiometrically rich with epoxy functional groups (Figure 1). During the primary cure, the epoxy rich (ER) resin mixes with the conventional resin, but the offset stoichiometry in the ER surfaces limits the advancement of molecular weight, and the resin on the faying surfaces remains flowable at elevated temperature with intact reactive groups even after the primary cure. In step 2, the composite panels are assembled with a ply of hardener rich (HR) material between the ER surfaces. During secondary cure, the ER and HR plies intermix and cure to form a composite assembly with no discernable interface, analogous to a conventional laminate. During both cure processes, increased temperature reduces the viscosity of the uncured resin allowing flow, diffusion, and consolidation. During the secondary cure step, intermixing of the HR and ER resins occurs, which eliminates material discontinuity at the joint. By combining the HR and ER resins, stoichiometric equivalence is achieved, and the molecular weight of the resin can advance until vitrification occurs.

The successful fabrication of an HR/ER joint depends on multiple, interdependent material and process parameters including precursor selection, stoichiometric offset, initial degree of cure, fiber volume fraction, ply thickness, number of plies, and cure cycle temperature profile. Previous work using rheology and calorimetry indicated an ER *r*-value ≤ 0.15 prevented gelation during primary cure where *r* is defined in equation 1 as:

Equation 1: $$r = \frac{eq_H}{eq_E} \equiv \frac{molar\ equivalents\ of\ hardener}{molar\ equivalents\ of\ epoxy}$$

In conventional resin formulations, the *r*-value is typically 0.8 in order to obtain complete cure.[3]

This report describes a sub-set of over 20 experiments conducted to optimize materials and processes to maximize mechanical properties of the assembled joint. Infrared (IR) spectroscopy was used to measure the chemical state of the ER surface after primary cure. Laminates were fabricated with various HR and ER layer thicknesses, inspected using ultrasonic testing, and mechanically tested to measure fracture toughness.

Experimental

Epoxy resins were formulated from two components: API-60® (part A) epoxy resin supplied by Kaneka North America with an epoxy equivalent weight of 131 g/mol and diethyltoluenediamine (DETDA, part B) hardener supplied by Alpha Chemistry as shown in Figure 2.

Resins were formulated from parts A and B in a resin kettle in batches of 0.25-1.2 kg by heating to 100 °C and agitating with an overhead mechanical stirrer for 60-90 min under a nitrogen atmosphere. To fabricate mechanical test specimens, prepreg was prepared from HexTow® IM7G 12K carbon fiber from Hexcel Corporation and offset resins with *r*-values of about 0.15 and 2.5 for the ER and HR plies, respectively. Methyl ethyl ketone (MEK), obtained from Sigma Aldrich, was used to dilute the resin for prepreg preparation. Hexply® IM7/8552, 35%, 190 gsm unidirectional tape was obtained from Hexcel Corporation® and used as backing for the mechanical test specimens.

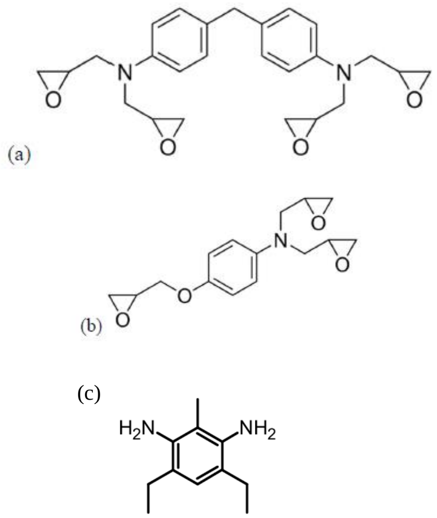

Figure 2: Structures of API-60® epoxy resin including the tetrafunctional epoxy, 4,4′-methylenebis(N,N-diglycidylaniline) (a) and the trifunctional epoxy, N,N-diglycidyl-4-glycidyloxyaniline (b), and the tetrafunctional hardener diethyltoluenediamine (DETDA) (c). Mole ratio of the monomers (a) to (b) was 3:1.

Differential scanning calorimetry (DSC) was conducted on offset resins using a TA Instruments Q20 modulated DSC (MDSC®) with a heating rate of 3 °C/min. Samples of approximately 3 mg were hermetically sealed in aluminum pans and cured at 180 °C for 2 h before cooling to -40 °C and ramping to 280 °C to measure the glass transition temperature (T_g) and residual heat of reaction.

Unidirectional prepreg tape was prepared using a custom prepregger from a resin solution of 70-85 wt.% solids and the compliment of MEK. Twenty-three-ply composite panels were prepared by laying up the Hexcel® Hexply® 8552 prepreg and ER prepreg in a 30 cm by 15 cm format according to $[\text{Hexcel}_9,\text{ER}_2,\overline{HR}]_\text{s}$. In addition to prepregging, HR material was also prepared by hand painting the MEK/HR resin solution (30% to 50% solids in MEK) onto a plain weave, e-glass fiber fabric. Each panel was cured in an autoclave using the two-step process in Figure 1. Primary cure produced two “half-panels” each with 11 plies. The half-panels were then assembled with a ply of HR material in contact with the ER surfaces and returned to the autoclave for secondary cure. All cure cycles had a final hold of at least 1 h at 178 °C. Various intermediate hold conditions (time and temperature) were tested to optimize primary and secondary cure processes.

Resin chemistry was characterized by IR spectroscopy to determine the *r*-value at the surface after primary cure. The *r*-values were calculated based on the relative peak heights at 907, 1514, and 2961 cm^{-1} using an empirical calibration curve developed from a series of resin samples of known *r*-value and degree of cure. Ultrasonic inspection in pulse-echo mode was conducted on a MISTRAS® UPK-T60-HS high speed C-scan system fitted with a NDT Automation® 10.0 MHz/13 mm immersion transducer (IU10G1). End-notched flexure testing (ENF) test was conducted according to ASTM D7905-14 to measure mode II fracture toughness using six replicate specimens.[4] Figure 3 shows the test configuration using a 3-point bend fixture to load the specimen. The side of the specimen is painted white for visualization of the crack.

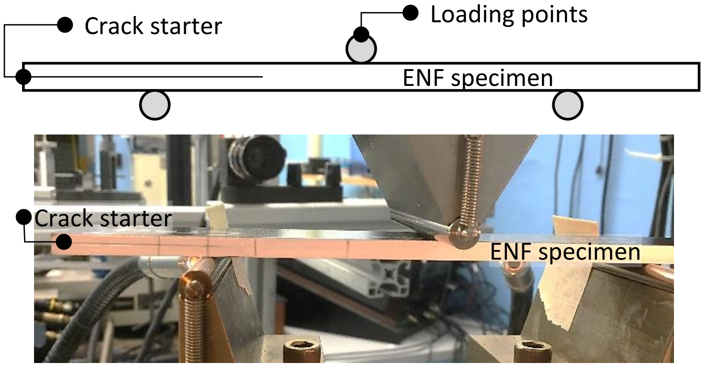

Figure 3. Specimen schematic and a photograph of test setup for the ENF test

Results and Discussion

The results of four experiments are presented in detail, and additional learnings from several preliminary experiments are referred to without supporting data due to page limitation. In the four presented experiments, *r*-values for the ER and HR resins were 0.15 and 2.5, respectively. The primary cure cycle included a 1 h hold at 107 °C before the final hold for 3 h at 178 °C. The resin areal weight (RAW) was varied for the ER and HR plies used in the four experiments according to Table 1. Additionally, two carrier materials were tested in the HR ply. From Table 1, it appears that higher ER and HR RAW improves fracture toughness of laminate joints.

During the primary cure, the ER resin at the surface must not advance past the gel point (~45% conversion for this system) to maintain the mobility needed to affect mixing during the secondary cure. The *r*-value of the ER surface, inferred from IR spectral analysis (Table 1), indicates the relative advancement of the surface polymer due to ingress of hardener from the bulk of the laminate or homopolymerization of the epoxy. ER surfaces with *r*-values less than ~0.3 resulted in measurable joint properties whereas *r*-values greater than ~0.3 (data not included here) formed no joints.

Table 1: Test parameters and results used in experiments 1-4 (E1-E4). Scrim denotes the plain weave glass fiber scrim cloth and CFT denotes a unidirectional carbon fiber tape used as the HR resin carrier. The baseline fracture toughness used to calculate % of baseline values was 736 J/m^2. ER *r*-values were measured after primary cure. *Fracture toughness measured from samples with no precrack for E1 whereas all other values had a precrack.

Experimental #	1	2	3	4
Parameter Set	18	20	21	15
ER-RAW (g/m^2)	81	222	222	200
HR-RAW (g/m^2)	190	190	117	240
HR carrier	Scrim	Scrim	CFT	Scrim
ER *r*-value	0.128	0.290	0.175	0.238
G_{II} (J/m^2)	88±33*	372±61	280±34	616±127
% of Baseline	12	51	38	84

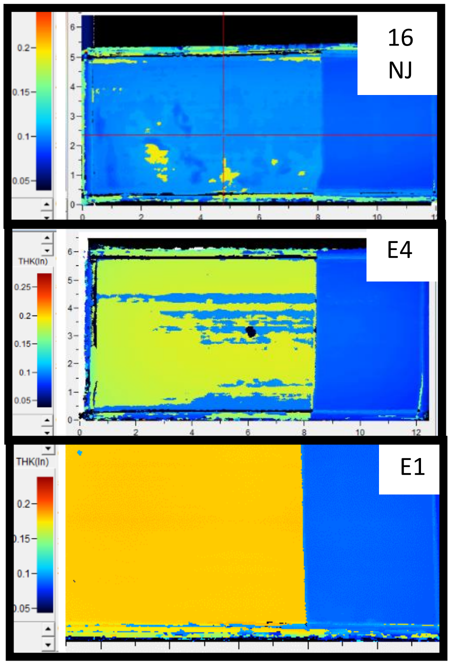

Figure 4: Time of flight C-scan images of three laminates prepared for ENF testing. E4 and E1 coorespond to the experiment numbers in Table 1. Panel 16NJ formed no joint and saw therefore not included in Table 1. All scales are in inches.

Figure 4 shows time of flight C-scan results for three experiments with vastly differing joint properties. A blue pixel indicates the largest reflection occurred at the mid-plane and a yellow pixel indicates the largest reflection occurred at the bottom surface. In each image, the dark blue field on the right ¼ of the image is due to the crack starter film, which creates an intentional disbond in the joint needed for ENF testing. The image labeled NJ formed no joint and the disbond in the C-scan image is readily apparent as the light blue field in the left ¾ of the image. Image E4 shows a large region of yellow color indicating most of the panel has uniform properties through the thickness with small blue areas that have measurably different acoustic properties. Finally, E1 indicates a uniform laminate with no significant variations in properties through the thickness. The C-scan results were successful at finding joined and delaminated panels prior to mechanical testing, but the C-scan data was not a good predictor of joint mechanical performance, but more an indicator of joint homogeneity. Contrary to the images, fracture toughness of E4 greatly exceeded those of E1 (Table 1).

In Figure 5, a microsection taken from E4 shows the resin rich interlaminar region between the ER and HR plies. The bright circles are the polished cross sections of carbon fibers, approximately 6 microns in diameter. The microsection shows the successful diffusion and mixing of the ER and HR resins in E4 such that no interface or inhomogeneity is visible in the joint.

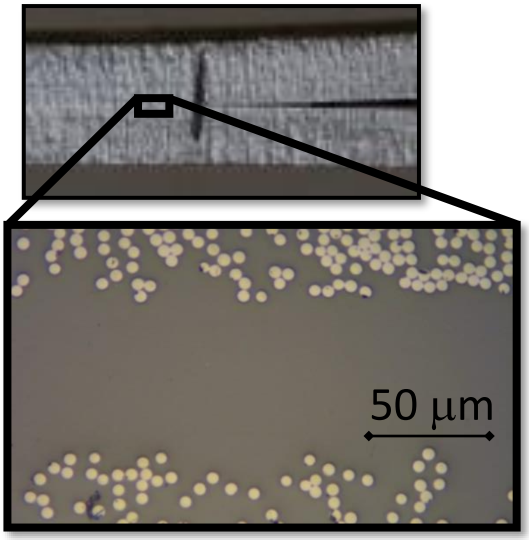

Figure 5: Images of E4 composite ER/HR joint showing the entire side of the specimen (top) and a polished cross-section of the combined and cured ER and HR layers (bottom).

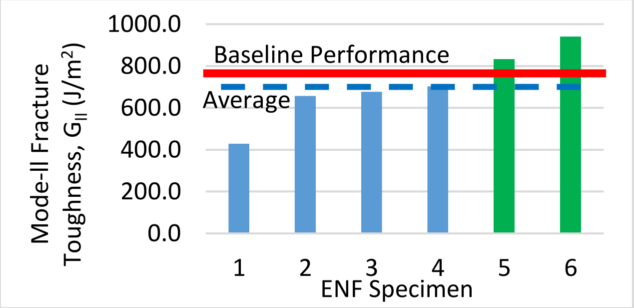

Figure 6: Fracture toughness results per specimen for E4. Blue bars are tape activated cracks and green bars are for scrim activated cracks.

The fracture toughness of individual specimens from E4 is shown in Figure 6. The blue bars were obtained using a tape activated test scheme where the crack was driven into the ER ply. The green bars were measured using a scrim activated setup meaning the crack front was driven into the woven glass carrier of the HR ply. The scrim activated tests exceeded the baseline laminate fracture toughness because the crack may have propagated through the scrim fabric.

Conclusions

Stoichiometrically offset epoxy resins were used to assemble composite laminate joints with no discernable bondline in optical micrographs after reflow and mixing of resins at the interface during cure. Laminates with sufficient RAW of ER material on the surface after primary cure maintained a surface *r*-value below 0.3 and retained sufficient mobility to intermix and polymerize during the secondary cure. Increasing the RAW of both the HR and ER led to improved facture toughness, which reached 84% of baseline fracture toughness measured from conventional laminates.

Acknowledgements

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