

MODIFIED EPOXY MATRIX RESINS FOR REDUCED DEPENDENCE ON REDUNDANT FASTENERS IN SECONDARY-BONDED COMPOSITE STRUCTURES

Frank L. Palmieri¹, Tyler B. Hudson¹, Austin J. Smith¹, Roberto J. Cano¹, Jin Ho Kang², Yi Lin², Kathryn M. Crossett³, Bryson Clifford³, Isaac J. Barnett³, and John W. Connell¹

¹NASA Langley Research Center, Hampton, VA, 23681, USA

²National Institute of Aerospace, Hampton, VA, 23666, USA

³NASA Internships Fellowships and Scholarships Program, Hampton, VA, 23681, USA

ABSTRACT

In structural bonds, the interface between adherend and adhesive is nearly two-dimensional making it susceptible to minute quantities of contamination that can lead to weak bonds. No methods currently exist to measure the strength of an adhesive bond nondestructively. For these reasons, regulating organizations such as the Federal Aviation Administration (FAA) often require redundant load paths in secondary-bonded, primary-structures to achieve certification for civil transport aircraft. To meet this requirement, manufacturers commonly install redundant fasteners (~10⁵ fasteners in a twin-aisle airframe with composite fuselage and wings), which add tremendous complexity, time and cost, and significantly reduce performance of the airframe. Under NASA's Convergent Aeronautics Solutions (CAS) Program, the Adhesive Free Bonding of Composites (AERoBOND) project is investigating reformulated aerospace epoxy matrix resins to enable reflow and diffusion of the resin at the interface during a secondary bonding/cure process. The mixing process eliminates the material discontinuity at the interface, thereby removing the dependence of bond performance on adhesion across a nearly two-dimensional boundary. The AERoBOND interface is similar to the interlaminar region formed during a co-cure process, so joint performance depends on the cohesive properties of the matrix resin, which can be measured, inspected non-destructively, and certified for flight with fewer redundant fasteners. This presentation describes the ongoing development of stoichiometrically-offset epoxy resins to control the degree of cure in composite joints and enable interfacial mixing during secondary bonding/curing. Details on the resin formulation, laminate fabrication, and mechanical testing will also be presented. The precracked mode-II fracture toughness measured from preliminary AERoBOND joints was similar for joints fabricated with conventional epoxy matrix materials.

Keywords: thermoset, hardener, prepreg, assembly

Corresponding author: Frank Palmieri – frank.l.palmieri@nasa.gov

DOI: (will be filled by SAMPE)

Copyright 2020. Used by the Society of the Advancement of Material and Process Engineering with permission.

SAMPE Virtual Conference Proceedings, 2020. Society for the Advancement of Material and Process Engineering – North America.

Copyright 2020. Used by the Society of the Advancement of Material and Process Engineering with permission.

SAMPE Conference Proceedings, Seattle, WA, May 4-7, 2020. Society for the Advancement of Material and Process Engineering – North America.

1. 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].

1.1 Example Assembly Process

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).

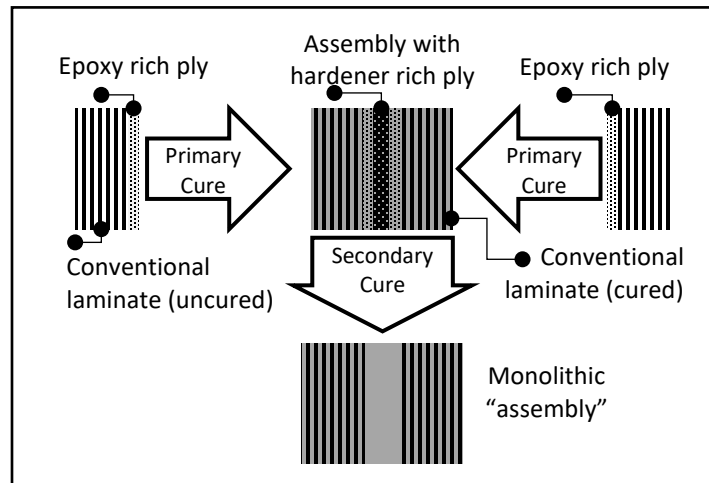


Figure 1. Schematic of assembly process using offset resin and reinforcing fiber.

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.

1.2 Critical Material and Process Parameters

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

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.

1.3 Considerations for Aerospace Implementation

The goal for joints assembled using offset resin chemistry should be similar in mechanical performance of co-cured assemblies, not necessarily bonded joints, for implementation in future aircraft structures. The inherent reliability and predictability of co-cured and analogously offset resin assembly is the critical factor in moving from bonded joint with redundant fasteners to monolithic laminate structures with minimal fastener requirement. Therefore, the goal of this research is not to exceed the mechanical performance of joints structures, but rather to work toward similar performance and reliability of co-cured joints.

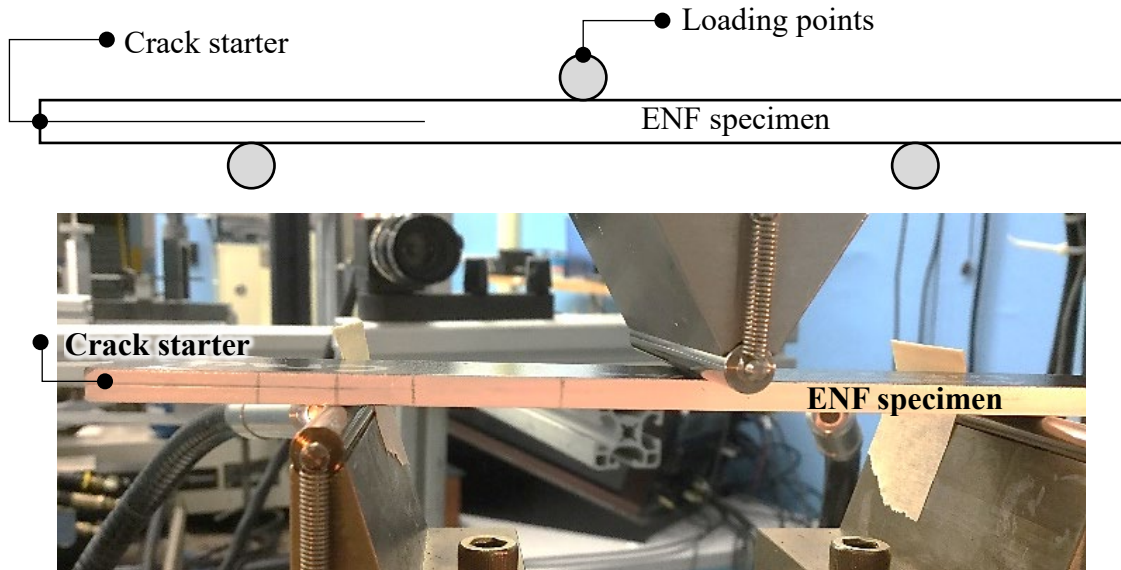
2. EXPERIMENTATION

2.1 Materials and Methods

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.

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 (ENF) testing 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 configuration to load the specimen. The sides of the specimen are painted white for visualization of crack extension.

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

3. RESULTS

Process development for fabricating joints from offset resins followed an iterative experimental method. Critical findings from several preliminary experiments are summarized in section 3.1. Detailed results from four experiments are presented in section 3.2 where r -values for the ER and HR resins were 0.15 and 2.5, respectively.

3.1 Preliminary Process Development

Preliminary experiments indicated that extremely high hardener concentrations ($r > 5$) and crystalline solid hardeners (DDS) hampered diffusion and bonding in the secondary cure process. During the primary cure, the ER resin at the surface must not advance past the gel point ($\sim 45\%$ 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. Early testing indicated that the ER layer required a minimum fiber areal weight ($>150 \text{ g/m}^2$, FAW) and resin content ($\sim 55\%$ RC) to remain sufficiently flowable and reactive after the primary cure. Further, the final hold time at $178 \text{ }^\circ\text{C}$ was limited to 1 h to prevent excessive etherification of the ER matrix.

3.2 Detailed Experimental Data

Table 1 shows results for experimental joints. In all cases, the primary cure cycle included a 3 h hold at $107 \text{ }^\circ\text{C}$ before the final hold for 1 h at $178 \text{ }^\circ\text{C}$. The secondary cure had a 3 h hold at $178 \text{ }^\circ\text{C}$ to ensure complete cure of the DETA hardened system. 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 the laminate joint.

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 739 J/m^2 [5]. 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-PC} (J/m^2)	$88 \pm 33^*$	372 ± 61	280 ± 34	616 ± 127
% of Baseline	12	51	38	84

3.2.1 Non-destructive Inspection

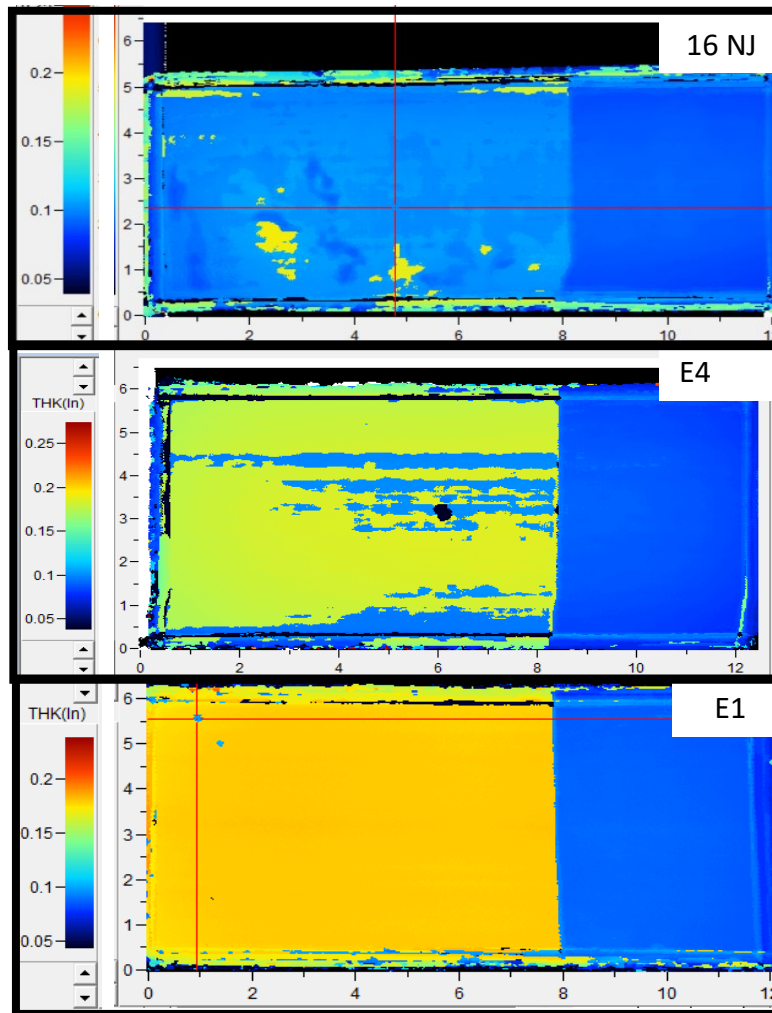


Figure 4. Time of flight C-scan images of three laminates prepared for ENF testing. NJ indicates an experiment that formed no joint and E4 and E1 correspond to the experiment numbers in Table 1. All scales are in inches.

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 $\frac{1}{4}$ 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 $\frac{3}{4}$ 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 measurable 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 2).

3.2.2 Microscopy

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.

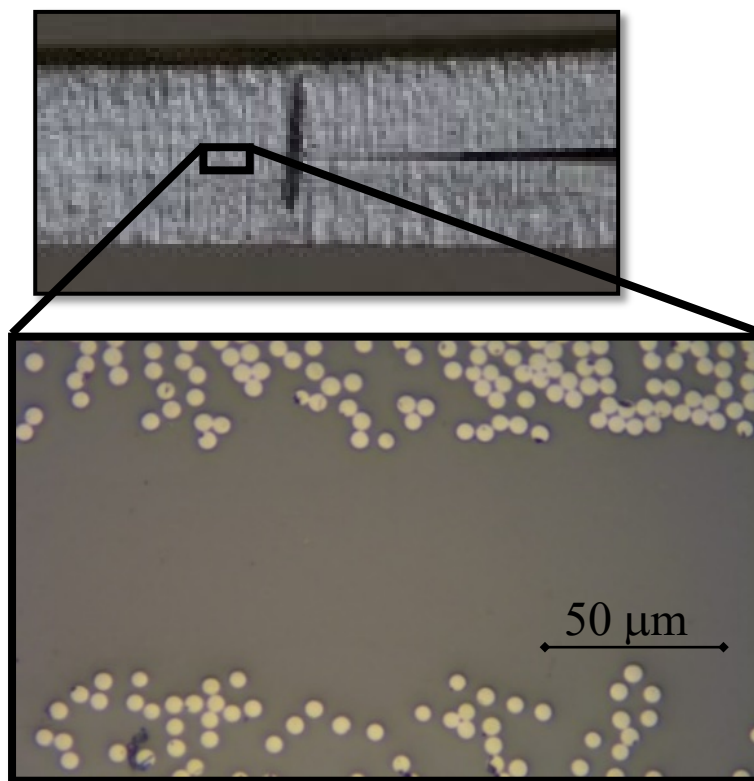


Figure 5. Images of E4 composite ER/HR joint showing the entire side of the specimen (top) and a polished cross-section of the combined and cured ER and HR layers (bottom).

3.2.3 Mechanical Performance

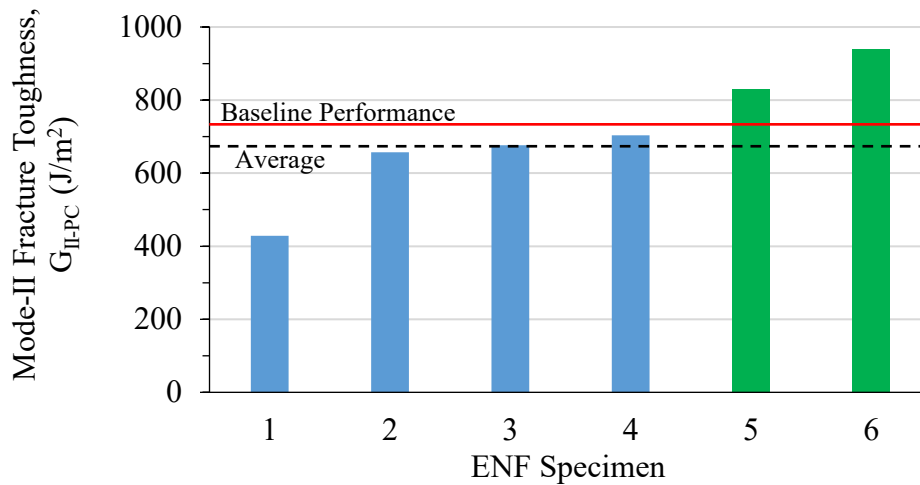


Figure 6: Precracked mode-II fracture toughness results per specimen for E4. Blue bars are tape-activated cracks and green bars are for scrim-activated cracks.

The precracked (PC) mode-II 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 tape 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 fabric architecture creates a more tortuous path for the crack as it extends, thereby increasing the resistance to crack growth at that interface.

4. 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 mode-II fracture toughness, which reached 84% of baseline fracture toughness measured from conventional laminates.

5. REFERENCES

1. Kruse, T., Fuertes, T. A. S., Koerwien, T. and Geistbeck, M. "Bonding of CFRP primary aerospace structures - boundary conditions for certification in relation with new design and technology developments," *Proceedings of the 2015 International SAMPE Tech. Conf.* Seattle, WA, 2014 Society for the Advancement of Materials and Process Engineering. CD-ROM.
2. Palmieri, F., Ledesma, R., Fulton, T., Arthur, A., Eldridge, K., Thibeault, S., Lin, Y., Wohl, C. J. and Connell, J. W. "Picosecond pulsed laser ablation for the surface preparation of epoxy composites," *Proceedings of the 2017 International SAMPE Tech. Conf.* Seattle, WA, 2017 Society for the Advancement of Materials and Process Engineering. CD-ROM.
3. Palmieri, F. L., Hudson, T. B., Cano, R. J., Tastepe, E., Rufeisen, D., Ahmed, L., Wohl, C. J. and Connell, J. W. "Adhesive Joining of Composite Laminates Using Epoxy Resins with Stoichiometric Offset," Hilton Head, SC, 2/18/19; 2019 Annual Meeting of the Adhesion Society.
4. Standard Test Method for Determination of the Mode II Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites, 2014, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
5. O'Brien, T. K., Johnston, W. M. and Toland, G. J., Mode II Interlaminar Fracture Toughness and Fatigue Characterization of Graphite Epoxy Composite Material, NASA/TM-2010-216838 NASA Langley Research Center. Hampton, VA, 2010.