

Adhesive Joining of Composite Laminates Using Epoxy Resins with Stoichiometric Offset

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Introduction

Polymer matrix composites are used in high performance 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 with adhesive, but uncertainty in bond strength requires manufacturers to install bolts or other crack arrest features to ensure safety in critical applications.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, composites made by co-curing, although limited in size and complexity, result in predictable structures that may be 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).

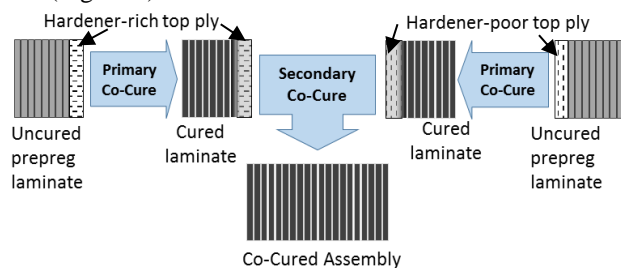


Figure 1: Schematic of assembly process using offset resin.

In one embodiment of this technique, composite components are prepared with a surface resin layer that is stoichiometrically rich in either hardener (Figure 1, left) or epoxy (Figure 1, right). In step 2, the composite panels are joined and the surface plies intermix and cure to form a composite assembly with no discernable interface. As with all prepreg lamination and cure processes, the primary co-cure step uses heat to decrease the viscosity of the uncured resin allowing the resin to flow and the part to consolidate. The resin reflow and consolidation steps are necessary to eliminate porosity and achieve full mechanical properties. Because of the offset stoichiometry in the hardener-rich (HR) and hardener-poor (HP) surfaces, the respective reac-

tive groups remain intact and the resins on the faying surfaces remain flowable at elevated temperature after the primary cure. During the secondary co-cure step, intermixing of the HR and HP resins occurs, which eliminates material discontinuity at the joint. By combining the HR and HP resins, the stoichiometric offset is reduced or eliminated, and the molecular weight of the resin advances until vitrification occurs.

A tetrafunctional diamine was selected as the hardener for this work, and the epoxy is a mixture of 25 mol% tri-functional and 75 mol% tetrafunctional glycidal epoxy species. The stoichiometric ratio, r , is defined as the ratio of molar equivalents of hardener reactive groups to the molar equivalents of epoxy reactive groups. Using equation 1, the ratios at gelation were calculated assuming full conversion of the limiting functional group.³

$$\text{Eq. 1} \quad r_{gel} P_{gel}^2 = \frac{1}{(f_e - 1)(g_e - 1)}$$

In Equation 1, P_{gel} is the conversion of the limiting monomer at gelation (assumed to be unity), r_{gel} is the ratio at the gel point, and f_e and g_e are the average functionality of the monomers, 4 and 3.75, respectively. By this model, the resin is predicted to gel for $0.12 < r < 8.25$. Gelled polymers were expected to diffuse less readily than ungelled materials, so resins with r -values near the HR ($r = 8.25$) and HP ($r = 0.12$) gel points were investigated to improve mass transfer across the interface.

This report describes the preliminary characterization and formulation of offset resins. Rheology and calorimetry were used to characterize the effect of stoichiometric offset on flow and cure properties. Mechanical testing of conventional laminates reported here provides a benchmark for co-cured joint properties.

Experimental

Epoxy resins were formulated from two components supplied by Applied Poleramic Inc. (now Kaneka North America): API-60[®] part A epoxy resin and 4,4'-diaminodiphenyl sulfone part B hardener shown in Figure 2.

Resins formulated from parts A and B were used for rheology and calorimetry testing. To measure baseline mechanical properties, prepreg was prepared from unsized, HexTow[®] IM7 carbon fiber from Hexcel[®] and pre-formulated API-60 resin with an r -value of about 0.8. Hexply[®] IM7/8552, 35%, 190 gsm tape was obtained from Hexcel

Corporation[®] and used as backing for the mechanical test specimens. Methyl ethyl ketone (MEK), used to dilute the resin for prepreg preparation, was used as obtained from Sigma Aldrich.

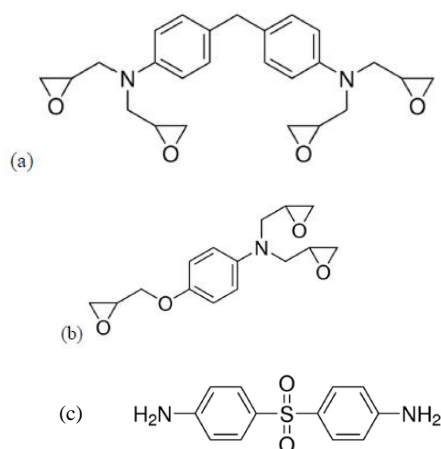


Figure 2: Structures of the tetrafunctional epoxy, 4,4'-methylenebis(N,N-diglycidylaniline) (a), the trifunctional epoxy, N,N-diglycidyl-4-glycidyoxyaniline (b), and the tetrafunctional hardener 4,4'-diaminodiphenyl sulfone (c).

A Thinky[®] planetary mixer was used to mix and degas all resin formulations at 100 °C by repeating a cycle with 4 min of mixing and 1 min of degassing 1-4 times. The HR resins required some hand mixing and multiple mixing cycles for homogeneity as visually assessed. Resins were cryogenically fractured at -79 °C to prepare powders for characterization tests. Rheology samples were prepared by pressing HR powder (~0.7 g) into disks while HP samples were heated to 90 °C and degassed under vacuum for 2 hours. Parallel plate rheology was conducted on an Anton Paar[®] MCR 502 rheometer with aluminum, disposable, parallel plate fixtures with a gap of 1 mm and a 25 mm upper plate diameter. The temperature was ramped at 3 °C/min from 70 °C to 180 °C and held isothermally for 2 hours before cooling to RT at 3 °C/min. An oscillatory test was used with a strain of 10% and a strain rate of 6.28 radians/s. A measurement was collected every 30 seconds.

Differential scanning calorimetry (DSC) was conducted on offset resins using a TA Instruments[®] Q20 modulated DSC 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 hours 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 for baseline properties testing was prepared using a custom prepregger from a resin solution of 70 wt% API-60 ($r = 0.8$) and 30 wt% MEK. Twenty-ply composite panels were prepared by laying up the Hexcel[®] prepreg and API-60[®] prepreg in a 30 cm by 30 cm format according to [Hexcel₉/API-60₁]_s. Each panel was cured in an autoclave using the Hexcel[®] recommended cure cycle. Double cantilever beam (DCB) and single-lap shear (SLS) panels were machined using a water jet and curved

beam (CB) panels were machined on a diamond wet saw to prepare 6 specimens for each sample. Testing and data reduction were conducted according to ASTM standards D5528-13 (DCB), D3165-07 (SLS), and D6415-06a (CB).⁴⁻⁷ Figure 3 shows the specimen configuration for each test.

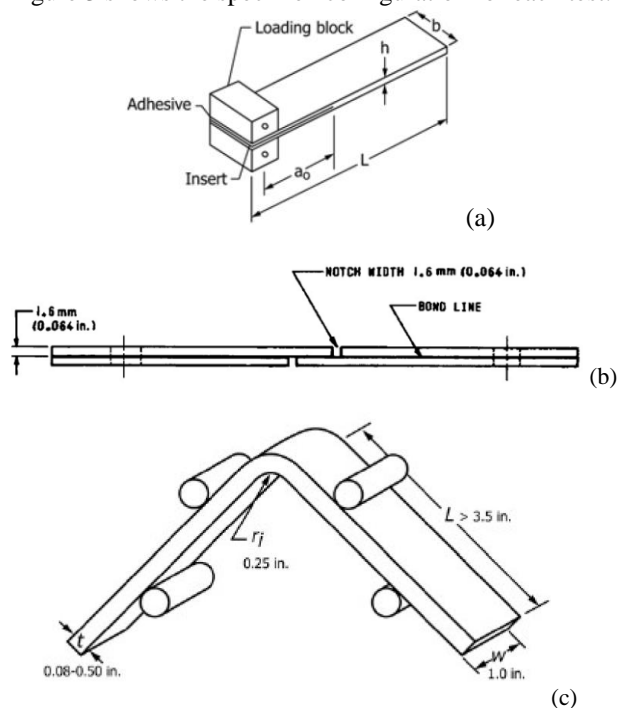


Figure 3. Specimen drawings for the three mechanical tests used to measure baseline properties: (a) DCB test, (b) SLS test, and (c) CB test.

Results and Discussion

The melt viscosities from rheology testing are presented in Figure 4 for the end of the isothermal hold at 180 °C and during the cooling ramp at 120 °C. The viscosity of the polymer melt increased smoothly for HP resin formulations as r approaches unity. In all samples, the storage modulus remained less than the loss modulus throughout the cure cycle indicating that gelation never occurred. Lack of gelation above the theoretical gel point ($r=0.12$) may indicate incomplete conversion of the limiting monomer.

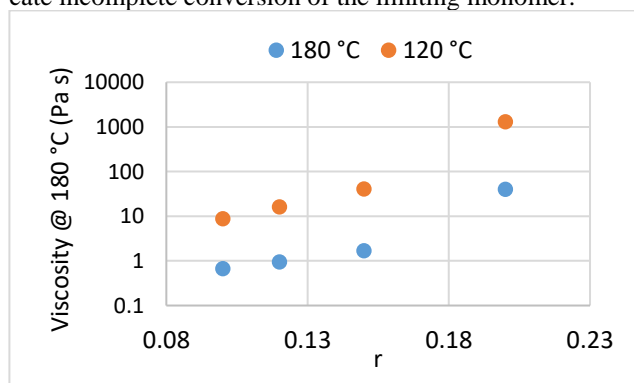


Figure 4. Dependence of melt viscosity on r for two temperatures: 180 °C and 120 °C.

Using the model derived by Miller and Macosko, the molecular weight was predicted as a function of r (Figure 5).³ Asymptotes appear at r -values of approximately 0.12 and 8.26 in agreement with Equation 1. The form of the $r < 0.12$ function appears to match the rheology data in Figure 4 although it is shifted to lower r -values.

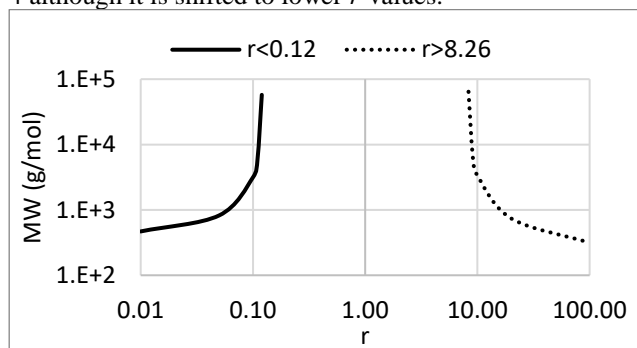


Figure 5. Predicted molecular weights for full conversion of the limiting functional group for various stoichiometric offsets.

Calorimeter results in Figure 6 show the temperature measured at the peak of the exotherm that occurred during polymerization with respect to r -value. The decrease in temperature with increasing r -value indicates that the amine-epoxy polymerization occurs at lower temperatures than the epoxy homo-polymerization. The homo-polymerization in HP resin formulations is anticipated to be limited using typical industrial cure conditions of 2 hrs at 180 °C.

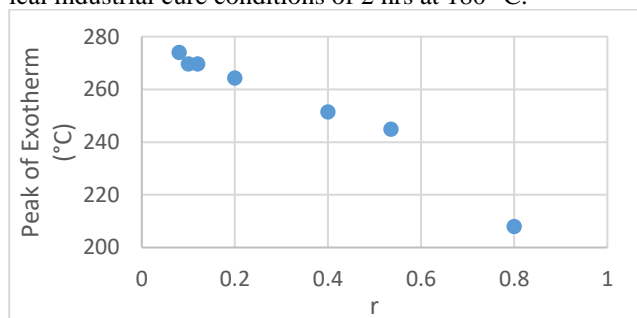


Figure 6. Peak temperature of the cure exotherm as a function of resin r -value as measured by DSC.

Mechanical test results are shown in Table 1 including the interlaminar fracture toughness (G_{IP}), the apparent shear stress (τ), and the interlaminar tensile strength (σ). The baseline properties measured here are representative of conventional materials made using the laboratory facilities available at NASA Langley Research Center to make the prepreg and laminates. These properties are for comparison with those measured from experimental joints, which remain to be fabricated and tested. The large error associated with σ is attributed to defects in the laminate that occurred during forming of the curved beam.

Table 1. Mechanical test results for baseline laminates.

Sample	G_{IP} (J/m ²)	τ (MPa)	σ (MPa)
Baseline	351±30	16.4±0.64	71.4±35.6

Figure 7 shows the bondline of a co-cured interface between two plies of conventional API-60 laminates with no visible polymer interface (left) in comparison with a co-bonded joint where the interface between the adhesive and substrate remains visible. During the cure process, consolidation occurs due to resin flow and diffusion, which eliminates the interfaces between plies. In comparison, secondary bonded joints have a clearly defined interface.

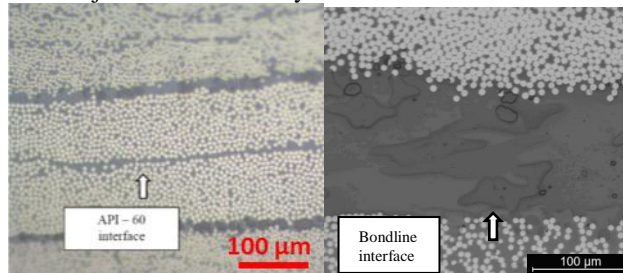


Figure 7. Cross-section micrographs of a baseline, co-cured laminate with API-60 plies at the center (left) and a secondary bonded interface (right).

Conclusions

Epoxy resins with large stoichiometric offsets prevented advancement of the resin significantly past the gel point at full conversion of the limiting reactive groups. Results indicated that resins with r -values predicted to gel at full conversion appeared to remain ungelled throughout a typical cure process. Baseline mechanical properties measured for conventional formulations ($r = 0.8$) are the benchmark for on-going mechanical testing with offset resin based laminates.

Acknowledgements

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