Evaluation of Low Viscosity Repair Resins for Delamination Injection Repair

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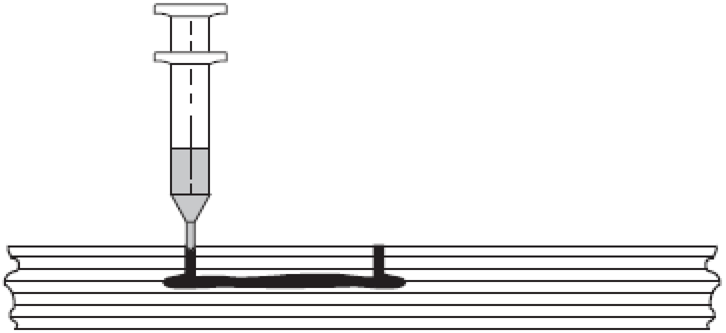
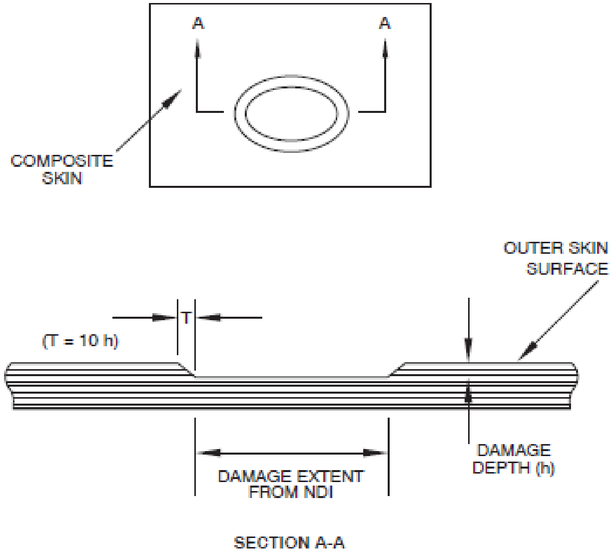
Problem Statement

- **Delamination is a common failure on polymer matrix composites (PMC)**
  - **Sources include manufacturing defects and in-service or maintenance damage**
- **Resin injection is a standard repair technique but NOT considered strength-restoring**
  - **Difficulty in characterizing and removing contaminants in small cracks**
  - **Multiple drilling attempts and heat application required to inject currently approved resins**
- **Benefit of resin injection: faster and cheaper compared to patch repairs**



Injection Repair



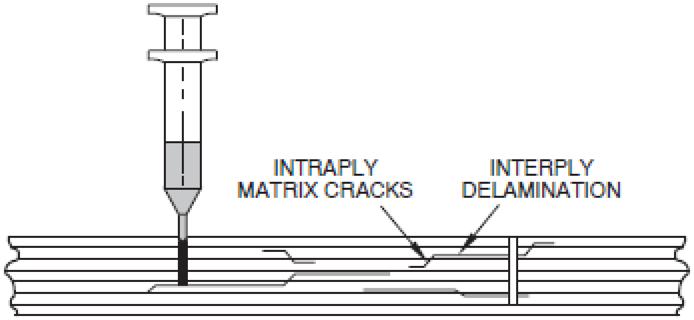
Patch Repair

Problem Statement, Cont.

- Per aircraft maintenance and repair manuals, resin injection is used to repair delaminated composite materials using laminating resins Henkel EA9396 and EA956.

- Filling small cracks (< 1 micron) is difficult due to the resins' viscosity (~3500 cP at 77°F)
  - Delaminated sections are rarely filled completely without heat application and multiple attempts
  - Current injection repair process are considered non-structural due to repetitive drilling and incomplete crack fill
  - Previous research diluted EA9396 with 10% and 20% w/w acetone to achieve lower viscosity at the expense of increased porosity [1]

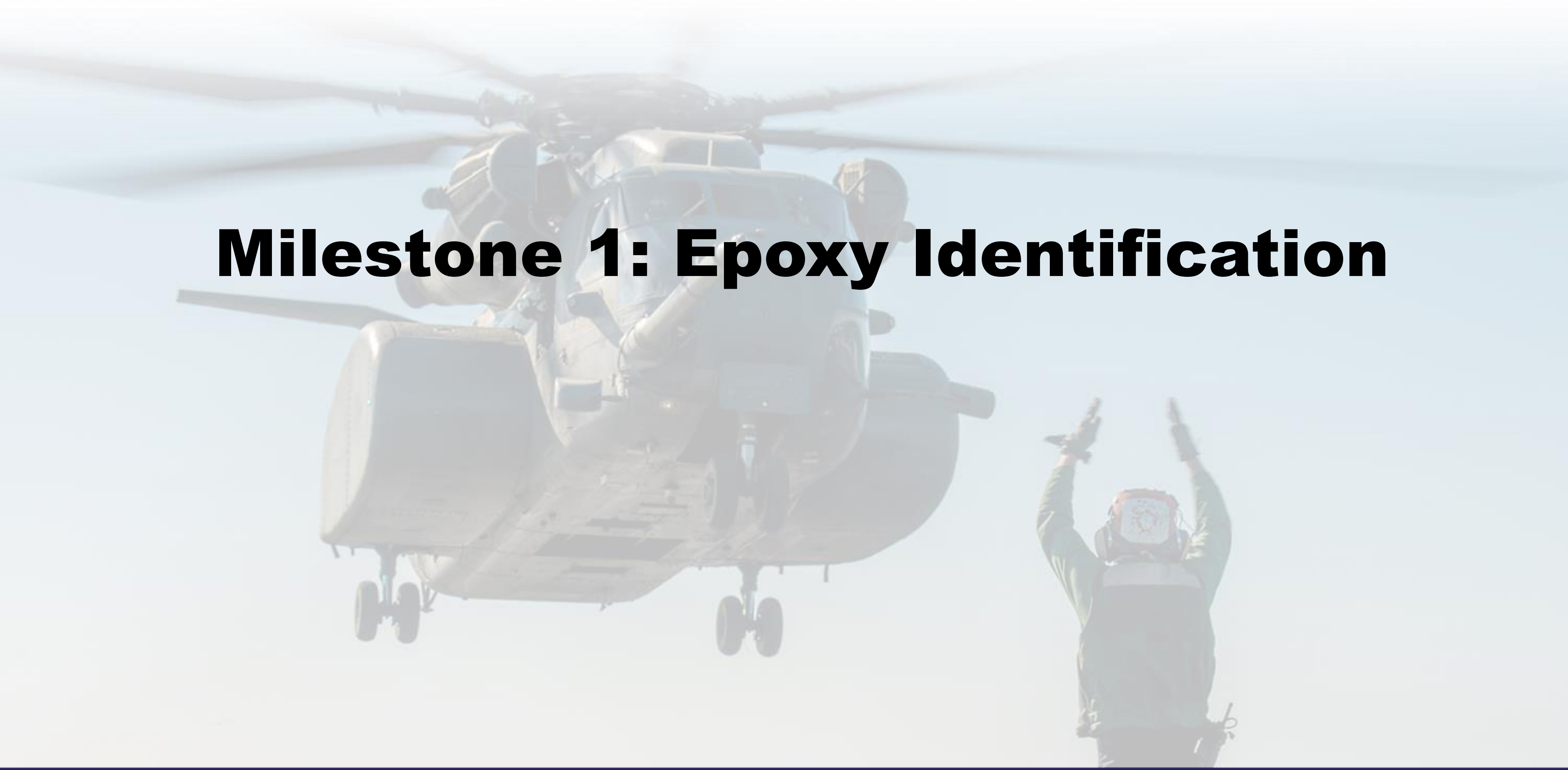
- FRCSW is investigating epoxies that:
  - (1) initially meet a viscosity of <650 cP, recommended by A.J. Russell (Canadian Defense Research Establishment Pacific) [2]
  - (2) comply with the in-service temperature and humidity conditions of multiple aircraft platforms.



Objectives

- **Milestone 1: Identify potential resin candidates that satisfy the following criteria:** ✓
  - **Viscosity < 650 cP**
  - **Tg (glass transition temperature) > 250°F**
  - **Pot life is ≥ 20 minutes**
- **Milestone 2: Characterize resin mechanical and chemical properties for convergence upon 2-3 resins** ✓
- **Milestone 3: Test Mode II interlaminar fracture toughness of the selected epoxies to compare to baseline unidirectional laminate values**
- **Milestone 4: Inject resins into laboratory-impacted coupons. Perform NDI and mechanical testing to converge upon final 1-2 resins that will be used for multiple platforms in the field**

Epoxy Identification	Epoxy characterization	Down-selection to 2-3 resins	Delamination characterization	Down-selection to 1-2 resins	Mechanical Testing (PAX)	Final Report
•Literature review •Procurement	•Porosity studies •Viscometer •Single lap shear •Differential Scanning Calorimetry (DSC) •Dynamic Mechanical Analysis (DMA)		•End-Notched Flexure testing •NDI repaired coupons to determine percentage fill		•Inject impacted coupons and NDI to determine percentage fill •Compression After Impact (CAI)	



Milestone 1: Epoxy Identification

Potential Epoxy Candidates

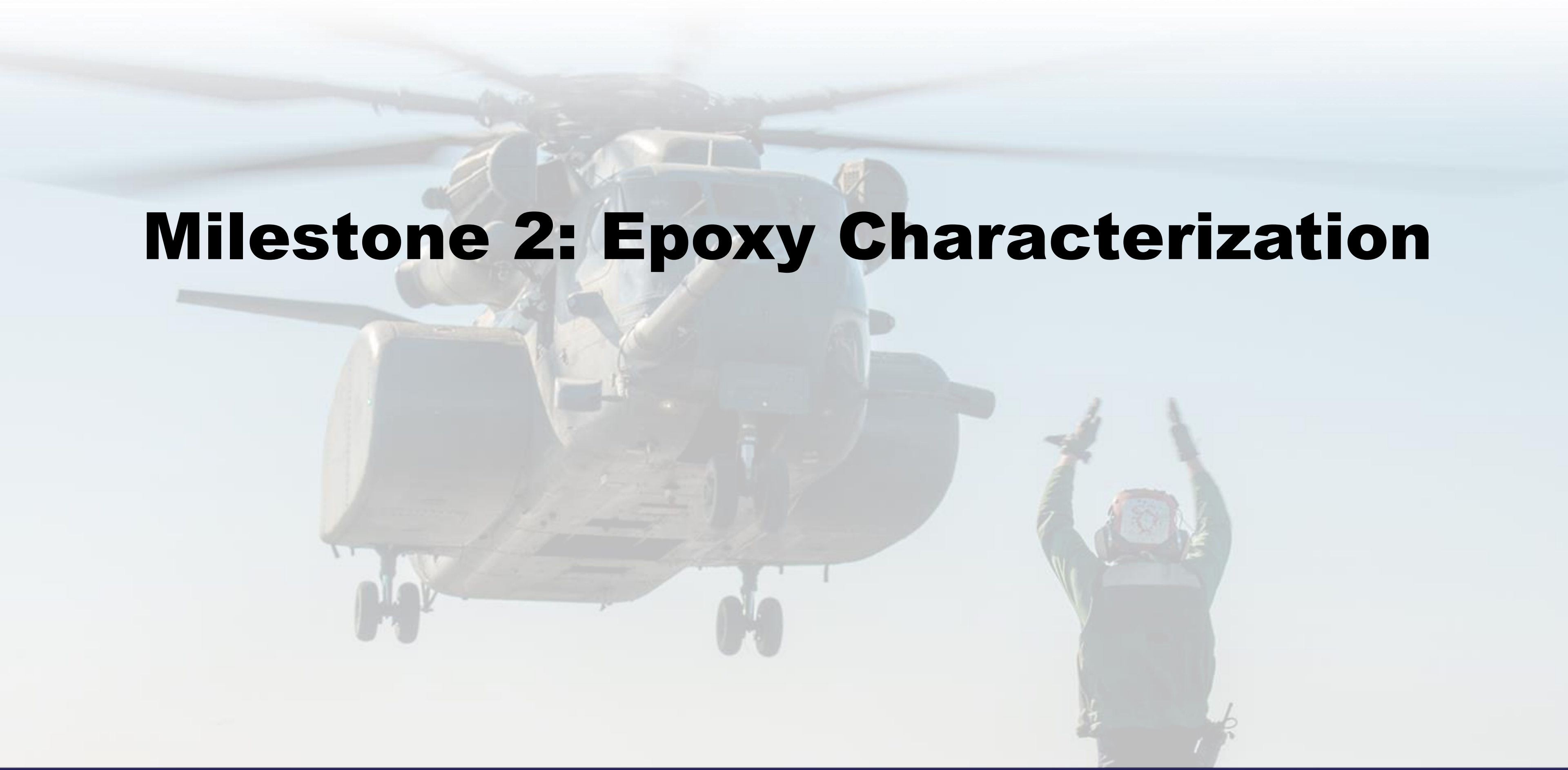
Table 1: Potential Off-the-Shelf Products

Product Name	Manufacturer	Initial Viscosity at 25°C/ 77°F (cP), Brookfield	Service Temperature/Tg (°F)	Service Temperature/Tg (Elevated Temperature-Wet)	Pot Life (hrs)
Masterbond SUP112 (Supreme 112)	Master Bond	50-200	550	N/A	48-72
Araldite LY 5052-1/ Aradur 5052 Hardener	Huntsman	600-700	248-273 (Tg)	N/A	4
Kaneka SR6400	Kaneka	80	262 (Tg)	199 (Tg)	0.33 (20 mins)
Kaneka IR6030	Kaneka	370	275 (Tg)	N/A	1.5

Table 2: Potential EA9396 Dilutions

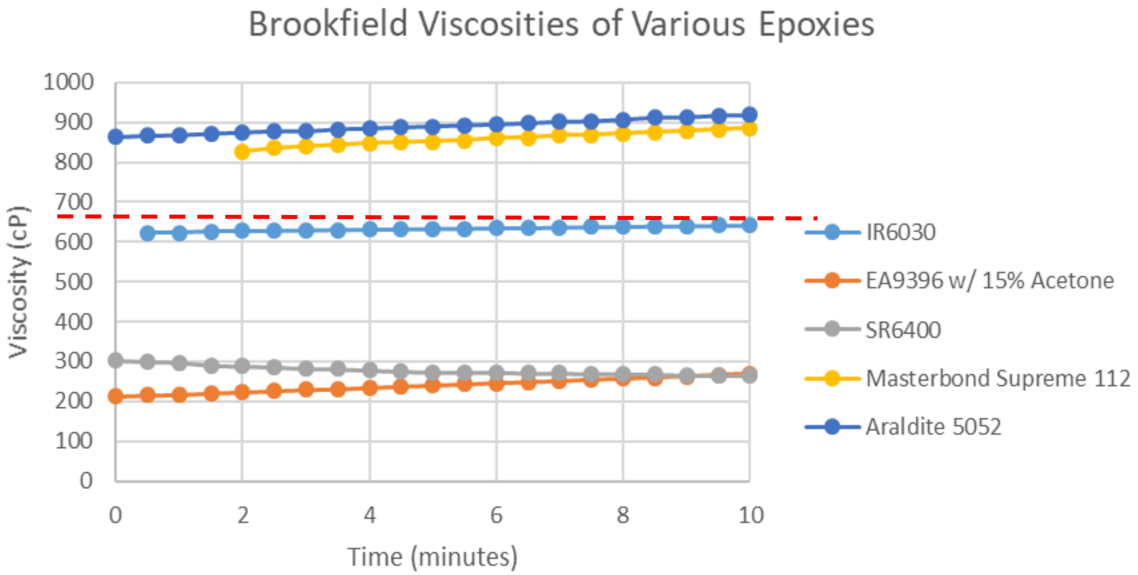
Solvent	Quantity (% w/w)
MIBK	10
	20
Acetone	15

- **Potential resin candidates need to satisfy the following criteria**
  - **Viscosity < 650 cP**
  - **Tg (glass transition temperature) > 250°F**
  - **Pot life is ≥ 20 minutes**
  - **Procurable (no excessive lead times or DOD-specific difficulties)**
- **Diluted EA9396 included for consideration due to all materials being readily available**



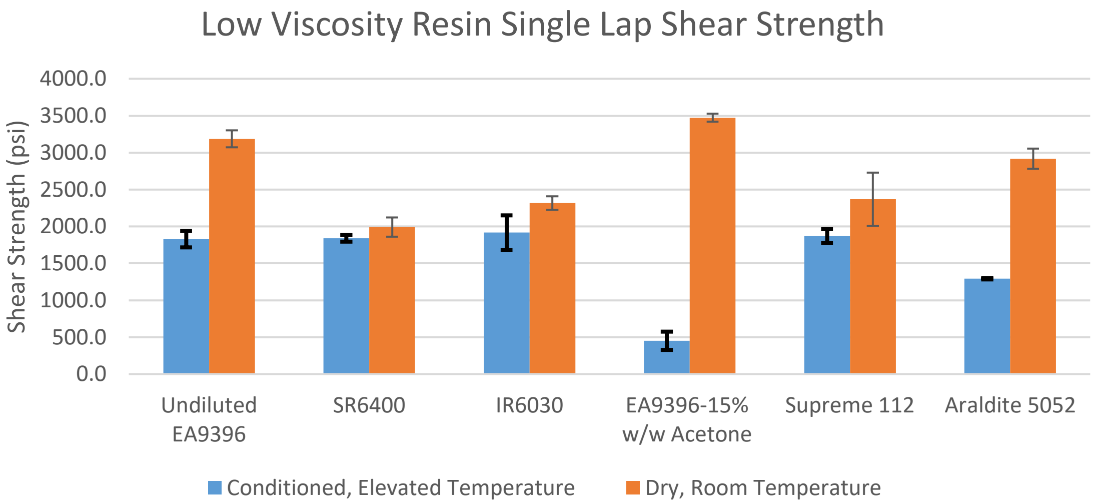
Milestone 2: Epoxy Characterization

Viscometer Testing



- **Evaluation of epoxy viscosity conducted with Brookfield Viscometer**
  - **Reading were taken over the span of 10 minutes after time of mix**
  - **Ambient temperature at 21°C versus the 25°C condition stated in TDS**
    - **Results are more viscous than values stated in datasheets, also more conservative and representative of actual conditions**
- **<u>Results</u>**
  - **SR6400 and EA9396-15% acetone display the lowest viscosity (200 – 300 cP)**
  - **Supreme 112 and Araldite well above the 650 cP of AJ Russell's epoxy (red line); IR6030 at the threshold**
  - **Not pictured: initial viscosity for 10% MIBK is 833.3 cP**

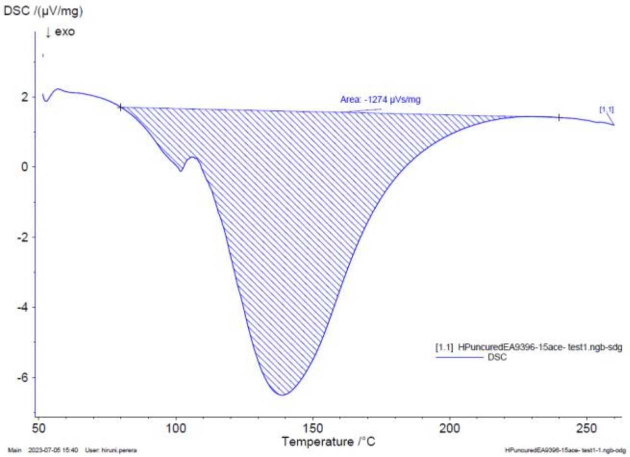
Single Lap Shear



	EA9396	SR6400	IR6030	EA9396-15% w/w Acetone	Supreme 112	Araldite 5052
% change from original mass to final mass (TC)	1.74	1.52	0.57	-1.32	0.27	0.46
Dry, RT shear strength (psi)	3186.7	1993.4	2317.5	3473.6	2369.2	2971.9
Conditioned, elevated temp shear strength (psi)	1829.3	1839.7	1916.8	451.2	1871.4	1291.8
% Difference From Average Dry RT Results	-42.6	-7.7	-17.3	-87.0	-21.0	-55.7

- **Conducted single lap shear (SLS) testing for dry and heat and humidity-conditioned samples**
- **Conditioned samples were in humidity cabinet at 140°F and 90% RH until moisture equilibrium achieved**
  - **Samples soaked for 10 minutes at 250°F immediately prior to testing**
- **<u>Results</u>**
  - **EA9396 variants and Araldite 5052 demonstrated the largest RT SLS and the most extreme change with hot-wet samples**
  - **Kaneka resins displayed the lowest deviation between the hot-wet and dry SLS**
  - **All coupons failed cohesively**

DSC Testing



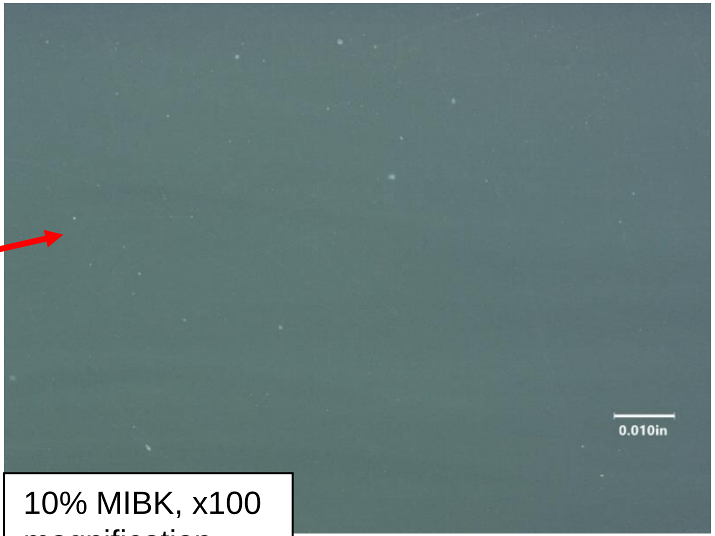
EA9396-15% Acetone- uncured sample example

Epoxy	Degree of Cure (%)
EA9396	92.1-94.9
EA9396 w/ 15% Acetone	95.9
SUP112	94.7
IR6030	95.2
Araldite 5052	96.6

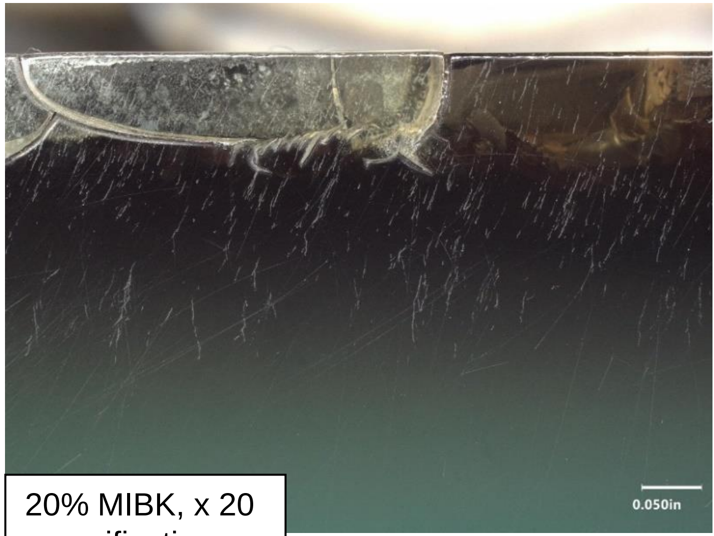
DSC sample containers for EA9396-15% acetone (left) and EA9396 (right) post testing

- **Using DSC to determine the degree of cure per the TDS-recommended cure cycles**
  - **Heating rate at 20°C/min**
- **Samples of known mass are heated and changes in heat capacity are tracked as a function of time**
- **Residual exotherm of cured and uncured samples are compared to get degree of cure**
- **Volatility of EA9396 diluted with acetone noted in epoxy egress from DSC container**

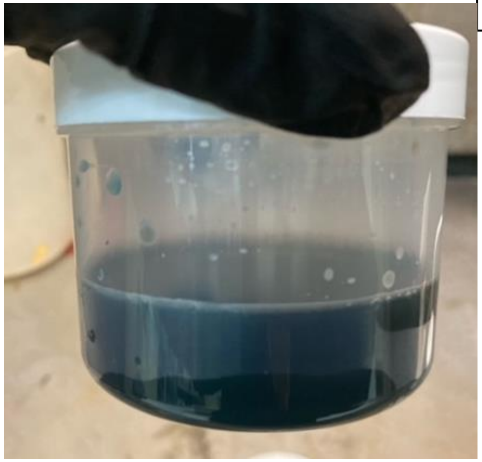
Porosity Studies- Diluted EA9396



10% MIBK, x100 magnification



20% MIBK, x 20 magnification



10% MIBK EA9396 Resin Puck

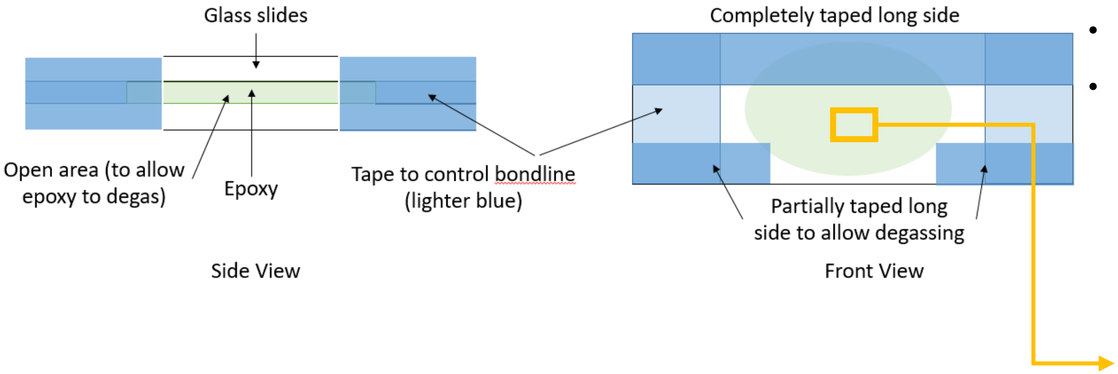
<u>Purpose</u>: characterize the bubble generation from diluting EA9396 with different solvents

  - **Excess bubbles could become trapped in small cracks from delamination**
  - **Cure 10% and 20% MIBK after 24 hr set time at room temp in containers with lid closed to simulate "worst-case" (arduous path for resins to outgas)**
  - **Pucks" cut in half; cross-section polished and examined under microscope**

<u>Results</u>

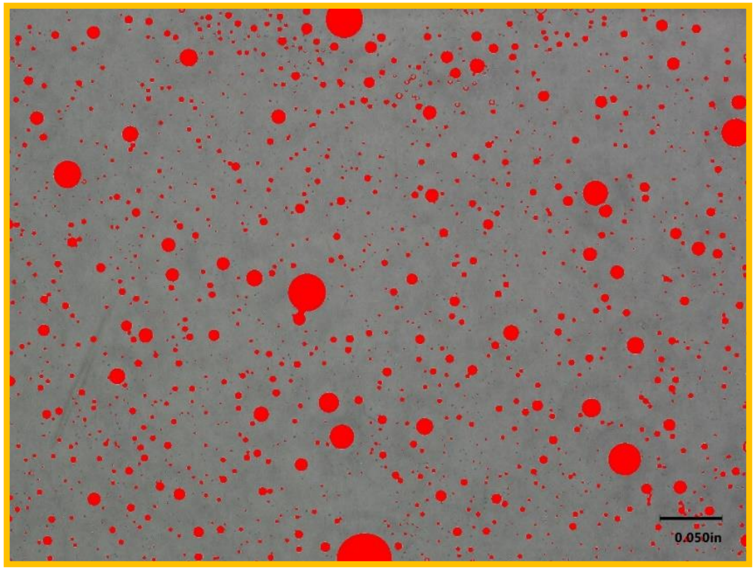
- **20% MIBK showed surface discoloration post cure and large voids at surface**
  - **Solvent concentration is rejected as a viable option**
- **10% MIBK puck shows very sporadic voids- fairly homogeneous surface**
- **MIBK as a diluent was eliminated due to volatility and 10% w/w only reduced viscosity to 833 cP**

Porosity Studies-All Potential Epoxies



- Used Keyence VHX-7000 digital microscope to analyze porosity generated from hand-mixing and curing epoxies
  - Areal porosity calculated using area of bubbles (red) with respect to specified area of coupon
- Micrographs taken with x20 magnification to yield more global view of coupon (i.e. EA9396 shown below)
- <u>Notes</u>
  - EA9396 variants showed the largest areal porosity
    - Mixing Parts A and B components that are very different in viscosity requires more motion for homogenous solution
    - High viscosity of Part A also seems to result in large amount of bubbles induced
  - Observed comparatively low porosity in remaining epoxies

Epoxy	Average Areal Porosity (%)
EA9396	8.32
EA9396 w/ 15% Acetone	6.61
SR6400	0.22
IR6030	1.42
SUP112	2.80
Araldite 5052	2.03



DMA Testing

Epoxy	Average Tg, E' (°C/°F)	Average Tg, E" (°C/°F)	Average Tg, tan δ (°C/°F)
Masterbond Supreme 112	107.2/224.96	111.4/232.5	131.9/269.4
Kaneka SR6400	125.8/258.5	132.5/270.6	156.9/314.4
Kaneka IR6030	126.1/256.0	134.5/270.0	145.0/293.0
EA9396-15% Acetone	74.7/166.5	84.2/182.6	143.1/289.6
EA9396	94.8/202.6	107.4/225.3	166.1/331.0
Araldite 5052	113.8/236.7	122.2/252.0	131.3/268.3

- **Stress applied to heated sample in 3-pt bend configuration**
- **Material response is measured; loss in elasticity is correlated to Tg**
- **Test parameters and results interpretation dictated by ASTM 7028**
- **3 samples were tested per epoxy**
- **<u>Results</u>**
  - **Both Kaneka resins exhibit average storage modulus Tg that is larger than expected Super Hornet service temperature (250 ° F)**
  - **All epoxies have comparatively larger Tg versus the currently-used EA9396**

Decision Matrix Scoring Criteria

Score Rating	Single Lap Shear Strength, Dry and RT (psi)	Single Lap Shear Strength, Elevated Temp (psi)	Viscosity (cP)	Tg, E' (°F)	Porosity (% areal porosity)	Pot Life (hrs)	Cost/qt. kit ($)	Procurement (months from order placement)
1	<2000	<1750	>700	<220	>5	<0.5	>1000	>2
2	2000-3000	1750-2000	300-700	220-250	3-5	0.5-1.5	500-1000	1-2
3	>3000	>2000	<300	>250	<3	>1.5	0-500	<1

- **Created a decision matrix (outlined on next slide) to converge upon 1-2 candidate epoxies to continue to evaluation process (repair strength restoration)**
- **Categories that epoxies' were evaluated upon outlined in table above**
  - **Epoxies were evaluated relative to each other- cut-off for each "score" reflects this**
  - **Epoxies with the largest total "score" will be used for further evaluation with ENF and CAI**

Decision Matrix

	Category Weights (Multiplier)	EA9396	SUP112	SR6400	IR6030	EA9396-15% Acetone	Araldite 5052
Single Lap Shear Strength, Dry	0.1	3	2	1	2	3	2
Single Lap Shear Strength, Hot-Wet*	0.1	2	2	2	2	1	2
Viscosity	0.2	1	1	3	2	3	1
Tg	0.2	1	2	3	3	1	3
Porosity Generation	0.15	1	3	3	3	1	2
Pot Life	0.05	3	1	1	3	3	2
Cost	0.1	3	1	2	3	3	3
Procurement	0.1	3	2	3	3	3	1
Total	1	1.80	1.80	2.80	2.60	2.10	2.00

Milestone 3: Fracture Toughness Testing (In Progress)/ Hot-Wet Tg Testing

End-Notched Flexure (ENF) Test

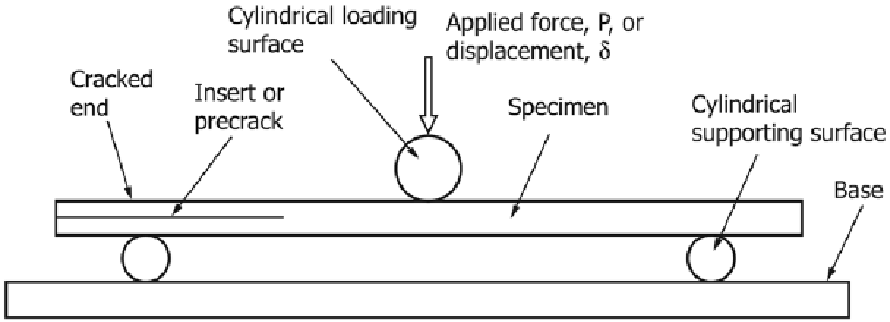
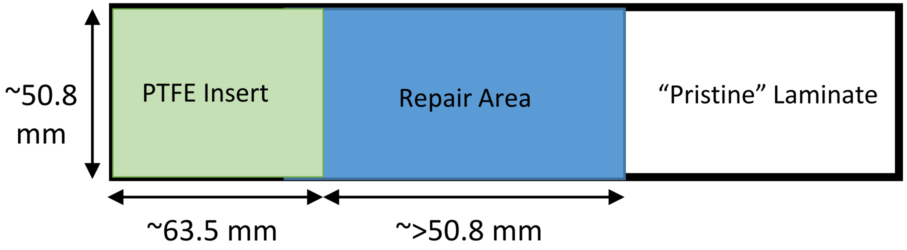


FIG. 1 ENF Test Fixture and Specimen Nomenclature



~50.8 mm

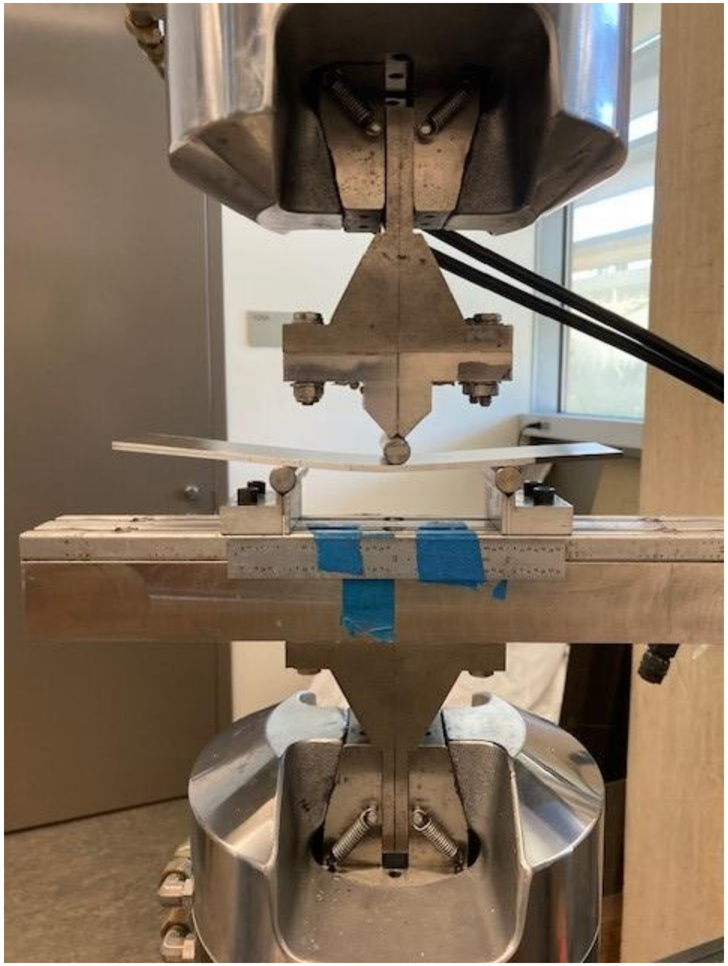
PTFE Insert

Repair Area

“Pristine” Laminate

~63.5 mm

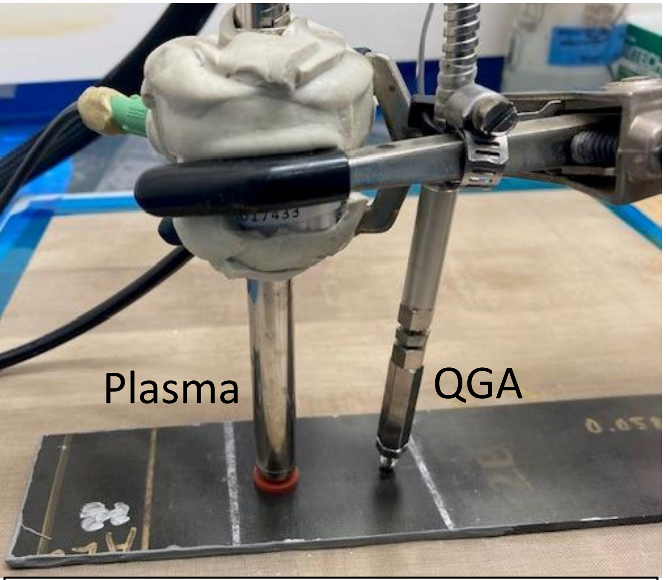
~>50.8 mm



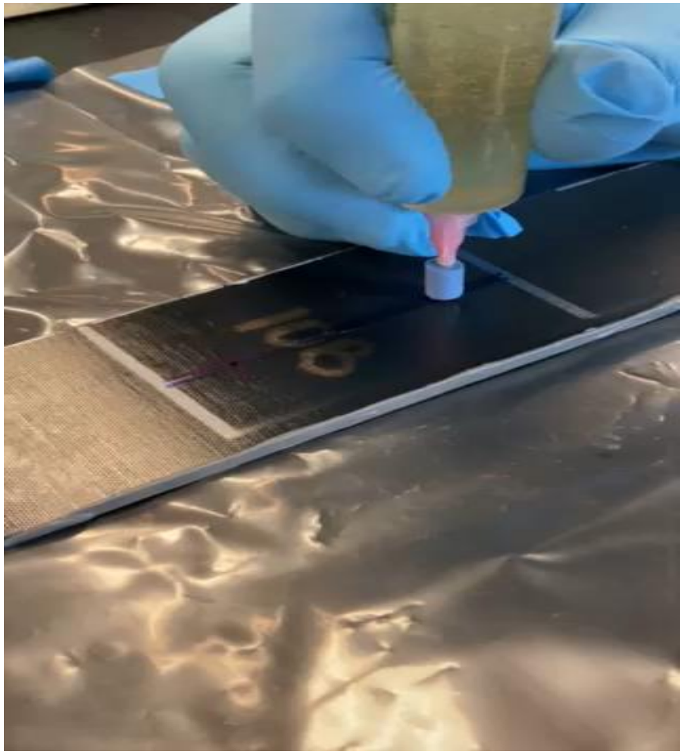
- **IM7/977-3 panels created with PTFE insert to simulate delamination**
- **Coupons are loaded under Mode II shear to propagate crack and measure fracture load**
  - **Fracture toughness is calculated as function of fracture load and geometric effects**

Cleaning and Resin Injection Process

- **Small cracks within delaminated components can be filled with common contaminants (hydraulic fluid, jet fuel, etc.)**
  - **Contaminants would compromise bonding of injected resin to c/ep coupon**
- **ENF coupons were injected with hydraulic fluid to simulate worst-case scenario**
- **Cleaning process involving acetone flush followed by nitrogen purge and atmospheric plasma surface treatment developed to reduce contaminant volume [2]**
  - **Plasma treatment done with Surfx Atomflo 500L**
  - **Reduction of HF elements were tracked using Hiden Quantitative Gas Analyzer (mass spectrometer)**
- **~15 mL repair resin injected into coupon immediately post cleaning**



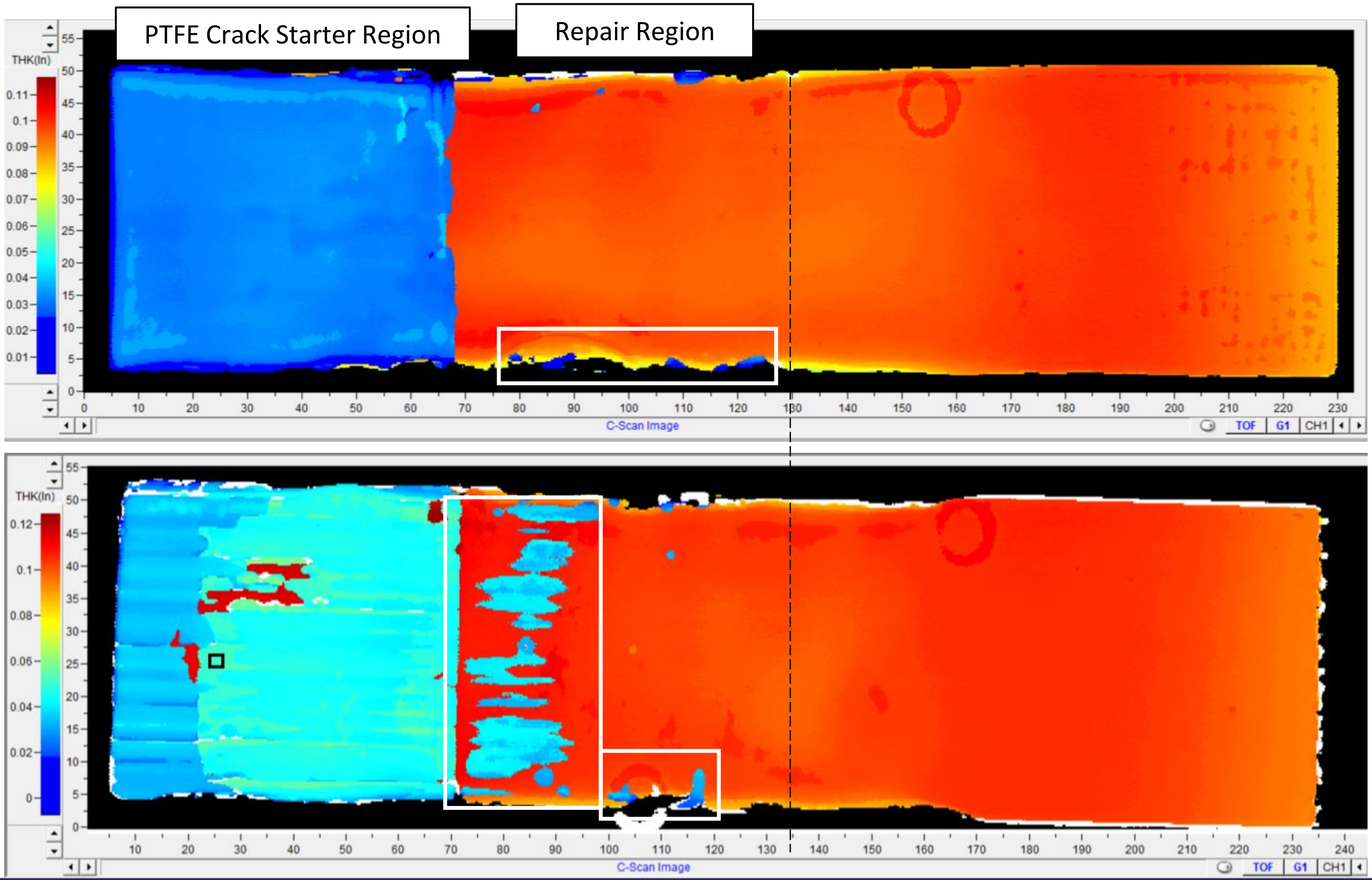
Plasma Cleaning Process with QGA



Coupon Injected with Kaneka IR6030

Sample Repaired Coupon C-Scans

- **Pulse-echo ultrasonic scans with 10 MHz transducer and water as couplant**
- **Edges of repair region tend to have pockets of under filled areas or voids (white boxes)**
- **Larger viscosity of IR6030 yields more effort in injection and filling of cracks**

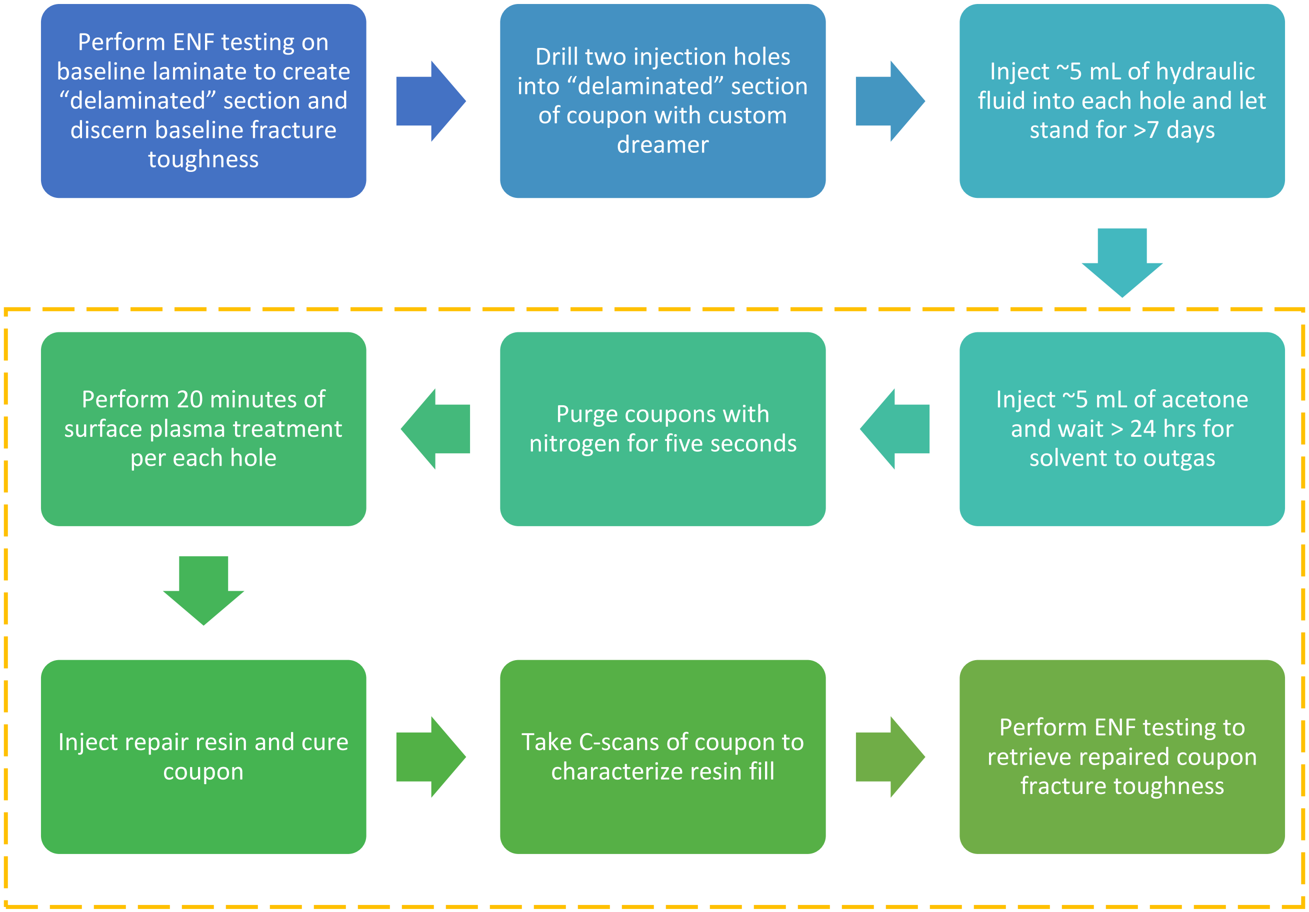

PTFE Crack Starter Region

Repair Region

Kaneka SR6400
~250 cP

Kaneka IR6030
~650 cP

Current Process Workflow Summary



Perform ENF testing on baseline laminate to create "delaminated" section and discern baseline fracture toughness

Drill two injection holes into "delaminated" section of coupon with custom dreamer

Inject ~5 mL of hydraulic fluid into each hole and let stand for >7 days

Inject ~5 mL of acetone and wait > 24 hrs for solvent to outgas

Purge coupons with nitrogen for five seconds

Perform 20 minutes of surface plasma treatment per each hole

Inject repair resin and cure coupon

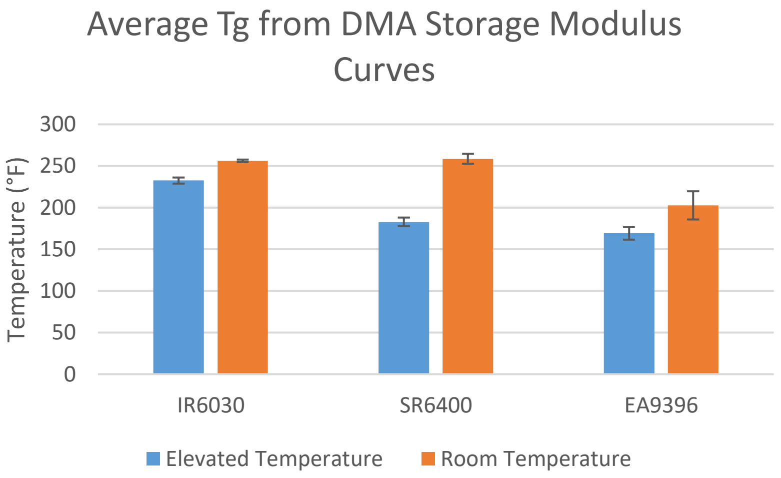
Take C-scans of coupon to characterize resin fill

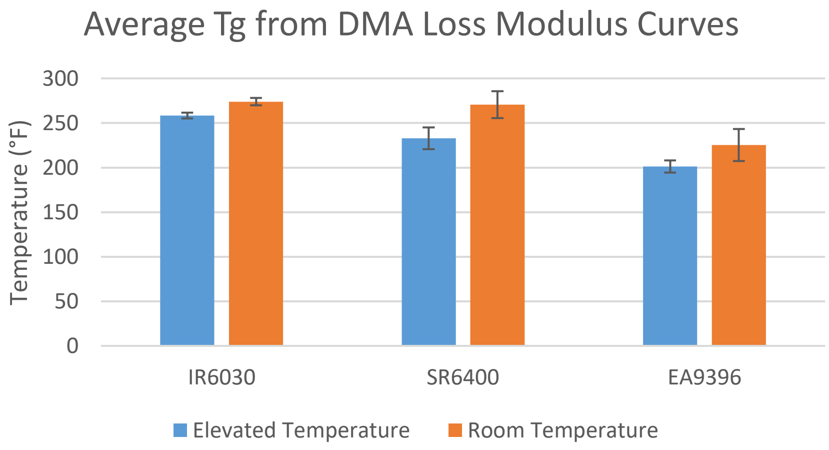
Perform ENF testing to retrieve repaired coupon fracture toughness

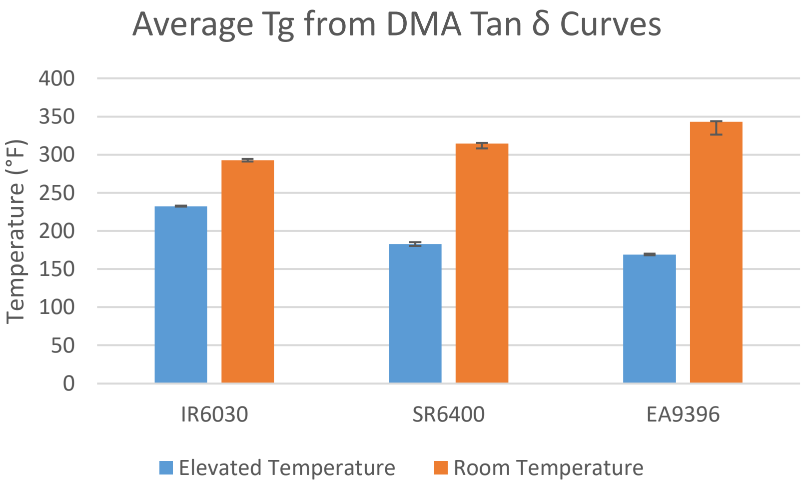
Work in progress

Elevated Temperature-Wet Tg

	Tg (E’, °C/°F)	Tg (E’’, °C/°F)	Tg (tan δ,°C/°F)
IR6030	111.4/232.5	125.8/258.4	143.7/290.7
SR6400	83.8/182.8	111.6/232.9	158.8/317.8
EA9396	76.1/169.0	94.0/201.2	156.0/312.8


Average Tg from DMA Storage Modulus Curves


Average Tg from DMA Loss Modulus Curves


Average Tg from DMA Tan δ Curves

Path Forward

- **Milestone 3: Fracture Toughness Testing**
  - **Continue ENF testing to determine repaired coupons' fracture toughness**
  - **Analyze fracture surfaces to discern failure modes**
  - **Develop elevated-temperature test setup**

- **Milestone 4: NDI, Mechanical Testing of Resin-Injected Impacted Coupons**
  - **Inject repair resins into laboratory-impacted coupons**
  - **Perform pulse-echo UT to determine percentage fill**
  - **Compression-After-Impact (CAI) testing to be performed at PAX to determine strength restoration from repair**
  - **Converge upon the repair resin of choice**

- **Implementation**
  - **Present results to platform FSTs**
  - **Execute additional testing and/or perform demonstration on actual component as identified by FST**

References

[1] Russell, A.J. and Bowers, C.P., “Resin Requirements for Successful Repair of Delaminations”, Proceedings of the 36th SAMPE Symposium, 15-18 April 1991, San Diego, CA.

[2] Massey, J. T. (2023). Novel Quantitative Composite Delamination Injection Repair Procedure and Characterization for Strength Restoration. *UC San Diego*. ProQuest ID: Massey_ucsd_0033D_22445. Merritt ID: ark:/13030/m5m99dk2. Retrieved from https://escholarship.org/uc/item/17n8b3vz

[3] ASTM Standard D7905, 2019,“Standard Test Method for Determination of the Mode II Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites,” ASTM International, West Conshohocken, PA, 2023

Questions?