Methods to Understand, Monitor, and Extend Prepreg Shelf-Life

WP20-S1-1490

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-Characterize effects of storage time (ambient and freezer) on prepregs
-Measure (vs. track) accrued shelf-life of prepreg via in situ monitoring
-Extend prepreg shelf-life by adjusting cure process to overcome effects of protracted storage

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Motivation

The aerospace industry sends more than 10,000,000 lbs of unused prepreg to the landfill each year

Sources of Prepreg Waste:

- Storage life expiration
- Cutting table scrap
- Supply chain management
  - Large order sizes
  - Long lead times (> 6 weeks)
  - Requires tracking of history, roll-by-roll

Image source: Nilakantan G, and Nutt S. Reuse and Upcycling of Aerospace Prepreg Scrap and Waste. Reinforced Plastics 2015; 59(1): 44-51.
Image source: https://www.materialsforengineering.co.uk/engineering-materials-explore/composite-materials/features/recycling-carbon-fibre/160324/

Motivation

Project Goals

1. Characterize effects of storage time (ambient and freezer) on prepregs
2. Measure (vs. track) accrued shelf-life of prepreg via *in situ* monitoring
3. Extend prepreg shelf-life by adjusting cure process to overcome effects of protracted storage

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Motivation

Potential for Industry Impact:

- Restore value and performance to prepregs currently scrapped
- Reduce economic and environmental impact of prepreg waste disposal via landfill
- Enable complex parts – extend layup times

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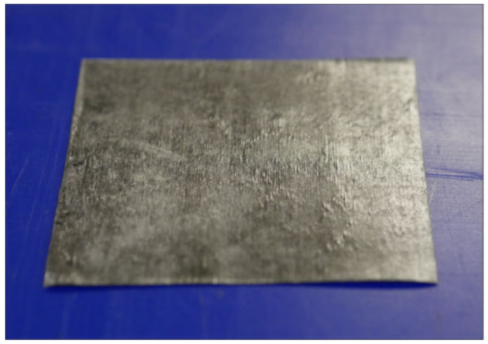
Image source: https://www.materialsforengineering.co.uk/engineering-materials-explore/composite-materials/features/recycling-carbon-fibre/160324/

Understanding Prepreg Aging: Characterization

Material Selection:
UD prepreg (Solvay 5320-1: 150 gsm)

Material Aging Status:
11.5 mo freezer storage (receipt)

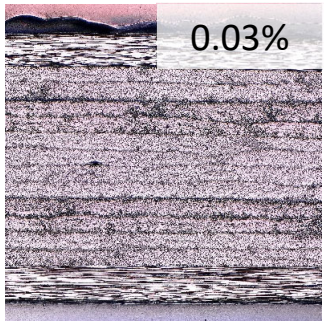


Characterization Goals:

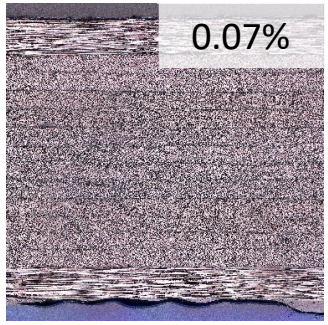
- ID onset of age-induced process or property decrease
  - At RT (out-time)
  - In freezer (storage time)
- Identify aging mechanism(s) causing process/performance deviation

RT Aged Laminates: Micrographs

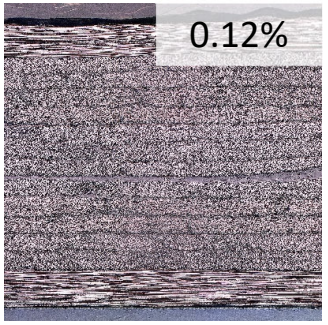
$F_{12}R_0$



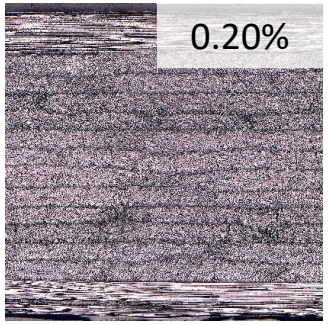
$F_{12}R_7$



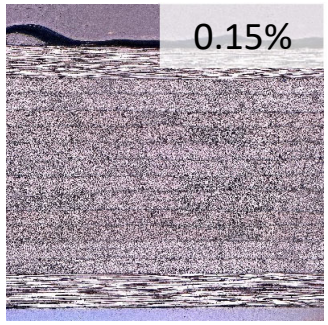
$F_{12}R_{14}$



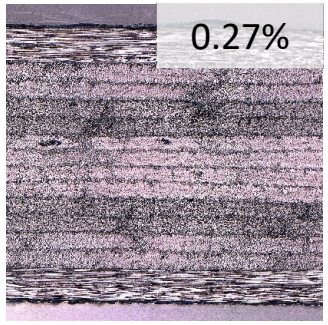
$F_{12}R_{21}$



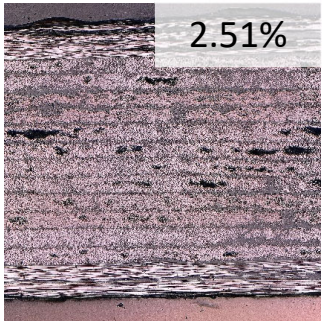
$F_{12}R_{28}$



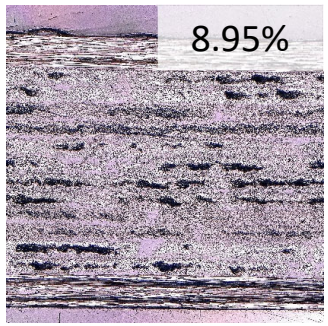
$F_{12}R_{35}$



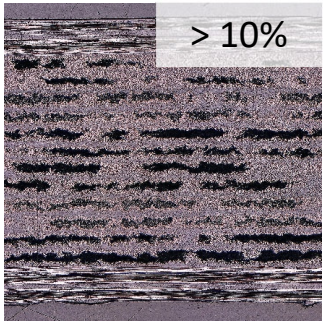
$F_{12}R_{42}$



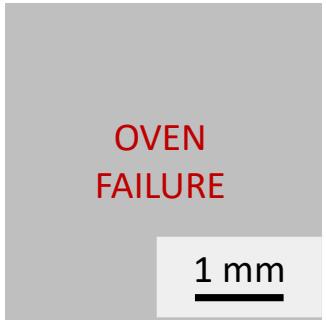
$F_{12}R_{49}$



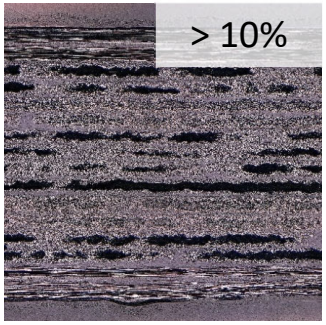
$F_{12}R_{56}$



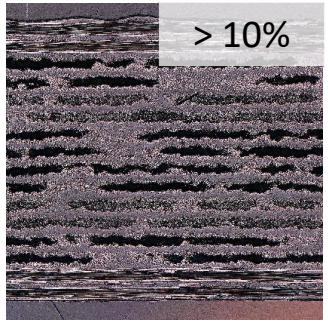
$F_{12}R_{63}$



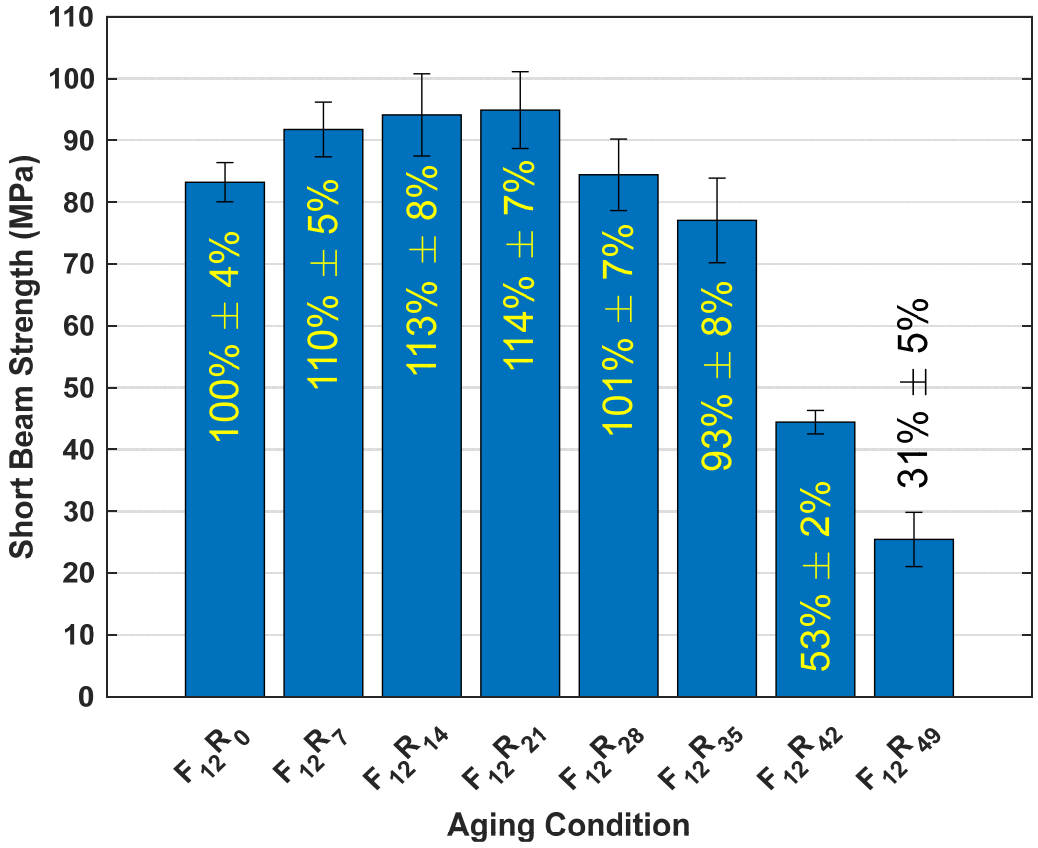
$F_{12}R_{70}$



$F_{12}R_{77}$



RT Aged Laminates: Mechanical Testing



Short Beam Shear Tests (SBS):

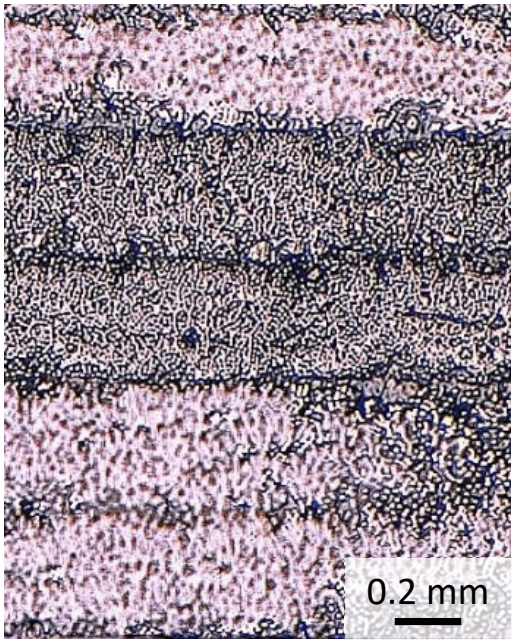
- Six samples from each laminate
- Normalized vs laminate with least age ($F_{12}R_0$)
- Error bars = std dev

Key Findings:

- Age-induced strength drop correlated with out-life spec
- SBS strength correlated with porosity

RT Aged Laminates: Defect Formation Mechanisms

Day 35



Day 42

Day 70

Key observations:

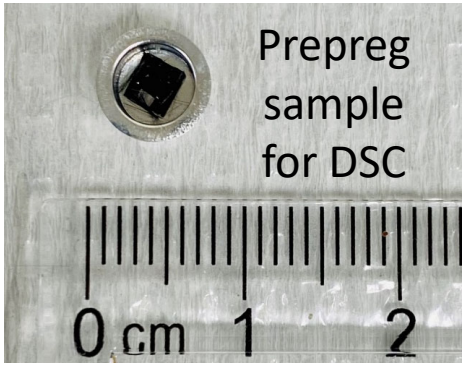
- Low porosity in *interply* regions
  - Not gas-induced
- Resin-rich regions remain:
  - Inter-tow, same ply
  - Inter-ply
- Excess resin adjacent to dry tows → flow-induced

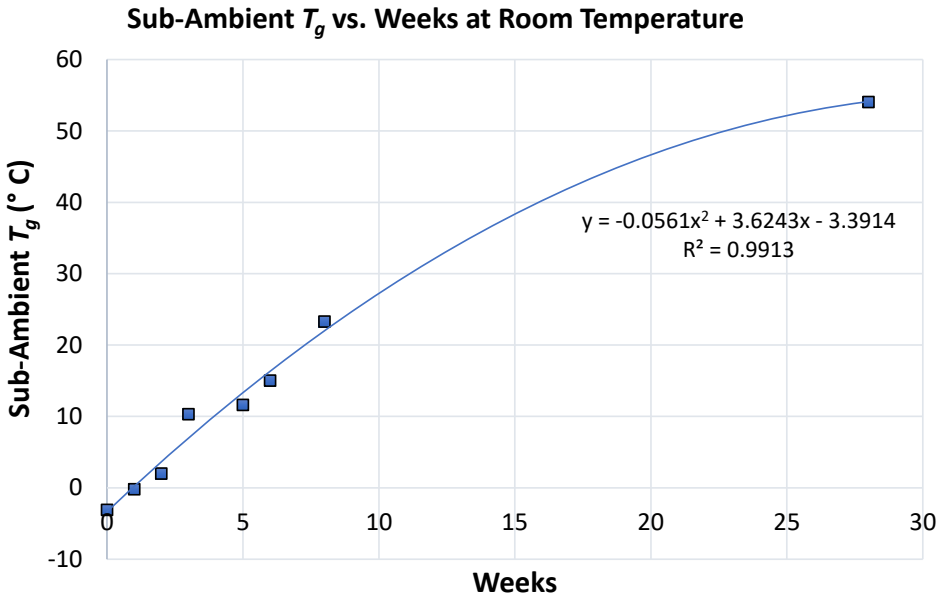
Primary defect formation mechanism: insufficient resin flow

Measuring Prepreg Out-Time: Sub-Ambient T_g

Differential Scanning Calorimetry (DSC)

- Small samples: 5-8 mg
- Fast process: sub-ambient T_g measured: 90 minutes

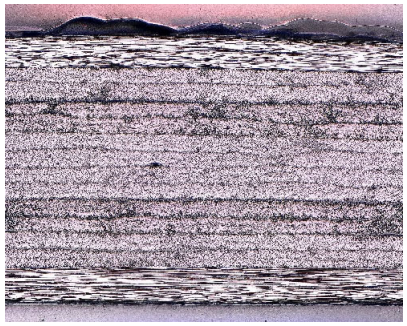




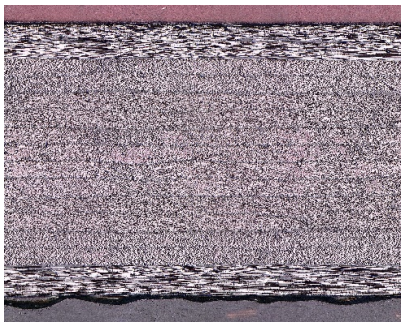
Key Finding: Sub-ambient T_g correlates with prepreg out-time

Freezer-aged laminates

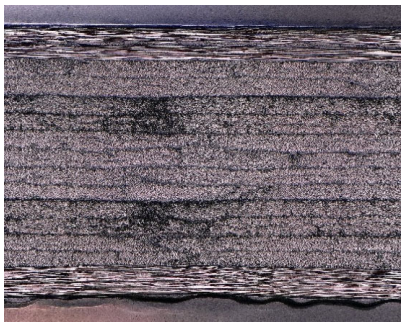
$F_{12}R_0$



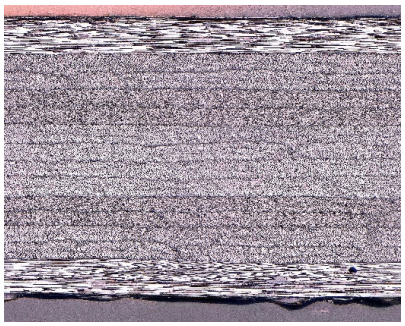
$F_{13}R_0$



$F_{14}R_0$



$F_{15}R_0$

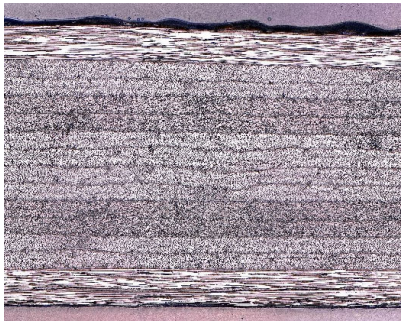


$F_{16\text{-}18}R_0$

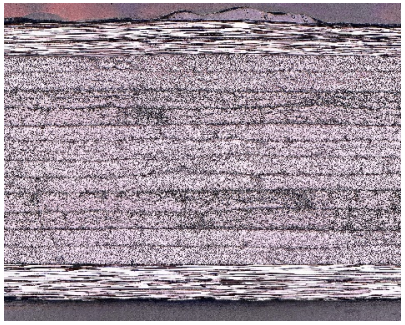
COVID-19
INTERRUPTION

1 mm

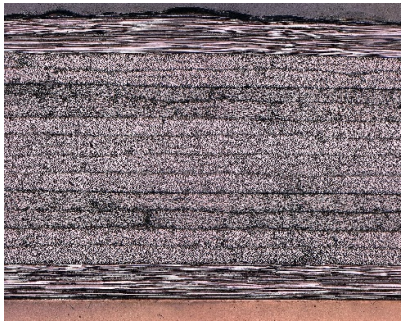
$F_{19}R_0$



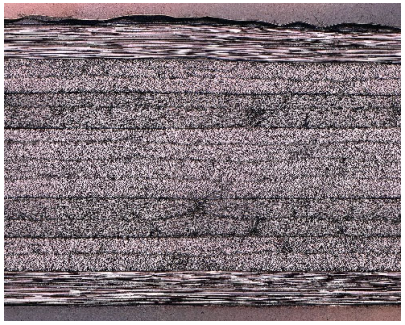
$F_{20}R_0$



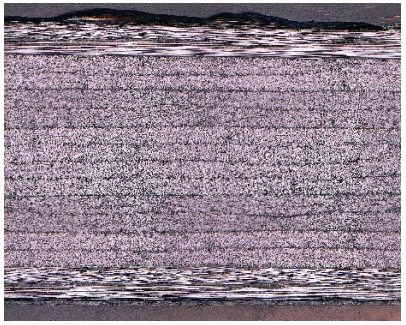
$F_{21}R_0$



$F_{22}R_0$



$F_{23}R_0$



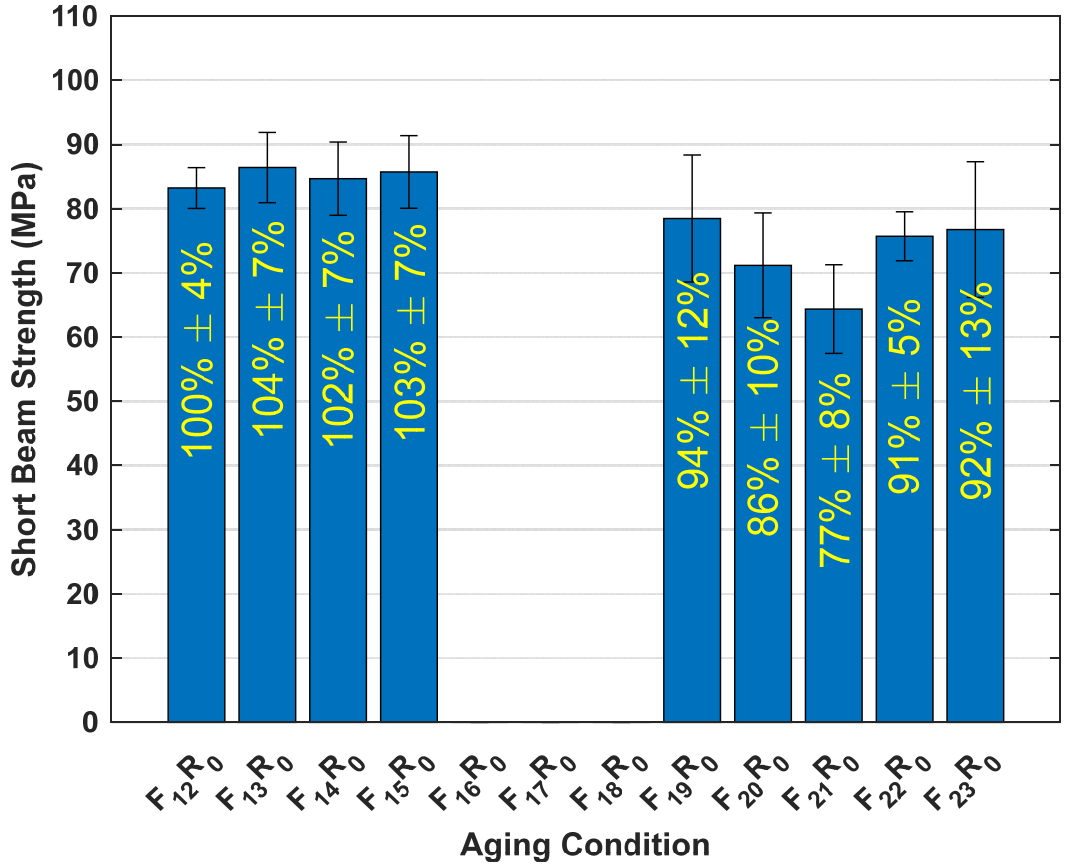
Freezer Aged Laminates: Mechanical Testing

Observations:

- Freezer-aged prepreg continues to produce defect-free parts **11 months *beyond* storage life spec**
- Knockdowns in SBS strength *not* due to increased porosity

Key Finding:

- SBS knockdown from freezer-storage *not* caused by flow-induced defects



Measuring Storage-Time

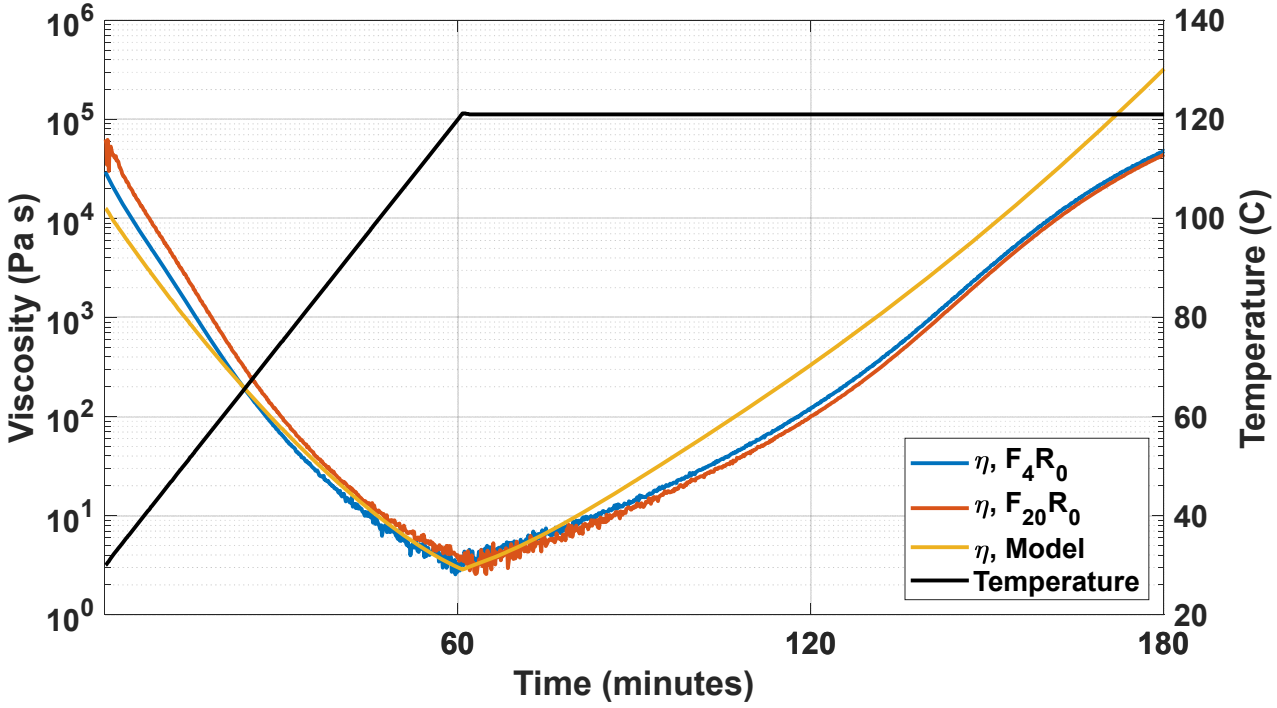
DSC Measurements:

- Sub-ambient T_g unchanged after 9 months of freezer storage
  - $F_{12}R_0$: -2.35° C
  - $F_{21}R_0$: -3.52° C

Key Finding:

Resin crosslinking is not the cause of strength knock-down from freezer storage

Rheometry indicates little processing behavior deviation



Understanding Prepreg Aging: Summary

Out-time Aging:

Onset process, strength loss:

- 28-25 days

Aging mechanism:

- Poor resin flow caused by crosslinking

Out-time can be measured via

- DSC (sub-ambient T_g)

Storage (Freezer) Aging:

Onset of age-induced process, strength loss:

- 16-19 months

Aging mechanism(s) responsible:

- Hypothesis: water (work needed)

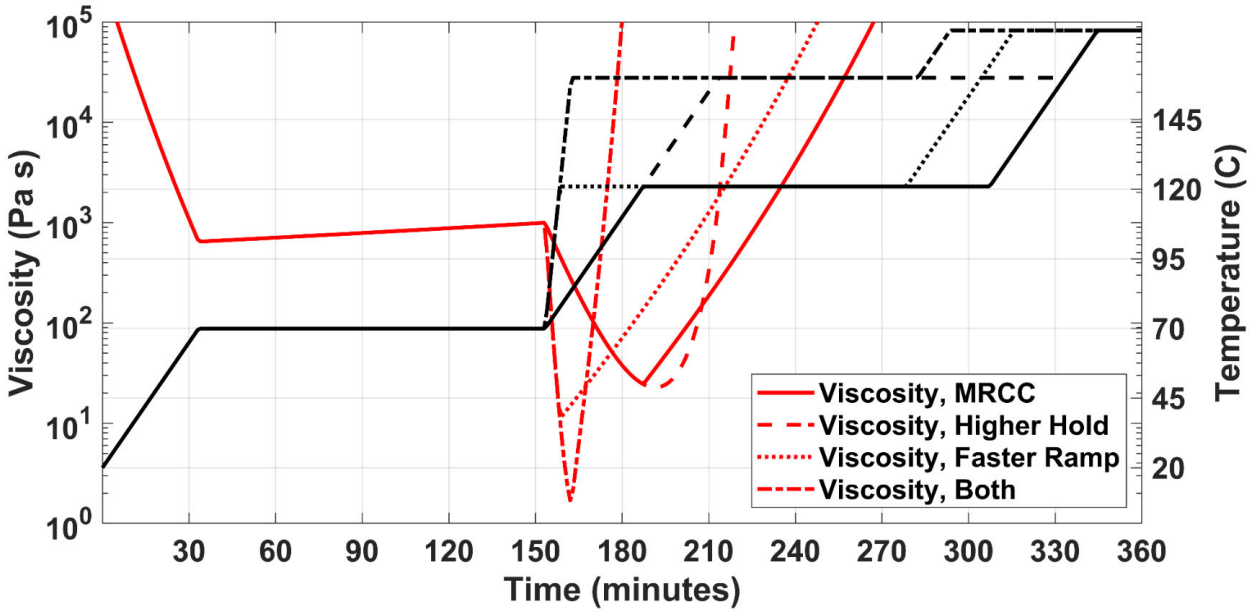
Storage-time cannot be measured using DSC

- Exploring other techniques (HPLC, NMR)

Cure Cycle Modification for Processing Over-Aged Prepreg

Cure Cycle Modification Goals:

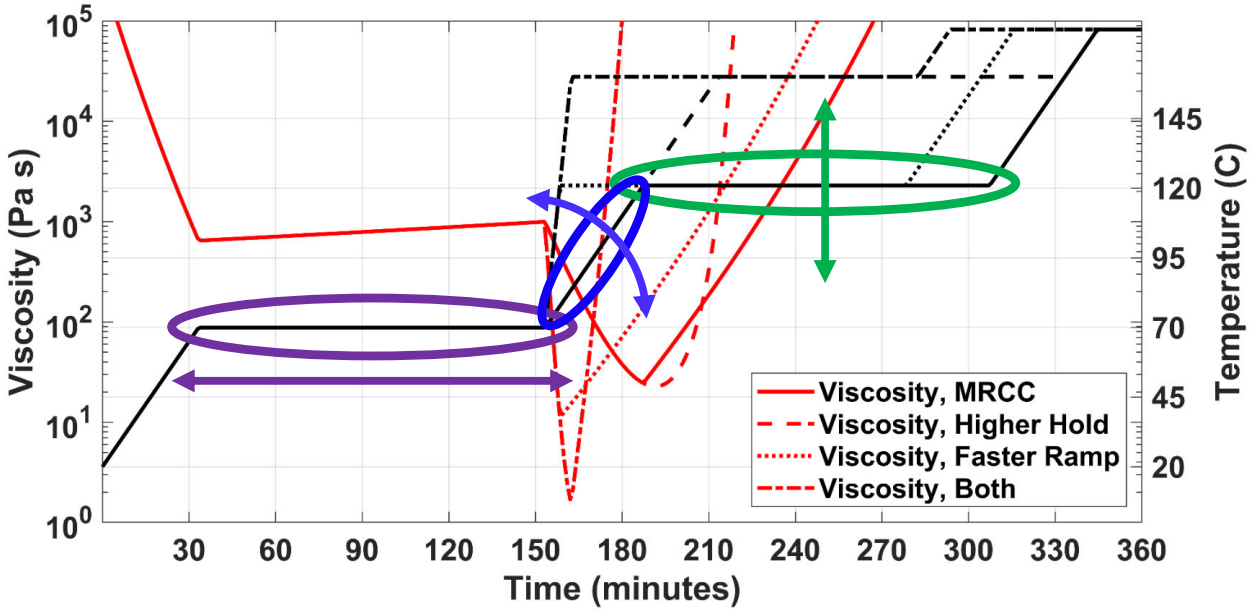
- Develop process design tool to modify cure cycle as function of aging
- Demonstrate modified cure cycles extend out-life, verifying
  - Low porosity
  - Strength retention



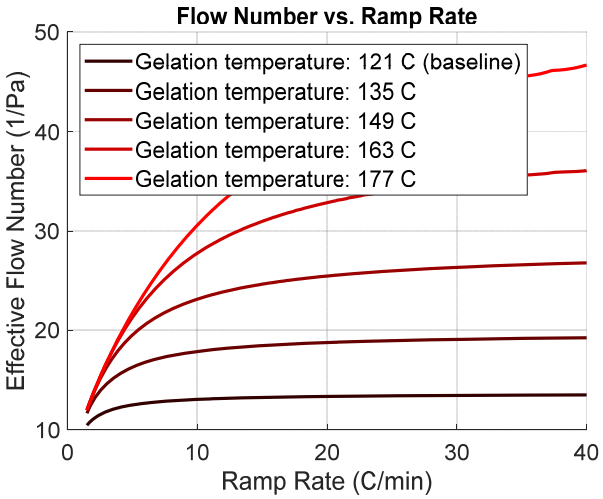
Cure Cycle Modification Parameters

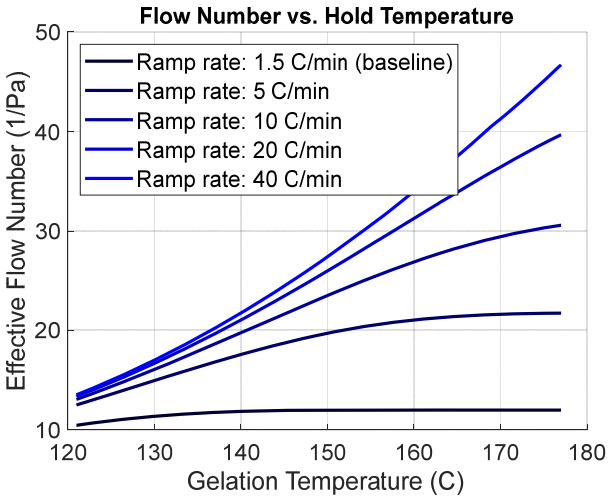
Cure Cycle Mod Script specifies:

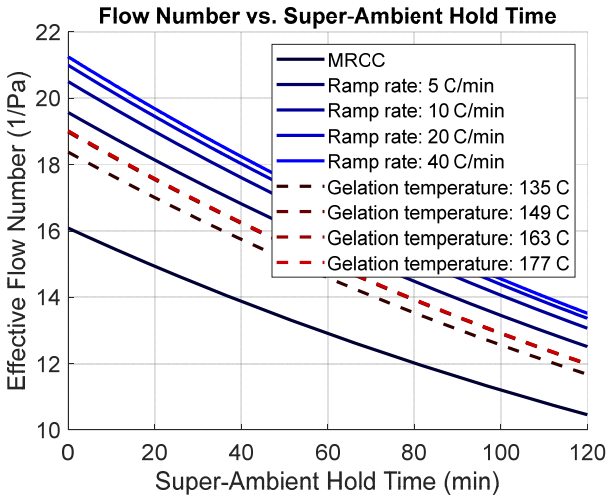
- Ramp rate
- Cure temperature
- Sub-ambient dwell time



Cure Cycle Modification Parameters





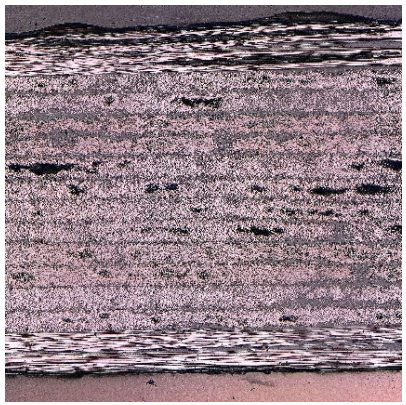


Key Observations:

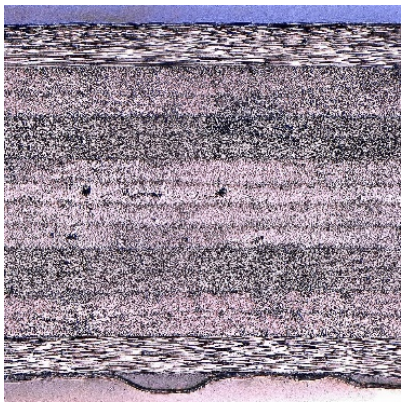
- Ramp rates > 20 ° C/min → marginal increases in Flow Number
- Cure T and super-ambient hold time → quasi-linear relations w/ flow number

Cure Cycle Modification Demonstration

Day 42, MRCC

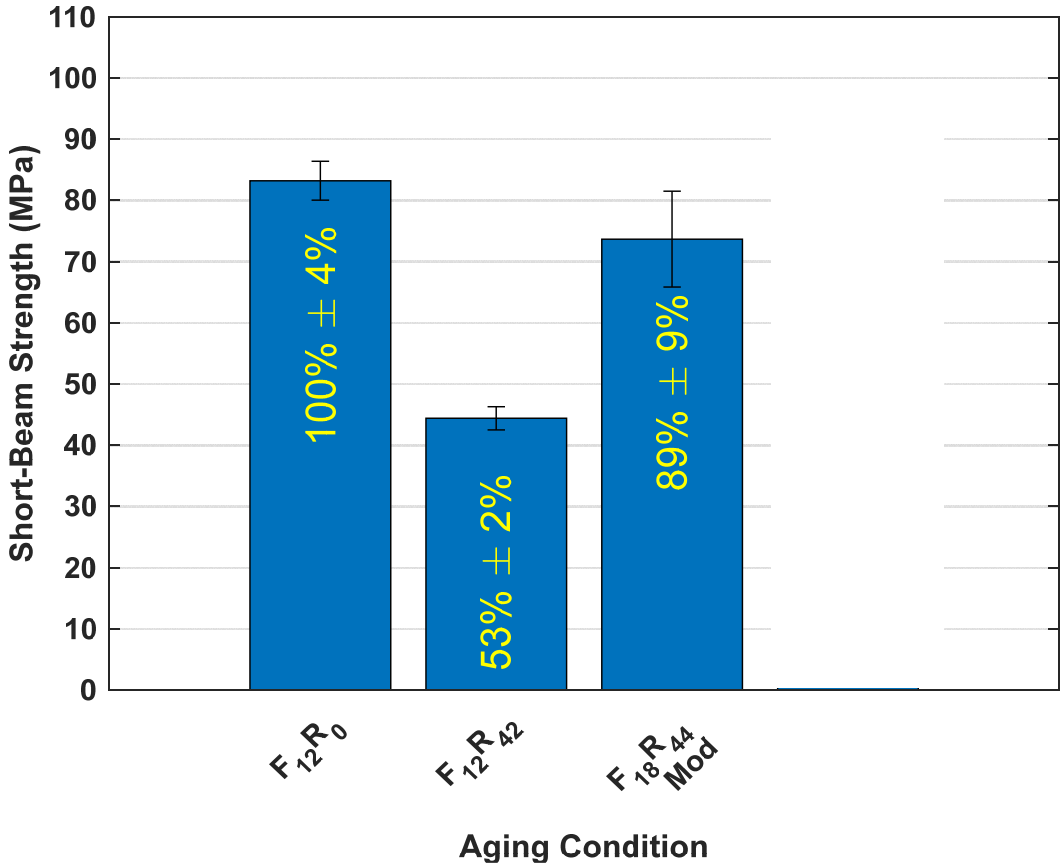


Day 45, Mod. CC



Cure cycle modification

- Reduced porosity
- Increased strength to ~90%



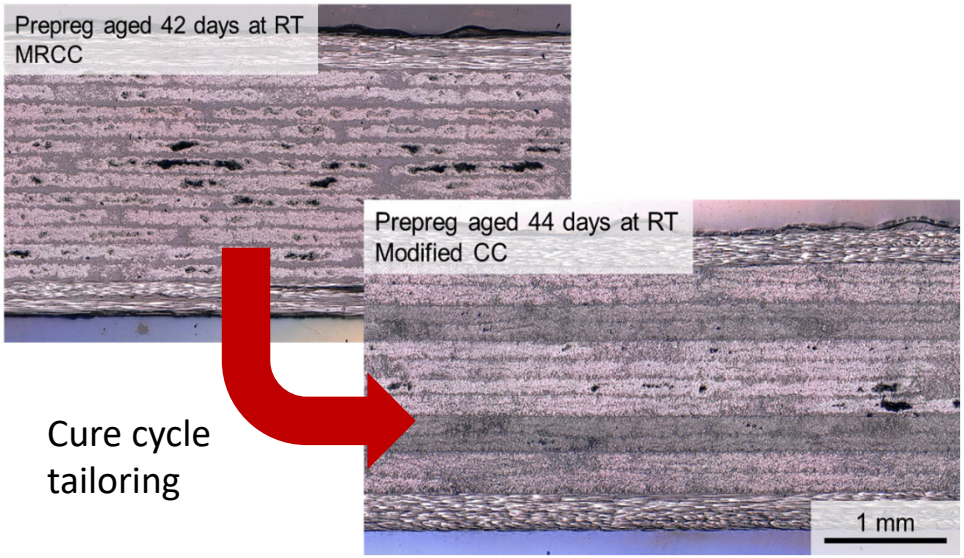
Conclusions and Future Work

Conclusions

- Sub-ambient T_g = useful indicator of out-time, measured rapidly and at low cost
- Cure cycle tailoring can extend prepreg out-life by 2 weeks (46%) - mechanicals retained

Future Work:

- Identify physical/chemical changes occurring during freezer storage
- Develop/demonstrate strategies to extend freezer storage life
- Demonstrate out-time diagnostic on prepreg formulations (BMI, PI, etc.)



Cure cycle tailoring

Broader Impact

- Recover value, performance of waste materials
- Reduce economic, environmental impact of PMC manufacturing