FINAL REPORT

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

SERDP Project WP20-1490

NOVEMBER 2020

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SERDP
DOD ▪ EPA ▪ DOE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
22-11-2020	SERDP Final Report	9/23/19 – 9/23/21

4. TITLE AND SUBTITLE

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

5a. CONTRACT NUMBER
19-P-0081

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Steven Nutt

5d. PROJECT NUMBER
WP20-1490

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Southern California
Los Angeles, CA 90089
USA

8. PERFORMING ORGANIZATION REPORT NUMBER

WP20-1490

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
WP20-1490

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT The objectives of this project were to (a) characterize the effects of freezer storage and out-time on thermoset polymer prepregs, (b) develop a method for measuring accrued shelf-life of prepreg using non-invasive in situ monitoring, and (c) identify and impose adjusted process conditions (cure cycles) to extend prepreg shelf-life to produce laminates with equivalent performance to material produced under recommended prepreg storage and processing conditions, thereby eliminating the detrimental effects of protracted storage. The methods developed during this project will restore full value and performance to most prepreg materials currently considered waste, while ensuring that fabricated parts will achieve equivalent performance and exhibit fewer process-induced defects arising from protracted storage. In doing so, this work will reduce waste streams associated with time-expired materials, reducing total production costs and environmental impact.

15. SUBJECT TERMS
shelf-life, prepreg storage, laminate microstructure

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Steven Nutt
UNCLASS	UNCLASS	UNCLASS	UNCLASS	18	**19b. TELEPHONE NUMBER** *(include area code)* 213-740-1634

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List of Acronyms

CFRP	Carbon fiber-reinforced polymer
DSC	Differential scanning calorimeter
MRCC	Manufacturers recommend cure cycle
RT	Room temperature
SBS	Short-beam shear
RW	Resin weight
UD	Unidirectional

Keywords

Composites, prepreg, aging

Acknowledgements

The PI acknowledges SERDP (WP20-S1-1490) funding, and the efforts of two PhD students – Bill Edwards and Xiaochen Li, who did all of the experimental work for the project.

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

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Abstract

Objectives: The objectives of this project were to (a) characterize the effects of freezer storage and out-time on thermoset polymer prepregs, (b) develop a method for measuring accrued shelf-life of prepreg using non-invasive *in situ* monitoring, and (c) identify and impose adjusted process conditions (cure cycles) to extend prepreg shelf-life to produce laminates with equivalent performance to material produced under recommended prepreg storage and processing conditions, thereby eliminating the detrimental effects of protracted storage.

Technical Approach: The effects of storage time on laminate quality were monitored for prepreg stored at freezer temperature (to simulate long-term storage) and room temperature (to simulate out-time) by periodically curing laminates using the manufacturer's recommended cure cycle (MRCC). Laminate microstructure was characterized for defect (void) content using light microscopy, and mechanical properties were measured using short beam shear tests. The onset of age-induced void formation or mechanical performance decline was identified for each prepreg storage condition, and—where possible—the nature and cause of deviations from expected performance were identified. Differential scanning calorimetry was used to measure the B-stage glass transition temperature of prepreg, and this metric was demonstrated to be an effective means for assessing the time accrued at room temperature. A relationship between B-stage glass transition temperature (T_g) and prepreg out-time was developed for the standard aerospace prepreg used in this study.

Results: Insufficient resin flow (due to resin crosslinking during exposure to ambient temperature) was identified as the primary mechanism by which prepreg aging due to out-time causes defects. Freezer storage of prepreg, however, did not cause significant crosslinking; resin T_g and rheological behavior were unchanged after 20 months of freezer storage. A method for increasing resin flow in over-aged prepreg was developed by using resin cure kinetics and rheology models to estimate how cure cycle modifications changed resin flow properties. Cure cycle modifications were tailored to measurements of prepreg B-stage T_g to minimize deviations in manufacturer's recommended processing conditions. Cure cycle tailoring was demonstrated on prepreg aged for 44 days, yielding laminates with increased mechanical performance (compared to a laminate with similar aging but cured using the MRCC).

Benefits: The methods developed during this project will restore full value and performance to most prepreg materials currently considered waste, while ensuring that fabricated parts will achieve equivalent performance and exhibit fewer process-induced defects arising from protracted storage. In doing so, this work will reduce waste streams associated with time-expired materials, reducing total production costs and environmental impact.

Introduction and Objectives

Most high-performance composite structures are produced from thermoset prepregs, which undergo an irreversible cure reaction. This reaction initiates in prepreg resin when it is mixed, prior to resin deposition onto a fiber bed, and the rate of crosslinking is determined by the (storage or processing) temperature of the resin. As the cure reaction progresses, a continuous physicochemical change occurs, altering resin properties and modifying handling and processing behavior, all of which can result in unacceptable part rejection rates [1–3]. Because the aging state of prepreg resin is critical for assuring the production of defect-free laminates, prepreg manufacturers specify the allowable out-time (time out of the freezer at room temperature) and storage time (time stored in the freezer) beyond which they provide no assurance of mechanical performance. Consequently, manufacturers must discard time-expired materials rather than dedicate additional resources to processing and inspection, and there is presently no effective or economical approach for reusing, recycling, or otherwise disposing of expired prepreg.

Technical Objective 1 – Determine the effect of storage (freezer and out-time) on prepreg properties and behavior during processing and identify specific changes are associated with protracted storage. To propose effective strategies for extending freezer storage life/out-life, the mechanisms by which performance is compromised as age accumulates must be identified and understood. While it is widely believed that the same mechanism (resin crosslinking) is responsible for age-related performance decline during out-time and freezer storage, results obtained here indicate that different aging mechanisms compromise prepreg quality for the two conditions.

Technical Objective 2 – Identify *in situ* monitoring strategies for determining effective age of prepreg. Current practices for monitoring prepreg age (out-time) accumulation rely on tedious, manual, roll-by-roll tracking of exposure time at various temperatures; manual tracking is error-prone and scientifically inaccurate because it does not directly measure prepreg state. Not only must each roll of prepreg be independently tracked, but tracking must persist as prepreg is cut from the roll, kitted, laid up, and finally cured, to assure that the out-life spec is not exceeded. Prepreg is considered usable when resin has not yet exceeded out-life or storage life, and unusable if it has. However, the discrete nature of this metric does not map well onto the continuous changes in resin chemistry that are occurring as a function of aging. The present work demonstrates that B-stage T_g is a good indicator of the out-time accrued at any point in time.

Technical Objective 3 – Design/test cure cycle modifications that extend the useful life of thermoset prepreg. Recent work has provided insight into defect formation mechanisms in aged prepreg, and how such mechanisms may be overcome. Centea et al. showed that cure cycles that correspond to lower resin viscosity resulted in fewer flow-related defects (the predominant type of defect observed in overaged prepreg kept at room temperature) [4]. Kim et al. demonstrated that increasing cure cycle ramp rates and hold temperatures can reduce viscosity in overaged prepregs, and showed that laminates with a defect-free microstructure can be produced from overaged prepregs [5]. In this work, a method for tailoring the cure cycle as a function of accumulated prepreg age is developed and demonstrated.

Technical Approach

All work for this study was conducted using a common DoD-qualified prepreg (Cycom 5320-1 IM7 12K 145gsm 33% RW UD, Solvay). At the time of this study, the MRCC for this material included a range of ramp rates and hold temperatures. The nominal MRCC used in this study was

selected from these guidelines and defined by the following steps: (1) four-hour, room-temperature vacuum hold, (2) ramp at 1.5° C/min to a super-ambient dwell temperature of 70° C, (3) hold at the super-ambient dwell for 2 hours, (4) ramp at 1.5° C/min to the gelation temperature of 121° C, (5) hold at the gelation temperature for 2 hours, (6) ramp at 1.5° C/min to the post-cure temperature of 177° C, (7) hold for 2 hours at the post-cure temperature, and (8) ramp at -1.5° C/min to room temperature.

Due to limited material availability, the prepreg used for this study had already been stored in the freezer for 12 months at the time that it was received by the project team. As such, all of the aging states discussed in this study are complex, in that they are the outcome of combined freezer and room temperature storage conditions (typically 12-24 months of freezer storage followed by 0-77 days of room temperature out-time). In subsequent sections, prepreg and laminate samples will be referred to using the nomenclature F_xR_y, where x is the number of months stored in the freezer, and y is the number of days of out-time accrued prior to layup.

Prepreg Characterization

Samples of prepreg were stored at room temperature and in the freezer to monitor differences in aging as a function of storage condition. Prepreg stored at room temperature was characterized via differential scanning calorimetry (Q2000, TA Instruments) at the time the material was received ($F_{12}R_0$) and every seven days thereafter for 11 weeks. The DSC data were collected from -40° C to 200 ° C with the ramp rate 5 ° C/min. Prepreg stored in the freezer was similarly characterized every 30 days for 12 months. B-stage glass transition temperature was extracted from DSC data and used as a metric for quantifying prepreg age.

Laminate Manufacturing and Characterization

Laminates were produced from room temperature and freezer aged prepreg on the same schedule as prepreg characterization work was conducted (weekly for room temperature aged, monthly for freezer stored). All laminates were cured in an oven (DC-1406C, Thermal Product Solutions) using the manufacturer's recommended cure cycle and standard VBO consumables. A layup sequence of $[0_2, 45_2, 90_2, -45_2]_s$ was used, and laminates measured ~ 165 × 165 × 2.3 mm.

After cure, laminates were sectioned, mounted, polished, and imaged at 150× using a light microscope (VHX-5000, Keyence). Two 20 × 2.3 mm cross sections were prepared from each laminate. Porosity was measured in each micrograph by binarizing the images to distinguish pores, then dividing the pore area by the total cross section area of the laminate. Void content was averaged between the two samples from each laminate to produce an indicator of laminate microstructure quality.

Samples were also taken from each laminate for mechanical testing. Short-beam shear (SBS) testing was conducted (in accordance with ASTM D2344/D2344M – 16) using a tabletop load frame (5567 Load Frame, Instron). Six SBS samples were tested from each laminate. A precision waterjet cutter (ProtoMAX Compact Waterjet, OMAX) was used to remove samples from each laminate. Samples measured approximately 13.9 × 4.49 × 2.26 mm and were oriented such that the fiber direction on top and bottom plies was parallel to the longest edge of the sample. The span of the test fixture was fixed at 9.2 mm for all samples. SBS strength was averaged across all six samples to determine a representative metric of mechanical performance for each laminate.

Laminate microstructure and mechanical performance as a function of prepreg storage condition were examined to determining the onset of age-related processing or performance issues. Where possible, the mechanisms resulting in these issues were identified such that appropriate steps to address them could be developed and demonstrated.

Cure Cycle Tailoring

An approach was developed to modify the MRCC to extend prepreg storage life. The basis of this approach relies on controlling the effective flow number of the prepreg resin. Effective flow number is defined according to

$$N_{Fl,eff} = \int_0^{t_{gel}} \eta(t)^{-1} dt$$

where η is resin viscosity. This relationship implies that viscosity profiles that have lower minimum viscosities and remain at low viscosity for longer periods are characterized by higher effective flow numbers. Because both parameters influence the ability of resin to flow into dry regions of fiber beds, higher effective flow numbers are associated with more efficient fiber bed saturation. As prepreg ages at room temperature, the flow number increases (because the initial degree of cure advances prior to cure and this is associated with increased viscosity at all processing temperatures). In the approach described below, increasing the effective flow number by modifying the MRCC can address the primary phenomenon responsible for void formation in room temperature aged prepregs (discussed in detail next).

To mitigate the decrease in flow number observed for room temperature aging, three processing parameters were considered for adjustment. A cure kinetics model developed in [6] was used to estimate the relationship between these parameters and effective flow number. The ramp rates of MRCC steps 4 and 6 were varied from 1.5° C/min to 40° C/min, step 5 gelation temperature was varied from 121° C to 177° C, and super-ambient hold time was varied from 0 to 2 hours. These ranges were fixed by the operational envelope of the processing equipment available. Ramp rates in excess of 40° C/min were not feasible, and researchers determined it was unsafe to allow gelation temperature to exceed the post cure temperature recommended by the manufacturer.

A script was written to sequentially adjust these parameters until a modified cure cycle was produced that achieved a desired effective flow number. This script first increased the ramp rate, then increased the gelation temperature, and then reduced the super-ambient hold time. The script proposes cure cycle adjustments to each step only until the target flow number was achieved or the limit of the allowable parameter range was reached.

The cure cycle modification tool accepts prepreg B-stage T_g as an input and specifies a modified cure cycle that will achieve an effective flow number associated with full fiber bed saturation. Prepreg age may exceed the manufacturer's recommended out-life so long as the degree of cure has not advanced to the point that sufficient resin flow is impossible within the available processing window.

Demonstration of Prepreg Life Extension via Cure Cycle Modification

The cure cycle tailoring tool described in the previous section was used to generate a modified cure cycle for production of a laminate from prepreg aged for 44 days at room temperature (RT). The laminate was laid up in the same stacking sequence as described all other samples with

standard VBO consumables and cured using a heat blanket. After cure, the laminate was analyzed for porosity and mechanical performance (SBS).

Results and Discussion

Room Temperature Aging

B-stage T_g. The B-stage T_g values extracted from DSC measurements are shown in Figure 1 for all room temperature aged prepreg samples available. The B-stage T_g for prepreg with zero out-time was -2.35° C, and increased to 54.1° C as out-time accrued up to 28 weeks (196 days). Figure 1 shows that B-stage T_g is a strong indicator of the out time accumulated by the prepreg studied in this project.

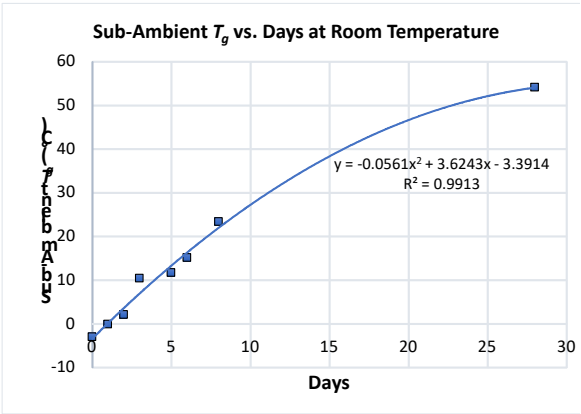

Figure 1: B-stage T_g temperature of prepreg aged at room temperature.

Laminate microstructure. Micrographs of the laminates produced from RT-aged prepreg are shown in Figure 2. Laminates aged up to 28 days exhibited nearly flawless microstructure (< 0.1% porosity) and uniform resin distribution. Beyond 28 days, laminate porosity increased as a function of out-time and was located predominantly within prepreg plies (intralaminar). The onset of porosity correlated with the presence of resin-rich interlaminar regions and (occasionally) resin-rich regions between adjacent fiber tows (intralaminar). Resin-rich interply and intertow regions are visible in sample $F_{12}R_{42}$ and those with additional RT aging in Figure 2. The timing of processing difficulty (porosity onset) with respect to RT aging is accurately predicted by the manufacturer's out-life spec of 30 days.

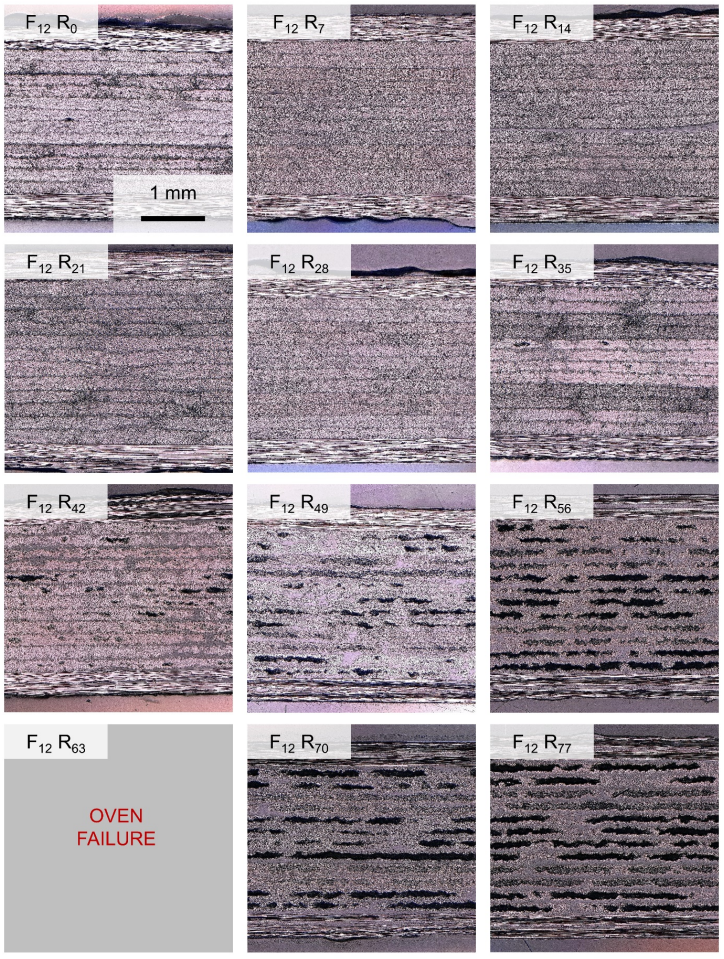

Figure 2: Micrographs of laminates produced from room temperature aged prepreg using the MRCC.

Short beam strength. The average mechanical performance of laminates cured from prepreg aged at RT is reported in Figure 3. Error

bars indicate standard deviation of SBS strength for the six samples tested, and labels indicate strength normalized against the performance of the sample with the least accumulated age ($F_{12}R_0$, referred to as the baseline case). The performance of samples $F_{12}R_{56}$ - $F_{12}R_{77}$ was omitted because (1) mechanical integrity was insufficient to be reliably measured or because (2) laminates did not survive SBS sample preparation (e.g., catastrophic delamination during water jet cutting). One can infer that such samples retained only modest mechanical performance.

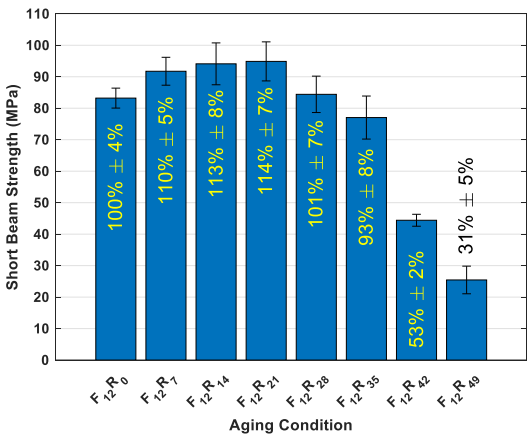

Figure 3: Average short beam strength of laminates aged at room temperature (labels indicate strength normalized against the $F_{12}R_0$ case).

Figure 3 shows that for the first three weeks that prepreg accumulated out time, SBS strength increased by 10-14%. Once prepreg accumulated 28 days of out-time, SBS strength declined back to the level of the $F_{12}R_0$ case. When the manufacturer's out-life spec was exceeded SBS strength decreased: the laminate aged for five days beyond the manufacturer's out-life spec ($F_{12}R_{35}$) exhibited a 7% reduction in SBS strength compared to the baseline case. Furthermore, samples $F_{12}R_{35}$ and $F_{12}R_{35}$ exhibited 47% and 69% knockdowns in SBS strength compared to baseline. Decreased strength in overaged laminates was associated with, and can be explained by, the presence and severity of porosity.

Aging mechanism during RT storage. B-stage T_g data and micrographs shown in Figure 2 provide evidence of the mechanism by which RT aging compromises the processability of the prepreg. As prepreg accumulates out-time, the resin degree of cure α, slowly advances. As α advances, resin viscosity increases. Increased resin viscosity has a two-fold effect on resin flow during subsequent cure. First, the viscosity minimum reached during processing is not as low as the minimum viscosity that would have been reached without RT aging. Assuming constant compaction pressure, increased viscosity slows the rate of resin flow into unsaturated fiber tows. Second, RT-aged resin remains at a low viscosity for a shorter period during processing than unaged resin (for the same cure cycle). A shorter time at low viscosity means a narrower processing window for fiber bed saturation. The impact of both of these phenomena can be captured in the resin effective flow number, which deceases as aging increases due to these viscosity changes. Ultimately, the consequence of increased resin viscosity (and corresponding decrease in effective flow number) is that resin flow fails to completely saturate dry regions of fiber bed, leading to porosity and diminished mechanical performance.

The understanding that resin degree of cure is advancing during room temperature storage is supported by increases in B-stage T_g, observed in Figure 1. The increase in B-stage T_g indicates that a chemical change is occurring in the resin during RT aging. Furthermore, previous studies have correlated B-stage T_g with degree of cure for the same type of prepreg as used in this study [7]. The assertion that insufficient resin flow causes porosity is supported by Figure 2, which shows that as RT aging time increases, the uniformity of resin distribution decreases. In this figure, it is not apparent that any resin flow occurred at all for samples $F_{12}R_{70}$ and $F_{12}R_{77}$. In these samples, resin-rich regions occur between plies, where resin was originally deposited during prepregging.

Inadequate gas evacuation was considered as a possible cause of porosity in samples $F_{12}R_{35}$ and beyond, but absence of interply voids and evidence outlined above support the assertion that insufficient resin flow is the primary cause of porosity.

Freezer Aging

B-stage T_g. No significant change in B-stage T_g was observed for prepreg freezer-stored for up to 20 months. B-stage T_g for prepreg with the baseline aging condition ($F_{12}R_0$) was -2.35° C, and samples stored in the freezer for up to an additional 8 months ($F_{13}R_0$ - $F_{21}R_0$) ranged between -3.52° C and -1.16° C.

Laminate microstructure. Micrographs of the laminates produced from freezer aged prepreg are pictured in Figure 4. None of the laminates produced from freezer-aged prepreg exhibited significant porosity (< 0.1%). Resin distribution was uniform, and no resin-rich regions appeared in laminates produced from freezer-aged prepreg. Several samples could not be produced due to disruption of lab access due to COVID-19. As material continued to age while labs were unavailable, this data could not be generated once lab access was restored.

Short beam strength. The average SBS strength of laminates cured from prepreg aged in the freezer is shown in Figure 5. In this figure, error bars indicate standard deviation of SBS strength for the six samples tested, and labels indicate strength normalized against the strength of the sample with the least accumulated age ($F_{12}R_0$, referred to as the baseline case). Several samples could not be produced due to disruption of lab access due to COVID-19, and blank spaces remain in their place to better visualize storage time on the x-axis.

Figure 5 shows that for the first three additional months that prepreg accrued storage time in the freezer, short beam strength did not change significantly. Once prepreg accumulated 19 months of total freezer storage time, SBS strength began to decline, with the $F_{19}R_0$ sample exhibiting a 6% reduction in

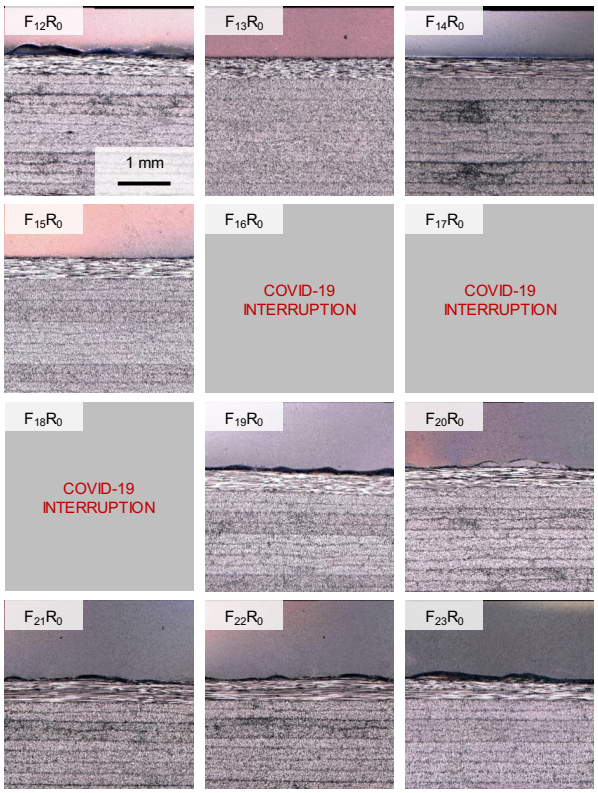

Figure 4: Micrographs of laminates produced from freezer aged prepreg using the MRCC.

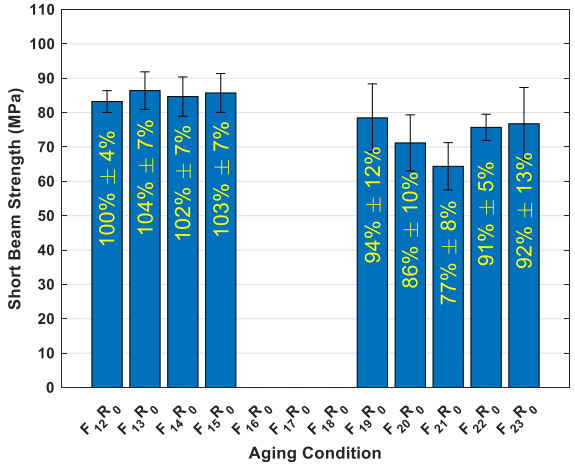

Figure 5: Average short beam strength of laminates aged in the freezer (labels indicate strength normalized against the $F_{12}R_0$ baseline case).

strength. This trend continued for samples $F_{20}R_0$ and $F_{21}R_0$, which were characterized with 86% and 77% of baseline strength, respectively. The manufacturer's storage life spec for this material was 12 months, but prepreg retained more than 95% of baseline strength even when the spec was exceeded by 58% (7 months).

Micrographs in Figure 4 indicate that decreased SBS strength in laminates produced from freezer-aged prepreg was not associated with porosity (no freezer aged laminates exhibited porosity) or other identifiable microstructure defects.

Aging mechanism during freezer storage. Prepreg stored in the freezer did not become unusable via the same aging mechanism as prepreg aged at RT. Invariant B-stage T_g data indicate that freezer storage over the period studied did not advance resin degree of cure. The rheology data in Figure 6 show that freezer aging had little effect on resin viscosity. Because resin viscosity is determined by resin temperature and degree of cure, Figure 6 also indicates that extended freezer storage did not alter prepreg degree of cure. Furthermore, the absence of porosity in the micrographs in Figure 4 indicates that resin flow was sufficient to saturate fiber tows, and the presence of porosity or other defects was not responsible for the decline in SBS strength shown in Figure 5.

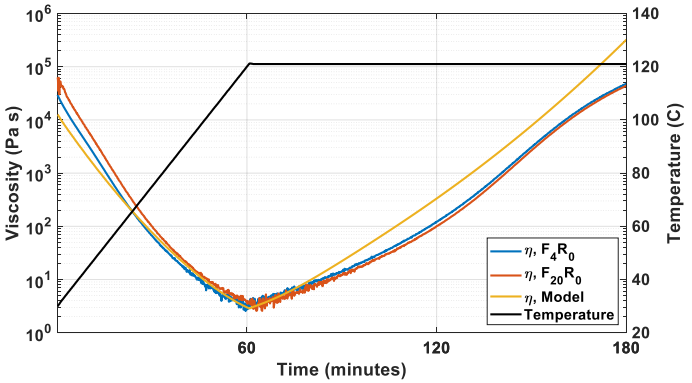

Figure 6: Viscosity profile of resin squeezed from prepregs with different aging conditions.

Further work is required to identify precisely how freezer aging impacts the chemical properties of various resin constituent components. This issue must be clarified before any informed attempt can be made to mitigate the aging and implement measures to extend freezer storage life. The results, nonetheless, provide important indications. It has been presumed by practitioners in the field that no significant chemical changes occur in resin stored below the B-stage T_g. Results reported here, however, indicate that a chemical change (not associated with advancing degree of cure) may be responsible for strength knockdowns associated with extended freezer storage.

Demonstration of Prepreg Life Extension via Cure Cycle Modification

The prepreg used for demonstration that cure cycle modification can extend storage life was aged for 44 days at room temperature. At the time of layup, the prepreg exhibited a B-stage T_g of 15.8° C, corresponding to a degree of cure of ~16%. The viscosity profile associated with curing such prepreg using the MRCC is shown in Figure 7. When cured using the MRCC, effective flow number was only 10.7 Pa^{-1}, and resin viscosity never moved below 150 Pa s. Previous results indicate that when prepreg is cured using the MRCC, unacceptable levels of porosity are observed due to insufficient resin flow into dry regions of the fiber bed (see sample $F_{12}R_{42}$ in Figure 2).

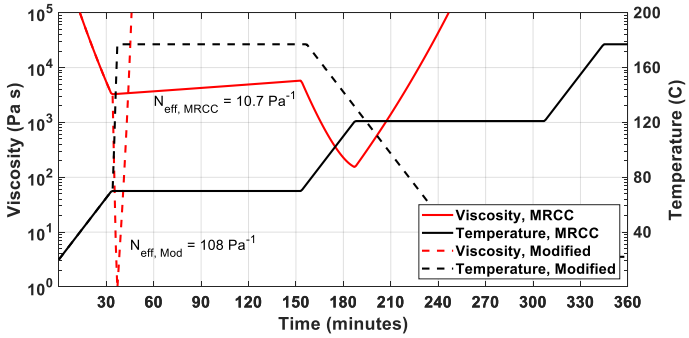

Figure 7: Viscosity profiles and corresponding effective flow number of overaged prepreg (T_g = 15.8° C) cured using the MRCC and a modified cure cycle.

To achieve fiber bed saturation in overaged prepreg, a modified cure cycle was proposed. The modifications were generated such that the resulting cycle corresponded to a target effective flow number ($N_{eff,\,T}$). The target was fixed at the same effective flow number achieved by the MRCC for prepreg aged at RT for one week (T_g = 0.5° C). An aging condition of seven days was selected to determine $N_{eff,\,T}$ because it assured that the cure cycle modification would achieve sufficient flow for fiber bed saturation. Using this approach, the target effective flow number was fixed at 108 Pa^{-1} for this study. This effective flow number was achieved by (1) increasing ramp rates to 40° C/min, (2) increasing the gelation temperature to 177° C, and (3) reducing the super-ambient hold time to just 50 seconds. The modified cure cycle, corresponding viscosity profile, and associated flow number are shown in Figure 7.

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)a}$$

The method used to identify appropriate cure cycle modifications was as follows. First, the B-stage T_g was correlated with degree of cure using the DiBenedetto relationship established in [1]. The relationship is reproduced, where T_{g0} = -8.4° C, $T_{g\infty}$ = 212° C, and λ = 0.66. The relationship for degree of curing and aging time calculated by the DiBenedetto equation is shown in Figure 8.

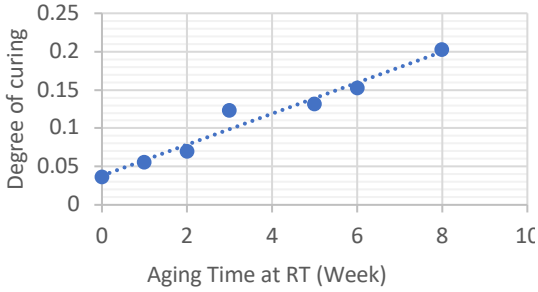

Figure 8. Relationship of degree of curing vs. aging time calculated by the DiBenedetto relationship

Next, the estimated initial degree of cure (α_0) and the MRCC were used as inputs to model the evolution of resin degree of cure and viscosity as a function of cure time according to the relationships established in by Kim et al. [6]. Resin viscosity was subsequently used to determine the effective flow number associated with the measured B-stage T_g and cure cycle. If the effective flow number associated with the MRCC was too low, the

cure cycle was iteratively modified until the estimated effective flow number reached the target flow number (or no additional modifications could be made). Modifications were made in the following priority, stopping as soon as the target effective flow number was achieved: 1) the ramp rate was increased, capped at 40° C/min, 2) gelation temperature was increased, capped at 177° C, and 3) super-ambient hold time was reduced, capped at zero. Each of these parameters was adjusted continuously over their respective ranges (determined by the physical or safe operation limits of the manufacturing equipment or resin chemistry) such as to not make more (or larger) changes than necessary to the MRCC. The cure cycle modifications shown in Figure 7 were specifically chosen for this report because they represent the extreme end of possible cure cycle modifications enabled by this approach (ramp rate and gelation temperature are both maximized over their allowable ranges, and super-ambient dwell temperature can only be reduced by an additional 50 seconds before reaching zero). Future work may consider the impact of additional cure cycle modifications (increasing the ramp rate of the ramp prior to the super-ambient dwell and/or the temperature of the super-ambient dwell) and the relative importance or priority of such changes.

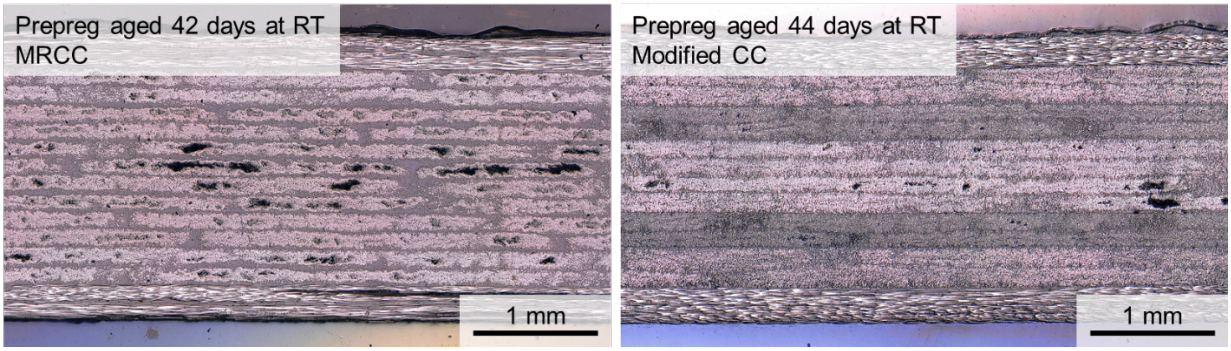

Figure 9: Comparison of microstructure in laminates produced from (left) prepreg aged for 42 days at room temperature, cured using the MRCC and (right) prepreg aged for 44 days at room temperature, but cured using the modified cure cycle show in Figure 7.

The microstructure of the laminate produced from the cure cycle tailored to its aging condition is shown in Figure 9, where it is compared against the microstructure of a laminate produced from prepreg of similar aging condition (42 days of out-time accrued, T_g = 15.1° C). The cure cycle modification resulted in more uniform resin distribution and fewer voids. The micrograph supports the contention that insufficient resin flow was primarily responsible for porosity in prepregs overaged at RT. Furthermore, the findings indicate that modifying processing parameters is an effective method to control laminate microstructure.

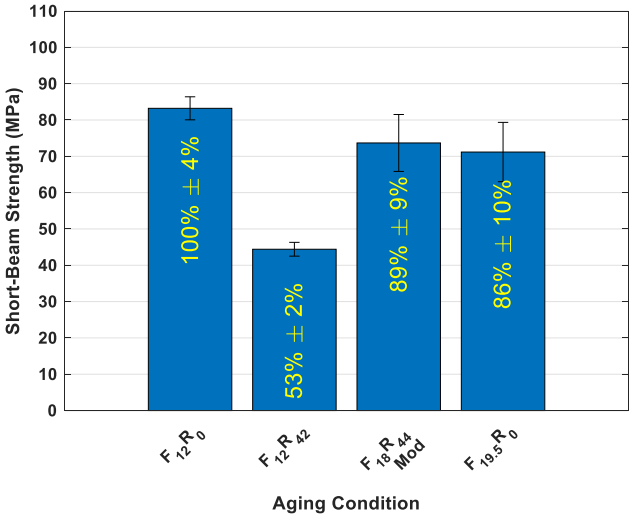

Figure 10: Short beam strength for laminates produced from prepreg with various aging conditions processed using the MRCC ($F_{12}R_0$, $F_{12}R_{42}$, $F_{19.5}R_0$) and a modified cure cycle ($F_{18}R_{44}$ Mod).

Figure shows the SBS strength of laminates produced from overaged prepreg using the cure cycle describe above. In the figure, the average SBS strength is compared against laminates produced from prepreg subjected to three different aging conditions, each cured using the MRCC. Error bars correspond to the standard deviation of strength measurements, and labels indicate short beam strength normalized against the baseline aging condition cured using the MRCC ($F_{12}R_0$). The average short beam strength of the laminate produced using the modified cure cycle ($F_{18}R_{44}$ Mod) was 74 MPa, while the SBS strength of the laminate with similar RT aging—but produced via the MRCC ($F_{12}R_{42}$)—was only 44 MPa. Processing via the modified cure cycle resulted in a 68% increase in short beam strength over processing via the MRCC. This increase did not restore the full SBS strength of the over-aged prepreg, however. Data in Figure also indicate that the laminate produced via the modified cure cycle showed a 12% knockdown in SBS strength relative to the laminate produced from fresh prepreg using the MRCC ($F_{12}R_0$). The difference between these two samples was attributed to the additional freezer aging of the $F_{18}R_{44}$ Mod sample. Prior to RT aging and subsequent cure, the prepreg sample was freezer-stored for ~18 months. SBS strength of a laminate produced using the MRCC from prepreg freezer-stored for 19.5 months (but with no accumulated RT out-time) is also shown in Figure as sample $F_{19.5}R_0$. This laminate exhibited a flawless microstructure, but a 14% reduction in strength compared to the baseline condition was nonetheless observed. These data support the assertion that the SBS strength knockdown (vs. fresh prepreg) observed in the $F_{18}R_{44}$ Mod sample was caused by extended freezer storage rather than process-addressable phenomena. Researchers anticipate that the full mechanical performance of fresh prepreg can be preserved in overaged prepreg that has accumulated less freezer storage, but additional work is required to explore this.

Together, Figure 9 and Figure demonstrate the efficacy of cure cycle modification for extending the useful life of prepreg that has exceeded the out-time spec. The example presented in this demonstration represents the extreme limit of aging condition (and associated B-stage T_g values) for which the approach described can produce a cure cycle that achieves the targeted effective flow number defined above. Prepregs exhibiting B-stage T_g values greater than 15.8° C require cure

cycles outside the available processing envelope to achieve the desired flow number. Prepregs exhibiting B-stage T_g values between -2.5° C and 15.8° C, however, require less extreme changes to the MRCC.

Summary of Results, Implications for Future Research, and Benefits

In this project, we analyzed process behavior of prepreg as a function of freezer storage time and out-time. During RT aging, prepreg advanced in degree of cure, and B-stage T_g increased linearly (for the first sixty days) with prepreg resin exposure time. Microstructural analysis and mechanical testing of laminates produced from RT-aged prepreg revealed that the onset age-induced porosity was correlated with reduced SBS strength. The primary mechanism by which porosity remained within laminates produced from prepreg exceeding out-time limits was identified as insufficient resin flow into dry regions of the fiber bed.

Freezer-stored prepreg did not undergo significant crosslinking, however, and resin B-stage T_g and rheological behavior were unchanged after 20 months of freezer storage (167% of the manufacturer's recommended storage life). All laminates produced from freezer-aged prepreg were nearly flawless; however, SBS strength of laminates declined after 16-19 months of freezer storage. Resin achieved uniform distribution in all freezer-aged laminates, indicating that insufficient resin flow was not the cause aging-induced performance decline. Instead, findings indicated different mechanisms were responsible for the mechanical knockdown in (1) prepreg aged in the freezer and (2) prepreg aged at room temperature. *This finding is contrary to the widely held belief that resin crosslinking is responsible for spoilage from out-time and freezer storage (with this reaction exhibiting temperature-dependent kinetics).* While this finding does not indicate that freezer storage entirely suspends resin crosslinking, the results of Figure 4 and Figure 5 demonstrate that crosslinking is not the primary cause of strength loss.

The relationship between processing cycles and resin flow properties was leveraged to develop a method for increasing resin flow in over-aged prepreg. A method for generating a modified cure cycle based on prepreg B-stage T_g was developed that relied on changing ramp rate, gelation temperature, and super-ambient hold time to achieve a desired effective flow number. This method was demonstrated on a prepreg aged for 44 days and shown to produce a laminate with increased strength (compared to a laminate with similar aging but cured using the MRCC).

Further work is required to identify phenomena responsible for prepreg aging during freezer storage. Because the mechanism by which freezer-aged prepreg spoils differs from out-time aging, the cure cycle modification approach also may have to be modified to extend prepreg storage life. Appropriate methods for storage life extension will be an objective of future research. More work will be devoted to refining cure cycle tailoring practices, including identifying an optimal effective flow number. Furthermore, the generality of the cure cycle tailoring approach for extending prepreg out-life must be demonstrated by adapting for use with other commonly used prepregs.

Objectives for follow-on research include:

1. Identify the aging mechanism responsible for prepreg aging during freezer storage
2. Develop a method to extend prepreg freezer life
3. Refine cure cycle tailoring practices by identifying an optimal effective flow number
4. Characterize the (freezer and room temperature) aging behavior of additional prepregs to
    a. Identify the relationship between B-stage T_g and aging condition

b. Demonstrate that cure cycle tailoring can be applied to other prepregs to extend useful life

Overall, we have shown that prepreg age can be measured, and by modifying the cure cycle accordingly, prepreg life can be extended, thus reducing scrap and waste. Deployment of the cure cycle modification approach requires minimal investment in infrastructure (e.g., a DSC) and little technical training, while providing environmental and economic benefits.

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