Effects of Alternative Jet Fuel Blends on Aerospace-Grade Carbon/Epoxy Composites

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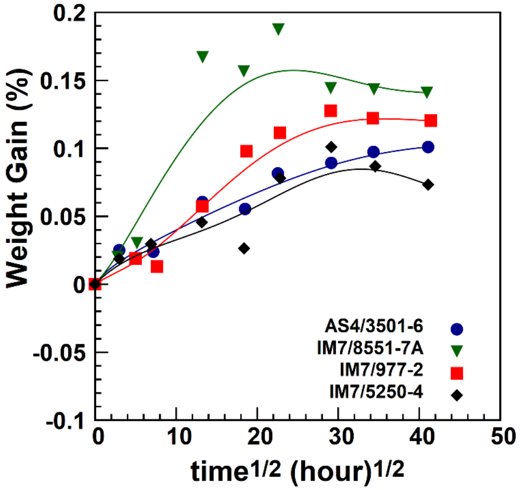
Background

- **Motivation and Key Issues**
  - The matrix phase of composites can absorb various fluids, including fuel leading to matrix swelling and matrix cracking
  - Fuel absorption can lead to the degradation of the thermal and mechanical properties of composites
  - Alternative fuels can have similar effects as typical Jet fuels, but not been reported in the literature extensively
- **Objectives and Scope**
  - **Determine whether the use of alternative fuels poses more risk on aerospace structural composites than the use of Jet A**
  - Investigate the effects of alternative fuels on carbon/epoxy composites
    - Fuel uptake
    - Thermal and mechanical properties
  - Develop a modeling framework based on the experimental data that can be used for complex, real-life geometries
- **Approach**
  - Experimental investigation of conventional and alternative fuels absorption of carbon/epoxy composites
    - Track the weight gain with time to determine the amount of fuel absorbed
    - Investigate the changes in the dynamic properties after absorption
  - Modeling the diffusion process using Finite Element Method

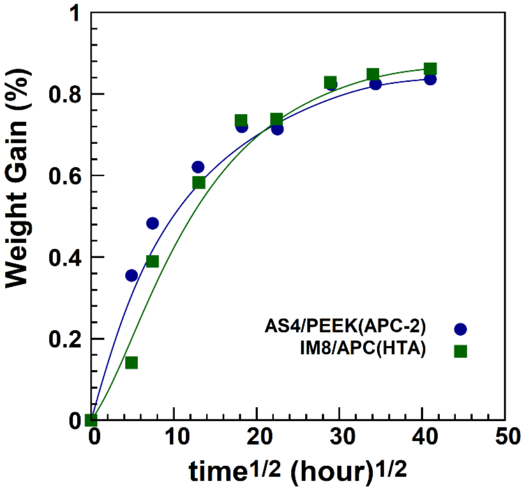
Literature Study: Effects of JP4 Fuel Uptake on Composites



% weight gain for composites with [±45]$_{2s}$ layup and thermoset matrix

- AS4/3501-6: carbon fiber with epoxy resin
- IM7/8551-7A: carbon fiber with epoxy resin
- IM7/977-2: carbon fiber with epoxy resin
- IM7/5250-4: carbon fiber with bismaleimide resin
- AS4/PEEK(APC-2): carbon fiber with polyetheretherketone resin
- IM8/APC (HTA): carbon fiber with aromatic polymer composite (high temperature amorphous)

Graphs reproduced from Ref 1



% weight gain for composites with [±45]$_{2s}$ layup and thermoplastic matrix

- Composites with a thermoset (cross-linked) matrix absorb less fuel than composites with a thermoplastic matrix
- The type of matrix and layup affect the fuel uptake

[1] Curliss, D.B., and Carlin, D., 1990, “Effect of jet-fuel exposure on advanced aerospace composites, II: Mechanical properties,” Final Report, no. WRDC-TR-90-4064, Air Force Wright Research and Development Center, OH, USA.

Material Systems: Composites

- Three aerospace-grade carbon/epoxy composites were considered:

Material system	Fiber type	Fabrication method	Layup
Hexcel SGP370-8H/8552	Eight harness woven carbon fabric	Autoclave cured	Cross-ply [0/90/90/0]
Hexcel SGP370-8H/8552	Eight harness woven carbon fabric	Autoclave cured	Quasi-isotropic [0/-45/45/90]
DMS2436/API-1078	Warp/knit carbon fabric	Resin-infused	[45/-45/0/90/0/-45/45]

- Specimens were cut from these composite panels into 2 (L) x 0.5 (W) in^2 dimensions

Red: carbon fibers
Blue: Epoxy

Fuels used

- Conventional jet fuel **Jet A** was used
- The alternative fuels (AF) used in this work were:

AF blend used	Process used	Blending ratio with Jet A	Aromatic content (AF only)
ATJ/Jet A	ATJ/SPK	50/50	0%
SPK/Jet A	HEFA/SPK	50/50	0-0.4%
Farnesane/Jet A	HFS/SIP	10/90	0%
S8/Jet A	FT/SPK	50/50	<0.2%

ATJ/SPK: Alcohol-to-Jet to Synthetic Paraffinic Kerosene

HEFA/SPK: Hydroprocessing Esters and Fatty Acids to Synthetic Paraffinic Kerosene

HFS/SIP: Hydroprocessed Fermented Sugars to Synthetic Isoparaffins

FT/SPK: Fischer-Tropsch to Synthetic Paraffinic Kerosene

Fuels used

ATJ/SPK: Alcohol-to-Jet to Synthetic Paraffinic Kerosene

Sugars/Cellulose

Fermentation

Alcohols

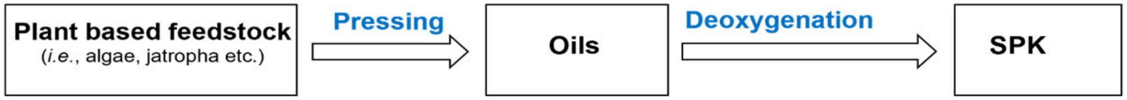
Hydration

Olefins

Hydrogenation

Paraffins

HEFA/SPK: Hydroprocessing Esters and Fatty Acids to Synthetic Paraffinic Kerosene



Plant based feedstock
(*i.e.*, algae, jatropha etc.)

Pressing

Oils

Deoxygenation

SPK

HFS/SIP: Hydroprocessed Fermented Sugars to Synthetic Isoparaffins

Sugars/Cellulose

Fermentation

Farnesene

Hydroprocessing

Farnesane

FT/SPK: Fischer-Tropsch to Synthetic Paraffinic Kerosene

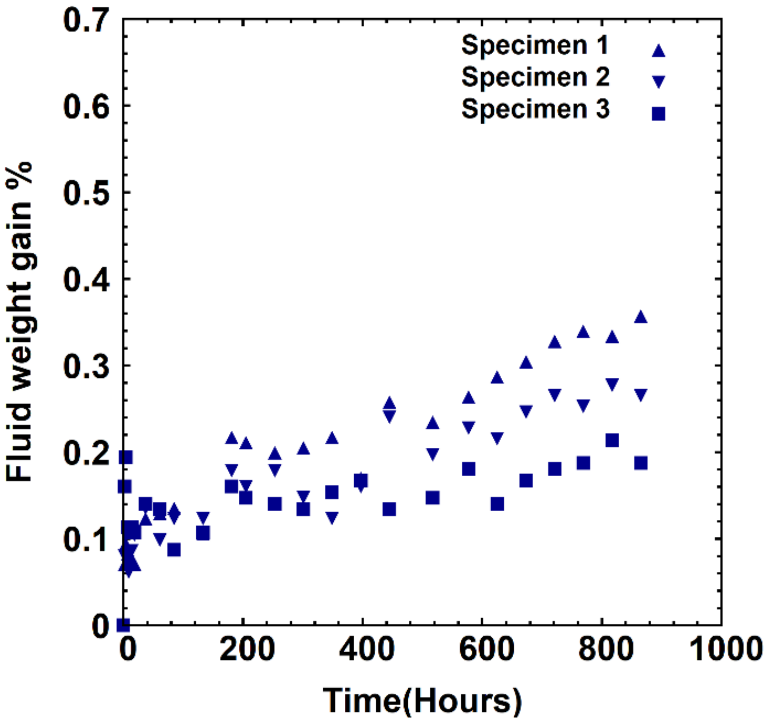
Biomass
(*i.e.*, forestry residues, grasses, municipal solid waste etc.)

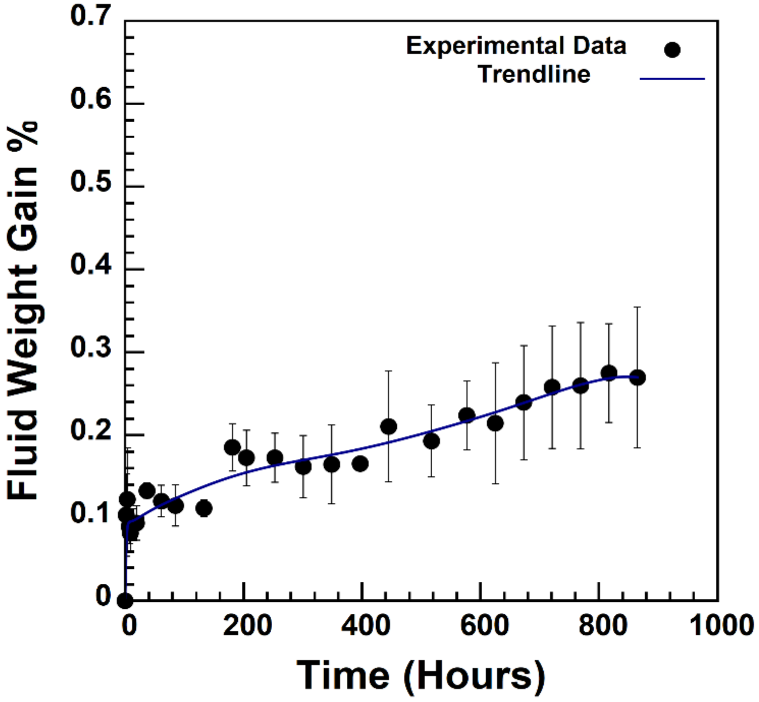
Syngas

Fischer-Tropsch

Alternative fuel

Weight Gain with Time for Autoclave Quasi-Isotropic Hexcel SGP370-8H/8552 Carbon/Epoxy immersed in Jet A fuel



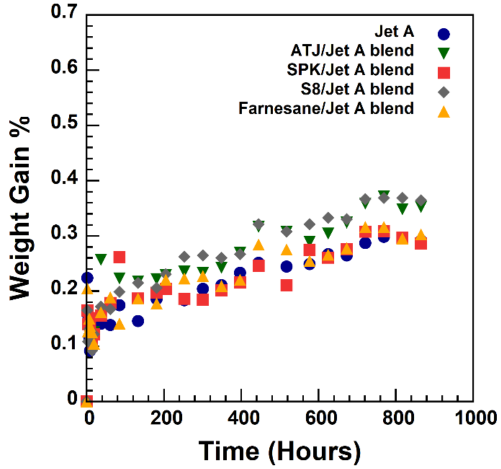


The ***average fuel uptake*** and a Bezier trendline. Error bars represent the standard deviation.

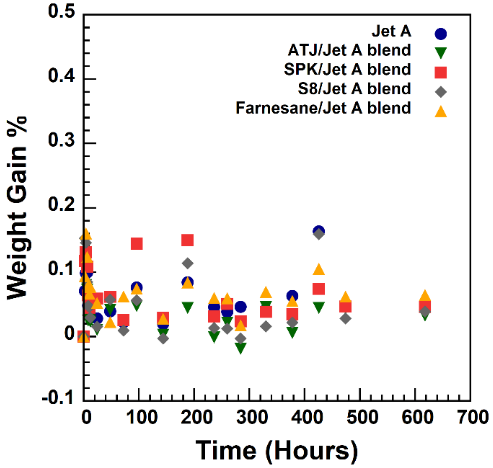
- Faster **absorption** in the **early stages** of the fuel immersion
- The equilibrium weight gain was of ≈0.27% and the range [L-H] of [0.18 - 0.35] %

Summary of Average Weight Gain for All Specimens and Fuels Used

- Total fuel uptakes were low for all three composite types [2, 3]
- No notable difference was measured in fuel absorption for specimens immersed in Jet A fuel versus the alternative fuel blends
- Composites fabricated using woven fabric plies absorbed more fuel than composites fabricated using warp-knitted unidirectional plies



Woven fabric specimens



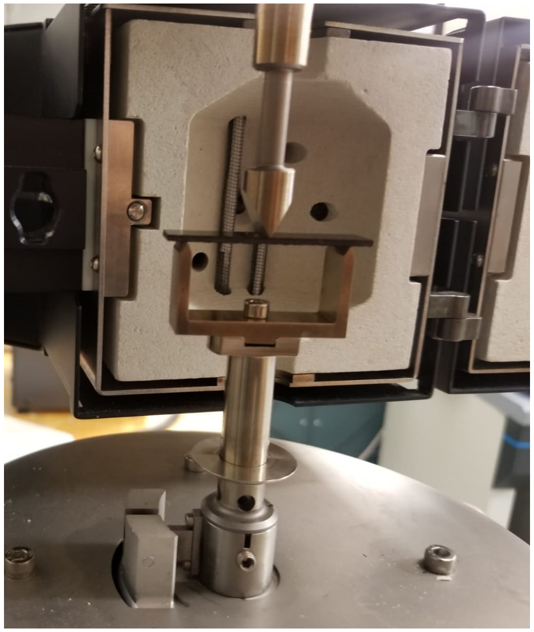
Warp-knitted specimens

[2] Harich, Naoufal, et al. *Effects of New Jet Fuel Exposure on Aerospace Composites–Phase 1 Final Report*. No. DOT/FAA/TC-21/53. United States. Department of Transportation. Federal Aviation Administration. William J. Hughes Technical Center, 2022.

[3] Harich, Naoufal, et al. "Effects of alternative jet fuel blends on aerospace-grade carbon/epoxy composites." *Materials & Design* 221 (2022): 110993.

Dynamic Mechanical Analysis (DMA)

- The effects of fuel absorption on the thermomechanical properties of composites are studied using Dynamic Mechanical Analysis (DMA).
- DMA was performed on neat and fuel-immersed specimens using an RSA-G2 Solids Analyzer with the three-point bending mode.
- The analysis was performed following the ASTM D7028-07.

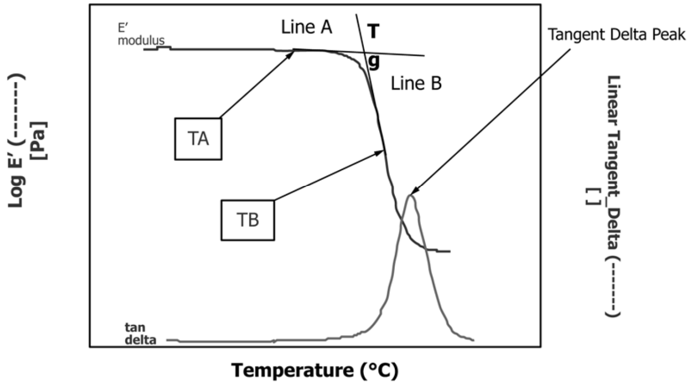


DMA parameters used

Test method	Frequency	Heating Rate
Three-point bending	1 Hz	5 °C/min

Dynamic Mechanical Analysis (DMA)

- **Thermomechanical properties** of interest:
  - **Storage modulus E'** measures the **elastic response**
  - **Loss modulus E''** measures the **viscous response** (dissipation in the system)
  - **tan(δ)** is the **ratio of E''/E'**
- The **ASTM D7028-07**[3] define **two temperatures** of interest for the **glass transition temperature:**
  - The **intersection of the two tangent lines** from the storage modulus gives **DMA T_g**
  - The **maxima in the tan(δ)** curves is the glass transition temperature, T_t



Obtained from ref [2]

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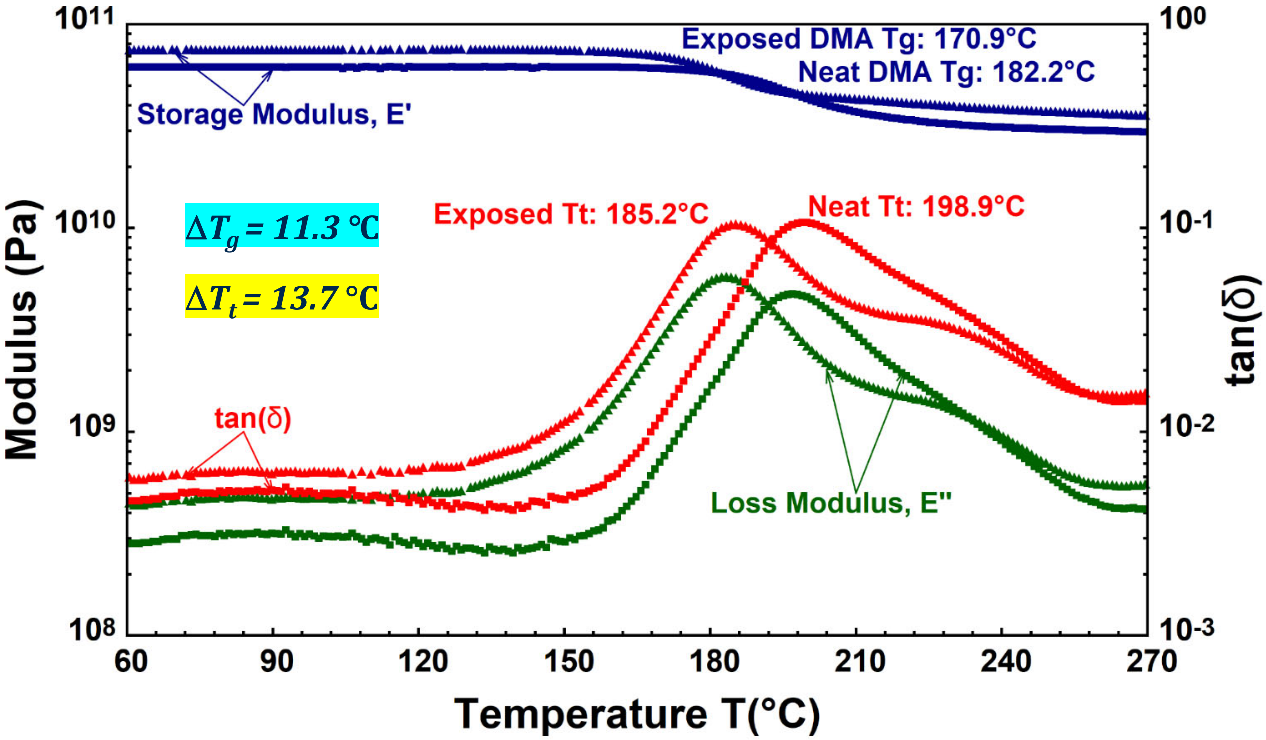
[2] Sperling, L. H. (2005). *Introduction to physical polymer science*. John Wiley & Sons.
[3] ASTM International. (2007). ASTM D7028-07-Standard Test Method for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA).

DMA Results for Autoclaved Cross-ply Hexcel SGP370-8H/8552 Carbon/Epoxy Specimens: Neat and Immersed in ATJ/Jet A Blend



- Both DMA T_g and T_t decreased after fuel absorption: $\Delta \mathbf{DMA}\ \boldsymbol{T_g} = \mathbf{11.3}$℃ and $\Delta \boldsymbol{T_t} = \mathbf{13.7}$℃

- **DMA T_g and T_t** for specimens **saturated** with **four alternative fuel/Jet A blends** were **impacted** to the **same extent** as those saturated with **100% Jet A fuel**.

Summary of DMA results for All Specimens and Fuels Used

- DMA T_g and T_t for specimens saturated with the four alternative fuel blends were impacted to the same extent as those saturated with Jet A fuel.

- Both DMA T_g and T_t decreased after fuel uptake in the range of 3.1-19°C for DMA T_g and 1.8-20.6°C for T_t.

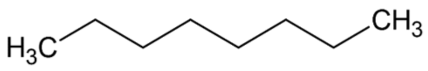
- The DMA T_g and T_t for woven fabric composites degraded more than for composite specimens with warp-knitted unidirectional plies.

Motivation for Considering Alternative Fuels and Cyclic Absorption/Desorption Cycles

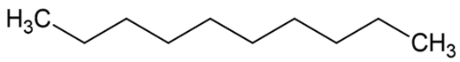
- The **pure alternative fuels** are comprised **mostly of paraffins and olefins** and have almost **no aromatics**
  - MSU has limited access to alternative fluids, particularly unblended ones
  - Investigate **model fluids** with **similar chemical structures** as the **pure alternative fuels**
- **Cyclic fuel absorption-desorption** experiments were performed:
  - Composites' **encounter with fluids** is a **cyclic** and **not continuous** process

Model Fluids Used

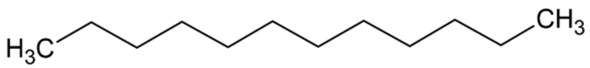
- Model fluids to be used:



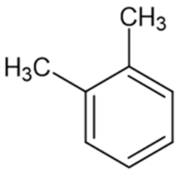
Octane



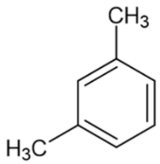
Decane



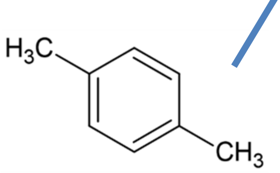
Dodecane



Ortho-Xylene (1,2)

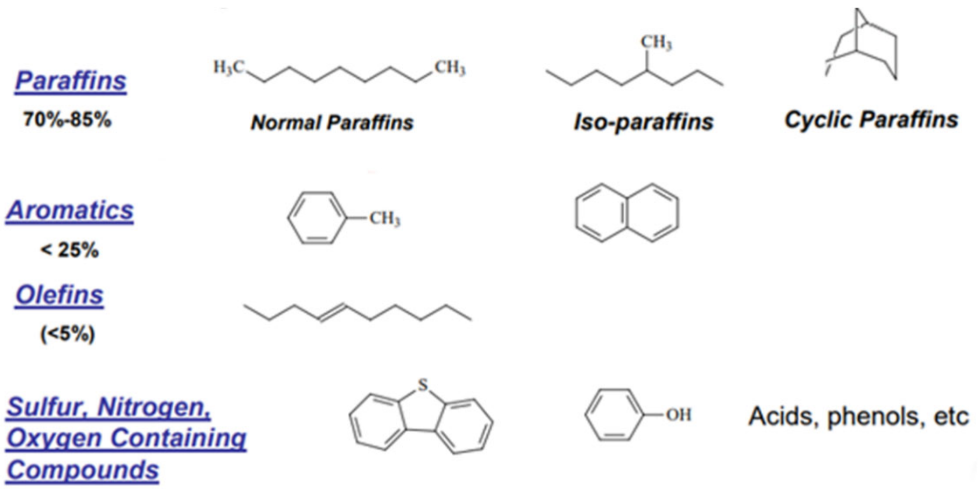


Meta-Xylene (1,3)



Para-Xylene (1,4)

Xylene Isomer Mix



Jet Fuel Composition [4]

[4] Sustainable bio-derived synthetic paraffinic kerosene (Bio-SPK) jet fuel flights and engine tests program results. *9th AIAA aviation technology, integration, and operations conference (ATIO) and aircraft noise and emissions reduction symposium (ANERS)*, (p. 7002).

Material Systems/Composites Used

- Two aerospace-grade carbon/epoxy composites were used:

Material system	Fiber type	Fabrication method	Layup
Hexcel SGP370-8H/8552	Eight-harness woven carbon fabric	Autoclave cured	Cross-ply [0/90/90/0]

- Hexcel SGP370-8H/8552 is an eight-harness woven fabric made from IM7 fibers
- Specimens were cut from these composite panels into 2 (L) x 0.5 (W) in^2 dimensions

Red: carbon fibers
Blue: epoxy

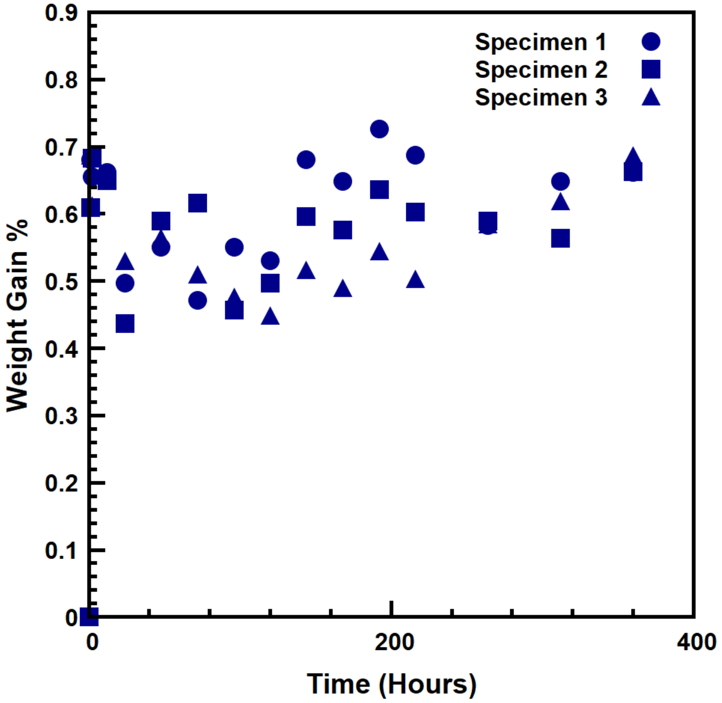
Experimental Details

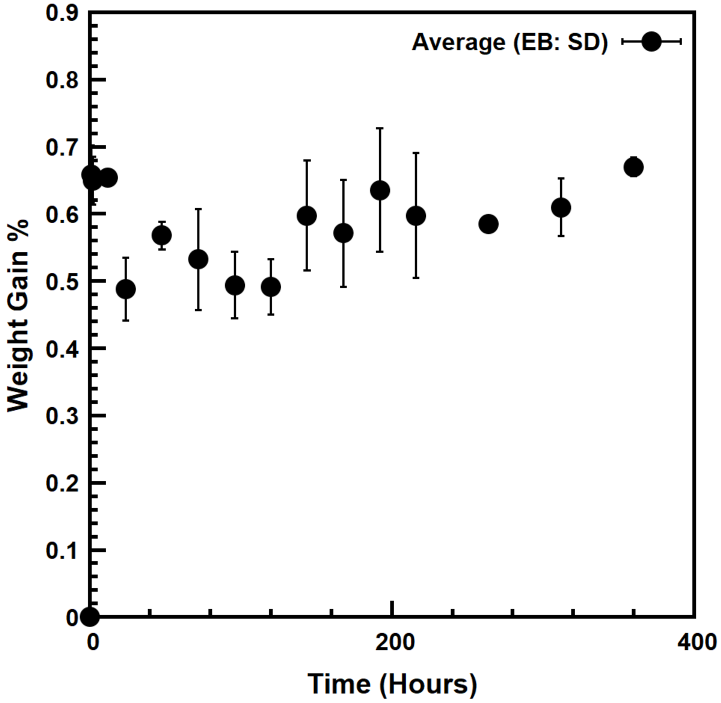
- Maximum three fuel absorption-desorption cycles were performed:

Set 1	Immersion	DMA				
Set 2	Immersion	Desorption	Immersion	DMA		
Set 3	Immersion	Desorption	Immersion	Desorption	Immersion	DMA

- DMA was performed once saturation was reached
- Vacuum drying was used to accelerate desorption
- Each set consists of three replicas for each model fluid

Weight Gain with Time for Autoclave Cross-Ply Hexcel SGP370-8H/8552 Carbon/Epoxy Immersed in Dodecane - 1st Absorption Cycle



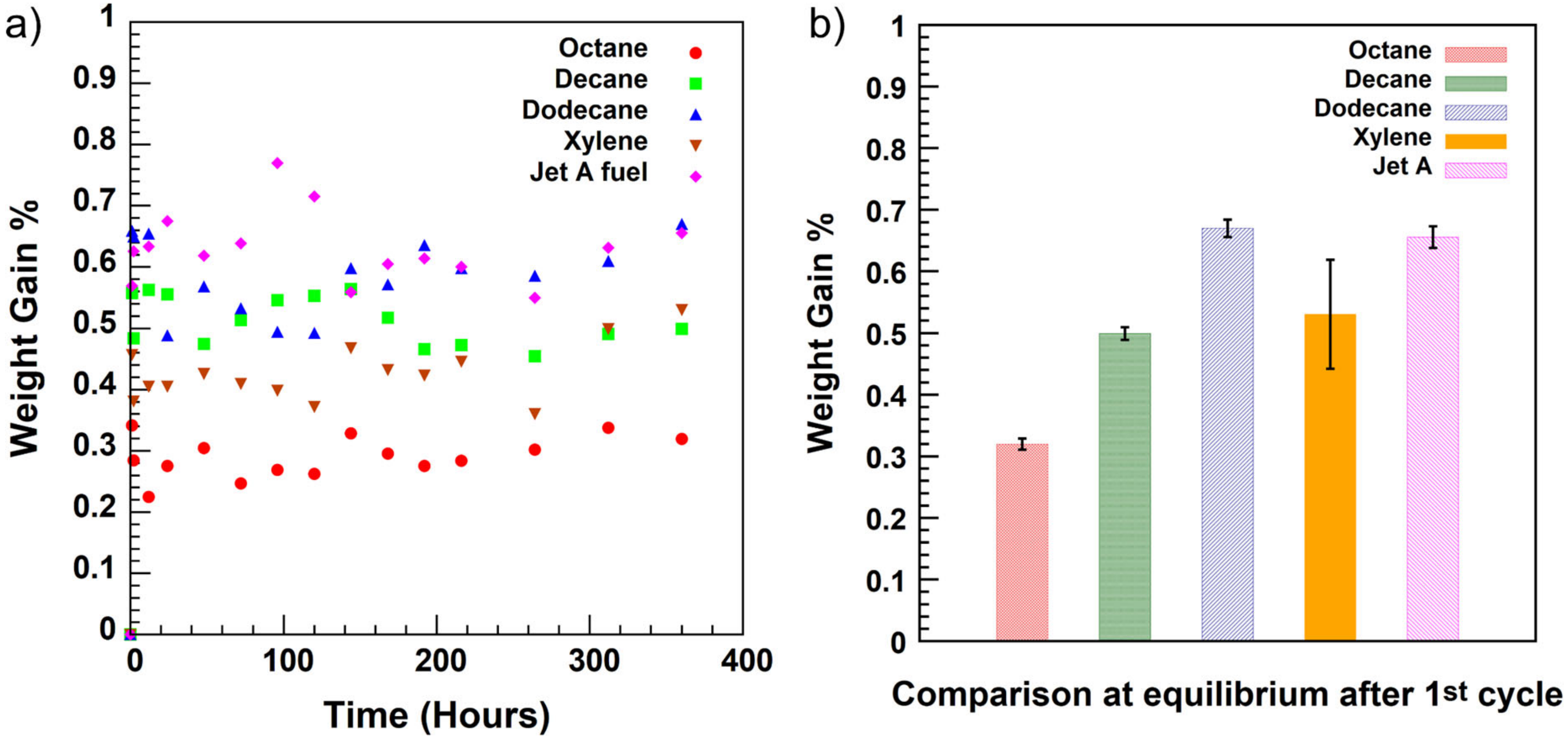


The ***average fuel uptake*** with error bars representing the standard deviation

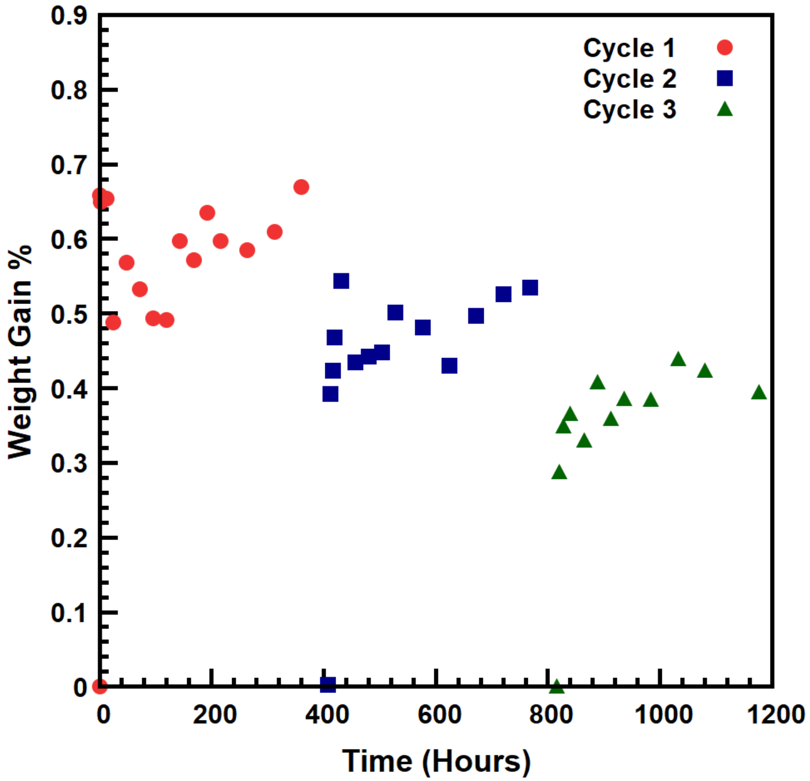
- Faster **absorption** in the **early stages** of the fuel immersion
- The equilibrium weight gain was of ≈0.69%

Weight Gain with Time for Autoclave Cross-Ply Hexcel SGP370-8H/8552 Carbon/Epoxy Immersed in All Fluids - 1st Absorption Cycle

- Faster **absorption** in the **early stages** of the fuel immersion
- The equilibrium weight gain for all specimens was in the range of 0.3 - 0.7%

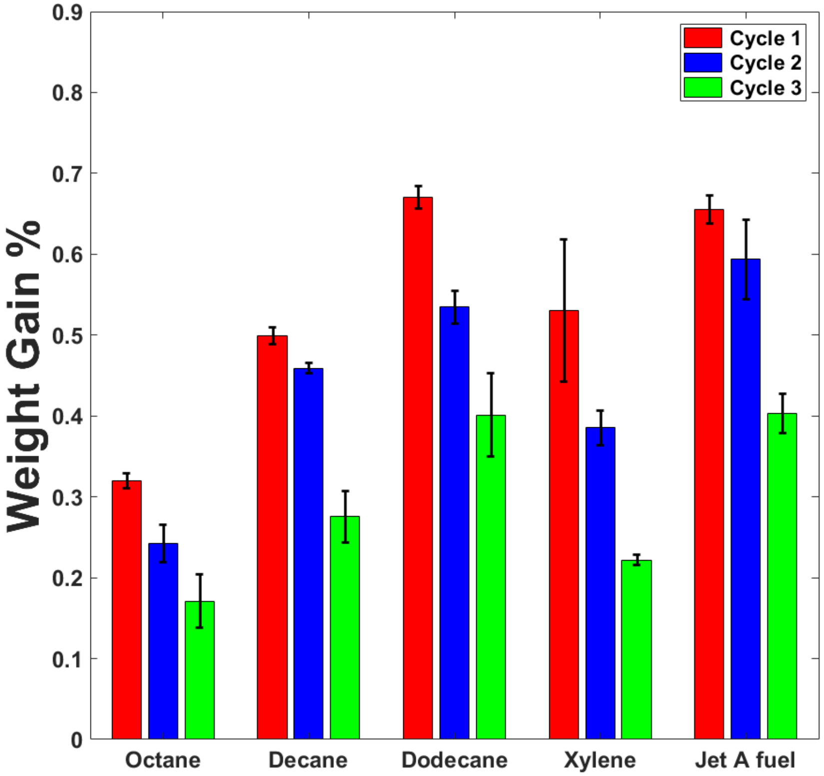


Weight Gain with Time for Autoclave Cross-Ply Hexcel SGP370-8H/8552 Carbon/Epoxy Immersed in Dodecane - All Cycles



- Faster **absorption** in the **early stages** of the fuel immersion
- The equilibrium weight gain *slightly* decreases after each cycle

Weight Gain Comparison for Autoclave Cross-Ply Hexcel SGP370-8H/8552 Carbon/Epoxy Immersed in All 5 Fluids - All Cycles



- The **equilibrium weight gain slightly decreases** after **each cycle** for all fluids
- **Dodecane** and **Jet A** have the **highest** equilibrium weight gain for all 3 cycles
- **Octane** has the **lowest** equilibrium weight gain for all 3 cycles

Number of Moles Absorbed of Each Model Fuel

- The number of moles absorbed was calculated using the mass absorbed
- Xylene had the highest moles absorbed
- Octane had the lowest moles absorbed

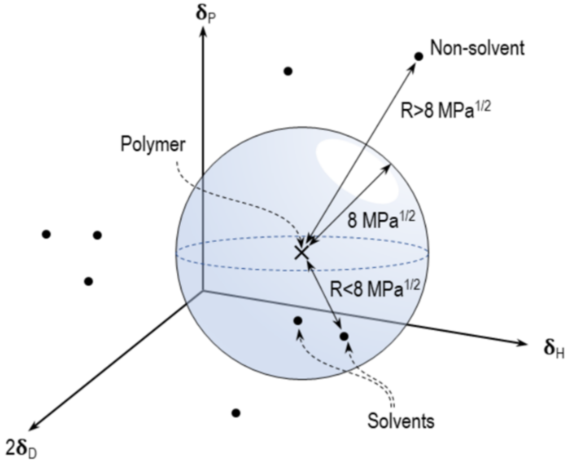
	Weight gain %	Molecular weight (g/mol)	Moles absorbed (mol)
Octane	0.32 ± 0.01	114.23	4.20 ± 0.15 x 10^{-5}
Decane	0.50 ± 0.01	142.29	5.22 ± 0.15 x 10^{-5}
Dodecane	0.67 ± 0.01	170.33	5.91 ± 0.03 x 10^{-5}
Xylene	0.53 ± 0.09	106.16	7.44 ± 1.30 x 10^{-5}
Jet A fuel	0.66 ± 0.02	N/A[1]	N/A

[1] Jet A fuel is a mixture of different compounds, its molecular weight was not obtained

Solubility Parameters

- Solubility parameters: Hansen solubility parameters (HSP)
- Contains a dispersion δ_d, polarity δ_p and hydrogen bonding δ_h capability of each molecule and compare it to the polymer
  - Hansen Parameters

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2$$



- R_a is the distance between the polymer and the molecule
- Relative energy difference RED is defined as:

$$\text{RED} = \frac{R_a}{R_0}$$ with R_0 is the interaction radius

- RED <1 the molecule will dissolve
- RED =1 the system will partially dissolve
- RED >1 the system will not dissolve

[5] Hansen CM. Hansen solubility parameters: a user’s handbook. 2nd ed. Boca Raton: CRC Press; 2007.

Solubility Parameters (Cont.)

	δ_D	δ_P	δ_H	R_0	δ	R_a	RED
Polymer	18.1	11.4	9	9.1	23.21		
Octane	14.9	0	0		14.9	15.9	1.74
Decane	15.7	0	0		15.7	15.3	1.68
Dodecane	16	0	0		16	15.1	1.66
Xylene	17.8	1	3.1		18.1	11.9	1.32

- Xylene is expected to be the most absorbed fluid
    - RED closest to 1
- Octane is expected to be the least absorbed fluid
    - RED farthest from 1

Summary of Absorption Results

	Weight gain %	**Molecular weight (g/mol)**	**Moles absorbed (mol)**	**δ ($MPa^{1/2}$)**
Epoxy	N/A	N/A	N/A	23.2
Octane	0.32 ± 0.01	114.23	4.20 ± 0.15 x 10^{-5}	14.9
Decane	0.50 ± 0.01	142.29	5.22 ± 0.15 x 10^{-5}	15.7
Dodecane	0.67 ± 0.01	170.33	5.91 ± 0.03 x 10^{-5}	16
Xylene	0.53 ± 0.09	106.16	7.44 ± 1.30 x 10^{-5}	18.1
Jet A fuel	0.66 ± 0.02	N/A[1]	N/A	N/A

[1] Jet A fuel is a mixture of different compounds, its molecular weight was not obtained

- Xylene is the fluid that was mostly absorbed but due to its low molecular weight it does not translate to the highest weight gain %
- Octane has the lowest # of moles absorbed and lowest weight gain %

Summary of Average Weight Gain for All Specimens and Model Fuels Used

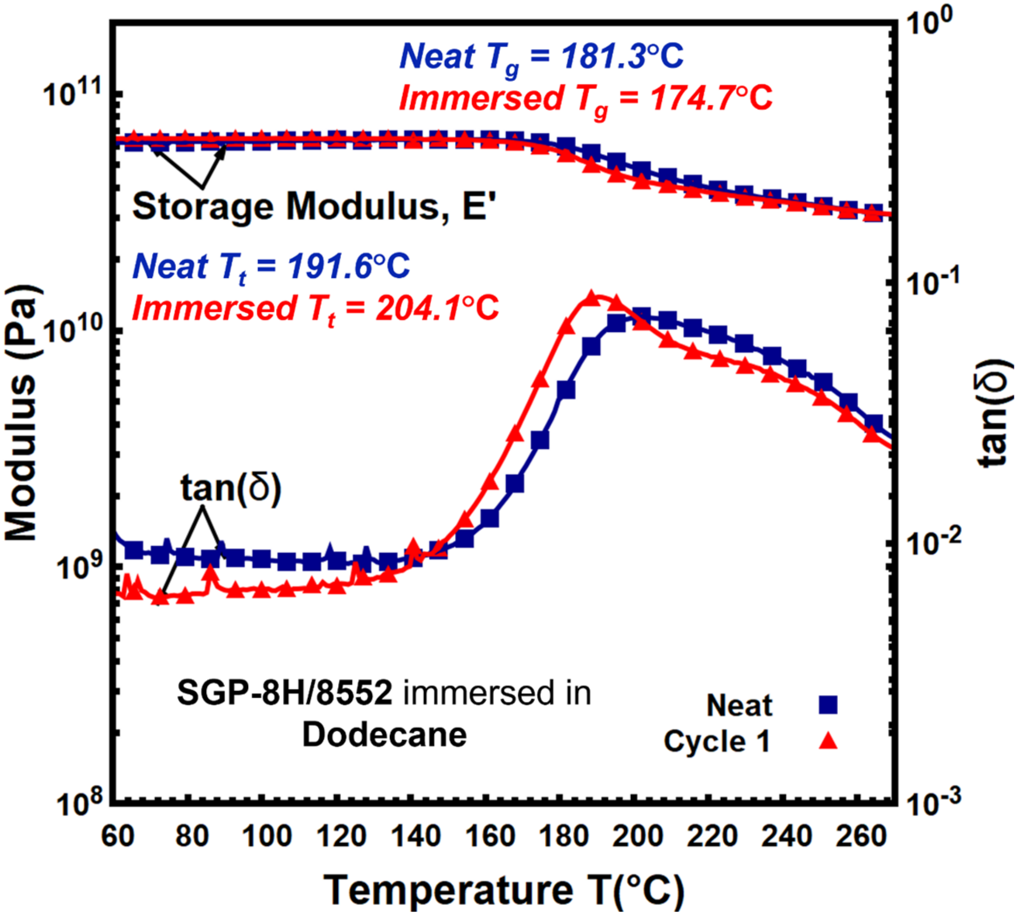
- The small differences in fuel absorption were explained using solubility parameters.

- The equilibrium weight gain decreased after each absorption-desorption cycle

- The saturation %WG was in the range of 0.32-0.67% for the 1st cycle, 0.24-0.59% for the 2nd cycle and 0.17-0.40% for the 3rd cycle.

- Octane had the lowest %WG for all three cycles while Dodecane and Jet A had the highest.

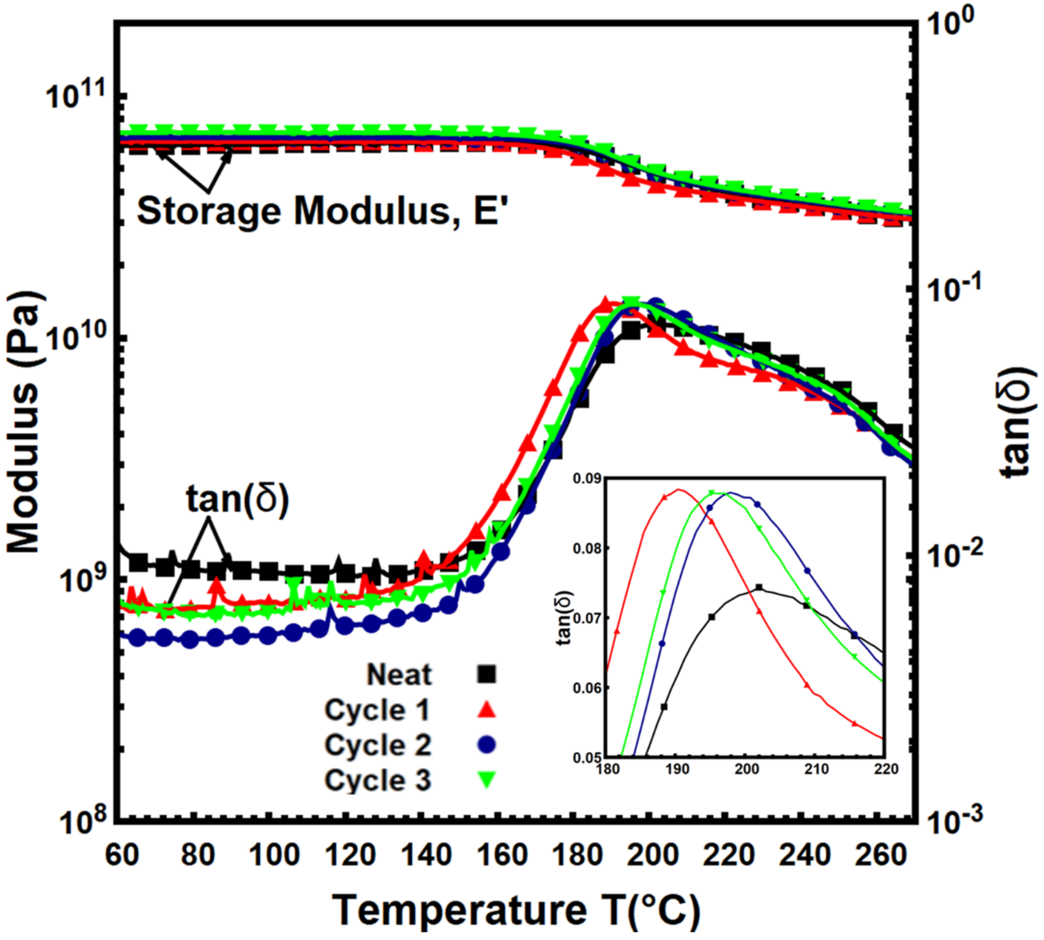
DMA Results for Autoclaved Cross-ply Hexcel SGP370-8H/8552 Carbon/Epoxy Specimens: Immersed in Dodecane for the 1st absorption cycle



- DMA T_g decreased after the first cycle of fluids absorption: $\Delta\mathbf{DMA}\ \boldsymbol{T_t} = \mathbf{12.5}$ ℃ and $\Delta\mathbf{DMA}\ \boldsymbol{T_g} = \mathbf{6.6}$ ℃

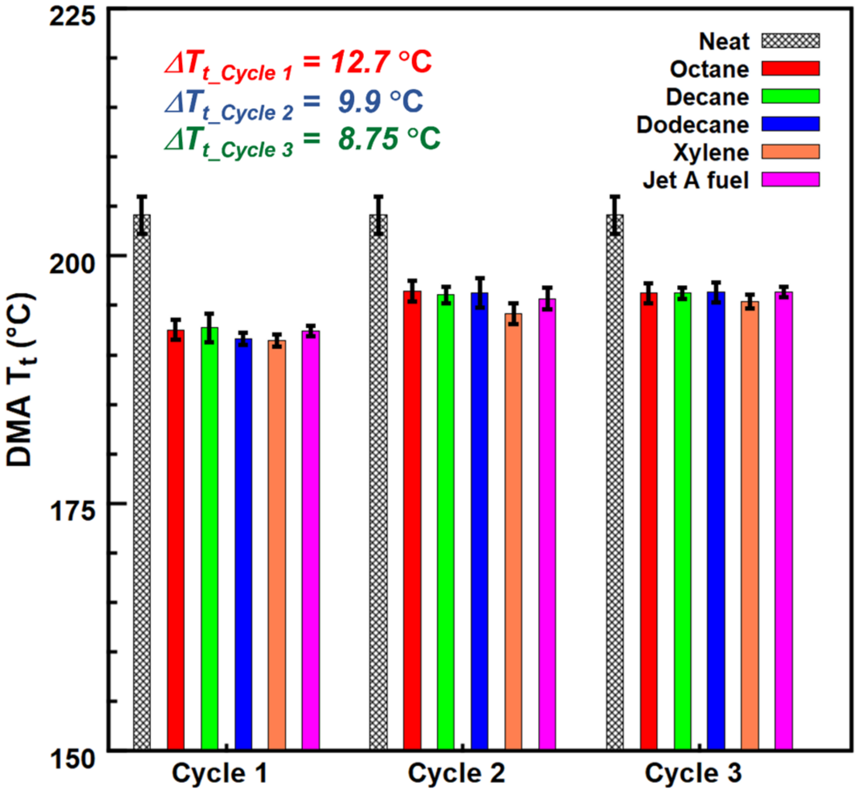
- **DMA T_g and T_t** for specimens **saturated** with **four model fuels** were **impacted** to the **same extent** as those saturated with **Jet A fuel**.

DMA Results for Autoclaved Cross-ply Hexcel SGP370-8H/8552 Carbon/Epoxy Specimens: Immersed in Dodecane for all absorption cycle



- DMA T_g decreased after the first cycle of absorption then increased after each absorption cycle
- **DMA T_g** for specimens **saturated** with **four model fuels** were **impacted** to the **same extent** as those saturated with **Jet A fuel**.

DMA Results for Autoclaved Cross-ply Hexcel SGP370-8H/8552 Carbon/Epoxy Specimens: Comparison of All Fuels and Cycles



- DMA T_t decreased after all cycles of absorption compared to neat specimen
- The DMA T_t drop for the 2nd and 3rd cycles was smaller compared to the 1st cycle
- This correlates well with the results from the weight gain
- T_g for specimens **saturated** with **four model fuels** were **impacted** to the **same extent** as those saturated with **Jet A fuel**.

Summary of DMA Results for All Specimens and Fuels Used

- DMA T_g for specimens saturated with the model fuels were impacted to the same extent as those saturated with Jet A fuel.

- DMA T_g decreased for the 1st, 2nd and 3rd cycle by 11.9, 8.4 and 8.0, respectively, when compared with the neat specimens.

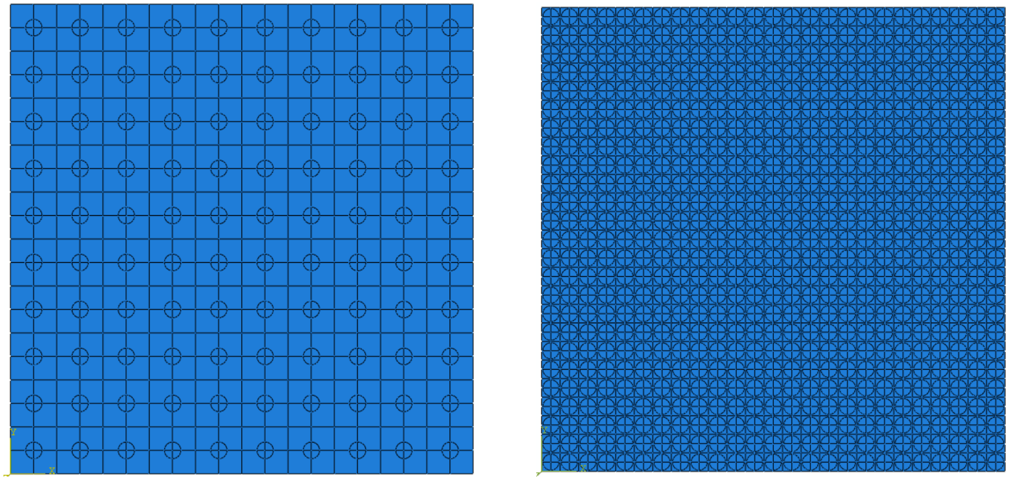
- The DMA T_g drop for the 2nd and 3rd cycles was smaller compared to the 1st cycle

- This correlates well with the results from the weight gain

Modelling Work

- The effects of fiber packing and fiber arrangement on the diffusion behavior of fluids in composite materials were investigated:
  - Three types of fiber arrangements were used (Square, Hexagonal, and Random Arrays)
  - Fiber volume fraction was changed to investigate the fiber packing ($10\ \% \leq V_f \leq 50\%$)
- Finite Element Analysis via ABAQUS was used (mass diffusion process)

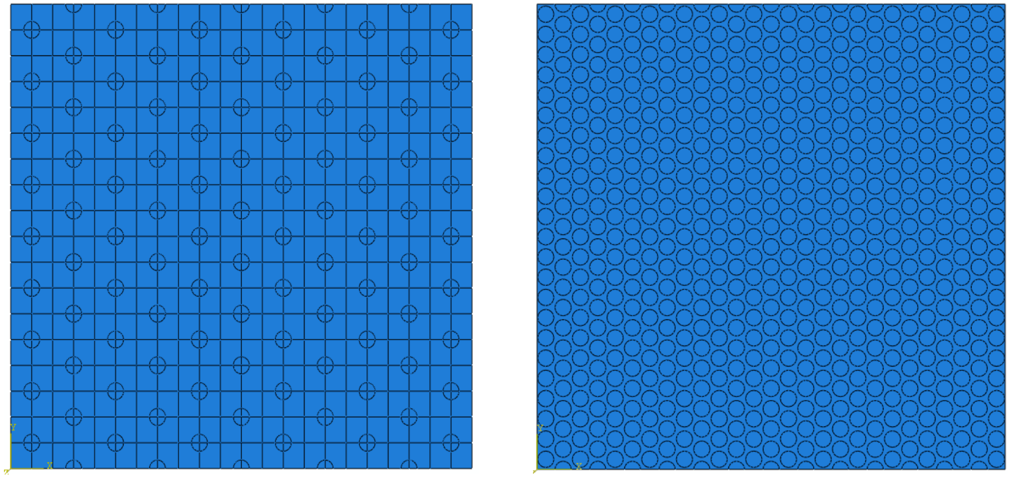
Geometry Details – Square and Hexagonal Array



V_f = 10%

V_f = 60%

Square Array

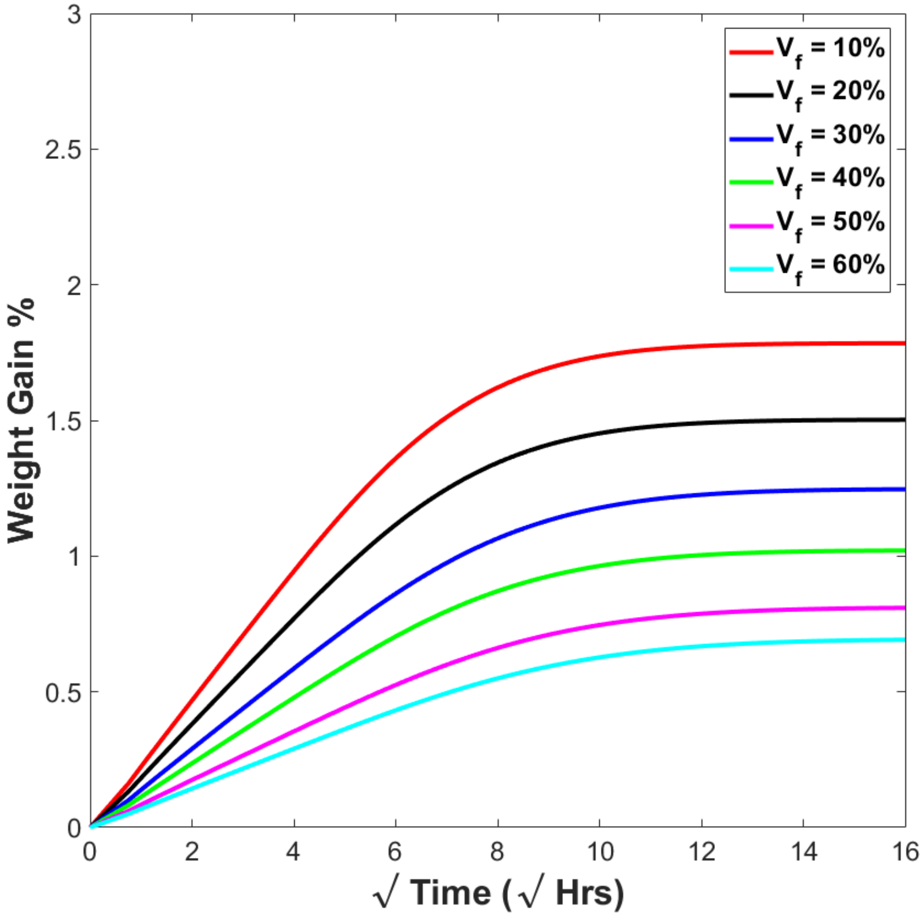


V_f = 10%

V_f = 60%

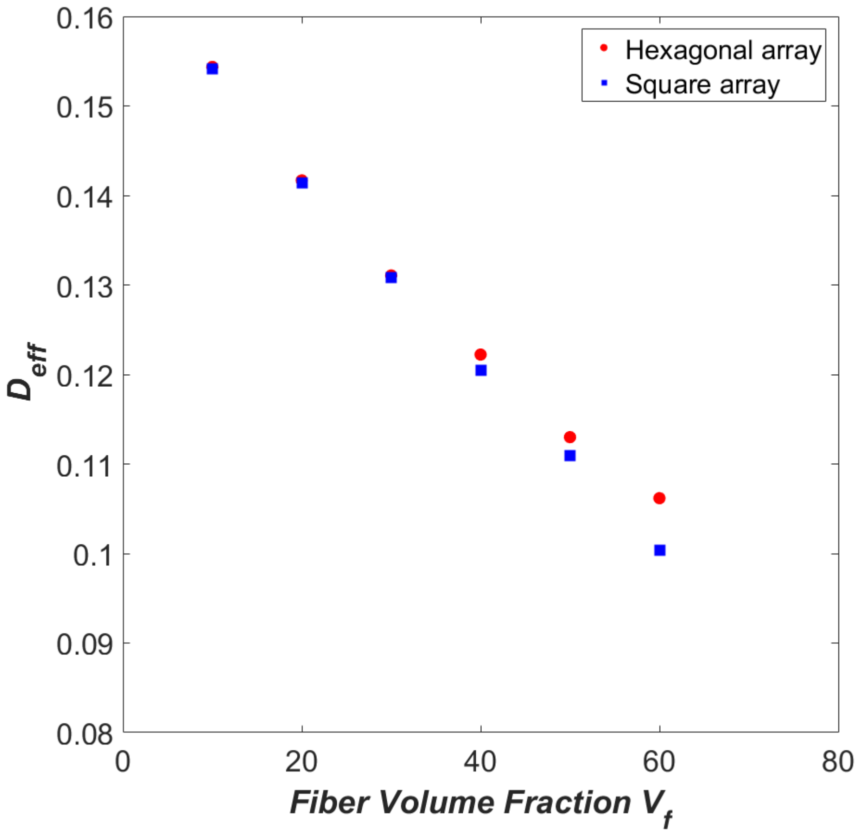
Hexagonal Array

Weight Gain % vs Time for Square Array



- Weight gain % $= \frac{Absorbed\ Amount}{Dry\ Weight\ of\ composite}$ x100%
- The weight gain % decreases with the increase in fiber volume fraction

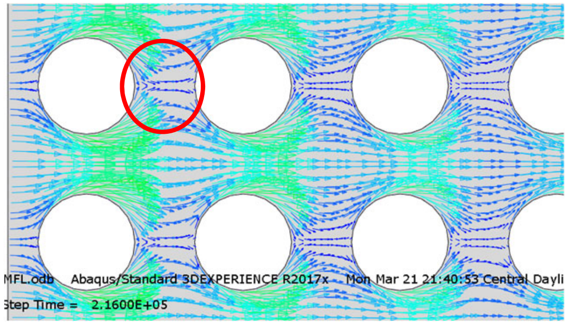
Effective Diffusivity Results



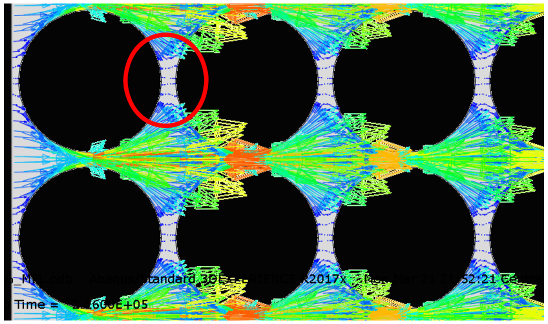
- The effective diffusivities obtained correlates well with the weight gain % results
- It decreases with the increase in the volume fraction
- At low V_f, the effective diffusivities are similar
- At high V_f, the hexagonal array has higher effective diffusivity values

Explanation of Effective Diffusivity Results

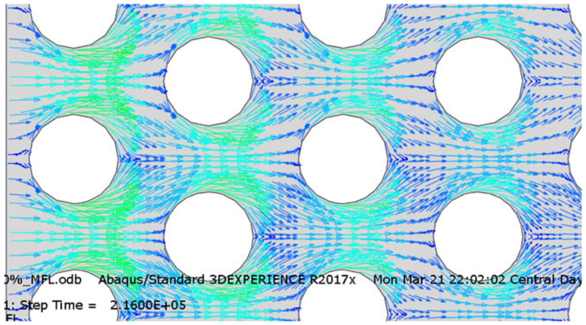
Square
$V_f = 30\%$



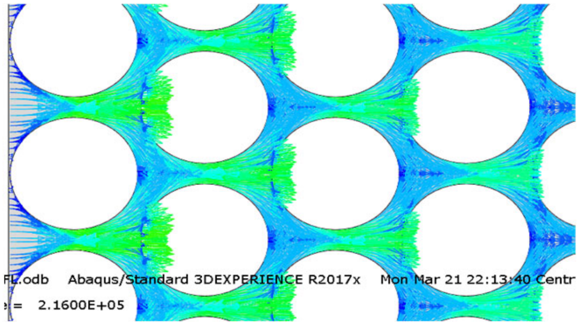
Square
$V_f = 50\%$



Hex
$V_f = 30\%$



Hex
$V_f = 50\%$



- At low fiber volume fraction, the square and hexagonal have similar effective diffusivities
- At high volume fraction, the hexagonal array had higher diffusivities
  - Likely caused by the different nature of fuel diffusion in the confined space

Concluding Remarks

- Alternative fuels blended with Jet A fuel within the ratios studied showed no different impact on composite materials than conventional fuel
- Model fuels used showed no differences in thermomechanical properties with Jet A
- Fiber packing impacted both the weight gain and thermomechanical properties
- From the research performed: **The alternative fuels represent a safe substitute for conventional fuels (effects of fluid vapor pressure not investigated)**

Publications

Technical reports

- Bassou, R., Harich, N., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., Kundu, S. *Effect of Jet Fuels Exposure on Aerospace Composites – Literature Review.* NO. DOT/FAA/TC-20/22. United States. Department of Transportation. Federal Aviation Administration. William J. Hughes Technical Center, 2021. **(Published)**
- Harich, N., Bassou, R., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., Kundu, S. *Effects of New Jet Fuel Exposure on Aerospace Composites–Phase 1 Final Report*. No. DOT/FAA/TC-21/53. United States. Department of Transportation. Federal Aviation Administration. William J. Hughes Technical Center, 2022. **(Published)**
- Harich, N., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., Kundu, S. *Effects of New Jet Fuel Exposure on Aerospace Composites–Phase 2 Final Report*. **(In preparation)**

Journal

- Harich, N., Bassou, R., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., & Kundu, S. (2022). Effects of alternative jet fuel blends on aerospace-grade carbon/epoxy composites. *Materials & Design*, *221*, 110993. **(Published)**
- Harich, N., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., & Kundu, S. Effects of cyclic absorption-desorption of model fuels by aerospace-grade carbon/epoxy composites. **(Submitted to Polymer Composite Journal)**
- Harich, N., Priddy, M. W., Lacy Jr, T. E., Pittman Jr, C. U., & Kundu, S. Influence of fiber packing and arrangement on the diffusion behavior of jet fuels in composite materials. **(In preparation)**