Properties of Phenylethynyl Imide Composites Fabricated Via VARTM

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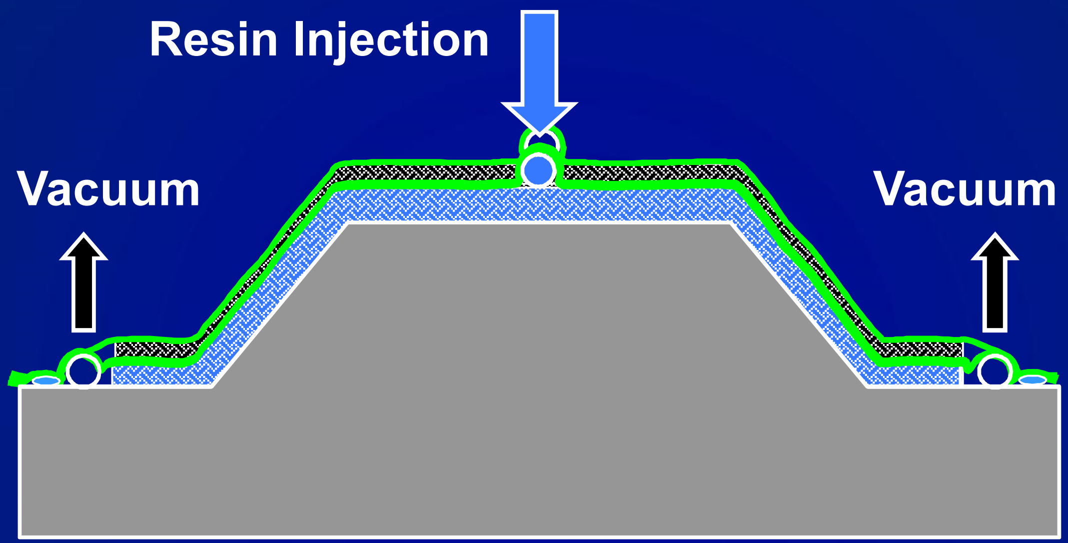
Outline

- Introduction to VARTM Processing
- Phenylethynyl Terminated Imide (PETI) Resins
- Past Research and Issues
- Current HT-VARTM Process
- Experimental
- Laminate Fabrication Results
- Mechanical Properties
- Structural Sub-Component Demonstration Article
- Summary

Vacuum Assisted Resin Transfer Molding



- Upper half of metal mold replaced by vacuum bag
- Atmospheric pressure provides both the resin driving force and the preform compaction force
- Distribution medium is used to facilitate resin flow
- Room temperature process

Ref: Seeman Composites Resin Infusion Molding Process (SCRIMP), TPI Composites, U.S. Patent 4,902,215 (1990)

VARTM Characteristics

- Strengths
  - Reduced cost
  - Complex shapes
  - Essentially no size limitation

- Weaknesses/Possible Issues
  - High fiber volume more difficult to obtain than in autoclave
  - Void content < 2% for aerospace applications (like epoxies)?
  - Most applications tolerate higher void content than aerospace
  - Applicable to high temperature resins?

- Controlled Atmospheric Pressure Resin Infusion (CAPRI)
  - Patented by The Boeing Company
  - SCRIMP variation
  - vacuum debulking and reduced pressure difference
  - minimizes thickness gradients and resin bleeding

Ref: J.A. Woods et al., U.S. Patent 7,334,782 (2008)

Selection of PETI Resins for HT-VARTM

- Precursor form offers
  - Low melt viscosity, large processing window
  - Long shelf-life
  - No solvent, no unreacted toxic monomers
  - Commercial availability in prepreg solutions and neat resin form (for RTM and RI)

- Cured resin offers
  - High temperature performance (>1000 h at 300 °C in air)
  - Composite mechanical properties including damage tolerance meet aerospace criteria

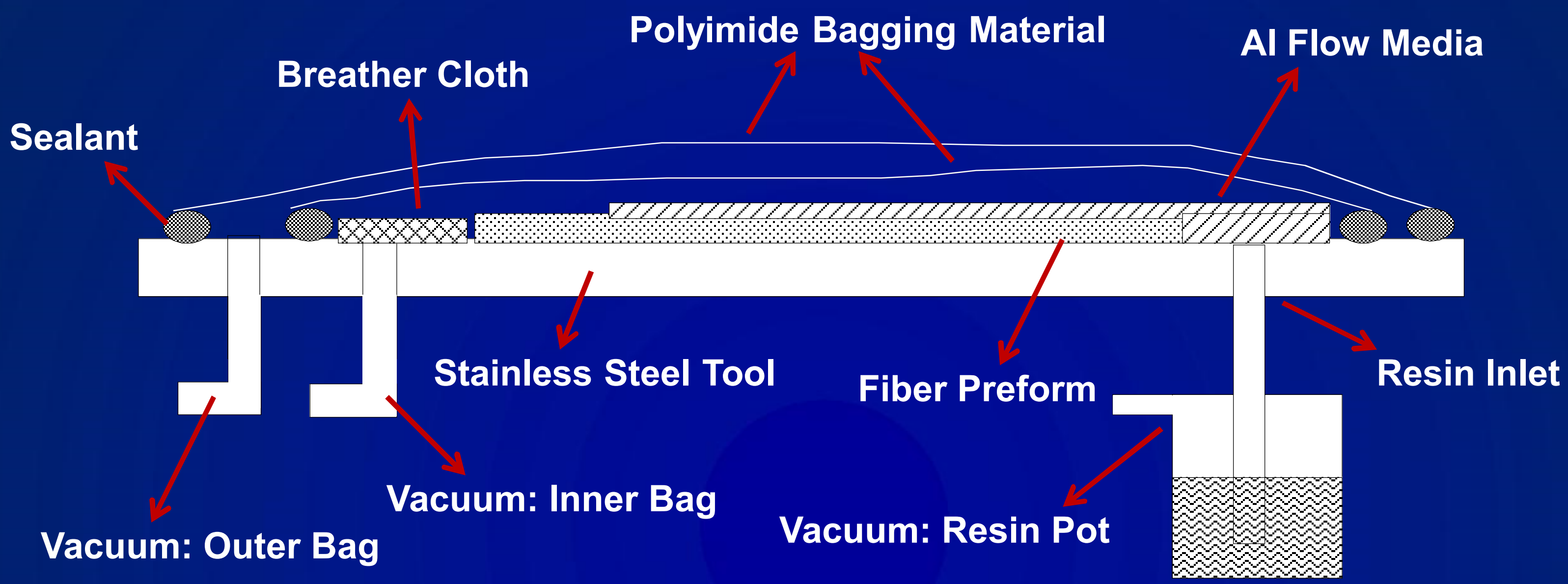
- Disadvantages
  - High temperature cure (typically 1-3 h at 371 °C)
  - High cost (relative to epoxies)
  - Niche market (jet engine applications, recent interest in airframe structure)

State of the Art

- PETI laminates from same resins (different mol wt) by autoclave (prepreg), RI and RTM, porosity levels of < 2% routinely achieved
- Difference between RTM and VARTM = pressure (1.4 vs. 0.1 Mpa)
- HT-VARTM laminate porosity by volume reduced from ~10% to as low as 1% by identification of porosity sources and processing modifications.

Ref: S. Ghose, et al.; "High Temperature VARTM of Phenylethynyl Terminated Imides," High Performance Polymers, 21 (5), 653 (2009)

Experimental

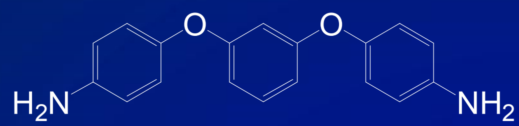


- Steel plate with 3 holes to provide one resin inlet and two vacuum outlets
- Polyimide bagging material (Thermalimide™)
- Inner bag with several layers of carbon fiber preform, 5 layers of Aluminum (Al) screen distribution media (DM), Release Ease™ fabric - a breather material
- High temperature sealant to seal both an inner bag and an outer bag (for redundancy should a leak occur in the inner bag after infiltration)

Experimental

- Resins: PETI-9: cured T_g ~ 265 °C (Imitec, Inc.),
  PETI-330: cured T_g ~ 330 °C (Ube America, Inc.)
- Fabrics: T650-35-3K-8HS
  IM7-6K-5HS
  IM7-6K uniweave (unidirectional weave)
- Rheology
- C-scan
- Acid digestion
- Mechanical properties (unaged and aged, room temperature and elevated temperature)
  - Short Block Compression (SBC)
  - Open Hole Compression (OHC)
  - Compression After Impact (CAI)

LaRC™ PETI-330



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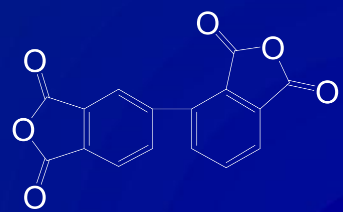
1,3-bis(4-aminophenoxy)benzene (1,3,4-APB)

1,3-diaminobenzene (m-PD)



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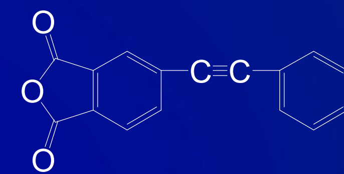


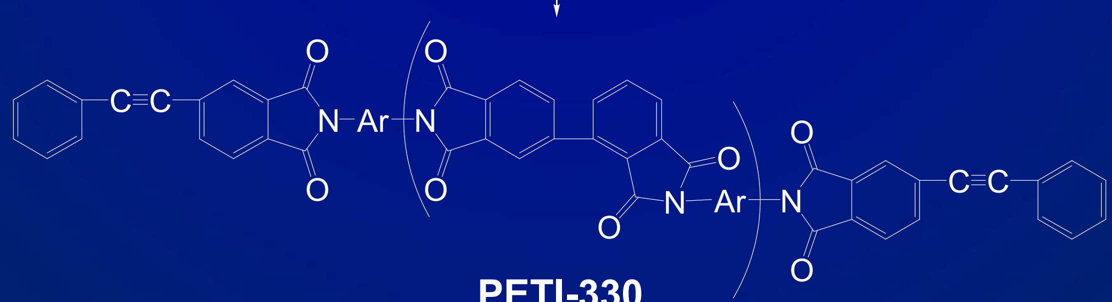
asymmetric biphenyl dianhydride (a-BPDA)

phenylethynyl phthalic anhydride (PEPA)

nitrogen
NMP

POLYAMIDE ACID

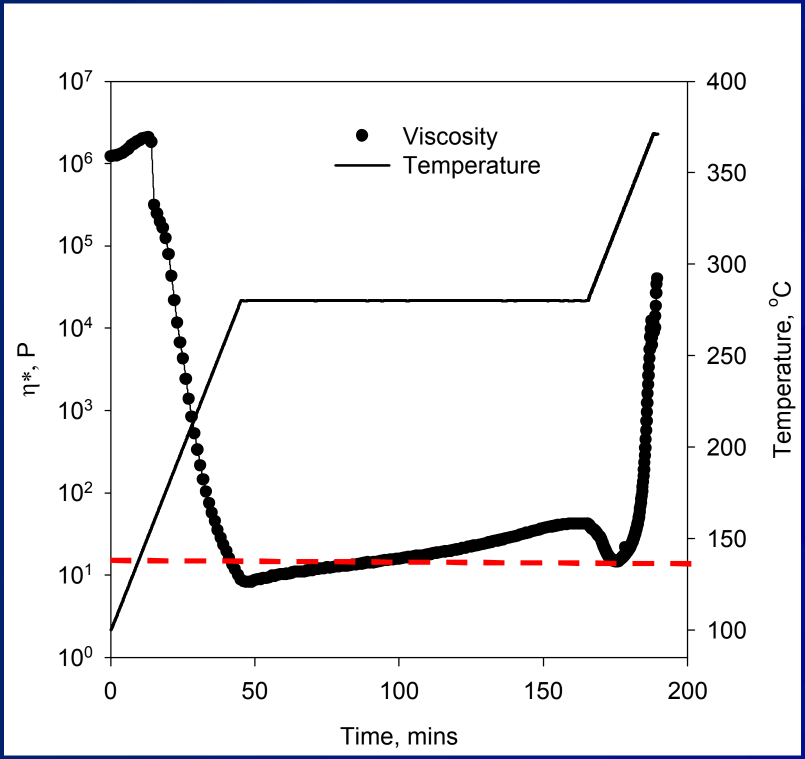
$-H_2O$

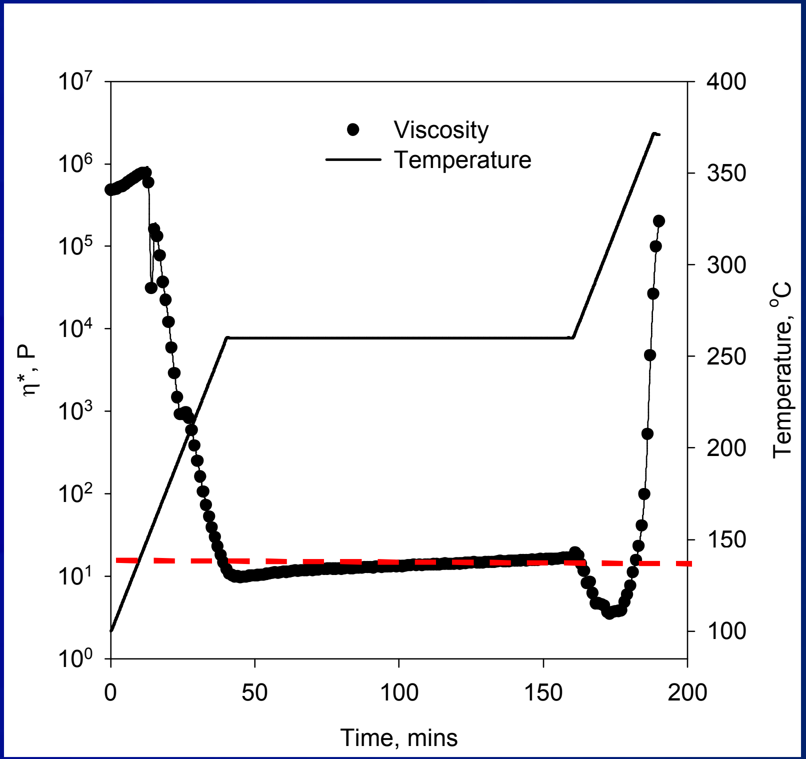


PETI-330

Where Ar = 1,3,4-APB and m-PD; 50:50 ratio, M_n ~1290 g/mol

Rheology Profile of PETI-330





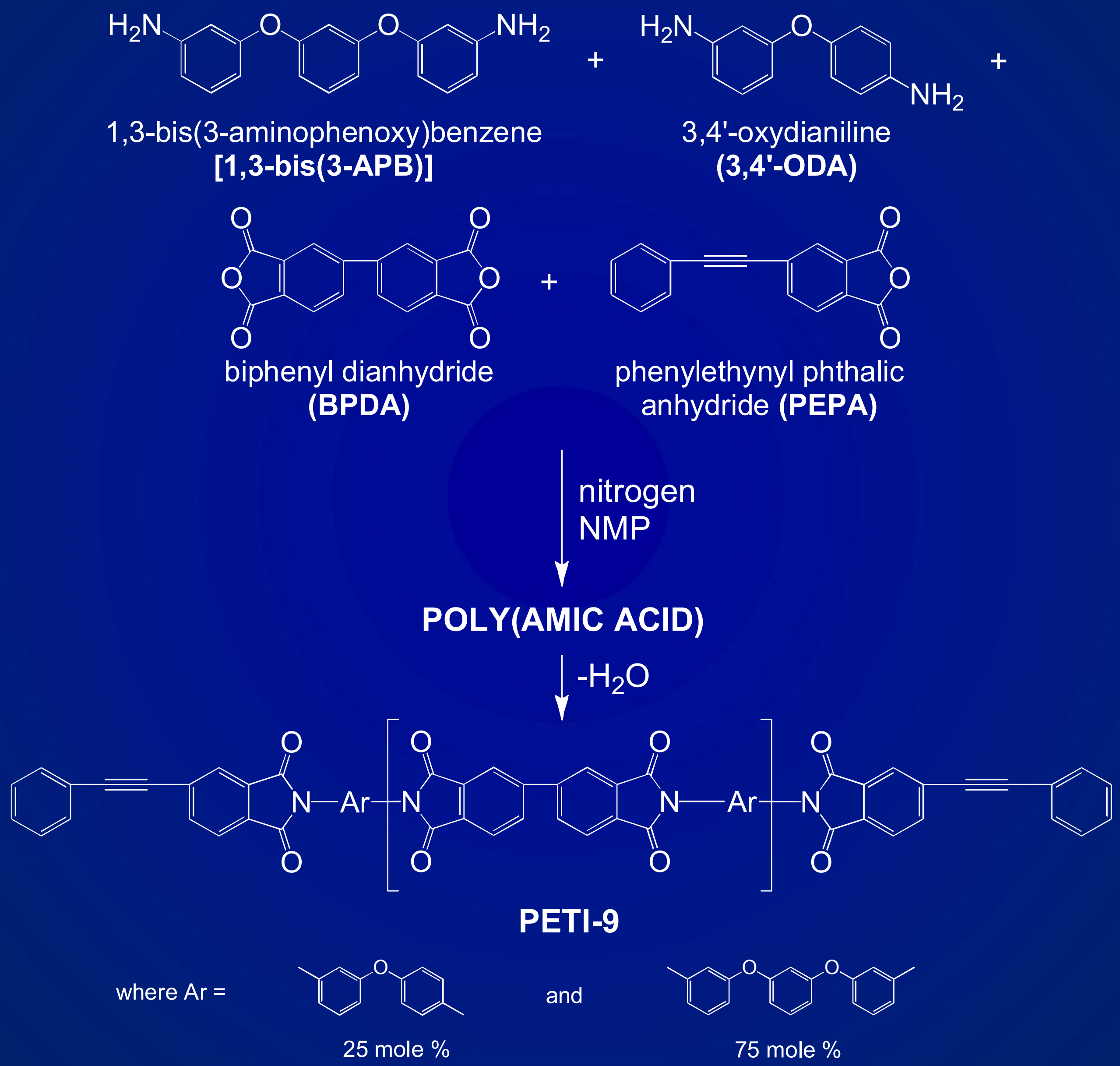
2 h hold at 280 ºC

2 h hold at 260 ºC

Larger processing window at 260 ºC for PETI-330

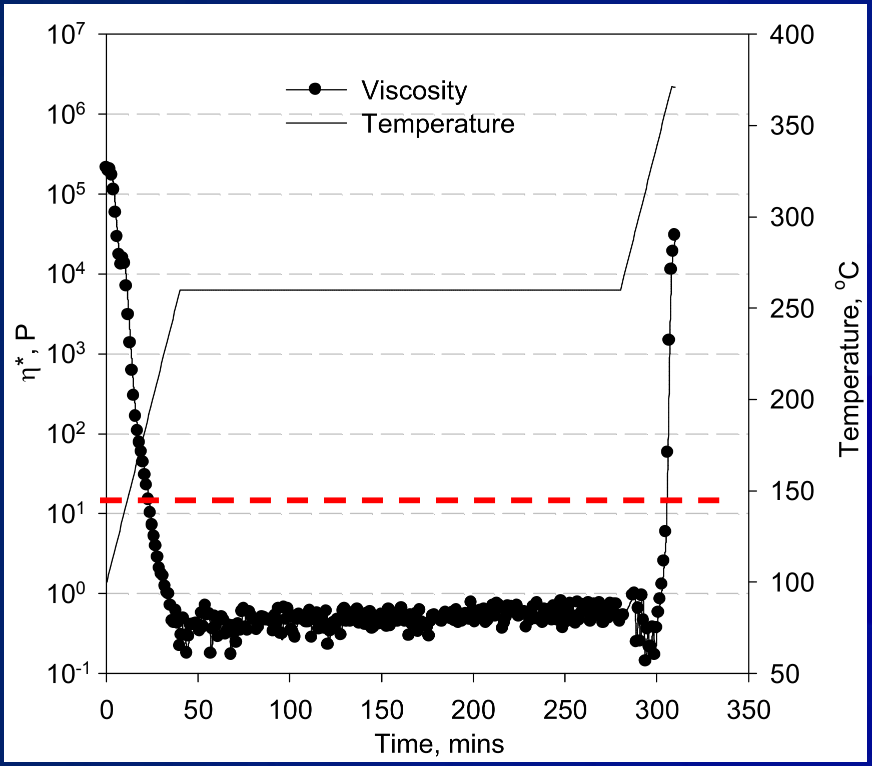
Rheology conditions: 100 – 371 ºC at 4 ºC/min; 2 h hold at infusion temperature, frequency of 10 rad/sec, autostrain

LaRC™ PETI-9



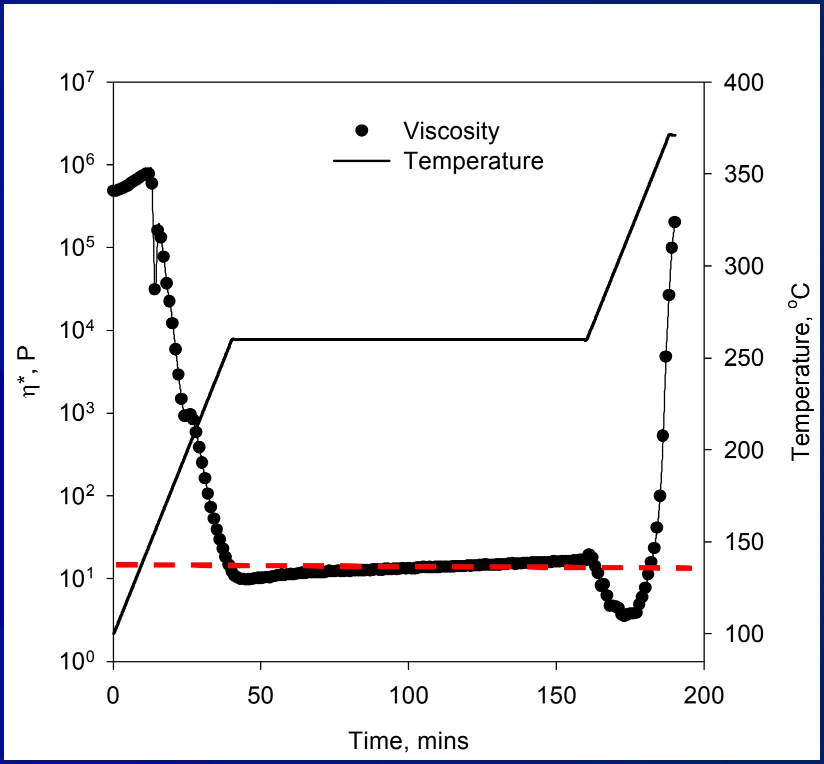
H2N
O
O
NH2
+
H2N
O
NH2
+
1,3-bis(3-aminophenoxy)benzene
[1,3-bis(3-APB)]
3,4'-oxydianiline
(3,4'-ODA)
O
O
O
O
O
O
+
O
O
O
biphenyl dianhydride
(BPDA)
phenylethynyl phthalic
anhydride (PEPA)
nitrogen
NMP
POLY(AMIC ACID)
-H2O
O
N—Ar—N
O
N—Ar—N
O
PETI-9
where Ar =
O
and
O
O
25 mole %
75 mole %

Rheology Profile of PETI-9 / PETI-300



PETI-9

4 h hold at 260 ºC



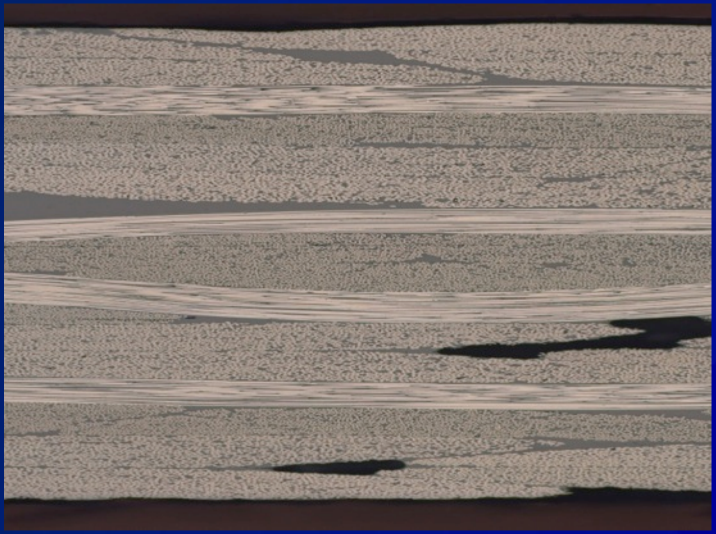
PETI-330

2 h hold at 260 ºC

Rheology conditions: 100 – 371 ºC at 4 ºC/min; 4 h hold at infusion temperature, frequency of 10 rad/sec, autostrain

Typical PETI Panels Quality

PETI-9/T650



Void – 3.6 %,
Fiber volume – 63 %

PETI-330/IM7

Void – 2.9 %,
Fiber volume – 57 %

Quasi lay-up: OHC $[\pm45/(0/90)/\pm45/(0/90)]_s$ (Biaxial Fabric)
OHC $[-45/0/+45/90]_{2s}$ (Uniweave Fabric)
SBC, CAI $[\pm45/(0/90)/\pm45/(0/90)]_{2s}$ (Biaxial Fabric)

- Heat treatment of C-fibers at 400 ° C
- Infusion at 260 ° C
- Staged cure cycle

Fiber and Void Volume Contents of PETI Laminates

	Material: Fabric / Resin					
Test	IM7-5HS/ PETI-9	T650-8HS/ PETI-9	IM7-Uni/ PETI-9	IM7-5HS/ PETI-330	T650-8HS/ PETI-330	IM7-Uni/ PETI-330
SBC RT	57.2 / 3.9	59.6 / 4.4	--	53.4 / 3.9	58.3 / 4.5	--
SBC ET	57.2 / 3.9	59.6 / 4.4	--	53.4 / 3.9	58.3 / 4.5	--
SBC Aged	57.2 / 3.9	59.6 / 4.4	--	53.4 / 3.9	58.3 / 4.5	--
OHC RT	58.7 / 2.7	63.7 / 3.6	57.4 / 2.7	57.5 / 2.9	62.4 / 3.2	56.5 / 1.7
OHC ET	57.6 / 2.4	60.0 / 3.7	57.5 / 3.1	53.5 / 4.2	63.1 / 3.4	53.5 / 3.8
OHC Aged	58.2 / 2.6	57.5 / 2.9	61.9 / 3.7	55.7 / 3.6	62.4 / 3.2	55.7 / 1.7
CAI RT	56.8 / 2.9	61.7 / 4.2	--	55.9 / 2.9	60.1 /3.8	--
CAI ET	56.8 / 2.9	60.8 / 4.2	--	55.9 / 2.9	60.1 /3.8	--

Fiber Volume % / Void Volume %

PETI-9 Aged for 1000 hr at 177° C

PETI-330 Aged for 1000 hr at 288° C

TGA/MS: Source of Volatiles

<u>Heating Ramp</u>

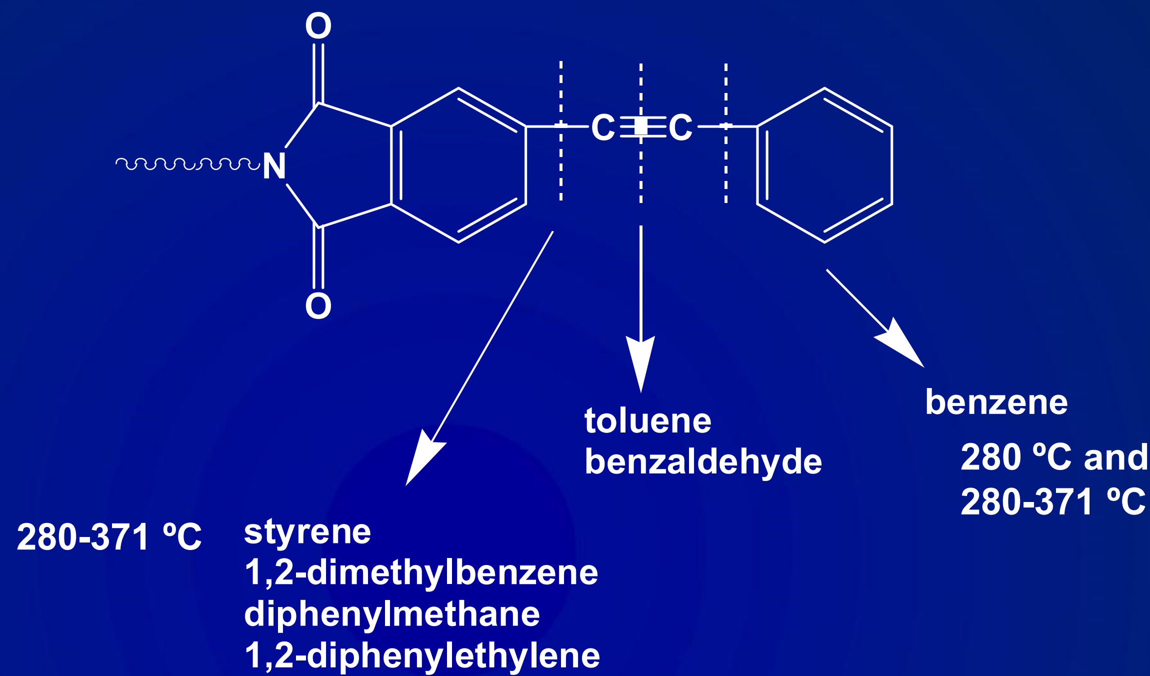
Heat to 280 ºC

Hold 1 h

Heat to 371 ºC

Rate 10 ºC /min

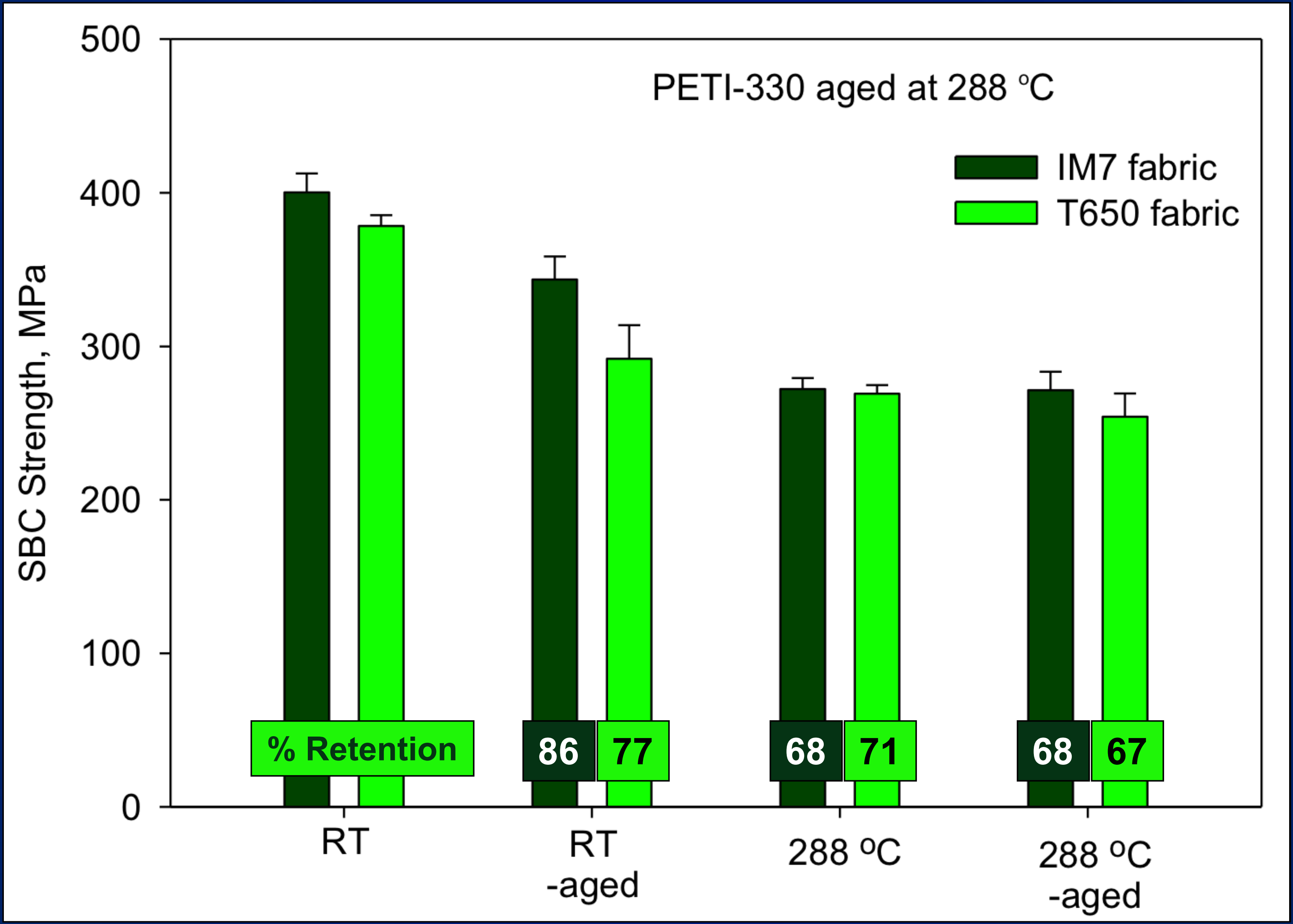
Atmosphere N_2



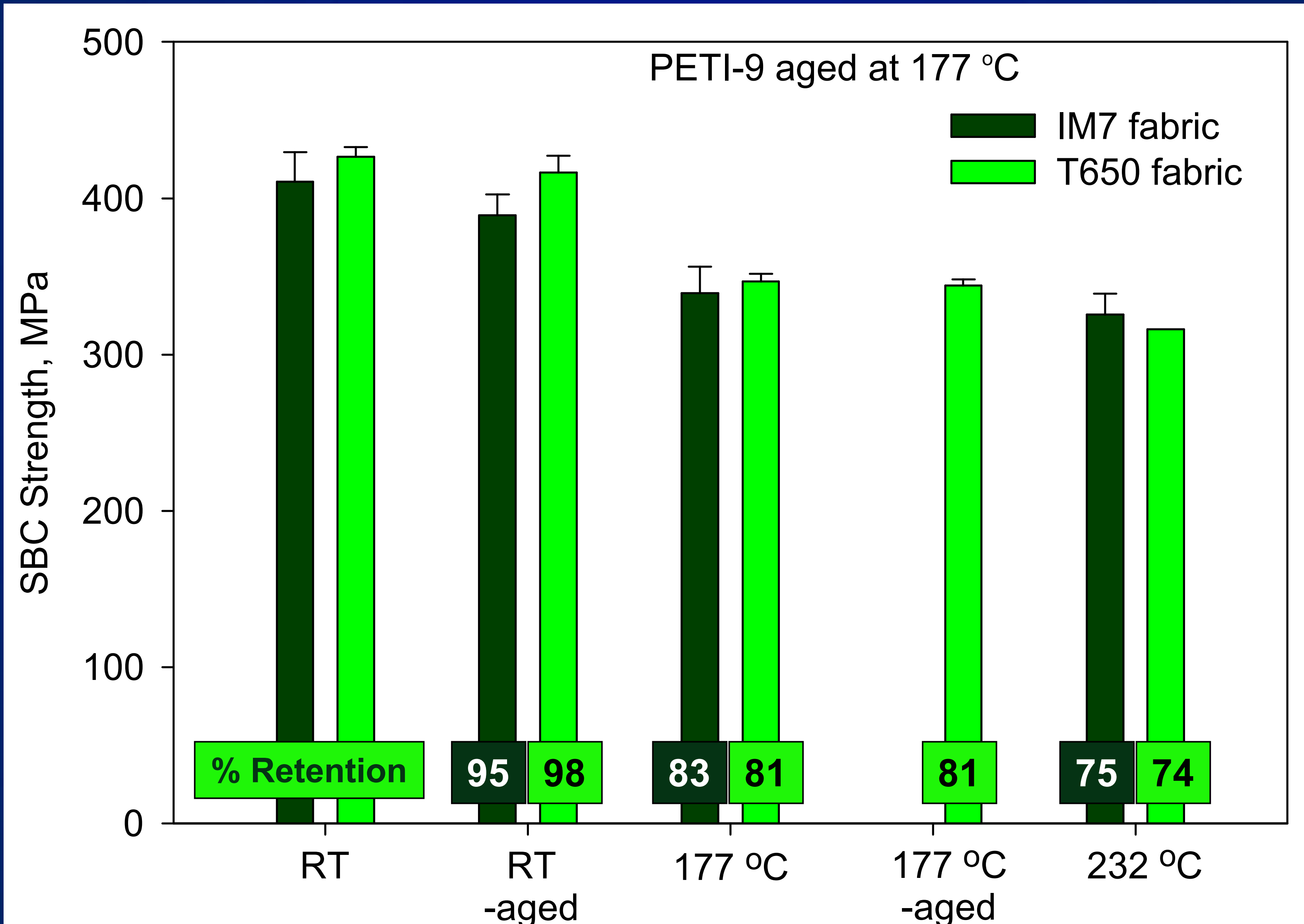
- Heating ramp designed to simulate laminate fabrication cycle (N_2 versus vacuum)
- Benzene, toluene and benzaldehyde detected during both heating ramps
- Other species listed evolved only during second heating ramp
- Total weight loss was 0.5-1.0 %

Ref.: Sayata Ghose, Kent A. Watson, Roberto J. Cano, Sean M. Britton, Brian J. Jensen, John W. Connell, Helen M. Herring, and Quentin J. Lineberry, High Performance Polymers, October 2009; vol. 21, 5: pp. 653-672

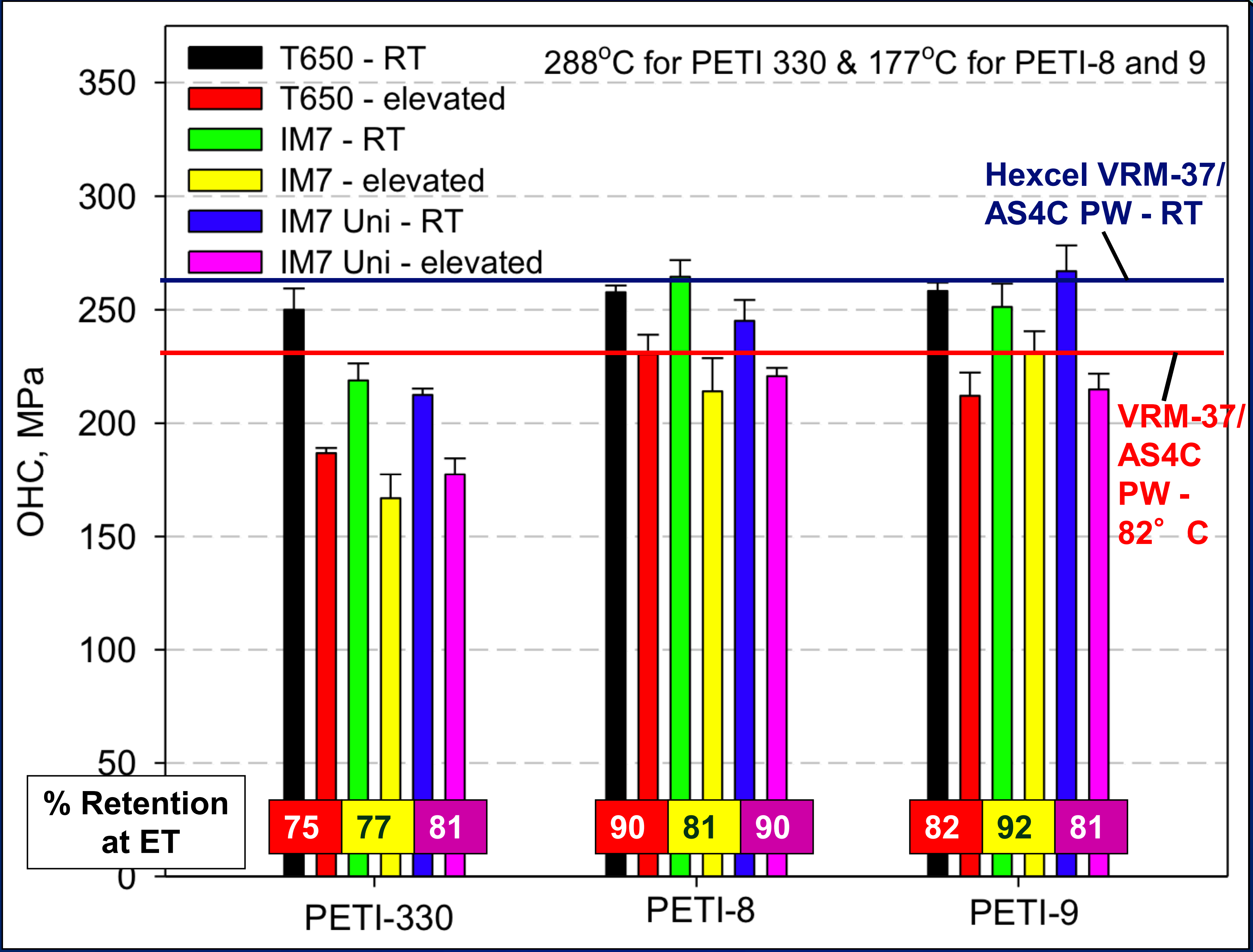
Short Block Compression Properties of PETI-330



Short Block Compression Properties of PETI-9

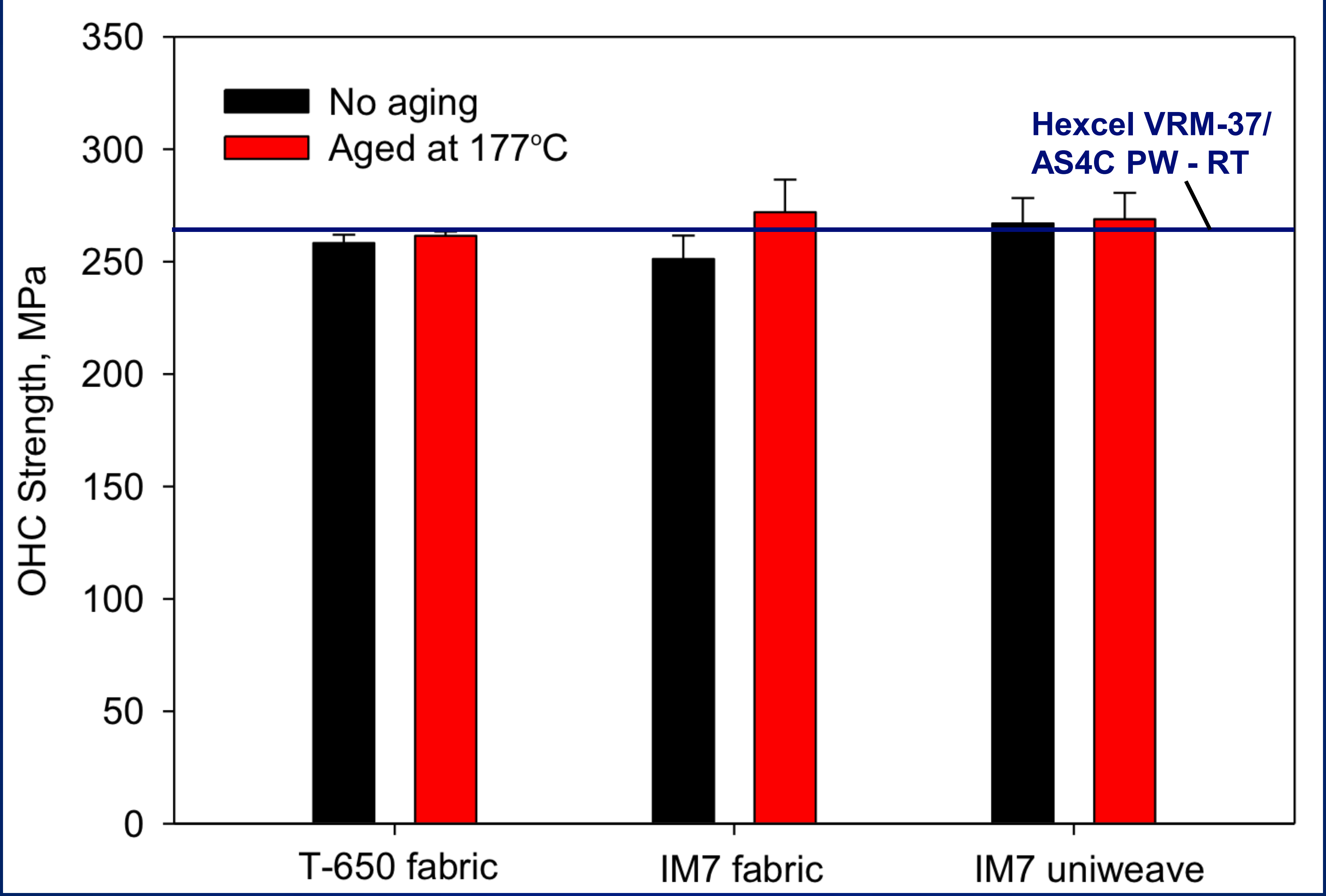


Open Hole Compression Properties

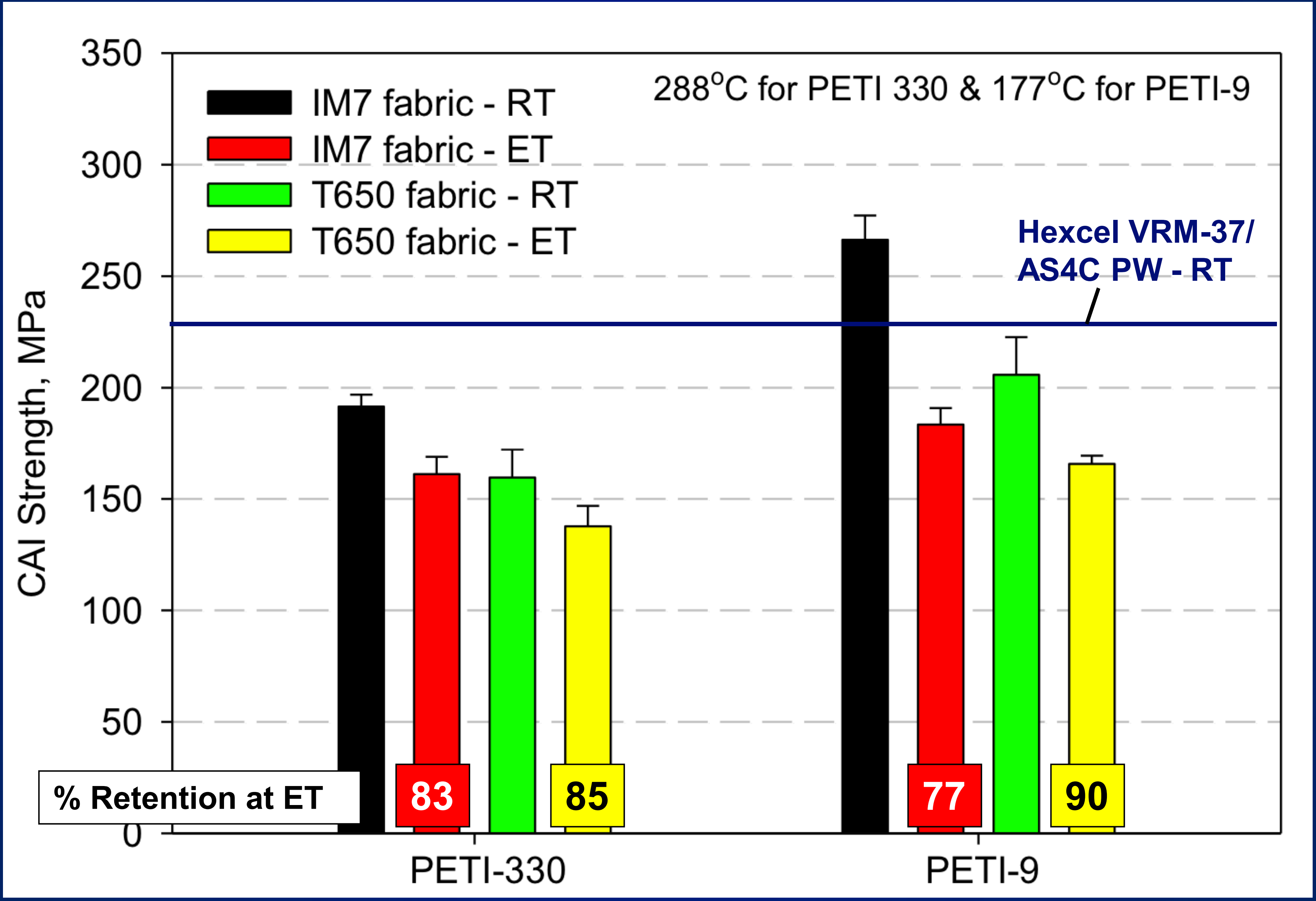


PETI-8 data from Ghose et al., SAMPE Proceedings, Long Beach, CA, May 2011.

OHC Properties of PETI-9 Aging Effects



Compression After Impact Properties



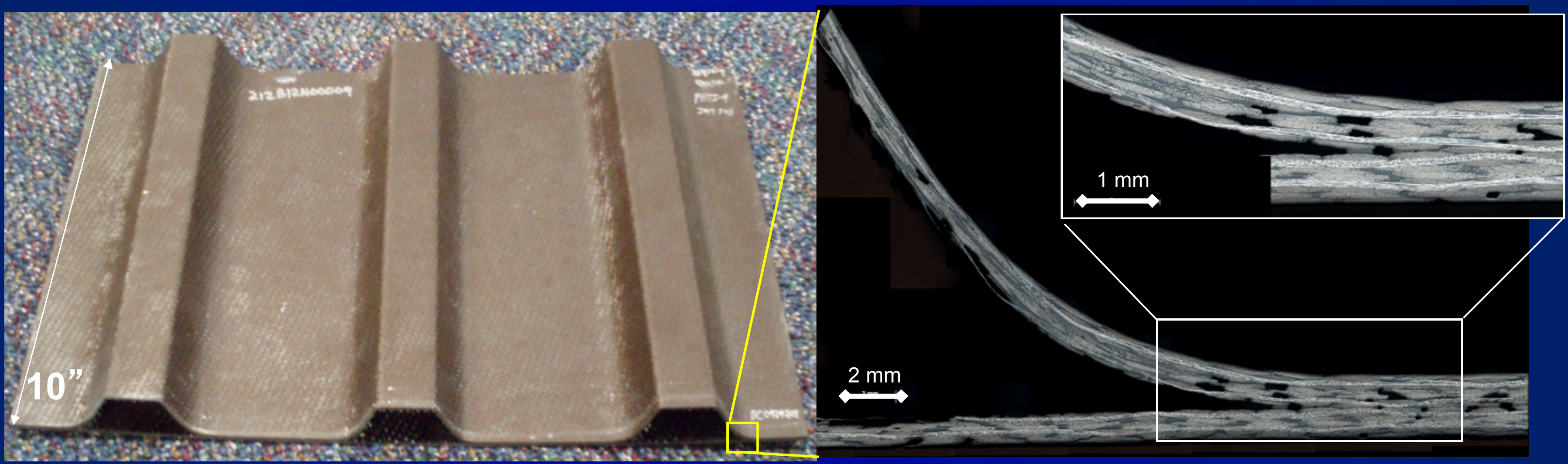
Compression After Impact

Test condition: dropped weight of 5.3691 kg and an indenter with a 1.59 cm diameter hemi-spherical tip

Material	CAI Test Temp., °C	Impact Energy, J	Drop Height, cm	Max. Force, N	Dent Depth, mm	Damage Area*, cm^2
PETI-330 / IM7 5HS	RT	399.54	63.24	25.41	0.62	3.16
PETI-330 / IM7 5HS	288	385.97	61.09	25.20	0.51	4.23
PETI-330 / T650 8HS	RT	448.04	70.91	28.26	0.96	8.70
PETI-330 / T650 8HS	288	460.61	72.90	27.51	0.45	8.56
PETI-9 / IM7 5HS	RT	375.98	59.51	25.38	0.45	1.92
PETI-9 / IM7 5HS	177	384.04	60.78	25.20	0.58	2.38
PETI-9 / T650 8HS	RT	447.82	70.88	27.63	1.05	3.90
PETI-9 / T650 8HS	177	451.00	71.38	25.94	1.06	3.14

*approximated from C-scan images post impact

Structural Sub-Component:
IM7/PETI-9 HT-VARTM Hat Stiffened Panel



3.6% Void Volume Fraction/
54% Fiber Volume Fraction

Conclusions

- LaRC developed polyimide resins with appropriate viscosity/ processing windows have been developed for HT-VARTM and HT-RTM
- With suitable hardware, infusion temperature, and cure cycle adjustments, LaRC™ PETI-330 and PETI-9 can be successfully processed by HT-VARTM
- HT-VARTM void contents of 1.3 to 4% are the lowest reported
- A database of compressive, OHC and CAI properties was developed on two resins and three types of carbon fabrics
- HT-VARTM composites demonstrated 67-100% retention of properties at elevated temperature (177 °C for PETI-9 and 288 °C for PETI-330) as well as after aging for 1000 h at those same temperatures
- Fabrication of a prototype part demonstrated that HT-VARTM has the potential to be a viable out-of-autoclave process for these polyimide systems

Acknowledgments

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