Selection of High Temperature Organic Materials for Future Stirling Convertors

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Collaborators and Contributors

This paper presents an overview of extensive work started at 2012 which involved numerous dedicated collaborators and contributors:

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- Mike Gorbulja, KOL-CAP Manuf.; Kerry Arnold, Cliff Fralick et al., Sunpower, Inc.; Mike Booker, CTL Inc.; Steve Hassman, Long-Lok Corporation.
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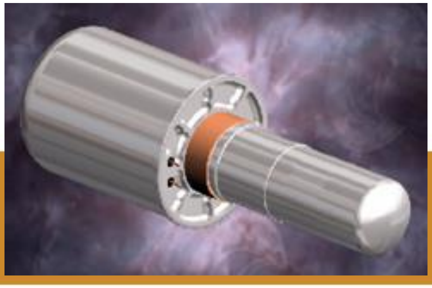
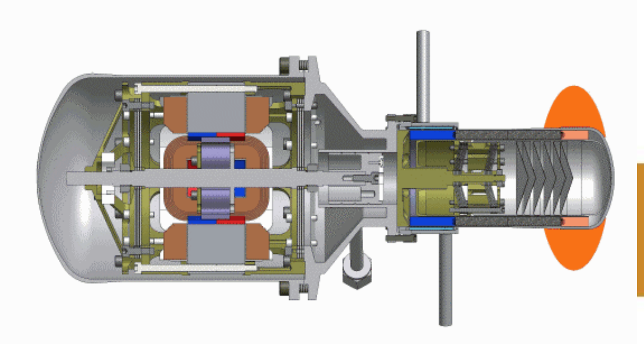




Backgrounds

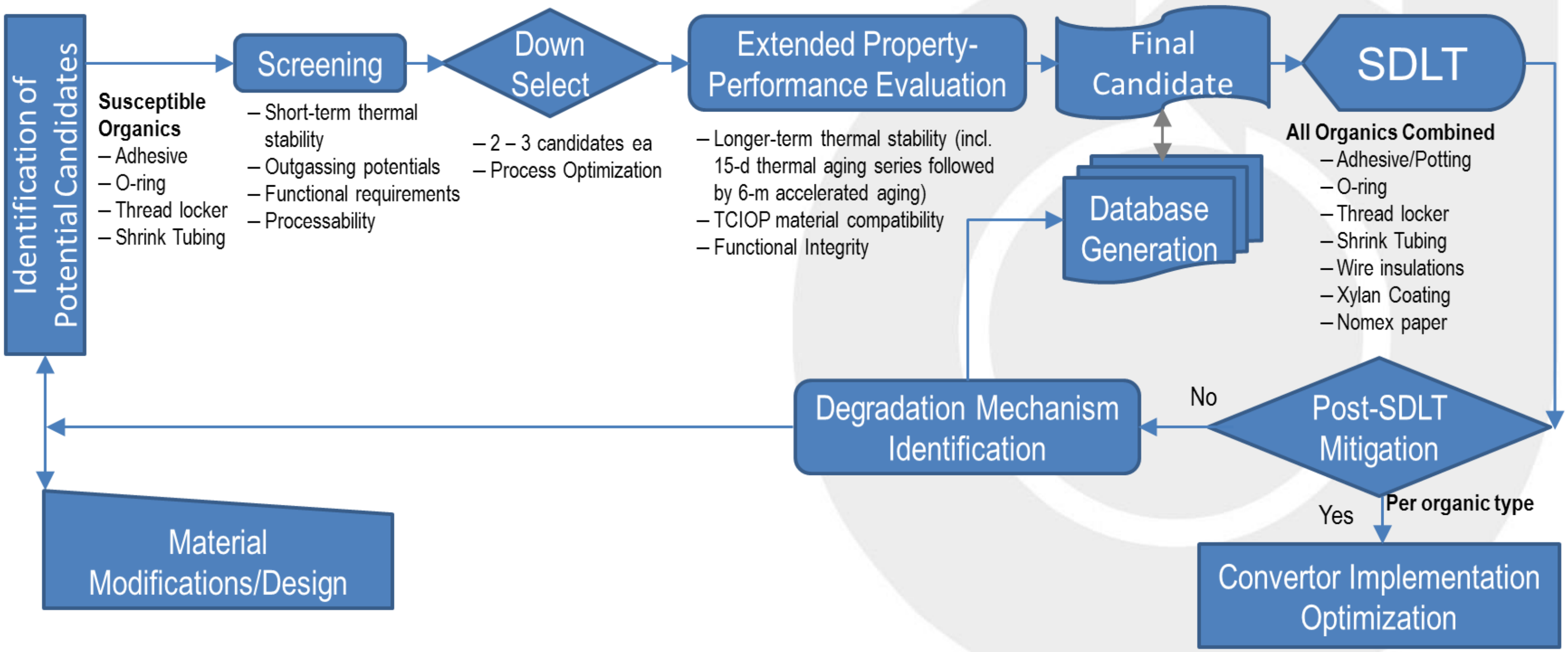
- Organics in Stirling convertors for design flexibility or unique properties and functionalities, such as bonding, potting, sealing, thread locking, insulation, and lubrication: a total of ~ 22 gram
- SOA Convertor operating environment
  - Pressurized with dry inert gas and hermetically sealed, but potential outgasses from organics or residual contaminants
  - Elevated temperatures, ~90 – 120 ºC, and radiation exposures
  - Long mission cycles up to 17 years, such as deep space explorations
- In future convertors, much higher operating temperature, ~ 165 – 200 ºC, for improved efficiency & performance

→ *HT organics should be screened & evaluated!*

Objectives

- Screen, evaluate, and validate high temperature organic materials for future Stirling convertor applications, more specifically in terms of
  - Performance, durability, and reliability
  - Material compatibility
- Identify application limits of the candidate materials, and develop their performance and lifetime predictions

Overall Program Plan



- The initial efforts focused on the most susceptible organics → the plan completed up to the "Final Candidate" step as of today

Materials and Processes

Candidate materials investigated, all commercially available

Material Class	Brand	Maker	Max. T °C	Install T °C	Product properties
Adhesive/ Potting Candidadates					
Epoxy	Hysol EA9394 C-2	Henkel	232	93/115	Two part epoxy paste filled with aluminum particle; long pot-life (8 hours at 25 °C)
Cyanate ester	FM2555	Cytec	232	177/227	Supported film adhesive on structural carrier; 0.06 psf film
	RS-4A	YLA		177	Unsupported film adhesive; 0.03 psf film
Epoxy	L-313U	JD Lincoln	204	135/213	Unsupported film adhesive; 0.05 psf film
Epoxy	AF191K AF191U	3M	204	177/204	Supported (0.08 psf) or unsupported (0.055 psf) film adhesive
Epoxy	AF131-2	3M	232	177	Flexible scrim supported film adhesive, 0.075 psf
Thread Locker Candidates					
Dimethacrylate ester	Loctite 266	Henkel	232	25 – 40	One part, surface insensitive, high strength, high temperature anaerobic material
	Loctite 294	Henkel	204	25 – 40	One part, low viscosity, high temperature anaerobic locking and sealing material
Epoxy	Resbond 507TS	Cotronics	260	25	Two parts epoxy-based thread locker & sealant, filled with PTFE particle for lubricity
Ceramic	Resbond 907TS	Cotronics	1148	25/121	Water-based proprietary material, cured by moisture removal
PET	Poly-Lok Patch	Long-Lok Fasteners	204	25	Solidified plastic locker patched on fastener at predetermined locations with optimum amount

Material Class	Brand	Maker	Max. T °C	Install T °C	Product properties
Shrink Tubing Candidates					
Polyimide	208X	Dunstone	220–400	350	Shrink ratio > 1.12:1; highest temperature shrinkable film commercially available
PEEK	PEEK	ZEUS	260	330	Shrink ratio > 1.4:1; excellent abrasion resistance and radiation resistance
Teflon copolymer	PFA	ZEUS	260	340	Shrink ratio > 1.4:1; improved thermal stability and radiation resistance
ETFE	RT-555	Raychem	200	220	Shrink ratio > 2:1; extremely resistant to hydrocarbons, low outgassing
Silicone	SRFR	Raychem	200	175	Shrink ratio > 1.5:1; extremely flexible
O-ring Candidates					
Silicone	70SLR	Marco	200	n/a	Baseline material for current SOA convertors
	S1151	Marco	315	n/a	High temperature formulation
Perfluoro-elastomer/ Fluoro-carbon Rubber (FFKM)	Kalrez	DuPont	260	n/a	Excellent chemical and temperature resistance
	Markez Z1028	Marco	300	n/a	Black, excellent chemical compatibility and high temperature capabilities
	Markez Z1307	Marco	275	n/a	Translucent, semi-crystalline nano-filled; low out-gassing; high temp capabilities

Materials and Processes, Cont'd

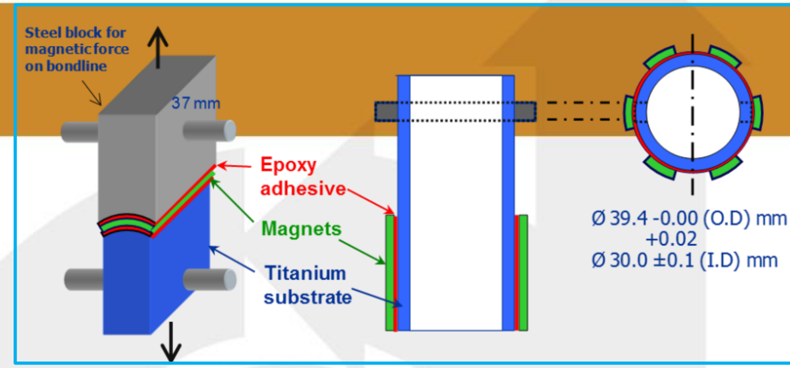
- Adhesive/potting candidates
  - Processed in a hot press or autoclave after conventional vacuum-bagging
  - Initial cure conditions per manufacturer's recommendations → optimized for final
  - Optimum mixing in a Thinky mixer for two part systems
  - Various sheet samples: thick (~ 1.5 mm) to mimic the potting; thin (~0.1 mm) or the thin sample but laminated between metal substrate to mimic bonding
- Thread locker candidates
  - Cure conditions optimized during initial screening evaluations
- Shrink tubing candidates
  - 3/16" OD – 1.12" (30 mm) long sections; shrunk snugly without metal core
- O-ring candidates
  - Nominal, 7/16" ID - 9/16" OD – 1/16" CS (Actual, 0.426" ID - 0.070" CS)

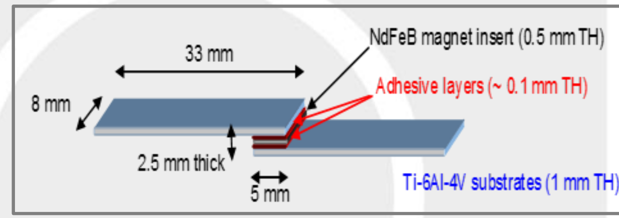
Experimental: Material Property Testing

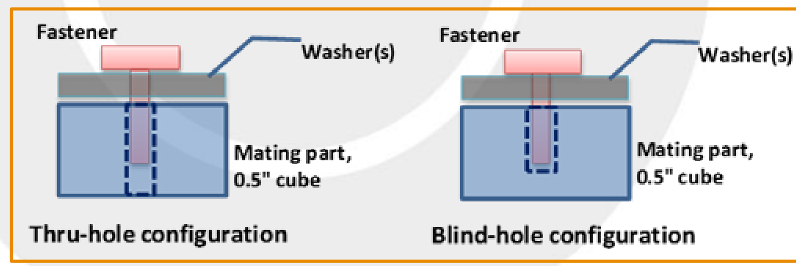
- Extensive and systematic material property characterizations (i) to compare candidates and (ii) to identify the degree of degradation and its mechanisms as a function of exposure conditions:
  - Physical properties, e.g., weight, dimensions, color, and surface microstructures
  - Thermal properties T_m, T_g, T_β, T_r, T_t, T_{end}, T_{exo}, ΔH, $\Delta Wt\%$, G’, G”, and % cure via mDSC, TGA, and DMA or TMA;
  - Other outgassing characteristics by isothermal TGA analysis, typically at 120, 150, or 200 ºC for 7 hours: initial wt loss, dwell wt loss, and wt loss rate at the last 100 minutes related to ASTM outgassing database
  - Molecular/chemical structural properties via FT-IR spectral analyses

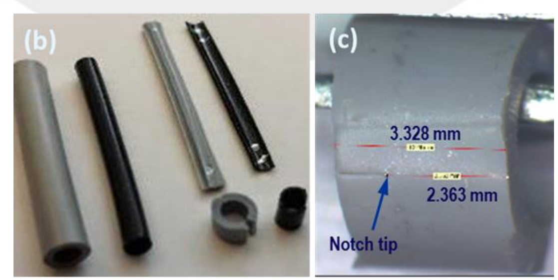
Material Property Testing, Cont'd

- Mechanical properties based on the functional requirements of the organics
  - ***Adhesive***: bonding integrity in shear and FWT mode using either component-level full-scale or subscale sandwich lap shear specimens for both static and fatigue loading modes,
  - ***Thread locker***: torque strengths in 3 – 4 representative joint types using the same materials, same dimensions, and configurations (esp. thru-hole vs. blind-hole) as the actual convertor components, based on the BS EN 15865 Standard,
  - ***Shrink tubing***: notched tensile properties, in both axial and radial directions
  - ***O-ring***: compression-set; hardness; tensile properties followed by the ASTM standards, D395, Method B; D2240, Shore A scale; D1414, Method B, respectively









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Experimental: Thermal Aging

- SOP for start-up & shut-down
- Inert gas environment, N_2 gas
  - Temperature & gas flow rate monitored and adjusted daily
- 15-day thermal aging up to 260 ºC
  - Two phases at 4 temperature ea.
- 6-month accelerated aging
  - Adhesive, shrink tubing, and o-ring candidates run together at 175, 200, and 225 ºC
  - Thread locker at 190 and 220 ºC

⇑ Blue M #5 or #6 or PC Oven for 175, 205, 220 & 260 °C Aging

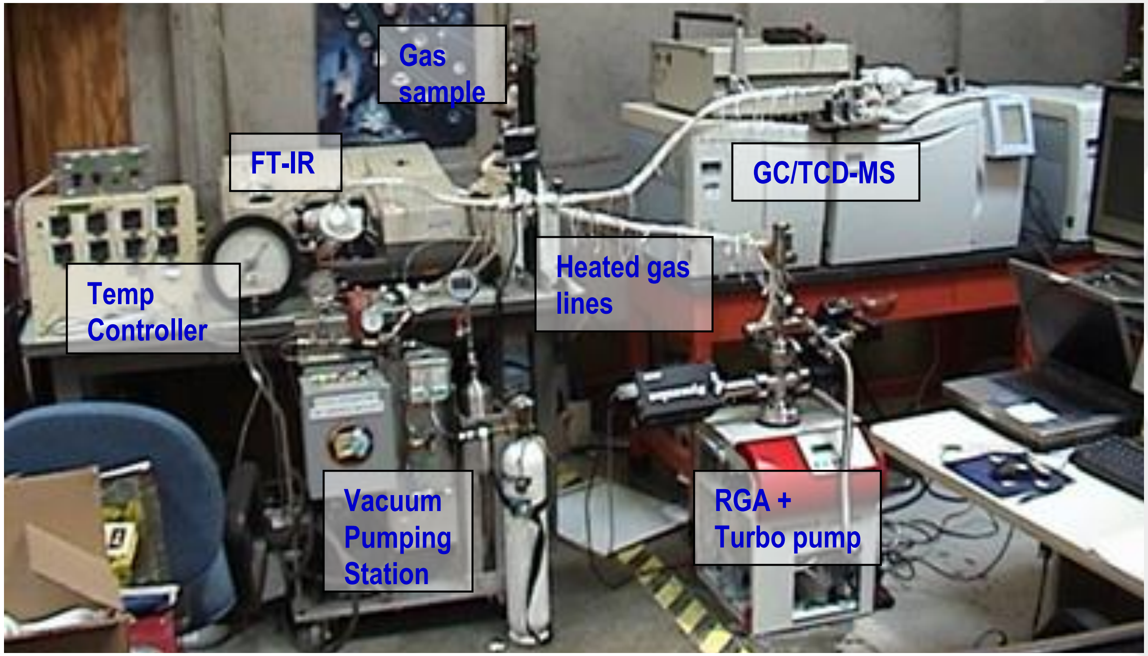
Lunaire Oven for 130°C Aging ⇒

⇐ Blue M N_2 Oven for 190°C Aging

Lunaire Gruenberg Oven for 160°C Aging ⇒

Experimental: TCIOP Testing

Integrated RGA-GC/TCD-MS-FTIR gas analysis system



- Systematic residual property characterizations of the TCIOP exposed samples → outgas-induced degradation and its mechanisms

<u>Standardized test procedure</u>:

1. loaded samples into PV, pulled vacuum
2. baked @ 90 ºC for 1 day under vacuum
3. charged with the pre-mixed gas, typical Stirling gas sample, to ~ 400 psi @ RT
4. leak-checked for 1 day
5. analyzed gas sample @ RT by all
6. heated to 100 ºC; dwelled 3 days
7. heated to 150 ºC; dwelled 2 days
8. heated to 200 ºC; dwelled 7 days

– heating rate @ 1 ºC/min
– during heating, outgas analysis only by FT-IR every 20 min
– during dwell, outgas analyses by all per day

Pre-mix gas: 107 ppm H_2, 1,060 ppm O_2, 3,081 ppm N_2, 312 ppm CO_2 in balance of He

Results & Discussions: Initial Screening and Down-selection

Overall ratings of adhesive/potting candidates

Properties \ Material type	L-313	RS-4A	FM2555	AF131-2	AF191K	EA9394C-2
Cure Condition	–	–	–	–	–	+
Processability/Applicability	0	–	–	0	0	+
Multi-purpose Application	+	–	–	–	–	+
Thermal Degradation Temperature/TGA	+	+	+	+	+	+
Weight loss/outgssing potential	–			+	0	0
Thermal Transisiton/mDSC	0	0	0	0	0	0
Shear Bond Strength	+	–	–	+	+	+
FWT Bond Strength	–			+		+
Final Selection				✓		✓

Note: 0, neutral or insignificant effect; +, positive performance; -, negative performance

- Superior thermal performance and stability for AF131-2
- Best multi-purpose system and large supportive database from the basic formulation, EA9394, for EA9394C-2

Overall ratings of thread locker candidates

Properties \ Material type	Loctite 266	Loctite 294	Resbond 507TS	Resbond 907TS
Cure Condition	+	+	+	+
Processability	0	0	0	0
FT-IR @ RT	0	0	0	0
Thermal Degradation Temperature/TGA	+	+	+	+
Weight loss/outgssing potential/iso-TGA	0	0	+	–
Thermal Transisiton/mDSC	0	0	0	0
Breakaway Torque	0	0	+	+
Max. Prevailing Torque	–	+	+	0
Final Selection		✓	✓	

Note: 0, neutral or insignificant effect; +, positive performance; -, negative performance

- Torque strength tested on M10 steel nuts & bolts at RT as a function of cure conditions
- Poly-Lok PET was also selected as an alternative because of its potential as a solid patch system

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Results & Discussions: Initial Screening and Down-selection

Overall ratings of shrink tubing candidates

Properties \ Material type		Viton (α)	PFA	SRFR	ETFE	PEEK	PI
Shrinking Temperature		+	+	+	+	–	–
Shrinking Ratio		+	–	+	+	–	–
FT-IR @ RT: on both OD and ID		0	0	0	0	0	0
Thermal Degradation Temperature/TGA		+	+	+	+	+	+
Weight loss/outgssing potential/iso-TGA		+	+	+	+	–	–
Thermal Transisiton/mDSC		0	0	0	0	0	0
Modulus-Drop Ratio at Temperature/DMA	Axial	–	–	0	0	+	+
	Radial	–	–	0	0	+	+
Notched Tensile strength:	Axial	–	0	0	0	+	+
Notched Tensile strength:	Radial	–	0	0	0	+	+
Final Selection				✓	✓		

- Shrinking process conditions optimized for each candidate
- Final candidates selected with less negative performance, thus need more thorough extended evaluations

Overall ratings of o-ring candidates

Properties \ O-ring type		70SLR	S1151	Kalrez	Z1028	Z1307
FT-IR		0	0	0	0	0
mDSC/DSC - Thermal transitions		0	0	0	0	0
TGA - Thermal degradation onset		+	+	+	+	+
TGA & Iso-TGA - Outgassing potential		–	–	+	+	+
DMA - Compression	Storage Modulus	0	+	+	+	–
Compression-set		0	0	0	+	+
Tensile properties:	Modulus	0	+	–	–	–
	Tensile strength	0	0	–	+	–
	Ultimate elongation	0	0	0	0	0
Max use Temp by Manufacturer		0	+	+	+	+
Final Selection			✓		✓	

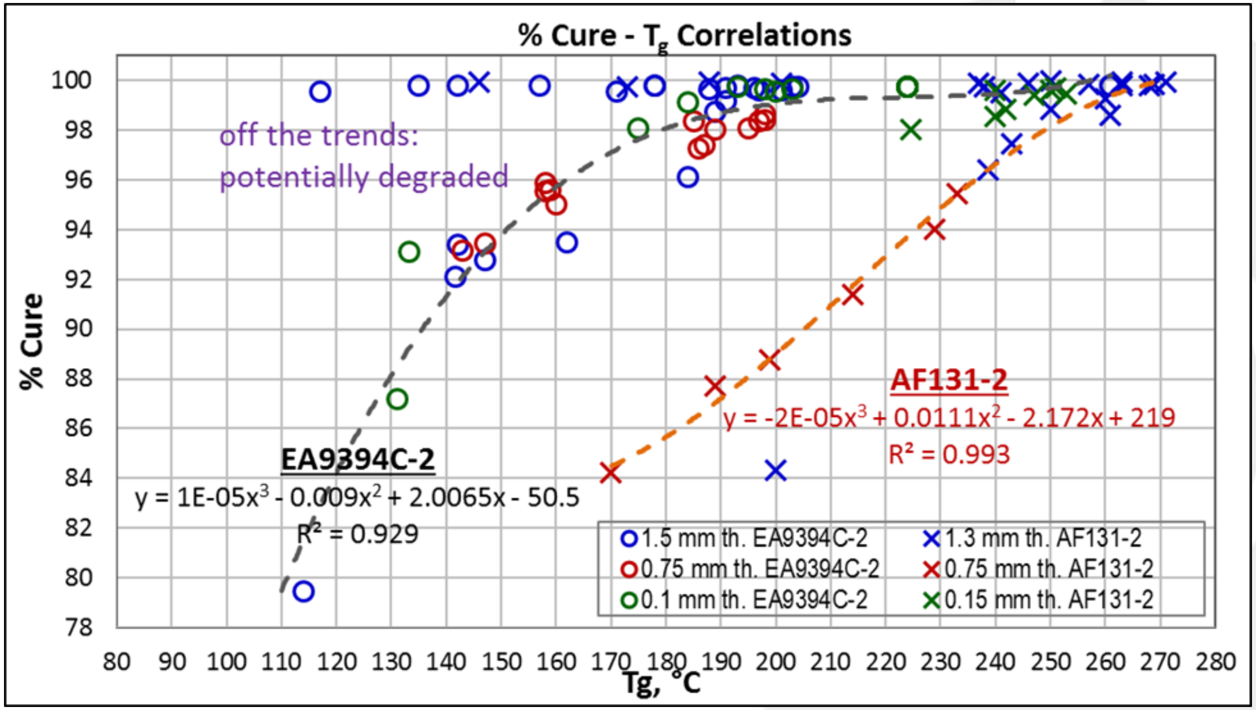
Extended Evaluations: Functional Performance

- Adhesive for magnet bonding identified as the most critical organic for the Stirling convertor due to its single point failure reliability assessment
- Extensive cure kinetics-% cure-property relations ascertained for optimizing cure conditions
  - investigated broad cure/postcure temperature-time conditions including the results from both 15-day thermal aging and 6-month accelerated thermal aging tests,
  - targeted the degree of cure higher than 99.5%
  - identified under-cured state or thermal degradation via. systematic property characterizations

  → The optimum conditions typically required higher cure temperatures or much longer cure time than the manufacturer's recommended conditions.

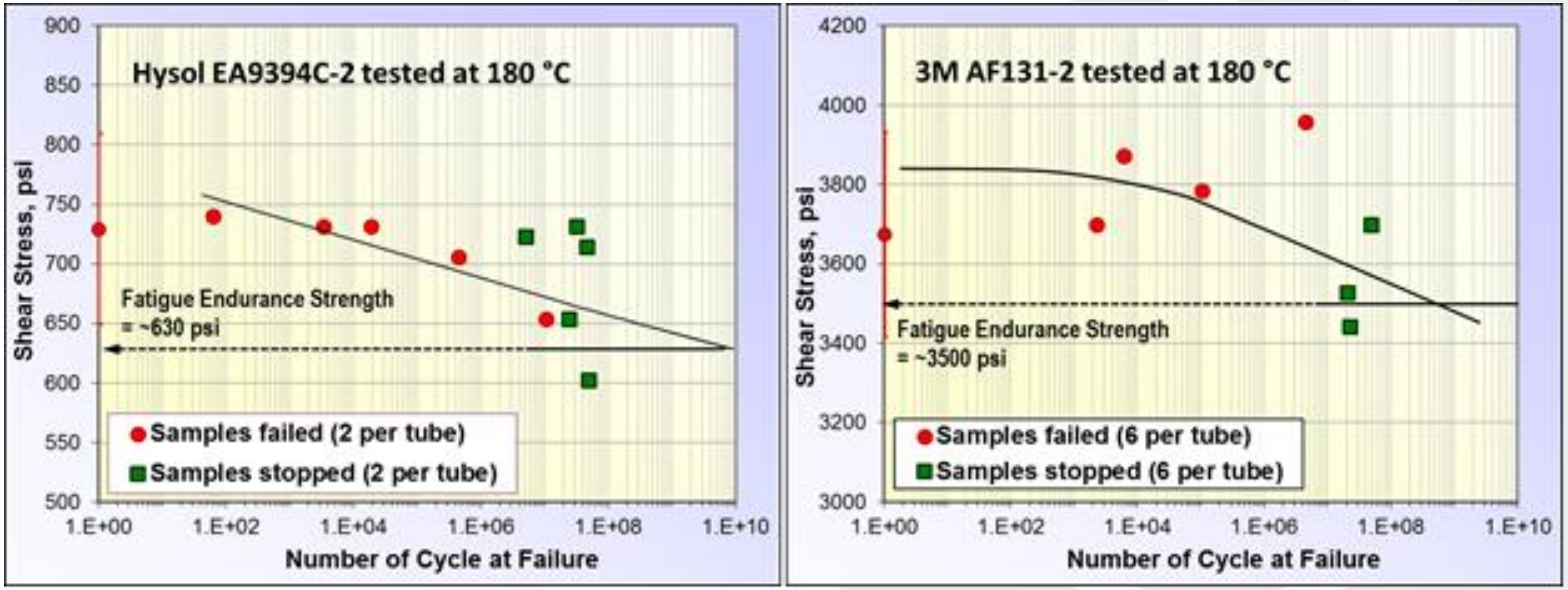
  → Increasing the postcure temperature to 190 – 205 ºC for up to 360 hours improved thermal stability of both candidates.

Extended Evaluations: Functional Performance



- ✓ Distinctive % cure-T_g correlation regardless of sample thickness → used for performance predictions
- ✓ The highest T_g achieved was fairly close for both adhesive candidates, 260 ºC vs. 270 ºC, but non-linear relationship for EA9394C-2 vs. linear relationship for AF131-2
- ✓ The initial cure conditions determined by the manufacturer's recommendations were acceptable

Extended Evaluations: Functional Performance



- ✓ Bonding performance via fatigue testing of full-scale component size coupons @ 180 ºC
- ✓ AF131-2 outperformed EA9394C-2, but their fatigue strengths were much higher than the theoretical strength needed
- ✓ Fatigue performance of the EA9394C-2 at 180 ºC was comparable to that of the regular EA9394 at 115 ºC, i.e., improved thermal stability

Extended Evaluations: Long-term Thermal Stability

Long-term performance and thermal stability

- 15-day thermal aging tests as a function of temperature up to 260 ºC

  Specific objectives:

  - to assess more meaningful but practical short-term thermal stability of down-selected candidates and
  - to determine the aging mechanism-based maximum temperatures for the 6-month accelerated thermal aging tests

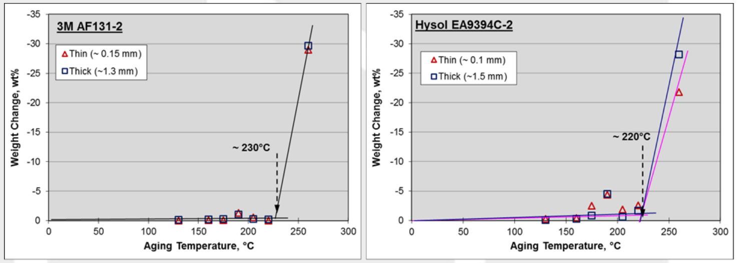
- 6-month accelerated thermal aging tests at 2 – 3 temperatures

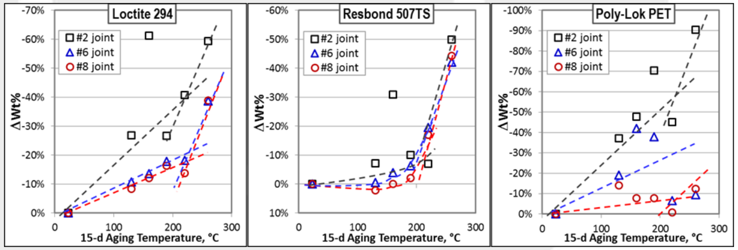
  Specific objectives:

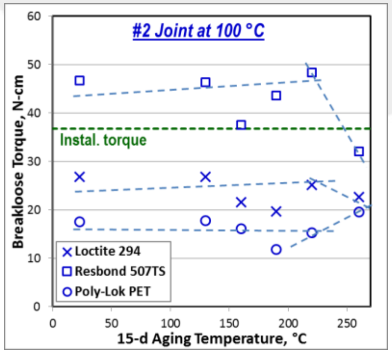
  - to assess longer-term thermal stability and integrity for life predictions
  - to determine the application limits of the down-selected candidates via extended and systematic property-performance characterizations, and subsequently select the final candidate

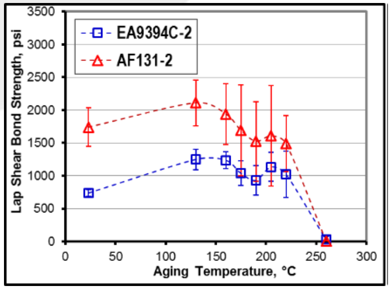
Extended Evaluations: Long-term Thermal Stability

- From the systematic physical-thermal-chemical-mechanical property characterizations as a function of 15-day aging temperature,
  - Good short-term thermal stability up to:
    - 220 – 230 ºC for both adhesives
    - 220 ºC for all TL candidates
  - and a distinctive change in aging mechanism
- T_{max} for the accelerated aging tests
  - 175, 200, and 225 ºC for adhesives, also for shrink tubing and o-ring candidates*
  - 190 and 220 ºC for TL candidates





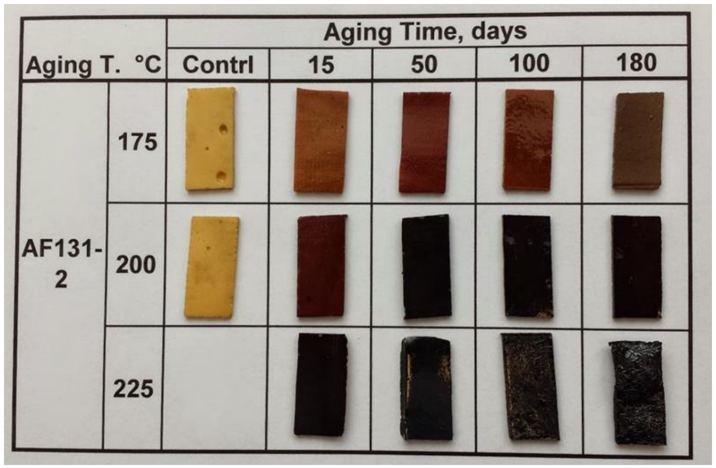


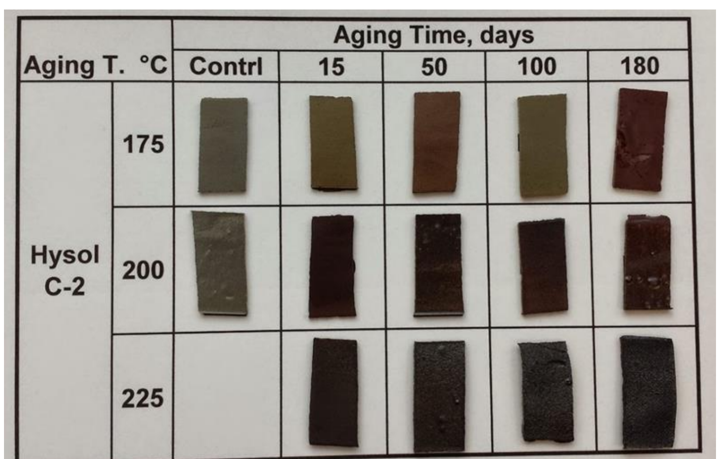


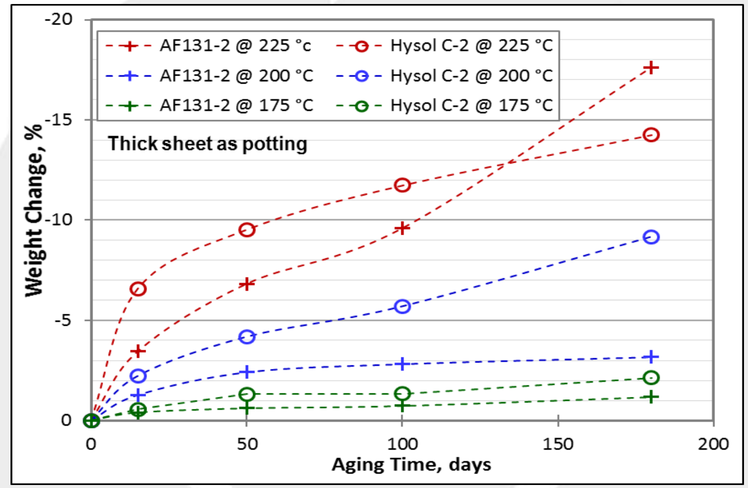
* Not tested due to logistics issues, but based on the initial screening test results, manufacturer's technical data, and max use temperature ratings

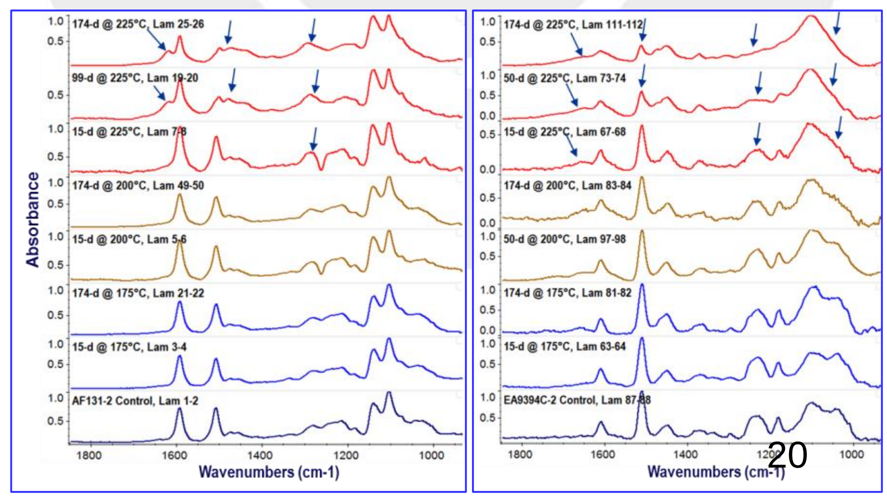
Extended Evaluations: Long-term Thermal Stability

6-m accelerated aging of *adhesives/potting* candidates*:* physical, chemical properties



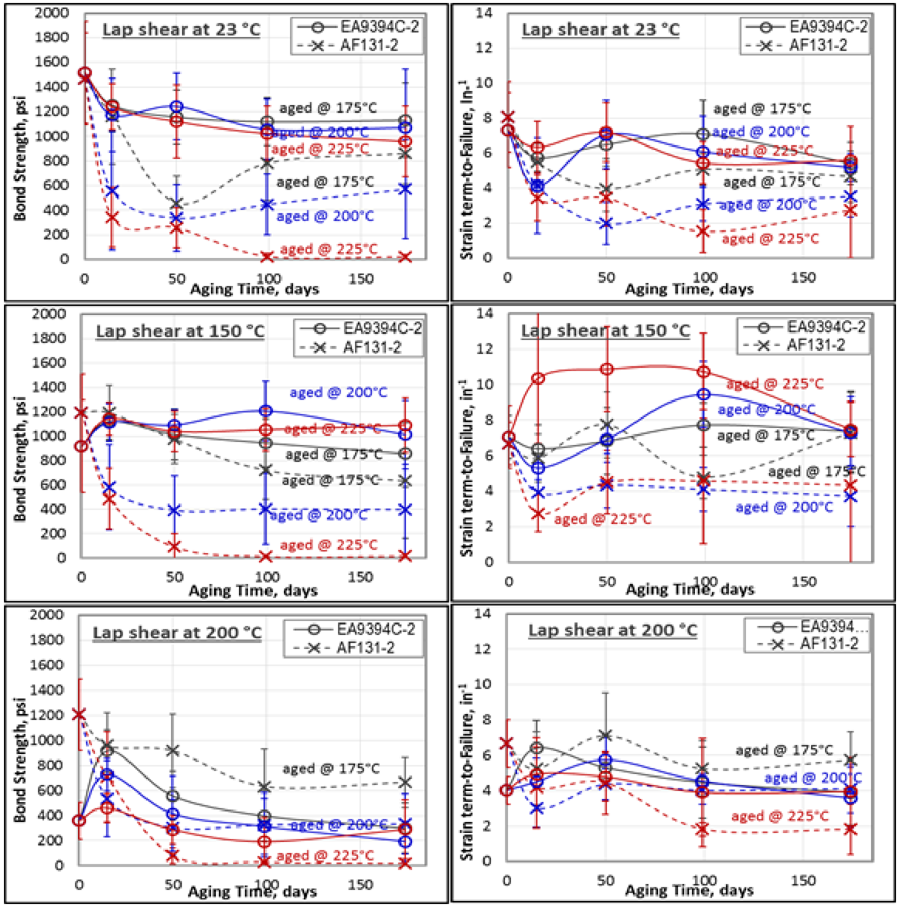


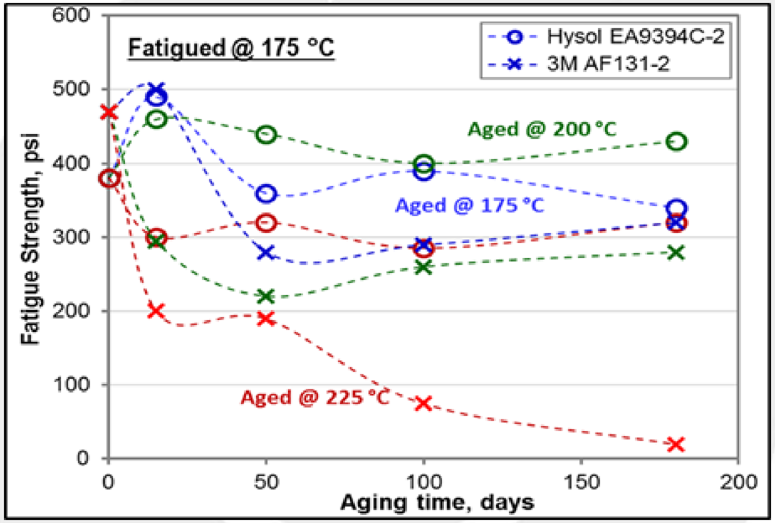




Extended Evaluations: Long-term Thermal Stability

6-m accelerated aging of *adhesives/potting* candidates: mechanical properties

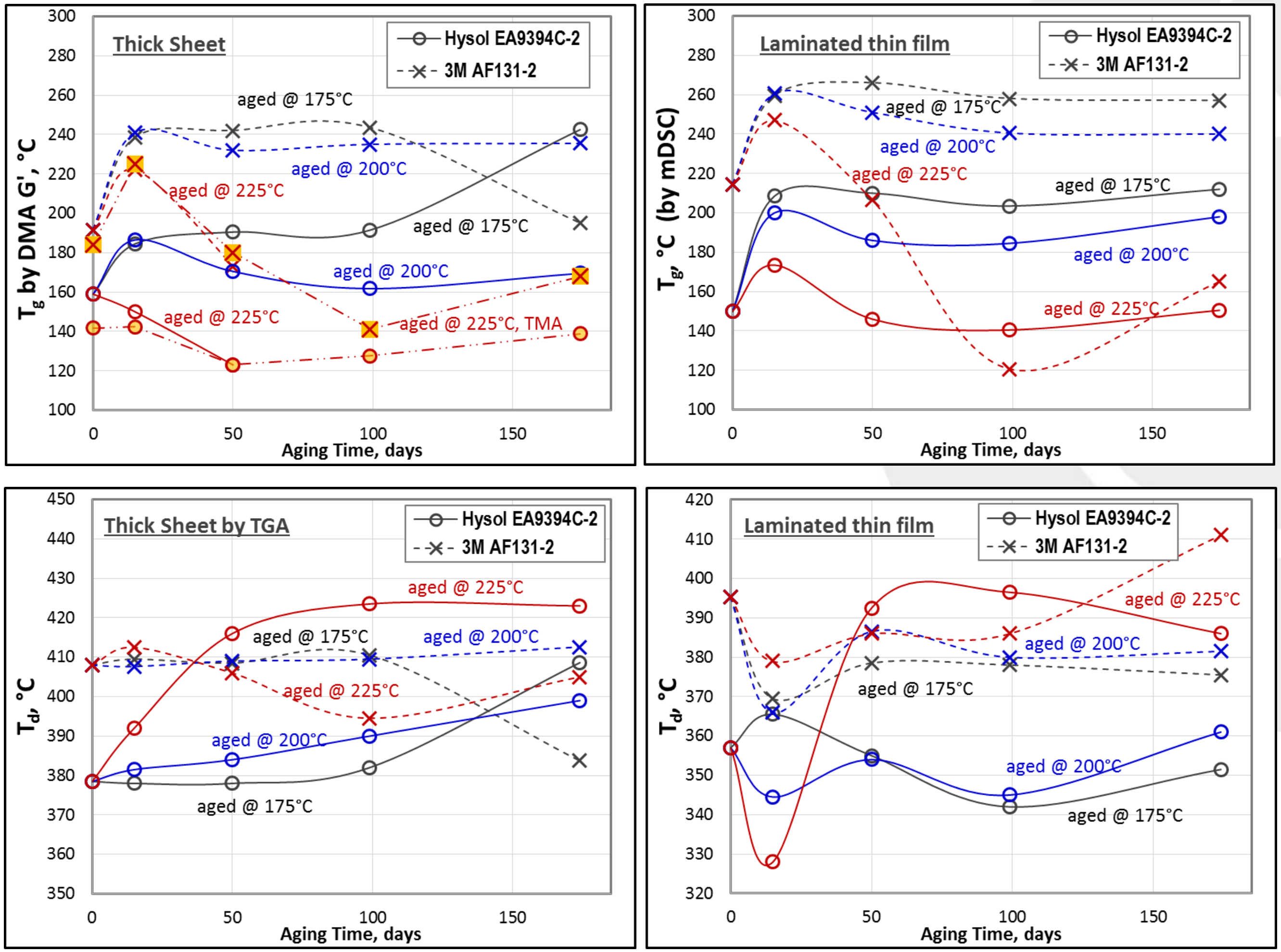




- Significant property degradation in AF131-2 when aged above 200 ºC
- Better thermal stability from EA9394C-2 regardless of aging or test conditions
- But, when aged below 200 ºC, bond strengths of both candidates were considerably higher than the required strength for the magnet bonding.

Extended Evaluations: Long-term Thermal Stability

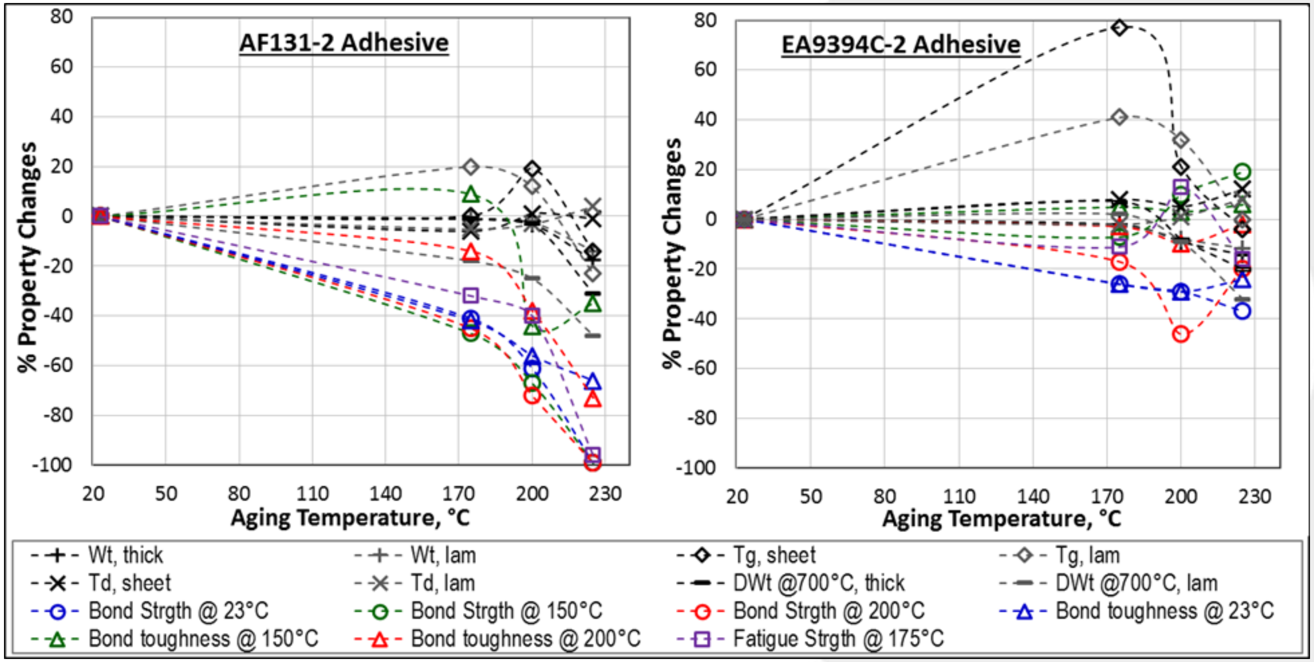
6-m accelerated aging of *adhesives/potting* candidates*:* thermal properties



- Most visible property degradation occurred when aged at 225 ºC in both candidates.
- The changes were greater for the AF131-2 in most cases.

Extended Evaluations: Long-term Thermal Stability

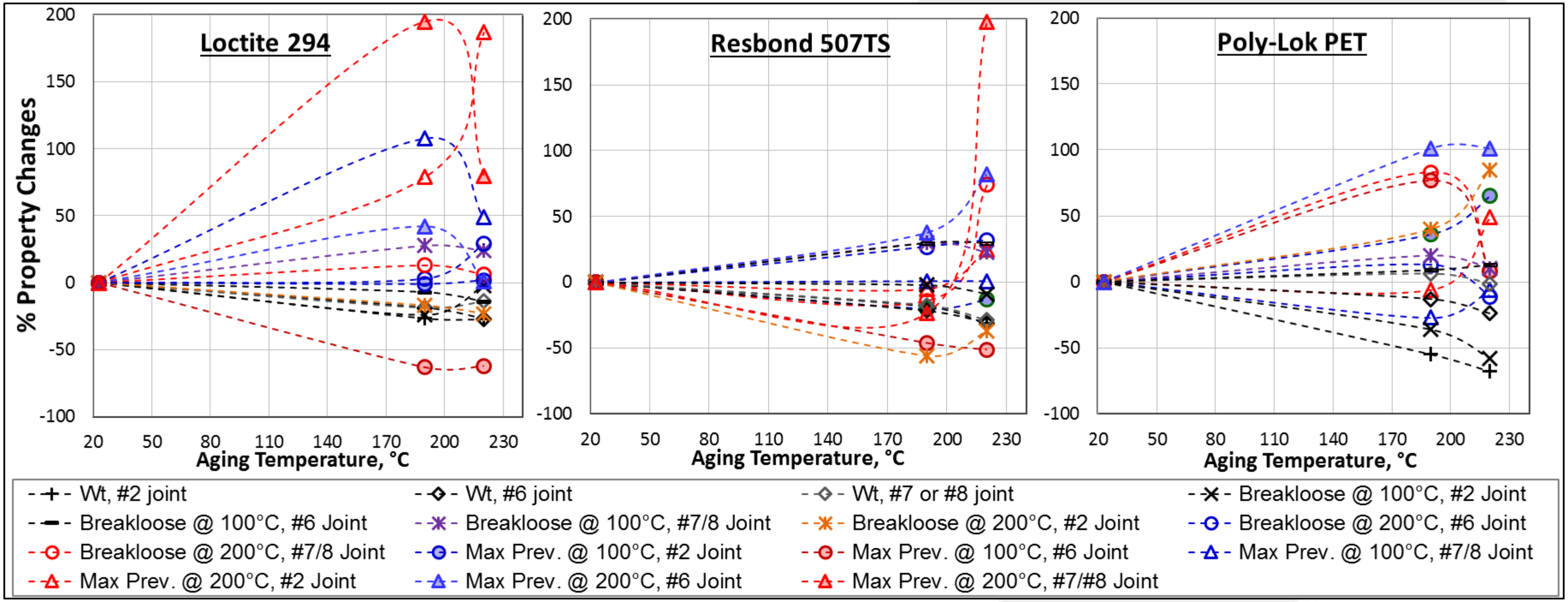
6-m accelerated aging of *adhesives/potting* candidates: overall property changes



- In most cases, changes in properties leveled-off or stabilized after 180 day regardless of aging T.
- AF131-2 suffered greater reductions in most properties than EA9394C-2, with sharper, more distinctive transitions at 175 – 200 ºC → Better thermal stability from EA9394C-2.
- Larger changes indicate greater effects of the thermal aging, esp., negative changes.

Extended Evaluations: Long-term Thermal Stability

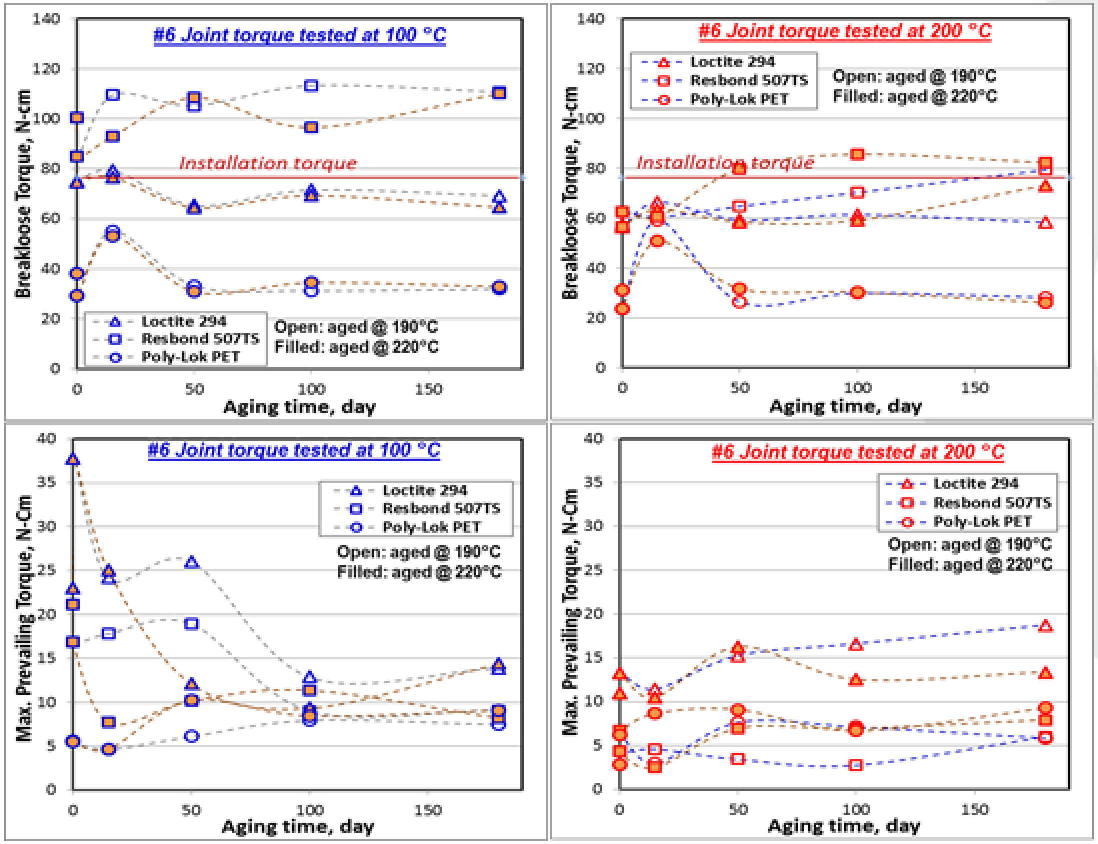
6-m accelerated aging of *TL* candidates: overall property changes



- More positive changes in Loctite 294 and Poly-Lok PET, but better thermal stability from Resbond 507TS

Extended Evaluations: Long-term Thermal Stability

6-m accelerated aging of *TL* candidates: mechanical properties



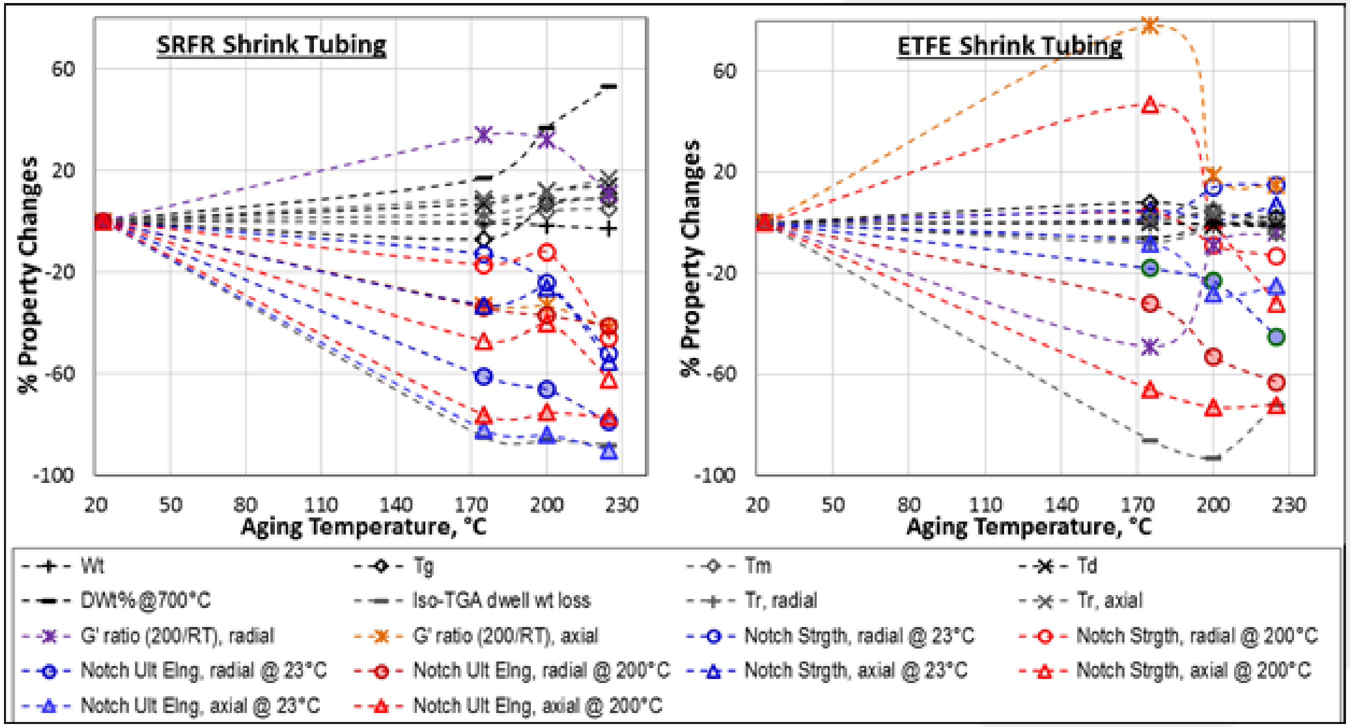
- Resbond 507TS outperformed other candidates regardless of aging condition, joint type, or test temperature.

  → the only candidate generating 100 ºC breakloose torques greater than the installation torques in all three joint types

- At 200 ºC, the Resbond 507TS suffered the most loss of breakloose torque even though its strength was still higher than others.

Extended Evaluations: Long-term Thermal Stability

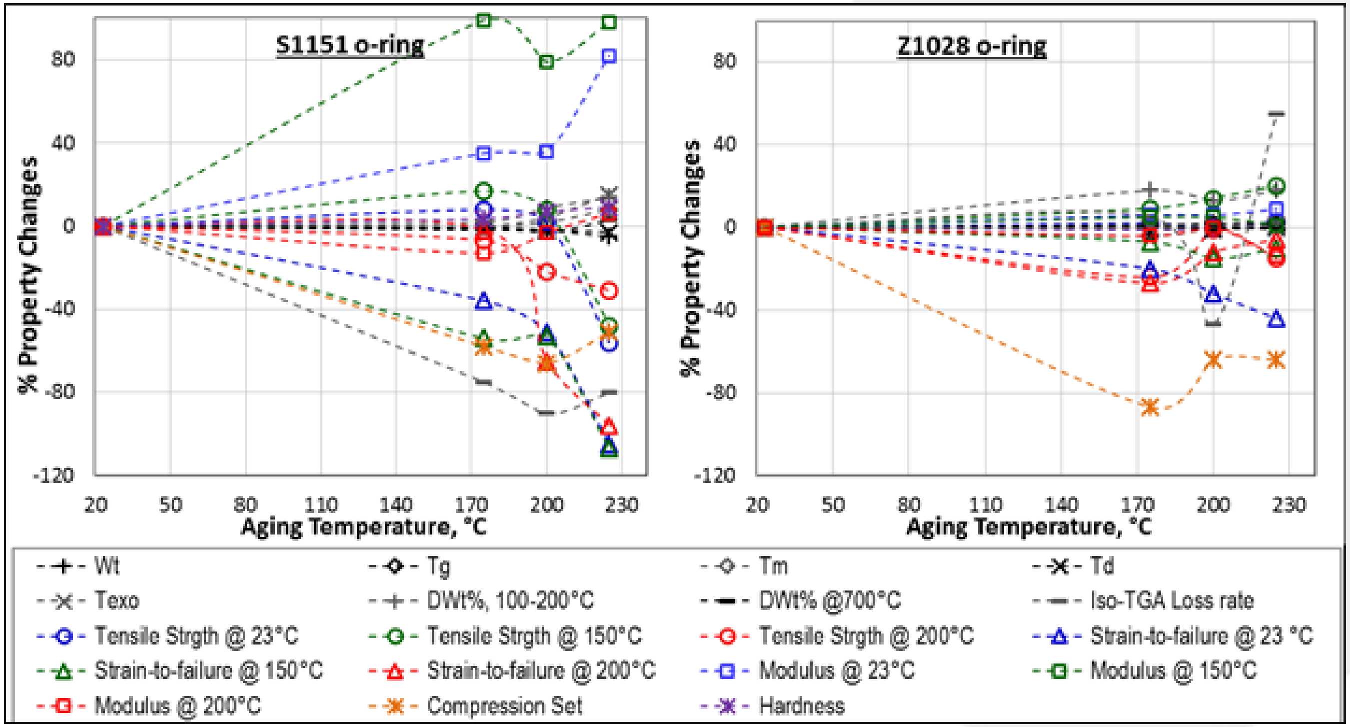
6-m accelerated aging of *shrink tubing* candidates: overall property changes



- ETFE performed significantly better in most mechanical properties and more thermally stable than SRFR regardless of sample direction (either axial or radial) and test temperature.

Extended Evaluations: Long-term Thermal Stability

6-m accelerated aging of *o-ring* candidates: overall property changes



- Overall, Z1028 was more thermally stable than S1151.
- Z1028 outperformed S1151 in most mechanical properties.
- Signs of thermal degradation in S1151 when aged above 200 ºC

Extended Evaluations: TCIOP Material Compatibility

Temperature-alone Combined In-situ Outgassing (TCIO) Test with Pre-mix gas

Specific objectives:

- to determine outgassing behavior of the down-selected candidates under the typical Stirling convertor pre-mix gas environment and its effects on their properties and performance
- to assess material compatibility for the Stirling application.

→ Material compatibility assessment made with two step process: (i) in-situ outgas analyses and (ii) residual property characterizations

Extended Evaluations: TCIOP Material Compatibility

Outgas Analysis Summary

Pre-mixed gas: 107 ppm H_2, 1,060 ppm O_2, 3,081 ppm N_2, 312 ppm CO_2, and the balance of He

Exposure temperature, °C		100	150	200
Exposure time, day		1 3	1 2	1 7
Adhesive /potting	EA9394C-2		CH-O-H↑	H_2↓; O_2↓; CH_4↑; H_2O↑; CO↑; CO_2↑
	AF131-2	no significant changes		
Thread Locker	Loctite 294			O_2↓; H_2O↑; CO↑; CO_2↑; -CH3/-CH_2-↑
	Resbond 507TS			O_2↓; H_2O↑; CO↑; CO_2↑; -CH_3/-CH_2-↑
Shrink Tubing	ETFE			CO↑; -CH_3/-CH_2-↑; C-F↑
	SRFR			O_2↓; CH_4↑; H_2O↑; CO_2↑; -CH_3/-CH_2-↑; Silicone vapor↑
O-ring	S1151			CO↑; -CH_3/-CH_2-↑; Silicone vapor↑
	Z1028	no significant changes		

* Outgassing from trapped volatiles vs. chemical reaction by-products vs. thermal degradation

Extended Evaluations: TCIOP Material Compatibility

Residual Property Characterizations Summary

	Properties*	Physical	Chemical	Thermal	Mechanical
Adhesive/ potting	EA9394C-2	ΔWt%↑	-	T_g↑; % cure↑; G'↑; T_d↑	Bond strength↓
	AF131-2	ΔWt%↓	-	T_g↑; % cure↑; G'↑; T_d↓	Bond strength↑
Thread Locker	Loctite 294	ΔWt%, joint #8↑	-	n/a	Torque strength↑
	Resbond 507	ΔWt%, joint #8↑	-	n/a	Torque strength↑
Shrink Tubing	ETFE	n/a	-	T_d↑	Notch strength↑
	SRFR	n/a	Δ↑, oxidation, side-chain	T_m↓; T_d↓; T_t↑	Notch strength↓
O-ring	S1151	n/a	Δ↑, oxidation, side-chain	T_{exo}↓; T_d↓; T_t↑	C_B↓; E_Y↑; σ_f↓; ε_f↓
	Z1028	n/a	-	T_{exo}↓	C_B↓; ε_f↓

*** TCIOP exposed against Temperature-only exposed under inert gas environment**

Summary and Conclusions

- Multi-step evaluation process was successfully performed to screen and down-select the best HT candidates for various organic materials for future Stirling convertor application.
- As a part of the evaluation, processing and installation conditions of the candidates have been optimized for their applications.
- The application limits of all material candidates were also identified based off the extensive property and performance data.
- The highest service temperature of the final candidates shall be further validated by the synergistic durability life testing (SDLT)

Summary and Conclusions, Cont'd

Organic Type	Down-selected Candidates	Application limit	Strength	Final Selection
Adhesive /potting	EA9394C-2	~ 225 ºC	Thermal stability	√
	AF131-2	180 – 200 ºC	Material compatibility	
Thread Locker	Loctite 294	~ 225 ºC	Thermal stability	
	Resbond 507TS	~ 200 ºC	Locking performance	√
	Poly-Lok PET	~ 225 ºC	Thermal stability	
Shrink Tubing	ETFE	~ 200 ºC	Thermal stability, material compatibility	√
	SRFR	~ 200 ºC		
O-ring	S1151	< 200 ºC		
	Z1028	~ 225 ºC	Thermal stability, material compatibility	√

Future Work Plan

- Selection of the best candidates thus far was primarily based on the extended thermal aging experiments performed under an inert gas environment and a short-term TCIOP test under a typical Stirling convertor gas environment.
- As per the overall program plan, the final candidates shall be further evaluated and validated via the synergistic durability life tests (SDLT) after combining all convertor organic materials in a simulated Stirling service environment. The tests will consist of radiation exposures (gamma and neutron) and subsequent thermal aging up to 3 years at three temperatures tbd. Three - four aging intervals, also tbd, are planned for outgas analyses and the extensive residual property characterizations.
- Once they are validated, the final process and installation optimizations, and implementation optimizations will be also followed.

Thank You for your attention!

Any Questions?

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