Evaluation and Validation of Organic Materials for Advanced Stirling Convertors (ASCs): Overview

Euy-Sik Eugene Shin[1]

Ohio Aerospace Institute, NASA Glenn Research Center, 21000 Brookpark Rd., MS 49-1, Cleveland, OH 44135de

Various organic materials are used as essential parts in Stirling Convertors for their unique properties and functionalities such as bonding, potting, sealing, thread locking, insulation, and lubrication. More efficient Advanced Stirling Convertors (ASC) are being developed for future space applications especially with a long mission cycle, sometimes up to 17 years, such as deep space exploration or lunar surface power or Mars rovers, and others. Thus, performance, durability, and reliability of those organics should be critically evaluated in every possible material-process-fabrication-service environment relations based on their mission specifications. In general, thermal stability, radiation hardness, outgassing, and material compatibility of the selected organics have been systematically evaluated while their process and fabrication conditions and procedures were being optimized. Service environment-simulated long term aging tests up to 4 years were performed as a function of temperature for durability assessment of the most critical organic material systems.

Nomenclature

ASC	=	advanced Stirling convertor
C_B	=	o-ring compression-set property
E_Y	=	Young's modulus
ΔH	=	enthalpy of transition
DMA	=	dynamic mechanical analysis
ε_t	=	tensile strain-to-failure
E' or G'	=	tensile or shear storage modulus from DMA
$FT\text{-}IR$	=	fourier transform- infrared spectroscopy
GC	=	gas chromatography
H_v	=	Vickers Hardness number
LLC	=	liquid locking compound
$mDSC$	=	modulated differential scanning calorimetry
MS	=	mass spectroscopy
OM	=	optical microscope
PV	=	pressure vessel
RGA	=	residual gas analysis
σ_t	=	tensile strength
$SARTA$	=	Stirling alternator radiation test article
$SDLT$	=	synergistic durability life testing
SEM	=	scanning electron microscope
T_β	=	sub T_g transition temperature
TCD	=	thermal conductivity detector
$TCIOP$	=	temperature-alone combined in-situ outgassing test with pre-mix ASC outgas
T_d	=	thermal degradation on-set temperature
T_e	=	endothermic peak temperature
T_g	=	glass transition temperature
TGA	=	thermo-Gravimetric Analysis
T_m	=	melting temperature

---

[1] Principal Scientist, Research Team Manager-Materials, Ohio Aerospace Institute (OAI).

American Institute of Aeronautics and Astronautics

T_r =   relaxation temperature
T_t =   transition temperature

I. Introduction

SINCE the ASC was identified as a potential candidate for various space applications because of its high radioisotope fuel efficiency in early 2000[1-3] , and subsequently advanced to a flight hardware development under the joint sponsorship of the Department of Energy (DOE) and NASA involving technical collaborations among Lockheed Martin Corporation of Valley Forge, PA, NASA Glenn Research Center (GRC) of Cleveland, OH, and Sunpower, Inc of Athens (recently merged to AMETEK), reliability and durability of every components and materials used in the convertor have been extensively and systematically evaluated and validated. Even though the typical ASC service environment was considered as benign, e.g., filled with dry and inert gas then hermetically sealed, because of its long-term operation at elevated temperatures also involving various radiation exposures, those organics used in the ASC have to be thoroughly evaluated for the final qualification.

Due to their inherent susceptibility to temperature and radiation as well as less predictable time-dependency on their properties and performance, the evaluations on the organic materials focused on thermal stability, durability, radiation hardness, outgassing behavior, and synergistic effects of various combined in-service conditions. Typically, thermal stability and durability of the organics was assessed by accelerated thermal aging experiments at a few elevated temperatures in conjunction with longer-term life testing. The rate of aging processes was normally accelerated by temperature, thus temperature was often used as an accelerator for the accelerated aging test in predicting longer term thermal stability of the organics. However, it could be only valid when the degradation mechanisms were not altered within the test temperature range. Thus the maximum aging temperature was determined with rigorous thermal exposure analyses involving series of short-term (10 to15 days) isothermal aging tests in dry Nitrogen environment as a function of temperature. Extensive and systematic residual material property characterizations of the aged or other simulation exposed samples were conducted based on their functional and in-service requirements in order to quantify the aging behavior, structural changes, or degradation, if any. Typical material properties and performances monitored were i) physical properties, e.g., weight, dimensions, and surface microstructures via OM and SEM; ii) thermal properties such as T_β, T_g, T_d, T_m, T_r, ΔH, $\Delta Wt\%$, G' or E', and %cure via mDSC, TGA, and DMA or TMA; iii) chemical properties or molecular network structure via FT-IR spectral analyses, and iv) mechanical properties including C_B, E_Y, σ_t, ε_t, H_v, and bond strength and toughness whenever applicable.

II. Materials and Processes

Organics in a typical Stirling convertor, primarily in the linear alternator, include potting compounds, adhesives, coil backing paper, thread locker, gasket seal o-ring, bearing surface coatings, coil wire insulations/coating, and wire connector insulations, and shrink tubing. Due to their export control and proprietary nature, all the organic materials involved in this study were only identified by their generic material type based on functionalities not by their specific brand name or locations. The organic materials tested in this paper were either purchased as final form, e.g., o-ring, backing paper, or coil wire insulation, or processed to test specimen or coupons from the raw materials purchased. Fabrication of test specimens and coupons of most organics followed the standardized conditions and procedures including pre-installation bake-out conditions implemented in fabrication of the actual parts or components which were based on either manufacturer's/supplier's recommendations or further optimizations developed and approved by the collaboration working groups. For the same reason, the specifics of the fabrication conditions and procedure won't be discussed in this paper. Other details including experimental approaches are available elsewhere[4-20].

III. Results and Discussions

A. Aging Behavior of Epoxy Adhesive

Since the epoxy adhesive used for both bonding and potting was identified as one of the critical organics in the ASC based on the overall system reliability assessment, most extensive and systematic evaluations were performed including mechanical bonding integrity in both static and dynamic fatigue mode, thermal stability and durability via thermally accelerated aging tests and subsequently longer-term in-service aging test up to 4 years. In order to maximize their properties and performances, its process conditions and procedures including mixing, cure, postcure bake-out, and application were optimized. While the bonding integrity evaluation and the optimizations of process conditions and procedures were presented earlier elsewhere[4], the results of various aging experiments for thermal

stability and durability are summarized in this paper. Long-term in-service aging tests up to 4 years were performed at two temperatures, 125 °C and 90 °C, which were selected as an upper limit and a normal median of the alternator operating condition, respectively[5]. The 15-day thermal aging tests ascertained that the adhesive was thermally stable and exhibited no changes in aging mechanism up to 180 °C. Thus, the 6-month accelerated aging tests were then performed at 180 °C and also at 150 °C as a bridging point to the long-term life testing[6]. Both aging tests were conducted under an inert gas environment to simulate the original ASC service conditions. Specific objectives of the tests were also to detect any sign of premature degradation or catastrophic failures and to establish mission service performance and lifetime prediction.

Key findings from those aging tests included:

- The overall weight loss of the epoxy was significant but strongly temperature- and thickness-dependent and the rate decreased significantly with the sealed specimens, Figure 1. The dependencies on temperature and thickness (or ratio of overall exposed surface area to volume) were consistent from both aging experiments, associated with diffusion-controlled processes as outgassing. Thus, the outgassing behavior of the ASC organics was extensively evaluated in a separate task, discussed in section E.
- Most noticeable change in thermal properties was only from T_g. The change was affected by specimen configuration, e.g., thickness or sealed state, but mostly by aging temperature, especially at the early stage due to combination of cure advancement and physical aging process. In most cases, the increases in T_g leveled off with increasing aging time and did not negatively impact its adhesive performance.
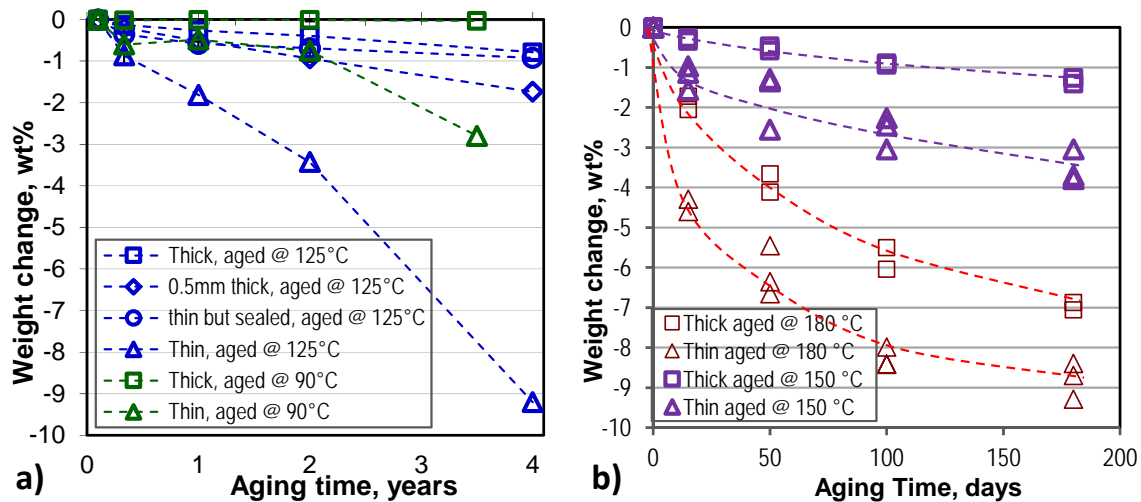

Figure 1. Weight loss of the ASC adhesive against aging time and temperature for various sample thicknesses (thin, ~0.15 mm; thick, ~ 1.5 mm): a) from the 4-year life testing, b) from the 6-month accelerated aging tests.

- No noticeable changes in FT-IR spectra, either peak locations or intensity, were observed, thus no changes in molecular network structures from either the 4-year life testing or 6-month accelerated aging test regardless of aging temperature or time.
- The overall bonding integrity of the epoxy adhesive was not compromised but rather improved with the thermal aging at all temperatures studied. Both the static lap shear bond strength and toughness in term of strain at failure tested at 23, 80, and 120 °C were stable and significantly higher than the required theoretical strength. Fatigue performance of the adhesive bond was also stable regardless of aging temperature and time. Figure 2 shows the steady fatigue strength or endurance limit of the bond at 115 °C in the lap shear mode regardless of aging conditions up to 180 °C.

Overall, the changes of most residual properties of the epoxy by the thermal aging exposures were either insignificant or positive except the weight changes showing considerably high weight losses, especially from thin sheet samples at higher temperatures. More systematic and quantitative outgassing analysis was warrantied for all ASC organic materials based on this study. In conclusion, the epoxy adhesive was thermally, structurally, and mechanically stable for the current ASC application. However, it should be also noted that all thermal aging tests were performed under a fully inert gas environment, i.e., the effects of outgasses from the ASC organics were not implicated in these evaluations.

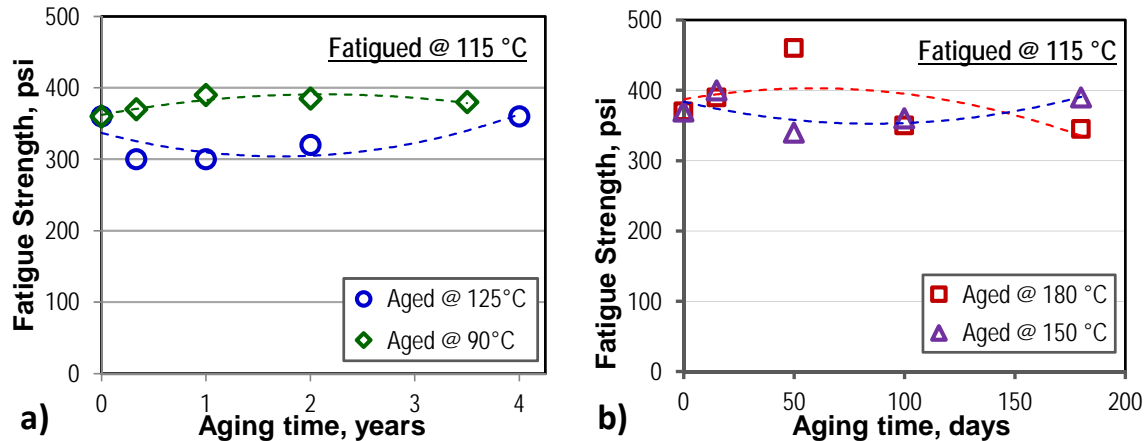American Institute of Aeronautics and Astronautics

Figure 2. Fatigue lapshear bond strength of the ASC adhesive against aging time at various temperatures: a) from the 4-year life testing and b) from the 6-month accelerated aging tests.

B. Aging Behavior of Other Susceptible ASC Organics

O-ring and shrink tubing materials used in current ASC were identified as thermally susceptible organics from a preliminary short-term thermal stability evaluations. Their longer-term thermal stability and reliability was assessed via thermally accelerated aging tests similar to the aforementioned procedure. In addition, a newly introduced ASC organic material, such as electrical insulation backing, feedthrough solder joint potting epoxy, and an alternative backup candidate for shrink tubing or wire insulation were also evaluated. For the o-ring and shrink tubing, 150 °C and 175 °C were selected for the accelerated aging tests based on the results of the short-term isothermal aging tests up to 225 °C under the inert gas environment[7]. On the other hand, the latter organics were aged at three temperatures, 130, 160, and 200 °C which were selected empirically based on the aging conditions used for other ASC organics previously and their thermal performance data from the manufacturer's technical datasheet[8]. From the extensive and systematic residual property characterizations of the organics as a function of aging temperature and time, the following key findings were drawn:

- The aging behavior of the o-ring was strongly size-dependent, e.g., small-size o-ring suffered significantly higher weight losses and thickness reduction than the large o-ring. This should be further evaluated for the ASC applications.
- Both o-ring and shrink tubing materials showed good thermal stability against the accelerated aging conditions, i.e., validated to use up to 175 °C or higher if used under an inert gas environment.
- The latter organic materials also showed good thermal stability, mostly up to 200 °C while the potting epoxy was thermally stable up to 160 °C, i.e., they were all suitable for current ASC applications if used under an inert gas environment.
- Notch sensitivity was one of the essential properties evaluated for the shrink tubing. Figure 3 shows the notched tensile strength and ultimate elongation to failure at 20 °C for both current and backup shrink tubing materials at various accelerated aging temperatures. While both shrink tubing showed good stability, the backup material was much stronger, i.e., more notch resistant.

Even though the 180-day accelerated aging experiments did not show any sign of degradation on most of the organics studied, it alone might not be long enough for more rigorous lifetime prediction or longer-term stability and reliability assessment for the ASC missions. However, the results could be more meaningful when they are correlated with data from other tasks, e.g., synergistic durability testing to investigate the combined effects of thermal exposure, radiation exposure, and outgas.

C. Evaluation of Thread Lockers

Two different types of liquid locking compounds (LLCs), designated as LLC1 and 2, were used for various ASC fastener joint systems to provide the secondary thread locking mechanism as required for a flight hardware. Since LLCs were not regularly used for a space flight hardware and their performance was strongly affected by installation and process conditions, a thorough and systematic evaluation was performed in terms of cure state, application method, joint conditions and configurations followed by the NASA specifications, NASA-STD-5017 and 5020, and the final report of NASA Engineering and Safety Center's (NESC) investigations, NESC-RP-04-092[9-10].
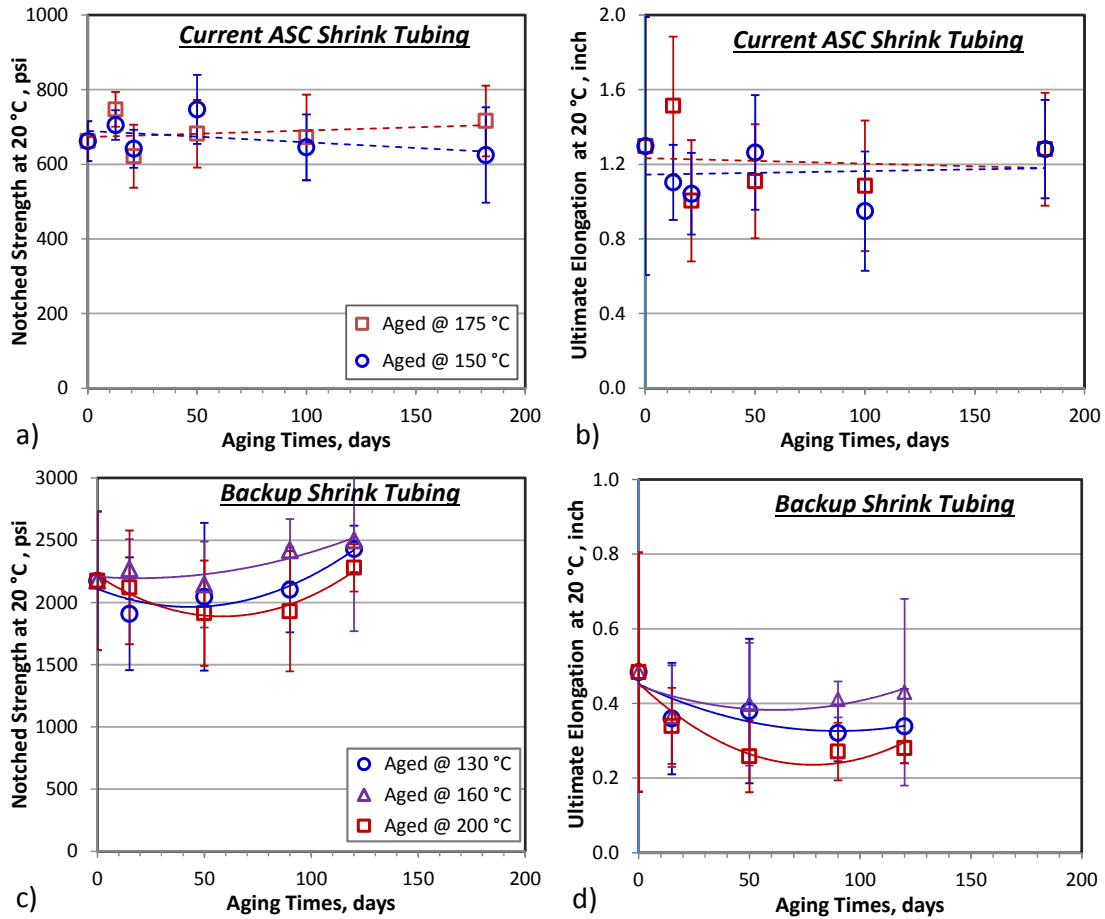
Figure 3. Notched tensile properties of the shrink tubing against aging temperature and time, a) & c) strength at 20 °C and b) & d) ultimate elongation to failure at 20 °C.

The overall program consisted of three phases including (I) determination of baseline control properties, (II) evaluation of installation variables and processes, and (III) evaluation of cure kinetics and thermal stability, Table 1. While the fastener locking integrity was assessed in phases I and II as a function of process and installation variables, thermal stability of the LLCs was assessed by a series of the 10-day thermal aging tests up to 200 °C followed by the 150-day accelerated aging tests at 165 and 185 °C as the standardized approach. Specific conditions and procedures for testing the ASC fastener joint designs were identified to determine processing sensitivities of the LLCs via test specimen fabrication, environmental thermal aging, torque strength, and other thermal, structural property testing. A full-scale component level torque testing system capable of testing up to 150 °C was developed and certified for this investigation. The designs of torque test specimens closely followed the actual ASC joint material, conditions, and configurations using the actual ASC fasteners on a 0.5 inch cube with a threaded hole, either thru-hole or blind-hole (for Joint 2, 3, and 4) configuration, while the actual ASC component was used for the joint 1. Among the eight ASC joint types, only the joint 1 was installed with LLC2 with low viscosity and capillary action because of its unique design and assembly procedure while all others used the LLC1, a more typical system. A total of about 720 torque test specimens were assembled by the Sunpower using the actual or replicated flight fasteners and threaded mating parts followed by the standard production procedures of the actual components. After torque testing, systematic postmortem was performed for OM failure analysis and FT-IR molecular network structure analysis, but only for a small subset of tested specimens representative of each test group per fastener type.

American Institute of Aeronautics and Astronautics

Table 1. Overall test program plan.

Phase	Experiments	LLC Type	Properties / Joint Type	23°C	90°C	130°C	150°C	Δwt%	sOM	FT-IR
				\# of Torque Test				Postmortem, \#		
Phase I	Baseline Control	LLC 1	Joint 2 - 8	24	21	21	18	7	7	7
		LLC 2	Joint 1	6	12	12	6	1	1	1
Phase II	Process validation: 7 variations - Cleaning solvent - Quantity & coverage - Alternative LLC*	LLC 1 Loctite242	Joint 2, 6, 7, 8	9	84	84	9	31	31	31
	- Other Preloads† - Application Blind Holes‡	LLC 2 Loctite246	Joint 1		21	15		5	5	5
Phase III	Cure kinetics - at 3 cure conditions§	LLC 1	Joint 6, 7, 8		27	27		9	9	9
		LLC 2	Joint 1		9	6		3	3	3
	10-d aging - at 5 temperatures¶	LLC 1	Joint 6, 7, 8		45	45		15	90	30
		LLC 2	Joint 1		5	5		5	5	5
	150-d Accelerated aging - at 2 temperatures, 4 times#	LLC 1	Joint 6, 7, 8		81	72		24	144	48
		LLC 2	Joint 1		9			3	9	4
			Total \# of test	39	314	287	33	103	304	143

* Loctite 242 for LLC 1 and Loctite 246 for LLC 2

† zero, lower, or higher than standard (1.35x for joint 1, 1.03 - 1.25X for all others)

‡ This applied only on Joint 2

§ 25-hour cure at 80 °C, 70 °C, and 22 °C vs. the standard cure, 25-hour at 60 °C

¶ 90 °C, 125 °C, 150 °C, 175 °C, and 200 °C under inert gas (N2)

165 °C and 185 °C for 10, 50, 100, and 150 days under inert gas (N2) determined from 10-d aging tests

Key findings from the Phase I included:
- LLC2 with the joint 1 tested with the actual component showed superior locking performance. Both breakloose and prevailing torques were much higher than the installation torque and thermally stable up to 150 °C. It was even verified that the high bake-out temperature, 245°C-1hr as required for component assembly, did not degrade its locking performance. However, the torque strengths were strongly affected by the condition of thread, e.g., gap thickness and contact material.
- Torque strengths of LLC1 varied significantly with the joint type, thermal exposure history, and test temperature. Typical breakloose torque was ranged from ~70 to 180 % of the installation torques which were varied from about 10 to 200 N-cm depending on joint type, and decreased with increasing test temperature. For a certain joint type, thermal stability of the LLC1 improved considerably with bake-out at elevated temperatures, e.g., 6 days at 115 °C
- Typical prevailing torque of LLC1 was much lower than that of LLC2 regardless of joint type, i.e., less or no significance in locking performance.

From the Phase II:
- For all four fastener joints studied, the optional cleaning solvent, Pro Strength Part Cleaner from Henkel, recommended by the LLC manufacturer did not improve but deteriorated the locking performance of LLC1 at both test temperatures, 90 and 130 °C, and thus was not recommended.
- Larger quantity/coverage of the LLC1, e.g., 2× of the baseline quantity, did not affect breakloose torques but increased prevailing torques at 130 °C considerably, especially for the joint 6 and 7. Thus, a larger quantity could be allowed if the excess LLC were properly handled during installation. This was consistent with the LLC manufacturer's recommendation.
- The alternative LLCs, a higher strength LLC from Loctite, did not improve breakloose torque but did increase prevailing torque in some fastener joints. However, the increase was rather insignificant.
- Increased installation torque did increase the apparent breakloose and prevailing torques in most cases, but showed no significant changes when the torque was compared in the percent of installation torque, i.e., less or no effects on the LLC secondary locking. The effect of higher installation torque on prevailing torques was inconsistent among fastener joint types.

- Other application methods developed by Sunpower were applied on the joint 2 with blind whole configuration, but showed no significant improvement. Regardless of all other options investigated in the Phase II, LLC1 on the joint 2 showed the poorest locking performance among all other joints.

From the Phase III:

- The cure kinetics study showed that the higher cure temperature was beneficial regardless of joint type. However, the initial cure at higher than ~ 70 °C was not recommended since it could cause thermal degradation of the raw material. Initial cure at ~ 60 – 70 °C followed by higher temperature bake-out, e.g., at 115 °C or higher, was recommended.
- From the 10-day thermal aging tests, it was found that failure mode was somewhat dependent on joint type, e.g., mostly cohesive mode for the joint 6, cohesive-adhesive mixed mode for the joint 7, or random modes for the joint 8 regardless of aging temperature, but didn't seem to be related to torque strengths.
- FT-IR analysis showed no sign of significant thermal decomposition for all aging temperatures up to 200 °C regardless of joint type.
- In general, torque strengths, both breakloose and prevailing, tested at either 90 or 130 °C, increased with increasing aging temperature initially but then decreased at certain temperatures, i.e., suggestive of potential change in aging mechanism. The onset of transition varied with joint type, e.g., 150 ~ 175 °C for the joints 6 and 8, but higher than 200 °C for the joint 7. Thus, 165 °C and 185 °C were selected as the two maximum temperatures for the 150-day accelerated aging tests.
- From the 150-day accelerated aging tests, both LLCs showed no sign of thermal degradation in terms of torque strengths, failure mode, or molecular network structure for both aging temperatures regardless of joint type.
- Gradual increases in the breakloose torque with aging time, especially at 185 °C, were probably due to cure advancement and densification, thus more aggressive bake-out of the joint systems at higher temperatures for longer time during ASC manufacturing was recommended.

In summary, the behavior and performance of the Loctite LLCs were strongly dependent on type of the fastener or mating part in terms of metal ion type, degree of thermal expansion, thread gap distance, and hole configuration, e.g., thru or blind besides preload, etc. Therefore, generalizing performance behavior and locking mechanism of the ASC LLCs would not be recommended. In conclusion, both LLCs were thermally stable and robust, thus were validated for the current ASC applications regardless of joint type. It was recommended, however, that more aggressive bake-out procedures at higher temperatures for longer time, in addition to the standard cure cycles should be applied for most ASC joint systems for improved thread locking integrity whenever possible.

D. Radiation Hardness of ASC Organics

Identification of radiation hardness of the organic materials was essential for the ASC applications because of the onboard radioisotope fuel as well as potential missions to deep space high radiation environments, and furthermore their greater susceptibility to radiations. It was required for both design qualification and reliability assessment. In spite of a large volume of the organics irradiation literature and database, most of them were typically tested in air and at room temperature, leading to new experimental validation being required since the effects of radiation on materials were strongly affected by the exposure conditions and sample configuration, e.g., thickness. Two representative radiations identified for the ASC system in the ASC specification were gamma as an ionizing radiation and neutron. Even though the combination of both radiations could be more realistic in-service exposure conditions, two separate irradiation exposure tests were conducted with either gamma[11-12] or neutron[13-14], in collaboration with High Flux Isotope Reactor (HFIR) spent fuel pool facilities, Oak Ridge National Laboratory (ORNL) or the Texas A&M University TRIGA reactor facilities, respectively, as a function of irradiation dose (from 100 krad to 15 Mrad) or fluence (up to 5×10^{14} n/cm^2) and temperature (125 and 150 °C) under the inert gas environment based on the ASC mission specifications for independent assessment. Additionally, in collaboration with the gamma irradiation facility (GIF), Sandia National Laboratories (SNL), radiation resistance of the organics was assessed in an ASC alternator subsystem, so-called the Stirling Alternator Radiation Test Article (SARTA) representing the linear alternator section of an ASC unit, which was designed and built by SunPower Inc.[11,15]. The test article operation in controlled thermal and radiation environments was used i) to screen for material or component failures that may not be evident in individual component material testing, ii) to evaluate overall radiation hardness of the unit at a subsystem level involving synergistic, combined irradiation responses of various materials, and iii) to identify potential radiation-induced component degradation or alternator performance degradation interactions. In all cases, the extensive residual property characterizations of the irradiated samples, coupons, or subsystem were performed at GRC and other testing collaborators such as Nanovea Inc, followed by NASA and

DOE radiation safety procedures while radiation exposure testing was conducted at the collaborating irradiation facilities.

Overall, most ASC organics tested showed a good tolerance to the combined thermal and gamma or neutron radiation exposures especially against the ASC specifications, and thus were validated as radiation hard for the application. Some of the organics such as o-ring or epoxy adhesive showed some changes in certain properties, but most of them were rather statistically insignificant or thermal exposure-induced. In the case of wire insulation material made of Teflon, the radiation caused considerable embrittlement and cracking, Figure 4, as expected from the literature, but the approximate threshold gamma dose for cracking was 25 Mrad at 125 °C or 15 Mrad at 150 °C which was much higher than the spec dose. Crystalinity of the insulation material increased significantly with irradiation which suggested some changes in crystalline morphological structure with irradiation. Even though it met the specification guidelines, the current Teflon insulation was replaced with more radiation resistant material based on the recommendation from this study in order to mitigate the potential risk associated with the uncertainties.
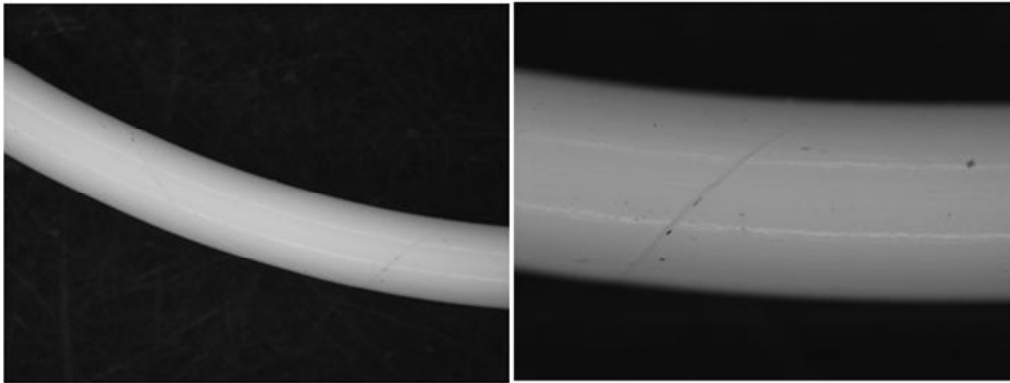
Figure 4. Spiral cracks on irradiated Teflon insulation sleeves.

The evaluation of the SARTA internal components revealed minimal degradation, chemically or physically, after operating in the radiation environment. Cracks were also observed in Teflon wires insulation but did not appear to contribute to changes in system response. Slight appearance changes, such as discoloration or the presence of rub marks, were observed but are comparable to changes that may be found in normal (non-irradiated) operation.

The SARTA operating performance changed insignificantly through the entire irradiation runs, amassing approximately 40 Mrad of exposure. However, post-operation measurements on the alternator suggested a shortage occurred when the SARTA was removed from the test cell. Evaluation also suggested that the shortage formed in the stator coil windings. Due to the nature of its construction, destruction evaluation of the coil did not seem feasible. Since the outer stator windings utilize a polyimide-based coating, a high-radiation tolerance would be expected from this component. It was recommended that further thermo-mechanical or irradiation testing of the outer stator be conducted in order to repeat the fault and isolate the failure mechanism.

E. Outgassing Behavior and Impact Assessment of ASC Organics

Stirling convertor was designed to operate under a pressurized medium but with dry and ultrahigh-purity inert gas for best performance with a hermetically sealed system. Potential outgassing from the thermally susceptible organics can contaminate the working fluid in the system and degrade overall convertor performance or even cause a system break-down. It was also evidenced that the outgasses, as evolved or further inter-reacted, caused premature degradation of certain ASC organics. As mentioned in Sections A and B, considerable weight losses have been detected from some of the ASC organic materials when they were thermally aged. Thus, in order to assess more reliable convertor performance and durability, in-situ outgassing behavior of the ASC organics was quantitatively tested and analyzed as a function of exposure time and temperature, individually[16] or combined all ASC organics together[17]. The effects of radiation on outgassing was also investigated as a function of irradiation temperature and dose rate of gamma, at GIF, DOE-SNL[16, 18]. Custom designed pressure vessels similar to the actual ASC PV capable of holding pressure up to 1000 psi at elevated temperatures up to 300 °C were built for those in-situ outgassing tests. All PVs were equipped with pressure gauge, internal thermocouples, relief valve, and variable leak valve to control amount of gas samples down to 10^{-5} torr. The test samples/coupons, either individual organic or all combined, were placed in the PV under pressurized inert gas as the actual ASC, then heated to predetermined temperatures while outgassing was monitored in-situ for typically 28 days or longer for temperature only tests.

Recently, an integrated RGA-GC/TCD-MS-FTIR system was developed and utilized for more accurate and reproducible gas analyses, Figure 5. The outgas-induced degradations or their mechanisms, if any, were assessed via the systematic residual property characterizations of the exposed organics after the in-situ outgassing experiments.
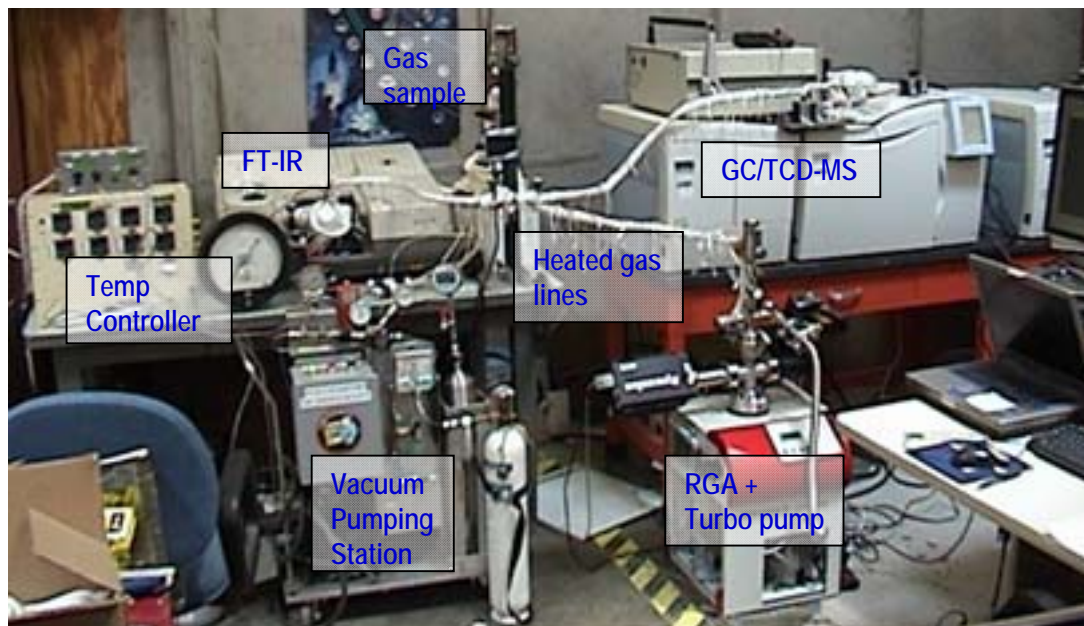

Figure 5. Integrated RGA-GC/TCD-MS-FTIR gas analysis system at GRC.

From the outgassing tests of individual organics, either the temperature-alone tests or the gamma induced tests, the most common outgas species observed were H_2, CH_4, H_2O, N_2, O_2, and CO_2. Among them, N_2 with molecular weight of 28 g/mole was the most dominant outgas but its concentration was not affected by exposure conditions. Only outgas species affected by the exposure conditions was CO_2 which its intensity increased consistently with increasing exposure conditions, but rather with temperature and time than gamma dose. It should note that part of the outgases were residual air contaminant left in the PVs even though they were vacuumed and purged with the inert gas several times. In the case of the shrink tube materials, especially at temperatures higher than 150 °C, two additional outgas species, possibly C_4H_{10} (n-Butane) and CF_4 (Tetrafluoromethane), were registered in the RGA. This suggested that backbone molecules of the material started to break down at or above 150 °C. The combined temperature and gamma radiation did accelerate outgassing of several organic materials, e.g., epoxy adhesives, o-ring, and shrink tube when exposed up to 20 Mrad accumulated even though the total exposure time was about 17 hours. Thus, temperature, time and gamma dose were all critical parameters that control outgassing of the organic materials. In general, high temperature capable organics showed less outgassing and appeared cleaner.

From the combined organics outgassing tests as a function of temperature alone (typically to 90 °C for 7 days, 125 °C for 7 days, 150 °C for 7 days , or 200 °C for 7 days or longer especially for an accelerated testing), up to 150 °C exposure, the outgases from the combined organic samples were almost identical to those from individual organic materials even though there were a trace of high molecular weight species that were not identified. Most organic samples after the outgassing tests showed no noticeable changes except slight discoloration of epoxy and thread locker samples. FT-IR and residual property characterizations also confirmed that most organics did not suffer any significant structural changes or degradation. However, it was evident that the shrink tube materials suffered outgas-induced thermal degradation and generated potentially harmful outgas containing fluorine. These findings suggest that the temperature limit of the shrink tube for longer-term use should be lower than 150 °C. The epoxy adhesive was another organic that possibly underwent outgas-induced molecular structural changes, but not necessarily involving significant degradation or decomposition. At 200 °C, several new outgas species with higher molecular weight, e.g., 47, 77, 81, 96, appeared as a result of thermal decomposition or chemical interactions among different outgas species and their concentrations increased considerably with aging time while other lower molecular weight species were decreased or leveled off. However, the most dramatic change was that the o-ring was completely degraded and disintegrated after the outgassing test at 200 °C as shown in Figure 6 b). Since the o-ring survived the same 200 °C exposure when exposed alone, it must be outgas-induced thermal decomposition. The MS

American Institute of Aeronautics and Astronautics

analyses identified much higher molecular weight outgas species at 225 g/mole and at 321 g/mole, which seemed to be resulted from degradation of the o-ring. In addition, the residual property characterizations indicated that the epoxy adhesive, shrink tube, and thread locker materials also experienced outgas-induced molecular structural changes or degradation, but less severe than the o-ring. Based on the available data, the suspected sequence of degradation mechanisms was suggested as follows: outgasses from the combined ASC organics at temperatures exceeding than 125 °C attacked and degraded the shrink tubing → additional fluorine containing outgasses were generated at ~150 °C or higher → other gas species via inter-gas chemical reactions were formed → o-ring and other organics were attacked, decomposed or de-polymerized at ~200 °C → additional higher molecular weight outgasses contained Si were generated → other organics, e.g., epoxy adhesive, thread lockers etc., were attacked. Even though the test temperature of 200 °C was much higher than that of normal convertor operation, the impact of outgas was clearly demonstrated. As a result, the shrink tubing and o-ring including potential backup candidates have been more extensively evaluated for the ASC applications.
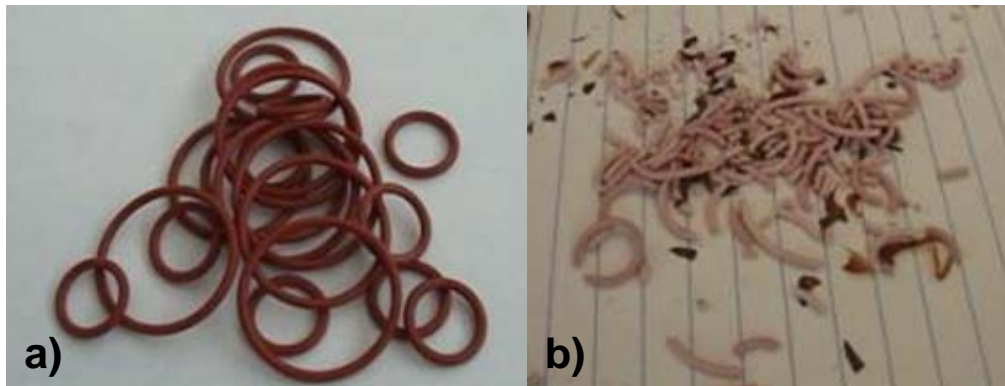
Figure 6. Effect of outgases on o-ring degradation, a) no degradation after exposures to 200 °C with or without gamma radiation, but individually, i.e., o-ring alone and b) after 200 °C exposure with other ASC organics together for 117 days.

Effects of gamma radiation on outgassing behavior of the combined ASC organics were also assessed experimentally following the conditions closer to the anticipated mission specifications, e.g., under lower dose rate (~0.1 rad-Si/sec), but for longer exposure time (24 days) at near the maximum alternator qualification temperature, 125 °C. Since the current shrink tubing material was considered as a potential source of major degradation of other organics, an alternative shrink tubing candidate was tested in a separate PV setup. The key findings include:

- The outgas species observed were consistent with those from previous outgassing analyses of either single individual organics or combined ASC organics or actual convertors, including the inherent residual air contaminations including a small trace of silicone vapor. Among them, only CO_2 increased in concentration with gamma dose.
- Outgassing behavior under gamma radiation between the current shrink tubing and the potential candidate material was similar.
- The most weight loss among ASC organics came from the o-ring followed by the coil backing paper regardless of shrink tubing type tested together. Their weight losses were considerably higher than those from other controlled thermal exposure tests, which was indicative of higher susceptibility to combined in-situ exposure of gamma irradiation, temperature, and outgas.
- From the residual property characterizations after the outgassing test, most organics showed no visible changes in properties or molecular network structures. Considerable decrease in T_g and T_m while a slight increase in T_d were observed from the o-ring, but no major chemical changes or degradations were detected. In the case of the shrink tubing materials, their thermal property changes were insignificant overall, but the current material showed somewhat greater changes than the alternative candidate. The bearing surface coating also showed more changes in some properties when exposed with the current shrink tubing material.

Overall, the most susceptible ASC organic to the combined temperature and radiation exposure was o-ring and possibly shrink tubing material, and the bearing surface coating. However, no major chemical structural changes or degradation of ASC organics was identified from the lower temperature outgassing tests.

F. Synergistic Durability of ASC Organics

The combined effects of irradiation, thermal exposure, and synergistic organic outgassing interactions on stability and durability of ASC organics were assessed with a simulated thermal aging test. The simulated thermal aging tests were designed to incorporate various service environments such as radiations and outgasses in addition to thermal exposure on the combined organics together in a tightly sealed pressure vessel. Various test specimens and sub-component coupons of the organic materials were pre-conditioned first under either gamma or reactor neutron radiations as described in the previous sections. The irradiation pre-conditioning conditions used were not based on the current ASC flight hardware specifications, but rather determined arbitrarily. Determining potential impact of the suspected reactive free radicals in most organic materials generated from the irradiation was one of the original objectives. The aging tests were performed at 130 °C, the maximum alternator qualification temperature, for 5 months and 16 months, respectively. Various outgas analyses and systematic residual property characterizations of the aged organics samples were performed to determine the synergistic effects on stability and compatibility of the organic materials.

The typical outgas species identified at the end of each aging tests included H_2, CH_4, H_2O, Ne, N_2, O_2, Ar, CO_2, small amount of acetone, C_3H_6O, and the host gas, almost identical to the typical composition of the gas samples from the actual ASC test units. As indicated earlier, they involved traces of trapped air and/or cleaning solvent. Their concentrations were ranged from 10 to 6000 ppm and varied with aging time. FT-IR analysis also suggested presence of Silicon vapor, Figure 7. Organics suffering the most significant weight loss after 16-month aging were the o-ring and shrink tubing. Most of other organics showed either insignificant or no changes during the entire aging duration. The aged o-rings also showed: i) some changes in FT-IR spectra which were indicative of possible side chain rearrangement and/or oxidization degradation, and might be related to the volatilization of silicone; ii) decreased thermal properties such as T_g, T_d, and T_m that were more prominent than when it was thermally aged under an inert gas, i.e., potentially outgas-induced changes; iii) considerable changes in TGA outgassing potential characteristics which supported the postulation of silicone volatilization, but no significant changes in compression-set property. The shrink tubing materials showed no noticeable changes in FT-IR spectra regardless of brand type or irradiation preconditioning conditions, no changes in mechanical properties, but considerable changes in thermal properties. It was not clear whether the changes were thermally-induced or synergistic effect-induced. Other organic materials showed insignificant changes in most residual properties.
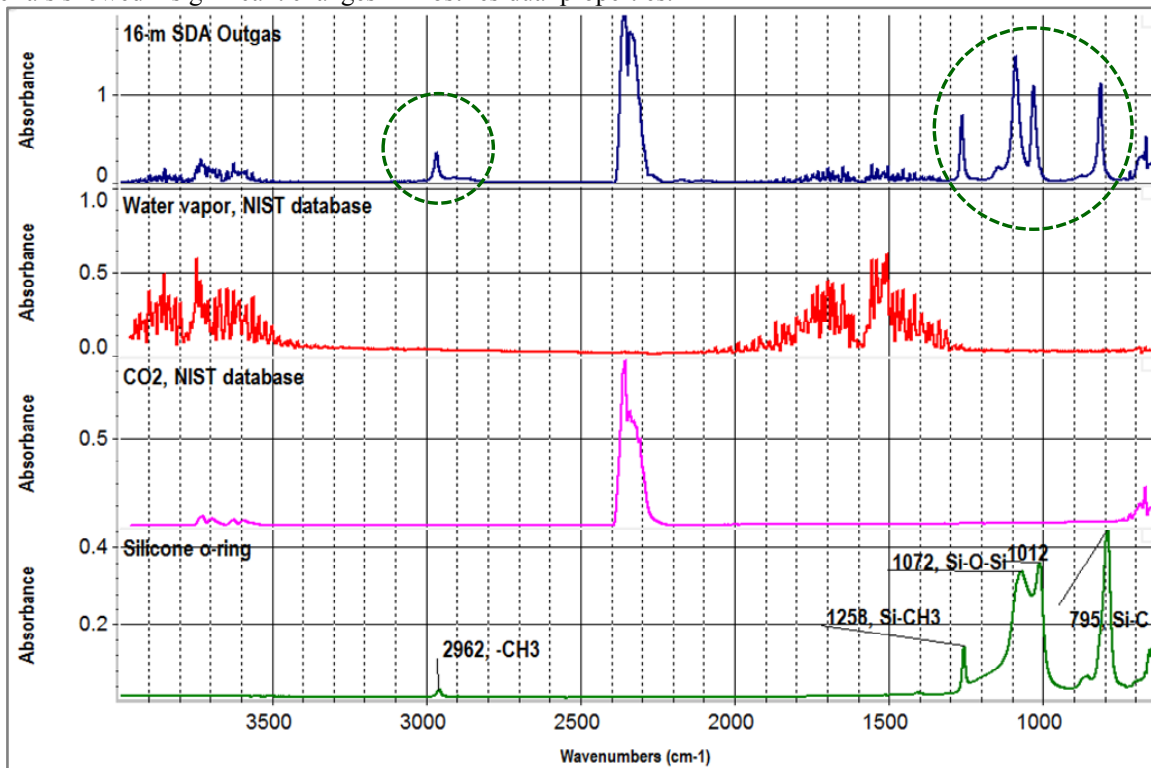

Figure 7. FT-IR spectra of the outgas samples from the16-month synergistic durability aging test, top, showing evidences of Si vapor, circled peaks in green dash, in addition to H_2O, CO_2.

In summary, most of the organics seemed to be stable and compatible with the ASC environment. The o-ring and shrink tubing did warrant some further evaluations as they had greater weight losses and more prominent changes in some material properties even though the test results showed no visible changes in their functional properties or chemical structures with no clear sign of degradation or decomposition.

G. Selection of High Temperature Organic Candidates for Future High Temperature ASCs

Efforts have been made to increase the operating temperature range of the current ASC by at least 20 °C. This increased operating range would allow the ASC to be used in additional missions, particularly ones that require a Venus fly by for a gravity assist. It should be also noticed that increasing the operating temperature and pressure improves efficiency and performance of the convertors. Thus, there are continued efforts to develop higher temperature ASCs, potentially 50 to 100 °C higher operating temperatures than the current ones. In any case, the future higher temperature ASCs requires organics with much higher temperature capability in the first place since organics are more susceptible to temperature changes. This task was also rationalized in that the higher temperature capable organics can significantly improve reliability margin of the current ASCs. Most of the aforementioned issues or concerns on the organic materials against the Stirling convertor applications are extremely temperature-sensitive. Screening and evaluation of higher temperature organics had been initiated in 2012. Based on the findings and extensive experiences from the current ASC organic evaluation and validation tasks, the more comprehensive and streamlined methodologies and work plans were developed, Figure 8. Figure 9 shows the detailed program plan for selecting the best high temperature adhesive candidate as an example. Various commercially available candidates were identified and screened for the most susceptible organics, such as adhesive, potting compound, o-ring, shrink tubing, and thread locker materials. As can be seen in the selection process, the initial candidates were evaluated first in terms of required properties and functions, processability, short-term thermal stability, and outgassing characteristics using the similar test approaches and methodologies described above. The down selected candidates, typically two to three, will be further evaluated for longer-term thermal stability via accelerated thermal aging tests, material compatibility by TCIOP testing, and key functional integrities followed by additional process optimizations whenever needed. As the final validation, the synergistic effects of the combined ASC in-service exposure conditions on the properties and performance of all the final ASC organics, therefore, overall system durability and reliability will be assessed. The synergistic durability life testing will consist of high temperature radiation exposures, both gamma and neutron, and subsequent extended thermal aging at three selected temperatures for up to 3 years in pressurized and hermetically sealed PVs. Once they were validated, the final organic materials will go through process and installation optimization, and implementation optimizations.
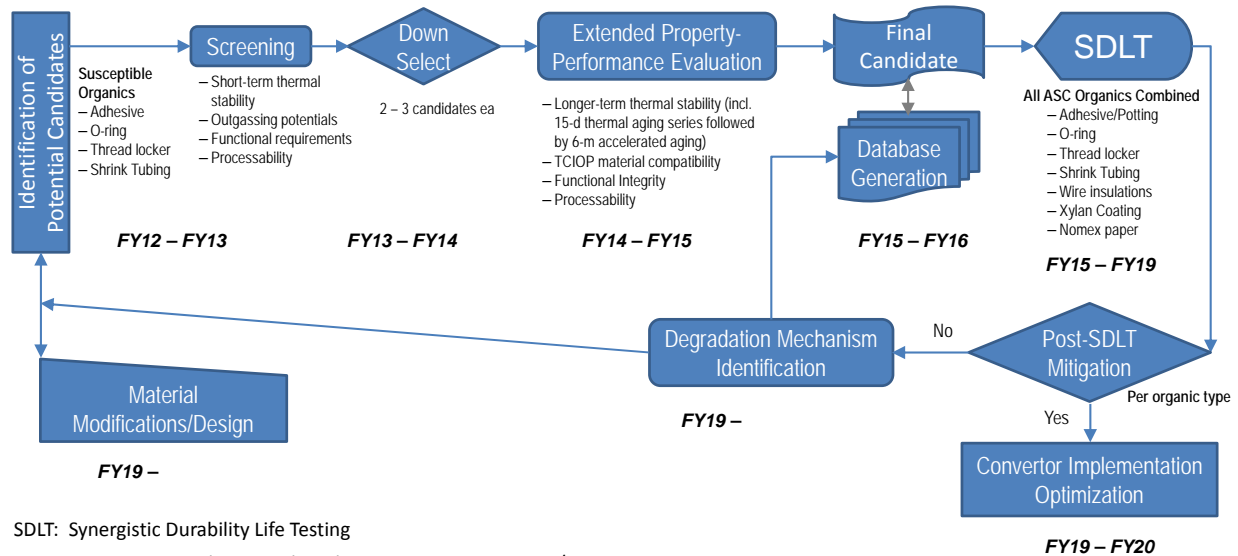

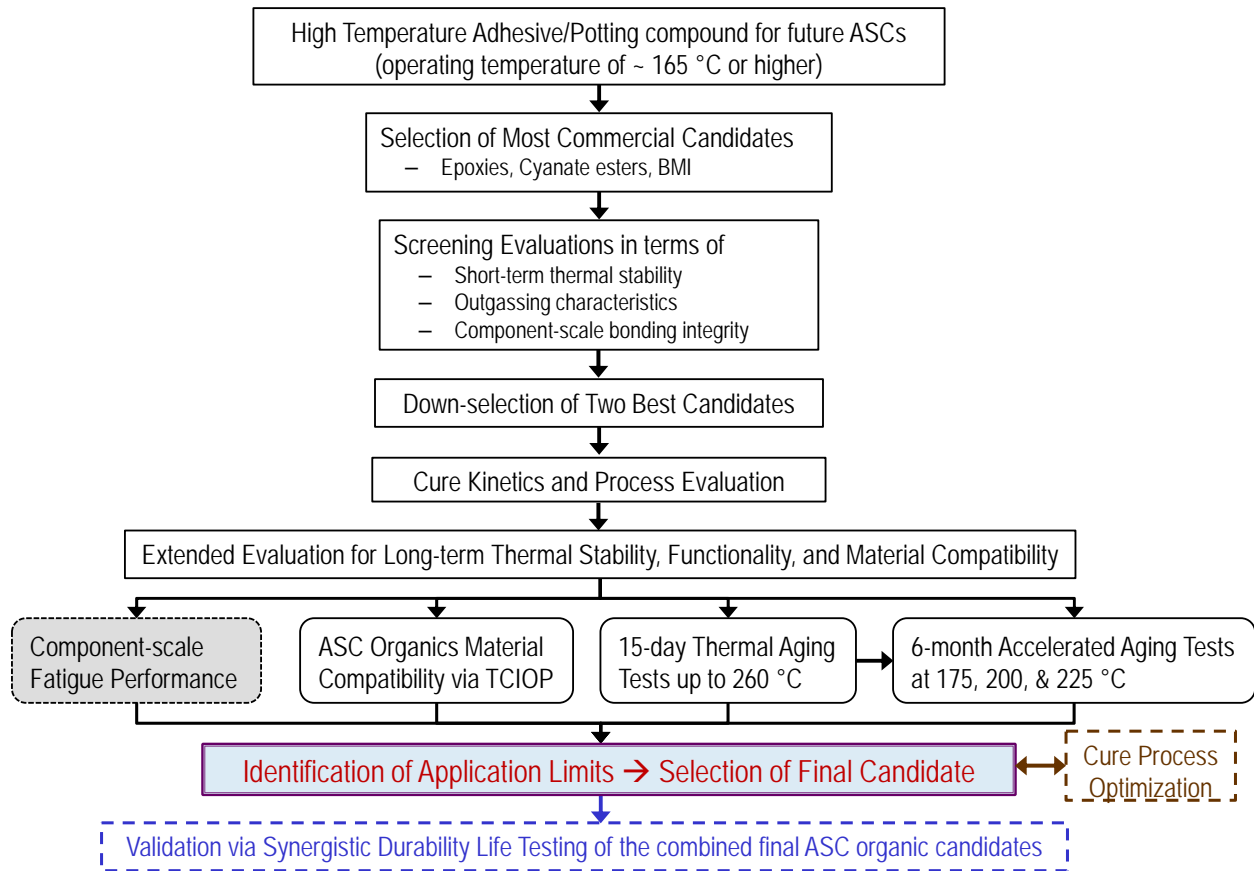**Figure 8. Overall program plan for best high temperature organics selection.**

Figure 9. Selection process of best high temperature adhesive candidate.

IV. Conclusions

The current ASC organic materials including certain backup candidates were extensively and systematically evaluated and successfully validated for various proposed missions after a few mitigation recommendations on a couple of organics such as shrink tubing and o-ring. The Teflon insulation material was replaced with more radiation resistant material. Practical and specific application limits of each ASC organics were also identified for any future ASC development.

Based on the findings and experiences from the current ASC organics evaluation and validation, the methodology and procedure of screening and down selecting the final candidates for the future higher temperature ASCs were streamlined and optimized.

Acknowledgments

References

[1]Chan, J., Wood, J.G., and Schreiber, J.G., "Development of Advanced Stirling Radioisotope Generator for Space Exploration," *proceedings of Space Technology and Applications International Forum (STAIF-2007)*, edited by M.S. El-Genk, AIP Conference Proceedings, 880, pp. 615-623, 2007.

[2]Wood, J.G. et. al., "Advanced Stirling Convertor (ASC) Phase III Progress Update," *Proceedings of Space Technology and Applications International Forum (STAIF-2007)*, edited by M.S. El-Genk, AIP Conference Proceedings, 880, pp. 313-324, 2007.

[3]Shin, E. E., Sutter J. K., Thieme L., "Organics Evaluated for Advanced Stirling Convertor (ASC)," *R&T Research and Technology 2006*, NASA/TM 2007-214479, GRC, Cleveland, OH, p252-253, 2006.

[4]Shin, E. E., Scheiman D.,, Cybulski M.,, Quade D., Inghram L., and Burke C., "Validation of Organics for Advanced Stirling Convertor (ASC)," in *Proceedings of Space Technology and Application International Forum (STAIF)-2008*, Albuquerque, NM, Feb 10 – 14, 2008, AIP Conference Proceedings, Vol 969, Edited by M. S. El-Genk, pp 570-581.

[5]Shin, E. E., "Final Report GFX A7-F Long-term Aging Test of Epoxy," NASA-GRC PIR ASRG-12-0012, NASA Glenn Research Center, Cleveland, OH, September 7, 2012.

[6]Shin, E. E., "Accelerated aging tests on epoxy," NASA-GRC Preliminary Information Release (PIR) ST-10-014, NASA Glenn Research Center, Cleveland, OH, March 5, 2010.

[7]Shin, E. E., "Final Report on Thermal Stability of Shrink Tube and O-ring," NASA-GRC PIR ST-11-032, NASA Glenn Research Center, Cleveland, OH, November 8, 2011.

[8]Shin, E. E., "Final Report GFX A7- G: Thermal Stability of Additional ASC Organics," NASA-GRC PIR RPS-15-0009, NASA Glenn Research Center, Cleveland, OH, August 21, 2014.

[9]Shin, E. E., "Interim Report GFX A7-A Evaluation of Thread Lockers and Fasteners," NASA-GRC Project Deliverable (PD) ASRG-12-0005, NASA Glenn Research Center, Cleveland, OH, February 25, 2013.

[10]Shin, E. E., "Final Report to GFX A7-A & B: Evaluation of Thread Lockers and Fasteners, Phase III," NASA-GRC PIR RPS-15-0005, NASA Glenn Research Center, Cleveland, OH, September 22, 2014.

[11]Shin, E. E., "Interim report on the Gamma Irradiation Testing of Advanced Stirling Convertor (ASC) Organics (Coupon Tests and Stirling Alternator Radiation Test Article)," NASA-GRC PIR ST-10-047, NASA Glenn Research Center, Cleveland, OH, July 30, 2010.

[12]Shin, E. E., "Final Report GFX A7-D: Gamma Irradiation Testing of Additional ASC Organics," NASA-GRC PIR RPS-15-00010, NASA Glenn Research Center, Cleveland, OH, September 11, 2014.

[13]Mireles O. R., Shin, E. E., and Bowman C., Vesudevan L., "Mixed Neutron & Gamma-Ray Testing of Stirling-Alternator Candidate Organic Materials," *Proceedings of IECEC 2010*, 8th Annual International Energy Conversion Engineering Conference, Paper# 769917, 25 – 28 July 2010, Nashville, TN.

[14]Shin, E. E., Bowman C., Mireles O., "Final report on the Reactor Neutron Irradiation Testing of ASC Organics," NASA-GRC PIR ST-11-030, NASA-GRC, October 31, 2011.

[15]Mireles O. R., Shin, E. E., and Bowman C., "Post-Irradiation Evaluation of the Stirling Alternator Radiation Test Article," *Proceedings of ICAPP 10*, San Diego, CA, USA, June 13-17, 2010, Paper 10008.

[16]Shin, E. E., "Interim report on the In-Situ Outgassing Assessment of ASC Organics under Radiation including Temperature-alone Baseline Analysis," NASA-GRC PIR ST-10-051, NASA Glenn Research Center, Cleveland, OH, August 10, 2010.

[17]Shin, E. E., "Interim report on the Outgassing Impact Assessment and Component Degradation of the Combined ASC Organics," NASA-GRC PIR ST-11-022, NASA Glenn Research Center, Cleveland, OH, September 27, 2011.

[18]Shin, E. E., "Final Report GFX A7-D: In-situ Outgassing Assessment of ASC Organics under Low Dose Gamma Radiation," NASA-GRC PIR RPS-15-0008, NASA Glenn Research Center, Cleveland, OH, August 1, 2014.

[19]Shin, E. E., "Final Report GFX A7-C: Synergistic Durability Testing," NASA-GRC PIR-RPS-15-0006, NASA Glenn Research Center, Cleveland, OH, April, 2013.

[20]Shin, E.E., "Synergistic Durability Testing of 5-m and 16-m Aging Data", NASA-GRC PIR-RPS-15-0007, NASA Glenn Research Center, Cleveland, OH, July 2014.