JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 48, No. 2, March–April 2011

Uniquely Customized Ultra-Low-Outgassing Silicones to Reduce Contamination

Vincent Malave,* Brian Burkitt,† Bill Riegler,‡ Roy Johnson,§ and Rob Thomaier¶
NuSil Technology, Carpinteria, California 93013

DOI: 10.2514/1.49476

Silicone materials for space and aerospace applications are continually in development and evaluation to limit and reduce the potential for outgassing contamination while maintaining essential physical and chemical characteristics. Several agencies, such as NASA, historically recommend the American Society for Testing and Materials ASTM E595 ["Standard Test Method for Total Mass Loss and Collected Condensable Materials from Outgassing in a Vacuum Environment," ASTM International, Std. ASTM E595, Alexandria, VA, 2007] test results of less than or equal to 1.0% total mass loss and less than or equal to 0.1% collected volatile condensable material. These levels provide an industry screening level for the acceptance or rejection of controlled-volatility materials for space applications. By a comparison of controlled-volatility product CV10-2568 and ultra-low-outgassing product SCV-2585, cured physical properties and outgassing profiles of these two products demonstrate that when incorporating specific fillers, the cured physical properties can remain consistent while still providing exceptional outgassing characteristics.

I. Introduction

THE aerospace industry has used silicones as adhesives and coatings for over five decades. Silicones are ideal materials for the protection of electrical components and assemblies against shock, vibration, moisture, dust, chemicals, and other environmental hazards that are particularly encountered in space environments. They also have the ability to maintain elasticity and a low modulus over a broad temperature range.

With the large amounts of adhesives/sealants currently used on spacecraft, manufacturers must pay close attention to material outgassing levels and carefully monitor cumulative contaminant levels. Selecting a material with outgassing levels below the industry standard of 1.0% total mass loss (TML) and 0.1% collected volatile condensable material (CVCM) could prove beneficial for many reasons. For instance, by employing materials with lower outgassing levels, manufacturers could use more of a material when necessary for mechanical reasons or as required by production techniques.

In recent years, the industry need for lower levels of outgassing led to the development of several silicone material systems that exceed the standard criteria for outgassing and meet the Ultra Low Outgassing™ requirements of $\leq 0.1\%$ TML and $\leq 0.01\%$ CVCM. Originally, these materials were all resin-reinforced silicone elastomers. While silica-reinforced systems generally have improved physical properties over resin-reinforced systems, silica contains a volatile component, and engineers were initially unable to develop a silica-reinforced material that met the ultra-low-outgassing requirements. Resin-reinforced silicone systems in the uncured state have lower viscosities, classifying them as low-consistency elastomers that will self-level and are transparent in the uncured and cured states. Resin-reinforced silicones have higher modulus values than silica-filled material of the same durometer, because the resin will form cross-links, whereas the silica filler gives much more stress relief and improved tensile values, mainly through hydrogen bonding. Extensive research and development provided SCV-2585, the first silica-reinforced ultra-low-outgassing silicone system. The next hurdle to jump was incorporating fillers into the silica-reinforced ultra-low-outgassing silicone system.

An ultra-low-outgassing material keeps processing time down, as no additional conditioning is required to achieve the desired outgassing values. There are also little-to-no changes in the mechanical properties when using ultra-low-outgassing silicones as compared to the controlled-volatility silicones. If device contamination is based on cumulative contaminant levels from all material in the device's vicinity, using a material with exceptionally-low-outgassing levels could allow use of other materials with higher outgassing levels in the same vicinity.

A major drawback with using silicone compounds in space applications is that silicone materials may outgas from the polymer matrix and cause subsequent contamination of expensive equipment and devices. In early NASA flights that used silicones around space capsule windows and other areas, oily residues of low-molecular-weight species were observed. These low-molecular-weight species had not cross-linked into the silicone polymer matrix and subsequently outgassed and deposited on cold surfaces. Based on these discoveries, NASA and other space agencies realized the importance of using low-outgassing materials, known as controlled-volatility (CV) materials, and recommended that all adhesives used in extraterrestrial environments be tested before use in space for volatile species that may outgas from the material.

An exemplary application for using ultra-low-outgassing materials can be found in solar cell arrays. The lower outgassing level produces lower contamination on the cell cover glass, preserving conversion efficiency, especially in low Earth orbit, where equipment is exposed to the detrimental effects of molecular oxygen [1]. In solar cell arrays, for example, lower-outgassing materials result in lowered levels of contaminants for interaction with solar cells, thus producing a more efficient solar cell by potentially extending the life of the cell. Chemical species can condense onto surfaces such as glass and interact with particles, causing decreases in clarity and signal strength. This phenomenon has shown to decrease the operation life of systems such as solar cells or sensors [2].

Iron oxide is a common filler incorporated into material systems, because it is known to aid in thermal stability [3] and has a long space-flight heritage. Filling a material with iron oxide can significantly increase the material's specific gravity, and this must be taken into consideration when selecting a silicone. Alternately, a filler package using iron oxide and microballoons can be incorporated into the material. The microballoons not only offset the increase in specific gravity from the iron oxide, but reduce the material's specific gravity to less than that of the unfilled material.

Received 19 February 2010; revision received 13 August 2010; accepted for publication 8 September 2010.

*Technical Sales, Engineering Materials, 1050 Cindy Lane.
†Technical Sales Supervisor, Engineering Materials, 1050 Cindy Lane.
‡Product Director, Engineering Materials, 1050 Cindy Lane.
§Chemist, Research & Development, 1050 Cindy Lane.
¶Research Director, Research & Development, 1050 Cindy Lane.

One of the most popular cure mechanisms used for aerospace applications is the tin-catalyzed condensation-cure system using alkoxy, oxime, or acetoxy cross-linkers. Condensation-cure chemistry requires moisture as part of the reaction that forms the cross-links, and the cure rate is dependent on available moisture, temperature, and exposed surface area. Condensation-cure systems produce reaction by-products that need to evaporate out of the silicone to ensure that the cure is complete, and this results in long cure times (greater than three days) as well as dimensional changes from the shrinkage caused by the evaporation of approximately 5–7% by weight of the cure by-product. The cure chemistry used in CV10-2568 is platinum catalyzed hydrosilation, also known as platinum cure or addition cure. One main advantage of the platinum-cure reaction is that it can be accelerated by heat and can also be formulated to cure at low temperatures. Other advantages for aerospace applications include the absence of chemicals released during the curing reaction, and they can be cured in thick sections, since the cure is not dependent on exposed surface area or atmospheric conditions such as temperature and humidity.

To date, CV10-2568 has been a widely used CV silicone material for space applications offered by NuSil Technology. It incorporates an iron-oxide/microballoon filler and is an excellent material for bonding, sealing, or potting, due to its silica-reinforcement and attendant mechanical properties. Key features include low density and low modulus for compensation, due to coefficient of thermal expansion mismatch and mechanical property stability over a broad operating temperature range, as required for materials used in extreme environments, where thermal temperatures can range from −115 to 300°C. A low-modulus, silica-reinforced, iron-oxide- and microballoon-filled, elastomeric silicone that meets ultra-low-outgassing requirements has not previously been achieved. This paper compares the cured physical properties of the CV silicone elastomer CV10-2568 with a comparable developmental Ultra Low Outgassing iron-oxide- and microballoon-filled silicone elastomer. The outgassing profiles of each material based on the American Society for Testing and Materials ASTM E1559 [4] test method are examined in detail.

ASTM E595 [5] is a widely accepted test standard used to screen materials for volatile content that may outgas from a material in a vacuum or space environment. NASA and ESA recommend testing outgassing materials per ASTM E595 before use in space. A maximum TML of 1% and CVCM of 0.1% are base requirements set by these agencies. Although a standard for many years, some question whether these specifications are stringent enough. In response, NuSil Technology developed an Ultra Low Outgassing line of silicone materials with limits set out at less than 0.1% TML and 0.01% CVCM. The characteristics and outgassing kinetics of many of these materials were recently discussed at length [5].

The primary goal of this study was to take a legacy material, CV10-2568, which has a complex formulation and is described as a platinum-cure diphenyldimethylsiloxane copolymer filled with microballoons and iron oxide, and to develop the next-generation ultra-low-outgassing silicone. After this developmental Ultra Low Outgassing silicone was created, the outgassing rates and CVCMs were then compared to standard ultra-low-outgassing silica-filled materials SCV-2585 and CV10-2568. The challenge was achieving TMLs at $\leq 0.1\%$ and CVCMs at $\leq 0.01\%$, but these goals were accomplished by achieving 0.070% TML and 0.005% CVCM for the developmental Ultra Low Outgassing material. The results for the developmental Ultra Low Outgassing material are 10 times lower than for CV10-2568.

II. Experimentation

A. Materials

The materials used for this study are listed in Figure 1. The critical contaminating species typically outgassed from silicone materials are primarily caused by the low- to middle-molecular-weight silicone cyclics and polymers that are not covalently bonded into the silicone matrix. These species are created during the polymerization process, and a common technique to remove these remaining uncross-linked siloxanes by the end user is to perform an extensive bake-out on the cured material. This bake-out process can cause many negative side effects such as contaminating the bake-out ovens and lowering the mechanical properties of the silicone. Using a silicone elastomer designed to be low-outgassing allows the end user to avoid additional processing.

Silicone Property	CV10-2568	Developmental Ultra Low Outgassing™ Material	SCV-2585
Silicone Polymer	Diphenyl-Dimethyl	Diphenyl-Dimethyl	Diphenyl-Dimethyl
Cure Mechanism	2-Part Addition Cure	2-Part Addition Cure	2-Part Addition Cure
Mix Ratio (A:B)	(1:1)	(1:1)	(1:1)
Reinforcing Filler	Silica	Silica	Silica

Fig. 1 Materials that are compared in this study.

There are a number of methods used to remove low- to middle-molecular-weight linears and cyclics from the polymer at various stages in the production process that involve heat and vacuum. To produce the ultra-low-outgassing materials, extensive processing time is needed to achieve lower levels.

B. Methods

Using ASTM E595 [5], the values for CVCMs and TMLs are obtained directly by measuring changes in weight before and after the test. The test is limited by the precision of the balances, but has proven to be an excellent method for screening a material's outgassing properties. ASTM E1559 [4] obtains these same values indirectly, whereby the volatile species will condense onto quartz crystal microbalances (QCMs) at specified temperatures. The calculated values for TMLs and VCMs are derived from algorithms designed to correlate the change in frequency of the QCM to the mass gain on the QCM. ASTM E1559 is able to obtain much more detailed information regarding outgassing rates and the molecular characteristics of the outgassing species. The materials in this study were analyzed using ASTM E1559 to obtain a more thorough understanding of the outgassing rate, but they are screened using ASTM E595 [5]. To clarify the nomenclature, ASTM E595 refers to the volatile condensables as *collected volatile condensable materials* and the ASTM E1559 [4] refers to them as *volatile condensable materials* (VCMs).

1. Test Method: VCM in Vacuum

This test method is used to determine the volatile content of materials when exposed to a vacuum environment (i.e., space). The two parameters measured are TML and CVCM. Water vapor recovery is an additional parameter that can also be obtained after the completion of the exposures and measurements required for TML and CVCM.

Each material sample is preconditioned at 50% relative humidity and ambient atmosphere for 24 h. The sample is weighed and loaded into the test chamber within the ASTM E595 [5] test stand. The sample is then heated to 125°C, and vacuum is pulled to less than 5×10^{-5} torr. These conditions are held for 24 h. The volatile species that outgas under these conditions escape through an exit port, and a portion of these may condense on a collector plate maintained at 25°C. Once the test is complete, the samples are removed from the chamber and the collector plate and samples are then weighed.

The TML, the percent of the total mass of the material outgassed, is calculated from the mass of the sample measured before and after the test. The CVCM is calculated as a percentage and is determined by calculating the difference in mass on the collector plate before and after the test and dividing this change by the initial sample mass.

2. Test Method: Contamination Outgassing

Outgassing Services International conducted ASTM E1559 [4] experiments and provided test reports. The isothermal outgassing test apparatus is explained in detail by Garrett et al. [6] and Glassford and Garrett [7] and will only be discussed here briefly. The material sample can range from 0.5 to 10 g and is placed in a temperature-controlled effusion cell in a vacuum chamber.

Outgassing flux leaving the effusion cell orifice condenses on four QCMs that are controlled at selected temperatures. The QCMs and effusion cell are surrounded by liquid nitrogen shrouds to ensure that the molecular flux impinging on the QCMs is due only to the sample in the effusion cell. The TML and outgassing rate from the sample are determined as functions of time from the mass deposited on an 80 K QCM and normalized with respect to the initial mass of the sample.

The amount of VCM is measured as a function of time from the mass collected on the 298 K QCM. After the outgassing test is complete, the QCMs are then heated to 398 K at a rate of 1 K/ min. As the QCM heats the deposited material evaporates. The species that evaporate can be analyzed by a quadruple mass spectrometer to quantitatively determine the species observed.

The CV10-2568 and developmental Ultra Low Outgassing version were cured at 150°C for 30 min into discs approximately 1.475 in. in diameter and 0.065 in. thick. The surface area is calculated for both faces and the edge of the disc.

One of the supplied discs of material was placed in the effusion cell as the test sample. The samples were tested with no additional preconditioning.

The parameters shown in Table 1 were set for each sample. The outgassing rates for species condensable on the warmer QCMs can be calculated from curve fits to the data. The total outgassing rate to the 80 K QCM can then be compared to the outgassing rates for species condensable on the warmer QCMs to determine the rates of very-high-volatility species (water and solvents) and the rates of the remaining species (high, medium, and low volatility).

III. Results and Discussion

A. Comparison of Physical Properties

In Table 2, the results for the typical material properties for each sample, measured according to ASTM protocols, are listed and compared. These properties were measured at NuSil Technology. A comparison of the physical properties of CV10-2568 and the developmental Ultra Low Outgassing material in Table 2 show that the desired cured physical properties are not compromised to achieve these requirements.

Table 1 Listing of test parameters

Test parameter	Value
Chamber pressures	$10^{-8} - 10^{-10}$ torr
View factor from QCM to sample	415 cm^2
Test duration	72 h
Sample temperature	125 °C
QCM temperatures	80, 160, 220, and 298 K
QCM sensitivity	4.43×10^{-9} $g/cm^2/Hz$

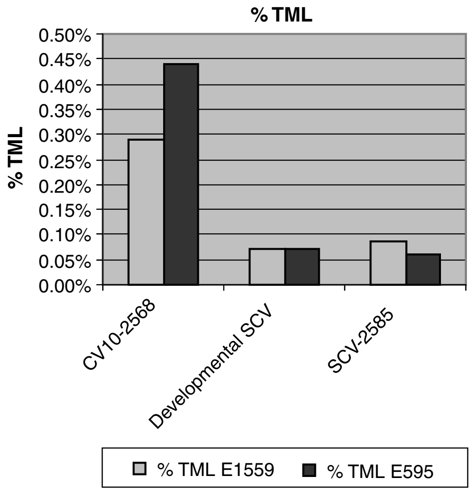

Fig. 2 Comparison of percentage of TML for each silicone elastomer and comparing the results from ASTM E595 [5] and ASTM E1559 [4] at the end of the test.

B. Percentage of Total Mass Loss

The percentage of TML of each sample for the results obtained from ASTM E595 [5] are compared in Fig. 2 to the results obtained from ASTM E1559 [4].

Figure 3 is a plot of the TML of each sample over the 72 h test period from the 80 K QCM, which represents essentially all of the possible outgassing species. Here, it is evident that the ultra-low-outgassing materials show a lower mass loss over the duration of the experiment and the rate is relatively stabile after 8 h versus CV10-2568, which is still stabilizing after 24 h.

C. Percentage of Volatile Condensable Material

Figure 4 is a plot of the VCM of each sample over the 72 h test period from the 298 K QCM, which represents the low-volatility species that tend to have a higher molecular weight than the condensable species collected on the QCMs at 80, 160, and 220 K. The low-volatility species have a higher likelihood to condense on surfaces, due to the lower vapor pressure. Again, the ultra-low-outgassing silicones' VCM percentages stabilize, and the VCM percentages have much lower levels of the low-volatility species compared to CV10-2568, which shows a change in outgassing rate after 16 h (ASTM E1559 [4]).

The volatility of a material is directly related to its average molecular weight: the lower the average molecular weight, the higher the volatility, and vice versa. Table 3 compares the percentages of

Table 2 Typical physical properties evaluated for silicone elastomers

ASTM	Typical property	CV10-2568	Developmental Ultra Low Outgassing material	SCV-2585
		Uncured		
——	Viscosity, cP	102,000	300,000	50,000
——	Work time, h	3	2	1
		Cured		
——	Cure time	30 min at 150°C	30 min at 150°C	15 min at 150°C
D792 [8]	Specific gravity	0.76	0.75	1.1
D412 [9]	Durometer, type A	40	45	36
D412 [9]	Tensile, psi	235	235	650
D412 [9]	Elongation, %	170	140	300
D1002 [10]	Lap shear, psi	175	175	500
E595 [5]	%TML	0.54	0.07	0.06
E595 [5]	%CVCM	0.06	0.005	0.001
E595 [5]	% water vapor recovery	Unknown	0.04	0.04

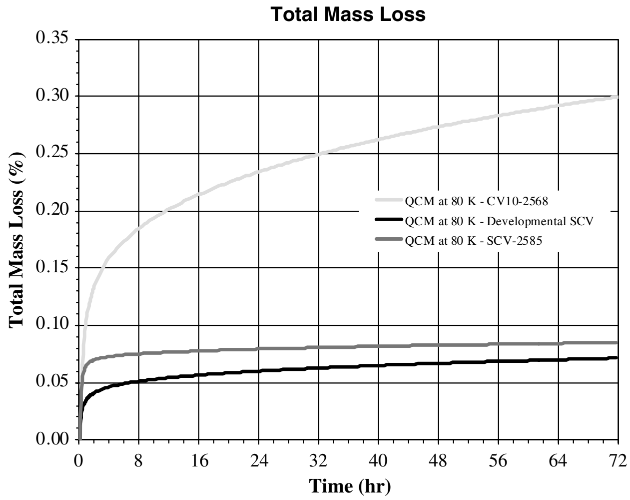

Fig. 3 Total mass loss of CV10-2568, developmental Ultra Low Outgassing material, and SCV-2585 as a function of time.

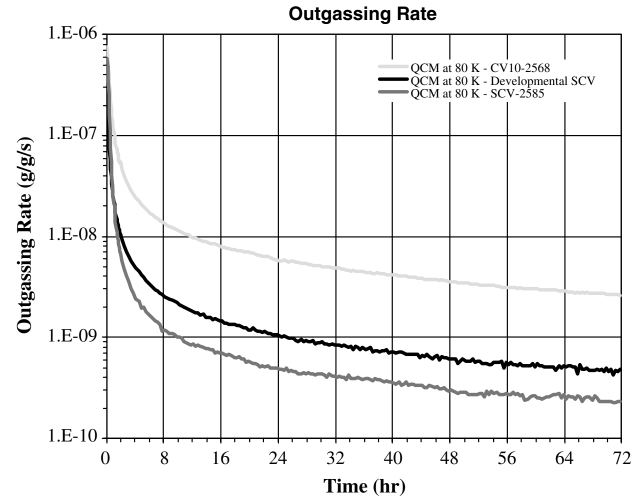

Fig. 5 Total outgassing rate for CV10-2568, developmental Ultra Low Outgassing material, and SCV-2585 as a function of test time (species condensable on 80 K QCM).

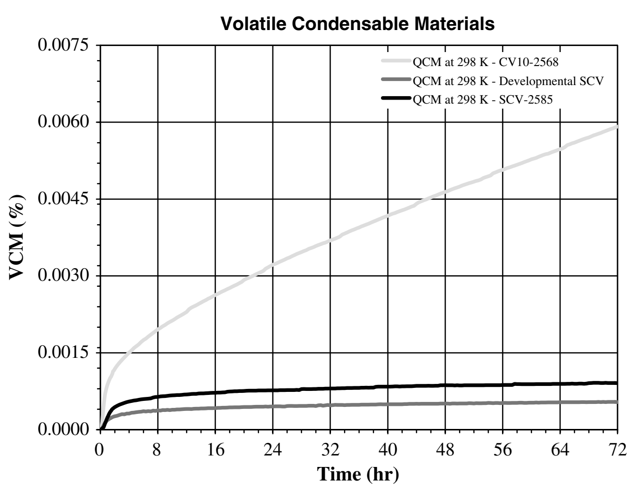

Fig. 4 Volatile condensable materials from CV10-2568, developmental Ultra Low Outgassing material, and SCV-2585 condensed on the 298 K QCM.

TML values, based on the 80 K QCM, to the molecular weight distributions derived from the QCMs at 160, 220, and 298 K, respectively. The table also shows that the normalized values based on the 80 K QCM. Molecular weight ranges for the species in the different volatility categories can be estimated based upon engineering experience related to species condensability and mass spectrometer data. The extremely-low-molecular-weight group of species, shown in Table 3, is highly volatile, primarily due to water and solvents. The low-molecular-weight species most likely have molecular weights of 50 to 200 amu, the medium-molecular-weight species fall in the 200 to 400 amu range, and the high-molecular-weight species have estimated molecular weights above 400 amu [5] and are the least volatile of all the species.

D. Comparison of the Total Outgassing Rate as a Function of Time

Figure 5 shows the total outgassing rate data as a function of test time for CV10-2568, the developmental Ultra Low Outgassing material, and SCV-2585. These outgassing rates are for species condensable at 80 K and thus would not include certain gases such as nitrogen and oxygen.

IV. Conclusions

As space system devices and processes become more advanced and sensitive to molecular contamination, more details of characterization of the construction materials must be obtained. The molecular weight characterization is complex and can be more fully explored to better characterize outgassing species and condensation kinetics. The TML results showed that the legacy space-grade material CV10-2568 had approximately four times more overall outgassing species compared to the two ultra-low-outgassing materials. The VCM data at 298 K also showed that the legacy space-grade material contained twice the amount of high-molecular-weight species than the next-generation space-grade silicone. The ultra-low-outgassing materials had not only a significantly lower level of TMLs, but also much less of the high-molecular-weight species that are most likely to condense onto cooler surfaces. In addition, it was also shown that achieving these lower levels does not compromise physical properties, and thus a broad range of silicone elastomers with unique and specific properties can be developed.

The results from kinetic outgassing data allows engineers to better predict the levels of contamination, migration, and deposition once the materials are in space. Achieving these lower levels does not

Table 3 Cumulative amounts of estimated volatility of different outgassed species

ASTM E1559 [4]		Cumulative amounts due to different outgassed species			
Silicone material	TML at end of test, %	Extremely low molecular weight, %	Low molecular weight, %	Medium molecular weight, %	High molecular weight, %
CV10-2568	0.3000	0.1000	0.1200	0.0700	0.0060
CV10-2568	100.0000	33.8600	41.3600	22.8100	2.0000
Developmental Ultra Low Outgassing material	0.0700	0.0600	0.0060	0.0080	0.0005
Developmental Ultra Low Outgassing material	100.0000	80.5600	7.8800	10.0000	1.0000
SCV-2585	0.0800	0.0800	0.0050	0.0030	0.0009
SCV-2585	100.0000	89.7400	5.5000	3.6900	1.0700

compromise physical properties, and thus a broad range of silicone elastomers with unique and specific properties can be developed. Ultra-low-outgassing specification requirements of $\leq 0.1\%$ TML and $\leq 0.01\%$ CVCM can be useful in the overall management of outgassing.

References

[1] Banks, B. A., de Groh, K. K., Rutledge, S. K., and Haytas, C. A., "Consequences of Atomic Oxygen Interaction with Silicone Contamination on Surfaces in Low Earth Orbit," *Proceedings of SPIE: The International Society for Optical Engineering*, Vol. 8784, 1999, pp. 62–71.

[2] Snyder, A., Banks, B., Miller, S., Stueber, T., and Sechkar, E., "Modeling of Transmittance Degradation Caused by Optical Surface Contamination by Atomic Oxygen Reaction with Absorbed Silicones," *Proceedings of SPIE: The International Society for Optical Engineering*, Vol. 4096, 2000, pp. 157–168.

[3] Hanu, L. G., Simon, G. P., and Cheng, Y. B., "Thermal Stability and Flammability of Silicone Polymer Composites," *Polymer Degradation and Stability*, Vol. 91, 2006, pp. 1373–1379. doi:10.1016/j.polymdegradstab.2005.07.021

[4] "Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials," ASTM International, Std. ASTM E1559, Alexandria, VA, 2009.

[5] "Standard Test Method for Total Mass Loss and Collected Condensable Materials from Outgassing in a Vacuum Environment," ASTM International, Std. ASTM E595, Alexandria, VA, 2007.

[6] Garrett, J. W., Glassford, A. P. M., and Steakley, J. M., "ASTM E 1559 Method for Measuring Material Outgassing/Deposition Kinetics," *Journal of the IEST*, Vol. 38, No. 1, Jan.–Feb. 1995, pp. 19–28.

[7] Glassford, A. P. M., and Garrett, J. W., "Characterization of Contamination Generation Characteristics of Satellite Materials," Lockheed Missiles and Space Co., Astronautics Div., Rept. WRDC-TR-89-4114, Sunnyvale, CA, 1989.

[8] "Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement" ASTM International, Std. ASTM D792, Alexandria, VA, 2008.

[9] "Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension," ASTM International, Std. ASTM D412, Alexandria, VA, 2006.

[10] "Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)," ASTM International, Std. ASTM D1002, Alexandria, VA, 2005.

D. Edwards
Associate Editor