New innovations in silicone technology for aircraft and aerospace

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WHITE PAPER

Over the last fifty years, the aerospace and aircraft industries have utilized silicone in an ever-growing number of applications for its unique properties. Inherently, silicone possesses high dielectric strength (≥ 500 V/mil, typically) and a large Coefficient of Thermal Expansion (CTE), allowing it to absorb stresses during thermal cycling. In addition, low modulus and low glass transition point enable silicone to remain elastic at low temperatures and resist breakdown at high temperatures or in UV light. Besides characteristics such as these, key to the legacy of silicone in an ever-expanding range of applications is the material's ability to be designed as needed to fulfill a particular role. New innovations in silicone technology that add to silicone's prolific resume and success in the aerospace and aircraft industries are fuel and solvent resistant silicone elastomers, silicone ice-release coatings for aerodynamic surfaces, and controlled volatility silicone film adhesives.

SILICONE CHEMISTRY

Silicone owes its versatility to its chemistry. Depending on an application's requirements, a silicone can be tailored for specific needs by filler incorporation and/or polymer alterations.

Silicone is comprised of repeating siloxane units, Si-O, with substituent groups attached to the open valences of the silicon atom. Having no carbon in the backbone, these repeating siloxane units are often referred to as a polysiloxane polymer, or a polyorganosiloxane polymer in reference to the organic substituent groups.

Typical substituent groups include methyl, phenyl and trifluoropropyl, which interact with the Si-O-Si units to cause the resulting silicone material to exhibit certain attributes. Conventional silicones, comprised of methyl groups, are commonly referred to as PDMS silicones because of their so-called polydimethylsiloxane polymers. Trifluoropropyl (fluoro) or phenyl groups are often added in varying degrees to form trifluoropropyl methyl polymers or diphenyldimethylpolysiloxane polymers, respectively. Phenyl influences refractive index, permeability, and operating temperature range. Fluoro-containing silicone products, also known as fluorosilicones, are often used for applications involving solvents and the need for swell resistance.

A silicone polymer is manufactured in several steps. Initially, a silicone polymer is produced via Ring Opening Polymerization (ROP). The process begins with polyorganosiloxane cyclics reacting with a chain terminating species, or "end blockers," in the presence of an acid or base initiator. The product of this polymerization reaction is a mixture of various molecular weight molecules, including cyclical and linear polymers of varying lengths; the concentrations of each species are based on a thermodynamic equilibrium. Because the uncrosslinked lower molecular weight species are often volatile and will migrate out of the cured matrix over time, resulting in contaminants, it is necessary to remove low-molecular-weight polymers and cyclics from the polymer mixture through a refinement process.

For applications that demand minimal outgassing, controlled volatility (CV) silicones may be ideal. Primarily for applications that exist in a vacuum, CV materials are processed to be tested per ASTM E 5951 and to meet specifications outlined in NASA SP-R-0022A and ESA PSS-014-702, which recommend a maximum allowable Total Mass Loss (TML) of less than 1% and a Collected Volatile Condensable Material (CVCM) of less than 0.1%2,3. With these materials, physical properties remain the same but volatiles are minimized. Mitigation of volatiles in space and many terrestrial applications is essential because a vacuum environment compounds the propensity of volatiles to condense on or around device components at elevated temperatures. For instance, the collection of volatiles within a solar cell's light path can cut off equipment's power generation. By greatly reducing outgassing, controlled volatility silicone adhesives and encapsulants significantly aid in the protection of equipment from debilitations to performance.

SILICONE FILM ADHESIVES

Advances in silicone technology have led to the development of controlled volatility, or low outgassing, silicone film adhesives. This is exactly what it sounds like: a tape-like silicone adhesive in film form. An alternative to (and arguably an improvement upon) the more traditional liquid silicone, the silicone film adhesive can be used in wire staking application or to bond optical solar reflectors (OSRs) or solar cells, as well as to adhere appliqués to substrates.

The film adhesive is a two-part curable silicone with an adjustable cure time that at the longest runs approximately 24 hours at room temperature. The Part B of the film adhesive is a liquid activator applied like a primer, and Part A is a calendered sheet of uncured silicone adhesive that begins to cure on contact with the activator. The properties of a two-part film adhesive can be adjusted at the manufacturer's level by adding fillers, such as carbon for static dissipation, to the part A component.

In adhesion strength, the film adhesive performs similarly to liquid silicone adhesives — and with greater processing efficiency. A peel-and-stick application replaces mixing and de-airing for easier processing, faster turn-around times, and controlled bond line thickness.

A lap shear test is typically conducted to quantify the adhesion strengths of silicone film adhesives. Per lot in three replicates, the films are bonded at .012 inches, cured at 65°C, and pulled apart at 0.02 cm/minute using an MTS loading frame. Figure 1 depicts the results for one of NuSil Technology's two-part, unfilled silicone film adhesives tested for lap shear via these parameters.

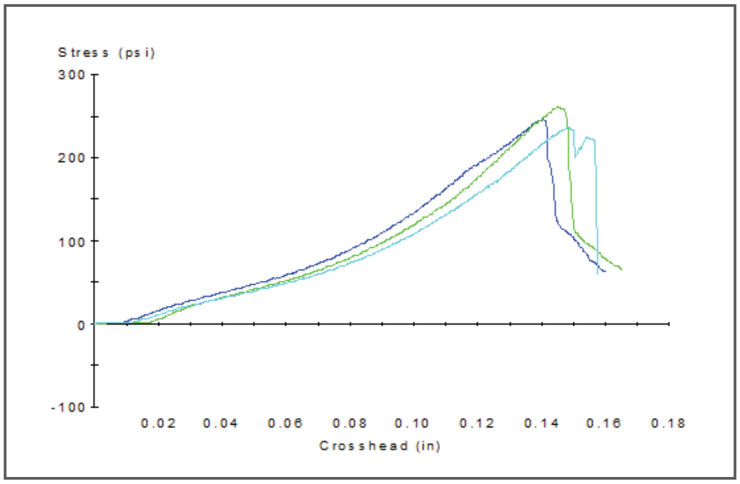

FIGURE 1: Lap shear test of unfilled film adhesive. Crosshead moves at 0.1in/min.

In form, the silicone film adhesive is a far cry from the liquid silicone adhesive, but in ability the two are very similar. The difference in form between these adhesives is a testament to silicone's material flexibility; the sameness in ability, to silicone's aptitude in extreme environments. Besides bonding, other uses attest to silicone's alterable and evolving canvas when it comes to ability in aerospace as well as aircraft applications.

FUEL AND SOLVENT RESISTANT SILICONE ELASTOMERS

Materials that resist swell when in contact with fuels, hydrocarbon solvents, and glycols are often required to maintain the effectiveness of integral parts in air or spacecraft, and by extension to preserve the functionality of the vehicle as a whole. Compared to conventional dimethyl silicones, fluorosilicones provide higher swell resistance and, therefore, even longer reliability even in prolonged exposure. Fluorosilicones are commonly used in aircraft and aerospace applications for their lack of swell in glycol de-icing fluids and fuels common to the aircraft industry, such as JP-8 and Jet A. Figure 2 offers a visual comparison of submersion in JP-8 jet fuel for a dimethyl silicone and a fluorosilicone. Swell resistance is an ability conferred by trifluoropropyl groups on the polysiloxane polymer chain. The resulting silicones, known as fluorosilicones, are just as subject to form flexibility as silicones containing no fluoro groups. Similar to other silicones, fluorosilicones can be provided as high consistency rubbers (HCRs), liquid silicone rubbers (LSRs), dispersions, gels and even foams; and they can be used as adhesives, molded parts, or protective coatings.

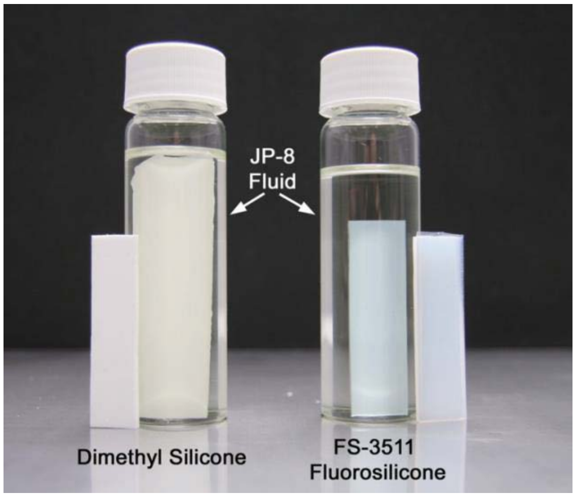

FIGURE 2: Swell comparison for PDMS and fluorosilicone formulation, prefixed "FS", in JP-8 jet fuel.

Using a test method based on ASTM D471 for swell, as well as one based on ASTM D792 for specific gravity, NuSil evaluated the percent swell of fluorosilicones versus dimethyl silicones in JP-8 jet fuel. The percent swell is depicted as the percent difference in specific gravity between t= 0. Cured samples were prepared at 1" x 1" x 0.070', and samples were tested for specific gravity before and after 24, 48 and 72 hours of exposure.

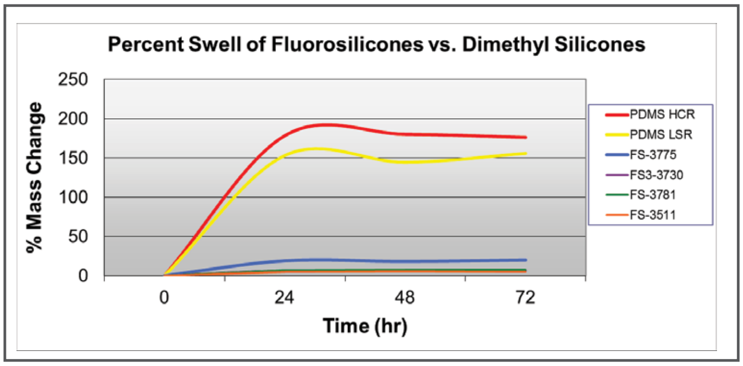

FIGURE 3: Percent mass change of fluorosilicones compared to dimethyl silicones.

The thermal stability data displayed in Figure 4 for one of NuSil's 100 mol % fluorosilicone elastomers represents fluorosilicones' endurance in harsh environments. Throughout suspension in an oven at 150 °C (302 °F), three specimens of this product were tested and their values averaged for durometer, Type A (ASTM D 2240) at 4, 8, 24, 48, 96 and 192 hours to determine the extent of change at these times. To be considered a passing data point each value had to be within a 15% range of the collective median. After 192 hours' exposure to 150 °C, this fluorosilicone demonstrated adequate resistance to high temperature, with a 14% increase in durometer after eight days.

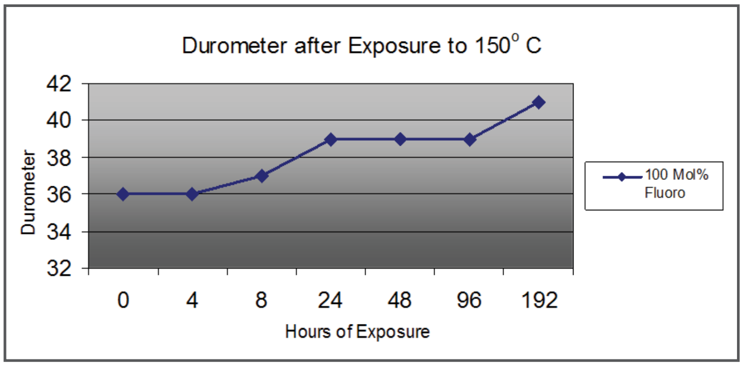

FIGURE 4: Type A durometer of 100 mol % fluorosilicone after exposure to 150 °C.

Results suggest swell resistance does not come at the price of temperature resistance. For certain silicone formulations, this environmental reliability extends to the ability to reduce the adhesion of ice to aerodynamic surfaces.

ICE-RELEASE SILICONE COATINGS

Ice adhesion is a major area of significance in the aircraft industry because ice buildup affects many aspects of flying. For instance, when ice accumulates on the wings of airplanes it decreases lift and increases drag. Wind tunnel tests have shown very thin ice sheets can reduce lift by as much as 30% and increase drag by 40%4. Using materials or applying coatings that reduce ice adhesion to surfaces is a practical and economical choice for aircraft manufacturers, but this is a difficult undertaking considering the adhesion strength of the ice must be less than the shear stress the ice exerts on the substrate.

In recent years, silicone coatings have gained popularity in the aircraft industry for their effective ice-release characteristics, in addition to a broad operating temperature range and resistance to many different aviation fluids. In events of ice buildup, silicone's ability to remain elastic at low temperatures has proven extremely valuable. Silicone ice-release coatings outperform other materials commercially available and marketed as ice-release materials, including Teflon®.

The U.S. Army's Cold Regions Research and Engineering Laboratory, also known as CRREL, has evaluated various materials for ice-release performance using the Zero Degree Cone Test, which quantifies ice adhesion strength as the force required to push a coated pin from an ice mold. NuSil Technology has worked with CRREL on multiple occasions for characterization of its silicone ice-release coatings using the Zero Degree Cone Test, which is discussed in detail in the Aerospace Information Report (AIR) 6232. The AIR is a new publication of SAE that provides information on methods for evaluating ice-release coatings.

To begin the Zero Degree Cone Test, water is added to a mold surrounding the coated test pin and then frozen. An O-ring placed at the bottom of the inner cylinder keeps any water from leaking out before it freezes. (See the image and schematic of the test stand shown in Figure 5.) After spending 48 hours at -10°C, the sample is tested on the equipment with a constant rate of 0.06 mm/min. The force required to push each pin out of the ice mold is at this point quantified to determine the adhesion strength of the ice.

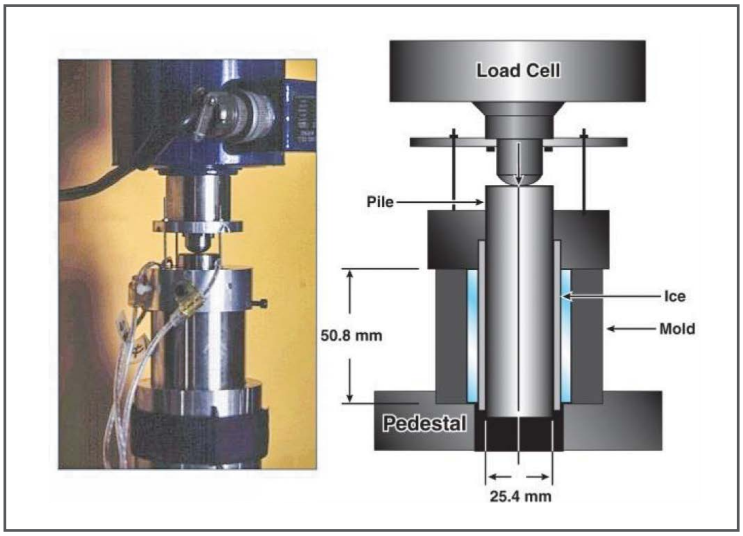

FIGURE 5: Instrumental sample pile and mold in testing machine (left) and Zero-Degree cone test stand configuration (right).

Figure 6 below displays Zero Degree Cone Test ice-release performance results for R-2180, R-3930, R-3975, R-1009, and R-1082 in which coatings were evaluated alone as well as in combination with R-1182, a one-part, fast cure room temperature vulcanizing (RTV) complementary silicone coating that prevents the silicone from being a particle gatherer. R-3930 and R-3975 are fluorosilicones, and the rest are dimethyl silicones. R-3975 had the lowest ice adhesion strength of the two fuel resistant coatings, as well as the lowest overall result when the coatings were tested in combination with R-1182. R-3975 also showed the least discrepancy in ice adhesion strength from being tested neat to being evaluated with R-1182 coated on top.

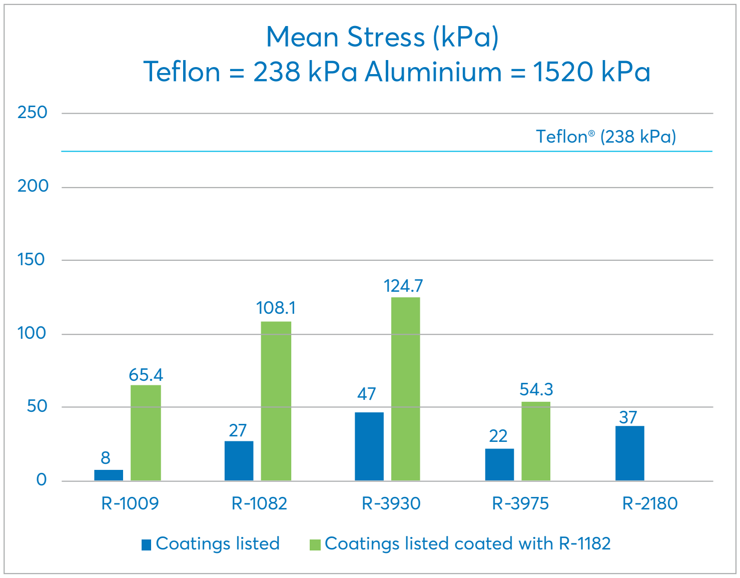

FIGURE 6: Ice adhesion results in kPa for silicone ice-release materials with and without R-1182 on bare 2024 aluminum.

CONCLUSION

Silicone's versatility makes it conducive to a wide range of applications. This capacity for optimization is why many engineers and manufacturers turn to silicone technology to serve their evolving and forward-looking innovations. Whether silicone is utilized as an ice-release coating to reduce ice adhesion to aerodynamic surfaces; a film adhesive for solar assembly or other applications benefiting from controlled bond line thickness; or as a fluorosilicone for swell resistance in contact with or immersed in engine fluids and other solvents, testing results show silicone is a particularly valuable asset to the aerospace and aircraft industries.

Resources

1. ASTM E-595, "Standard Test Method for Total Mass Loss and CollectedCondensable Materials from Outgassing in a Vacuum Environment."
2. NASA SP-R-0022A
3. ESA PSS-014-702
4. Mulherin, N.D., Haehnel, R.B., Jones J.F., "Toward developing a standard sheartest for ice adhesion" .Proceedings, 8th International Workshop on AtmosphericIcing Structures, Reykjavik, Iceland, 8-11 June 1998. IWAIS 1998.