NuSil SILICONE TECHNOLOGY

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SILICONE ADHESIVES AND PRIMERS ON LOW SURFACE ENERGY PLASTICS AND HIGH STRENGTH METALS

By Kyle Rhodes, Sr. Technical Sales, Bill Riegler, Product Director-Engineering Materials, Rob Thomaier, Research Director, and Henry Sarria, R&D Technician
NuSil Technology-Carpinteria, CA.

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ABSTRACT

This paper will demonstrate the ability of silicone adhesives, with the aid of primers, to adhere to low surface energy plastics and to high strength metals. In general, some plastics are difficult to adhere to because of their low surface energy, available bond sites, and chemical interaction. Most plastic have a surface energy under 50 dynes/cm while aluminum, an easier substrate to adhere to, is closer to 825 dynes/cm. Surface energy is a thermodynamic effect of how a liquid will 'wet out' on a surface. Low surface energy materials, like plastics, do not allow a liquid, like an adhesive, to 'wet out' on its surface. Adhesion chemistry tells us that the better an adhesive can 'wet out' on a substrate, the more surface area it can cover and allow more reactive groups to bond, making a stronger bond. Several low surface energy plastics and high strength metals were tested with silicone adhesives and primers to achieve cohesive bond failure when performing lap-shear testing. This list of substrates evaluated include polycarbonate, polyetherimide, polyamide, polyurethane, polymethylmethacrylate, polysulphone, titanium, stainless steel, and aluminum.

KEY WORDS: Adhesives, Silicones, Primers

1. INTRODUCTION

The aerospace engineer has many options to choose from for joining or sealing parts together. One of the common technologies used is bonding or adhesive technology, which is 5 parts chemistry, 3 parts physics, and 1 part art. Because there are so many different substrates available, each adhesive can not be actually tested before-hand by the supplier on each and every one. However, by testing on some novel substrates, or difficult to adhere to substrates, inferences can be made which can narrow the choices of adhesives and primers.

We can define adhesion as the physical and chemical bonding of two substrates. Substrates that have reactive groups available for bonding like OH or C=O groups on glass, plastics and aluminum make this chemical attraction greater through van der Waals forces or weak hydrogen attraction. Substrates with limited available bonding sites make adhesion difficult, such as Acetal, Nylon 24, or PTFE. Multiple other substrates fit somewhere in-between. This paper will investigate the substrates, adhesives and primers used to adhere to some of these difficult substrates.

2. SUBSTRATES

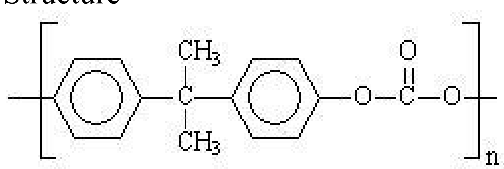
Some plastics are difficult to adhere to because of their low surface energy. Polytetrafluorethylene (PTFE), the basis for 'non-stick' cookware, has a surface energy of 18 dynes/cm(1). Most plastics are under 50 dynes/cm while aluminum, an easier substrate to adhere to, is closer to 825 dynes/cm. Surface energy is a thermodynamic effect of how a liquid will 'wet out' on a surface. Low surface energy materials, like polyethylene, do not allow a liquid adhesive to easily 'wet out' on its surface. Adhesion chemistry tells us that the better an adhesive can 'wet out' on a substrate the more surface area it can cover and allow more reactive groups to interact, making a stronger bond. Better 'wet out' also provides a means for greater penetration into the substrate to fill in those peaks and valleys found in the surface of a metal or plastic, allowing for better adhesion due to a mechanical interlock.

Table 1. Typical Surface Energy Dyne Levels (9)

Substrates	**Dynes/cm**
Polymethylmethacrylate	38
Polycarbonate	46
Polyamide	33-46
Polysulphones	41
Polyetherimide	40-45
Polyimide	40-50
Polyurethane	43
Aluminum	825
Titanium	>250
Stainless Steel	700-1100
Silicone Elastomer	24

Depending on the industry, some substrates are more common than others. A large growth area for polycarbonate is medical devices(2). Because of the established molding operations, ease of molding, and light weight, device manufacturers are incorporating it in many new devices. Polycarbonate can be found in applications from blood reservoirs for medical applications to automotive headlamp housings. Polycarbonate is often chosen for it excellent biocompatibility track record, high impact strength, and dimensional stability. For our experiment we looked at Bayer's Makrolon 2658-1112, which is a general purpose, FDA-Quality Grade polycarbonate without an internal mold release additive.

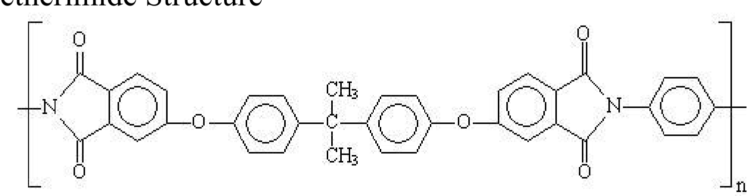
Figure 1. Polycarbonate Structure



Polyetherimides(PEI) are showing up in a number of industries including aviation and automotive. It can be found in automotive temperature sensors, medical connectors, flex circuitry, and circuit boards. GE Plastics, Ultem®, has become synonymous with the chemical name. This material is well suited for extreme service conditions, as it retains its excellent tensile, impact strength, and ductility properties at 190°C, high glass transition temperatures of 215°C, high volume resistivity, flame resistance, radiation and chemical resistance. Its surface energy is 52 dynes/cm makes it difficult for an adhesive to wet out onto the surface. We looked at GE Plastic Ultem 1000.

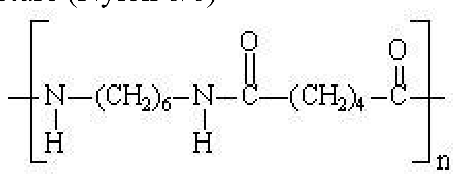
Figure 2. Aircraft cockpit showing Polyamide flight controls, PMMA displays, and polycarbonate & PEI flight consoles. Silicone adhesives can be used to seal the various components.

Figure 3. Polyetherimide Structure



Polyamide or its more common tradename, Nylon® is another common plastic with low surface energy, although slightly higher than Polycarbonate. It is probably the most diverse thermoplastic in its various applications and industries and can often be found in medical tubing, automotive wire harnesses, reservoirs, aviation control knobs, and even cable ties . Nylons have great wear, chemical and thermal resistance, and are inexpensive. Nylon 6/6 and 6 are the most common types with the numbers referring to the number of methyl groups occurring on each side of the nitrogen atom. A Dow Vydyne ECO315, Q3211-(RED) was used for these experiments.

Figure 4. Polyamide Structure (Nylon 6/6)



If you are a serious golfer, most likely you have titanium shafts on your golf clubs. Because of their favorable strength to weight ratio, they have become a staple in the orthopedic, aerospace and aircraft industry. Titanium also has excellent corrosion resistance to moisture and many acids and bases. Because of the nature of its protective oxide film it is erosion and cavitation resistance, twenty times more than copper-nickel alloys. Some applications require the use of an adhesive capable of bonding metals such as stainless steel, aluminum, or titanium. Examples range from the bonding of metal housings and turbine blades in aircraft engines and components, to sealing pacemakers. Titanium and stainless steel are often chosen for their strength, durability, and proven biocompatibility, whereas aluminum can be easily processed through molding, casting, or machining.

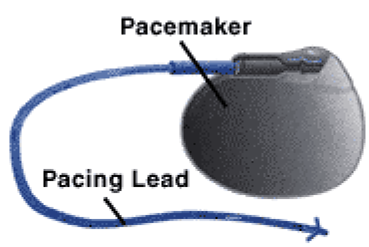
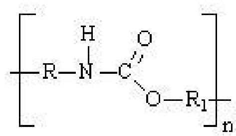


Figure 5. Generic Pacemaker and lead. Silicone adhesives can seal the lead to the pacemaker housing which is titanium.

Figure 6. Titanium turbine blades during processing and fabrication.

Polyurethane is certainly one of the most common substrates in use. From catheters to gaskets on boat engines to anesthesia masks to medical tubing to roller skate wheels, its excellent abrasion and chemical resistance make it a popular choice. Polyurethanes can be modified for different durometers depending on the application requirements, but retains excellent impact strength at low temperatures. We used a Dow Pellethane 2103-55D, a very common polyurethane, for these experiments.

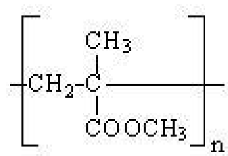
Figure 7. Polyurethane Structure



Polymethylmethacrylate (PMMA), more commonly referred to as Acrylic can be found in various applications, including aircraft windshields and aviation instrumentation, to lawnmower covers, to blood pumps and filters. Acrylic, also known as plexiglass®, is known for its excellent clarity and weatherability, often used in outdoor applications where non-yellowing or embrittlement is critical. Silicones can be used to provide a seal around the windshield. We used CYRO Industries Cyrolite G20 100.

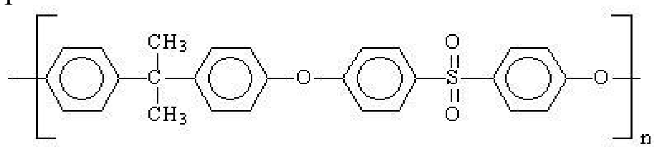
Figures 8. PMMA aircraft windshields are chosen for their excellent clarity and non-yellowing properties in outdoor environments.

Figure 9. Acrylic Structure



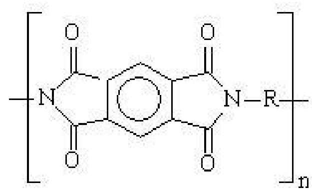
Polysulphones are very stable chemically and mechanically and have excellent thermal, electrical and creep resistant properties over a wide temperature range. Weathering is poor but can be improved greatly with selected pigments. This material is common in housings and reservoirs, aerospace, automotive, as well as components in business machines where good high temperature durability and electrical properties are important. Unfilled Polyethersulphone has a useful life of 4-5 years at 200°C, or approximately 20 years at 180°C. With reinforcing fibres, such as glass and carbon, very demanding applications can be met such as continuous performance under stress above 200°C.

Figure 10. Polysulphone Structure



DuPont High Performance Materials is a worldwide supplier of Kapton® polyimide film. Kapton® has more than 35 years of proven performance as the flexible material of choice in applications involving very high, 400°C (752°F), or very low, -269°C (-452°F) temperature extremes. Kapton is used in a wide variety of applications such as substrates for flexible printed circuits, transformer and capacitor insulation and bar code labels (3).

Figure 11. Polyimide Structure



3. MATERIALS

3.1 Primers

Primers have become a necessary evil for adhering to difficult substrates. Although often needed to aid in adhesion, this does add another step to the process. Silane primers are used to promote adhesion between two non-bonding surfaces. These primers are used with silicone adhesives but they can be used with other types of adhesives like epoxies. The primers usually consist of one or more reactive silane, a condensation catalyst and some type of solvent carrier. The reactive silane typically have two different reactive groups; one that is compatible with the substrate and the other with the adhesive. Some types of groups may be hydrophilic like a silanol (Si-OH) group or hydrophobic like a 1-octenyl group. These different groups form a compatible interface between the incompatible substrates and promote adhesion. The reactive silanes are usually added as moisture sensitive alkoxy silanes and, in the presence of water and a condensation catalyst, form the priming surface.

The reactive species are typically in concentrations of 5% to 20% in solvent. The main job of the solvent is to dilute the reactive species, the silanes and the condensation catalysts, on the surface of the substrate and promote a very thin film of these reactive species. The silanes and the condensation catalysts are now in position to form a very thin polymeric film on the surface of the substrate; the silanes begin hydrolyzing with atmospheric moisture and the condensation catalyst starts joining all the hydrolyzed groups into a primer film on the substrate. Some condensation catalysts, like organotitanates, are part of the primer film and also help promote adhesion.

Theoretically, the best primer film is a mono-molecular layer with the compatible groups facing the substrate and the organic groups facing the organic silicone adhesive surface. In reality, these monolayers don't exist but compatible bi or tri-layers do. This illustrates the importance of thin primer films and the necessity of solvent carriers in the primer formulation. Thick, overly primed surfaces tend to build chalky primer films that can be points of adhesive failure.

Application methods range from just wiping the primer on a surface to spraying the primer through a paint type sprayer. The primer is applied in a thin, uniform film, allowing the solvent to evaporate and the reactive groups to hydrolyze and condense into a film. The important considerations are a uniform film with no pooling or fisheyes. After the solvent evaporates there must be a minimum humidity in the air, typically from 30% to 60%. An excess of water will slow or stall the condensation. The usual recommended minimum time to permit the primer to cure is 30 minutes; this is the time from application to usage. It is possible to accelerate the primer cure process with heat from $35^{o}C$ to $80^{o}C$ but careful experiments must be performed to assure the primed adhesion doesn't suffer from this process. The primed surface should last a long time provided it is protected from contamination or abrasion.

The primers are moisture sensitive and poor handling of the bottles can affect the primer's performance. If the bottles are opened repeatedly, efforts must be made to prevent the entrance of water into the bottle. Humid room air must be displaced with either dry air or inert gases like nitrogen. Another method is to package the primer in the smallest size practical; this minimizes the number of times this particular bottle is opened. Another consideration during application is the build-up of residues on the applicators or spray heads. With time, the primer does form a chalky residues and this residue can be transferred to parts by using old applicators. Spray heads can be partially or completely obstructed by this residue. Some controls are required during application of primers on the production floor, such as changing applicators periodically during the day or inspecting spray heads every day.

While some simple cautions are required for working with silane primers, the result can be greatly increased adhesion of previously non-bonding surfaces. All that is required is some careful experiments initially and use of systematic manufacturing procedures to ensure successful priming applications.

To promote adhesion to novel substrates, a unique primer was developed called SP-270. It contains a proprietary blend of silanes, catalysts and solvents with a low surface energy to provide better wet out to the substrate surface. This unique blend also increases the wet out between the silicone adhesive and primer layer.

3.2 Treatment

The "difficult" substrates such as polycarbonate, polysulphone, polyetherimide, and polyimide, showed little improvement in tensile strength even when cleaned and primed. Various other techniques such as abrasion or solvent etching were evaluated, but modification of the bonding sites was more effective by flame treatment. Flame treatment of the substrate uses a propane flame from a torch to oxidize the surface of the substrate resulting in a high energy surface which is conducive to bonding. The flame generates excited species (radical oxygen molecules) which attack the polymer surface. Care must be taken not to over-heat the surface and cause damage; a cooler flame would be the better solution to prevent damage to the polymer. Analysis indicates the presence of alcohol, acidic and carbonyl groups present on the surface of the polymers. Flame treatment may also oxidize any hydrocarbon type contaminant. Plasma Treatment, or the deposition of specific reactive groups on the surface of the substrate, can also improve bondability and adhesion, however this method was not evaluated as part of this study. After treating and priming a substrate, the resulting bond is generally stronger.

3.3 Adhesive

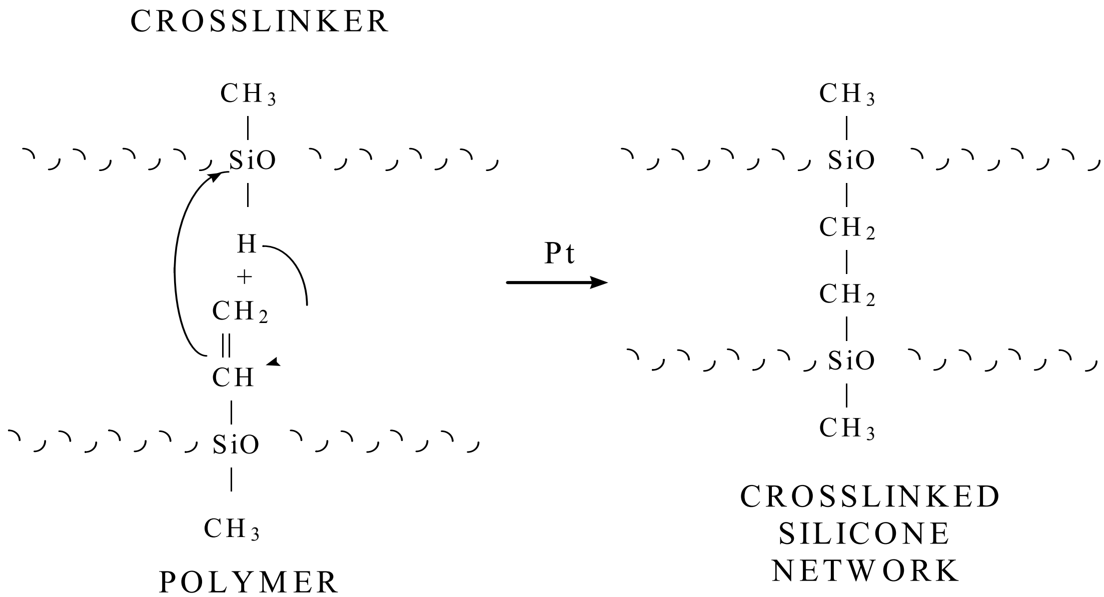
R31-2186, a fast-cure addition-cure adhesive(4), was used with this primer.

Table 2. R31-2186 Typical Properties

Viscosity, cP, 25^{o}C	80,000 cP
Work Time, hours, 25^{o}C	2 hours
Cure Time, 150^{o}C	15 minutes
Mix Ratio	10:1
Specific Gravity	1.10
Durometer, Type A	A-30
Tensile	900 psi
Elongation	600 %
Tear	70 ppi

The cure mechanism of this addition-cure system, involves the direct addition of the hydride functional crosslinker to the vinyl functional polymer forming an ethylene bridge crosslink.

Figure 12. Pt Cure Mechanism



Because this mechanism involves no leaving group, un-like the one-parts, these systems can cure in closed environments.

Most platinum systems can fully cure at room temperature in twenty-four hours or can be accelerated with heat. They can be partially cured, tack-free, with heat and packaged. Curing will continue in the sealed package with no adverse effects. Special care to eliminate the presence of contaminants that might have a negative impact on the catalyst may be necessary (4).

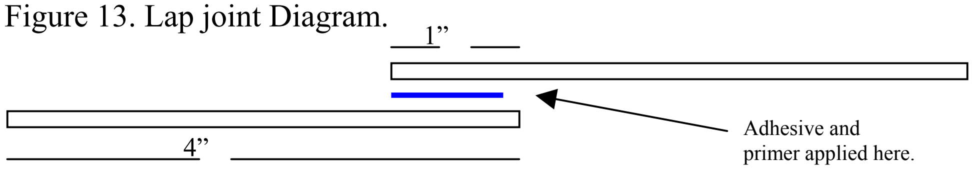
4. TESTING PARAMETERS

Each substrate of choice was cut into a lap shear configuration, 1 inch wide by 4 inches long. Six strips of each substrate were prepared to make 3 test panels. Panels were cleaned with isopropanol to remove dirt, grease or particulates. SP-270 was added to one square inch area on one end of each lap panel as described above and let to sit for at least 30 minutes. A bond thickness target of 5 mil (0.005in) was used for applying the R31-2186 to the primed area of the panels. The two panels were pressed together forming a sandwich (See Figure 13). We made sure not to overtly apply too much pressure over the bond surface. Sandwiched panels were placed in an air-circulating oven set at 70?C for a one hour cure. ASTM D-1002, Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading, was used as our test method reference.

“Difficult” substrates were flame-treated then primed with SP-270 silicone primer. The difficult substrates showed little improvement in tensile strength even when cleaned and primed. Difficult substrates were treated by passing a propane torch over the surface of the substrate. Care was taken to not damage or degrade the substrate due to excess localized heat.

The equipment used to test for lap shear value was an ISTRON Model 1011 with MTS data acquisition and 1000-lb load cell installed.

Figure 13. Lap joint Diagram.



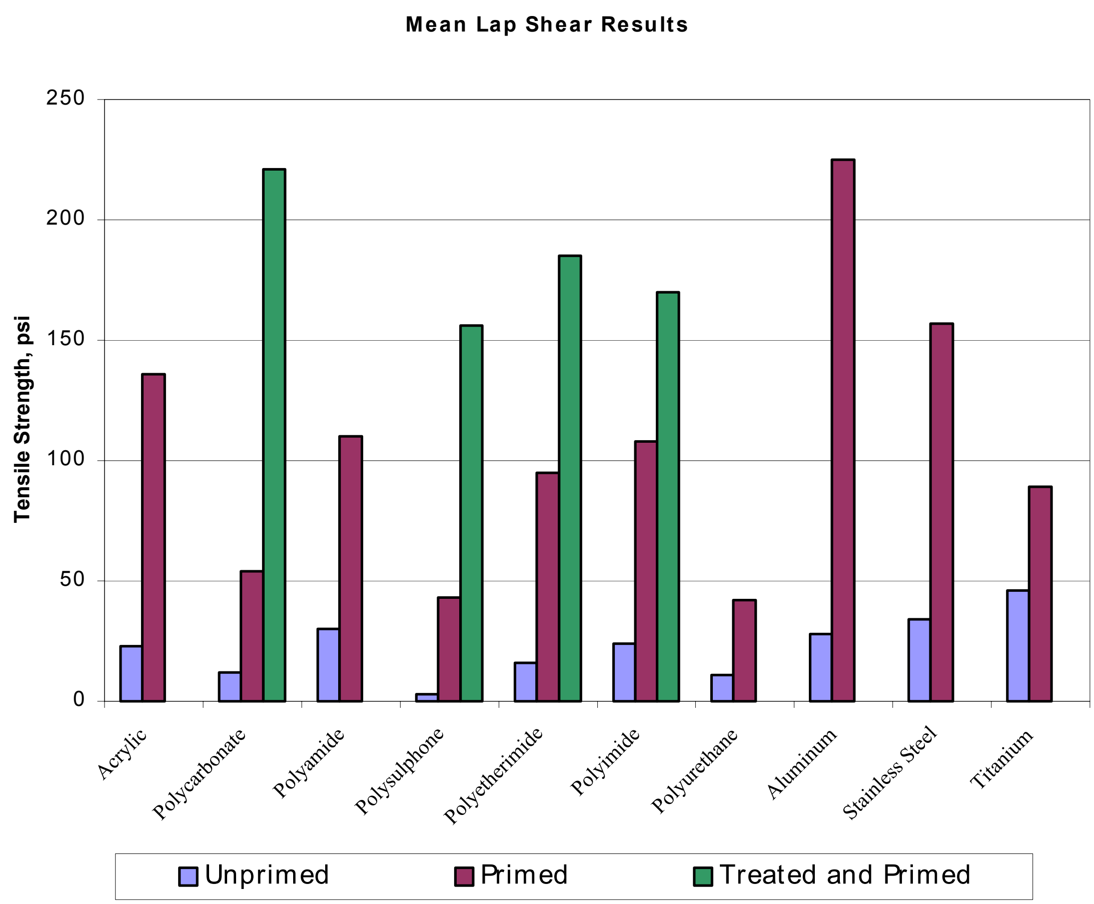
5. RESULTS

Table 3. Substrate Test Results

Substrate	Unprimed, psi		Primed, psi		Treated and Primed, psi	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
Acrylic	23	5	136	31	-	-
Polycarbonate*	12	5	54	13	221	35
Polyamide	30	7	110	41	-	-
Polysulphone*	3	1	43	7	156	2
Polyetherimide*	16	12	95	22	185	45
Polyimide*	24	0	108	22	170	70
Polyurethane	11	5	42	23	-	-
Aluminum	28	16	225	60	-	-
Stainless Steel	34	6	157	70	-	-
Titanium	46	18	89	7	-	-

* = Difficult Substrates Flame Treated

Chart 1. Mean Lap-Shear Results



6. CONCLUSION

The mechanisms of failure in adhesively bonded joints are usually substrate failure, adhesive failure or cohesive failure. Substrate failure is the fracture or internal failure within the substrate, indicating that the bond is stronger than the substrate. Adhesive failure is the interfacial failure between the adhesive and the substrate. It indicates a weak-boundary layer often from improper surface preparation or adhesive choice. Cohesive failure is the internal failure of the adhesive itself. This indicates that the strength of the bonded materials is greater than the strength of the adhesives own physical properties. Usually, the failure of joints is neither completely cohesive nor completely adhesive. Measurement of the success of a particular joint is based on the relative percentage of cohesive failure to adhesive failure (7).

For this silicone adhesive/primer system, mostly cohesive failure with all the primed and treated substrates was observed. For most applications requiring a hermetic seal or a bond that can be reworked or repaired as necessary, this is ideal. Although the lap-shear strength is lower with some substrates, such as Titanium and urethane, for applications requiring the most basic adhesion these adhesive systems would still work. The percentage of adhesion failure versus cohesive failure in the bond line is usually higher for these materials. Untreated and unprimed materials showed a tendency to exhibit mostly adhesive failure. While priming or treating a substrate does add an extra step to the manufacturing process, when working with unusual or difficult substrates, it may often be necessary. Future plans are to develop a primerless system for these substrates and to continue to find and develop new adhesives/primers that adhere to difficult substrates. Choosing the most effective adhesive system, technology, and process is the key to a winning project.

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Kyle Rhodes is the Senior Technical Sales contact for our Atlantic Coast & Canada Territory for NuSil Technology, the largest privately owned silicone manufacturer in the United States. Kyle has all adhesives background from his eight year career in both silicones and acrylates. Kyle has a Masters degree in Chemistry.

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Bill Riegler is the Product Director for Engineering Materials. Bill has been in the silicone industry for almost eighteen years with various R&D and technical sales positions at NuSil and the silicone division of Union Carbide which has become the OSi Specialties Group of GE Silicones. Bill has a B.S. in Chemistry from the University of California at Santa Barbara and a Masters in Business from Pepperdine University.

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Rob Thomaier is the Research Director at NuSil Technology. He has been in the silicone industry for twelve years, working in the R&D lab at NuSil Technology. Rob has a BS in Chemistry from UCLA.

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Henry Sarria is a R&D Technician at NuSil Technology. He has been involved with testing and statistical research for sixteen years. Henry has a BS in Mechanical Engineering from UC Santa Barbara.