Creative Partners in a Material World

Adhering to Difficult Substrates with Silicone Adhesives

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

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INTRODUCTION

Adhesive technology is equal parts chemistry and ‘black magic’. Because there are so many different substrates, each adhesive can not be actually tested before hand on each and everyone. However, by testing on some novel substrates, or difficult to adhere to, inferences can be made which can narrow the choices of adhesives.

We can define adhesion as the chemical bonding of two substrates. Substrates that have reactive groups available for bonding like OH groups on glass and aluminum make this chemical bond easier. Substrates with nothing to react to make adhesion difficult; graphite and PTFE. Multiple other substrates fit somewhere in-between.

SUBSTRATES

In general 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. Based on a standard, 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.

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 mold, and light weight, device manufacturers are incorporating it in many new devices. Polycarbonate can be found in applications such as blood reservoirs for medical applications, as well as 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. A general purpose, FDA-Quality Grade polycarbonate without an internal mold release additive.

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^{o}C, high glass transition temperatures of 215^{o}C, high volume resistivity, flame resistance, radiation and chemical resistance. Its surface energy is 52 dynes/cm making it difficult to stick to. We looked at two GE Plastic materials, Ultem 1000 and Ultem 2100-1000 with a loading of 10% SiO2.

Figure 1. Aircraft cockpit showing Polyamide flight controls, PMMA displays, and polycarbonate & PEI flight consoles. Silicone adhesives can be used to seal the various components.

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.

If your 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.

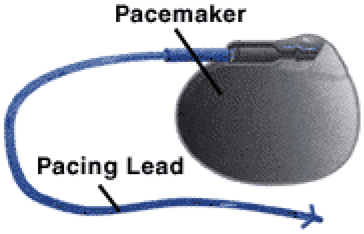


Figure 2. Generic Pacemaker and lead. Silicone adhesives can seal the lead to the pacemaker housing which is titanium.

Figure 3. 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.

Figure4. Polyurethane catheters and tubing

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. We used CYRO Industries Cyrolite G20 100.

Figures 5. PMMA aircraft windshields are chosen for their excellent clarity and non-yellowing properties in outdoor environments. Silicones can be used to provide a seal around the windshield.

Figure 6. PMMA blood filtration unit. Silicone adhesives can be used to pot the filters into the housing.

Figure 7. PMMA blood reservoir. Silicone adhesives can be used to seal the reservoir housings.

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^{o}C, or approximately 20 years at 180^{o}C. With reinforcing fibres, such as glass and carbon, very demanding applications can be met such as continuous performance under stress above 200°C.

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).

MATERIALS

Primers have become a necessary evil for adhering to difficult substrates. Although often needed to aid in adhesion, this does add another 'black-magic' 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 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 of 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 35C to 80C but careful experiments must be performed to assure the primed adhesion doesn't suffer form this process. The primed surface should last a long time provided it is protected from contamination or abrasion.

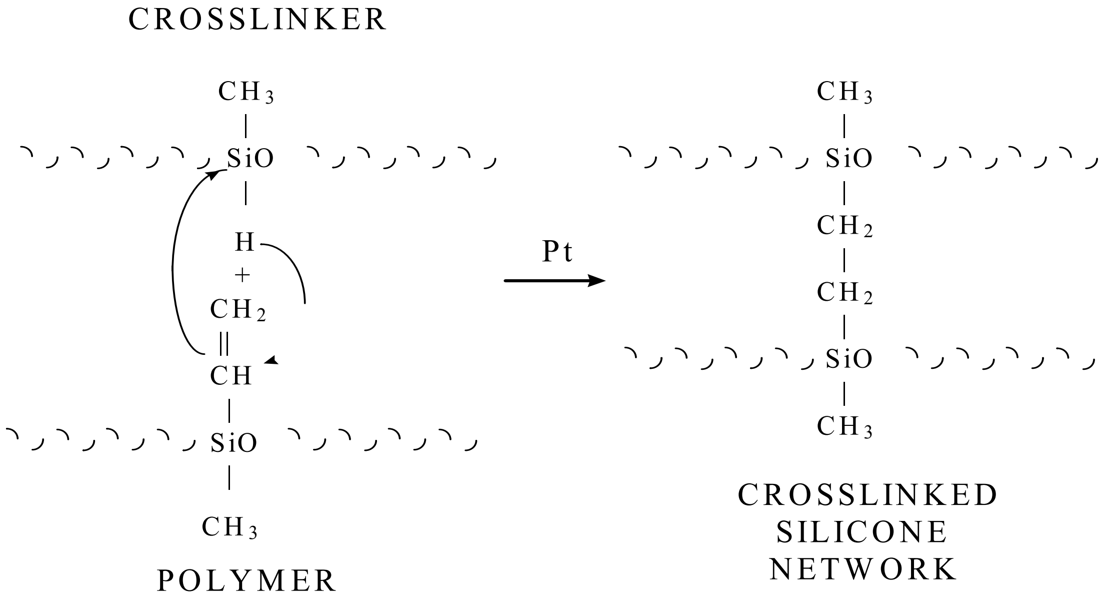
The primers are moisture sensitive and poor handling of the bottles can affect the primer's performance. If the bottles are opened repeatedly, efforts must be made to prevent the entrance of water into the bottle. Humid room air must be displaced with either dry air or inert gases like nitrogen. Another 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. R31-2186, a fast-cure addition-cure adhesive(4), was used with this primer. Typical properties:

R31-2186	Viscosity, cP, 25C	80,000
	Work Time, hours, 25C	2
	CURED-15 minutes@150C	Mix Ratio 10:1
	Specific Gravity	1.10
	Durometer, Type A	30
	Tensile, psi	900
	Elongation, %	600
	Tear, ppi	70

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.



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).

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 5ml(0.005in) was used for applying the

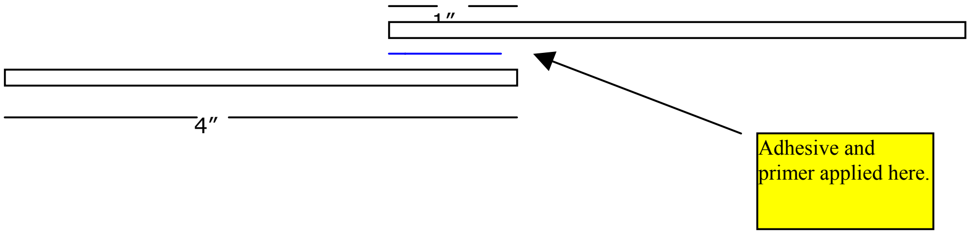
R31-2186 to the primed area of the panels. The two panels were pressed together forming a sandwich (See Figure 8). We made sure not to overtly apply too much pressure over the bond surface. Sandwiched panels were placed in an air-circulating oven set at 70?C for a one hour cure. ASTM D-1002, Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading, was used as our test method reference. This standard has been approved for use by the Department of Defense (5).

Difficult substrates were flame-treated then primed with SP-270 silicone primer. The difficult substrates are defined as the materials none of a variety of primers worked to improve adhesion, also none of a variety of adhesion techniques worked; cleaning with different solvents, partially dissolving the substrate with solvents, boiling in water or abrading the polymer surface. 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 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. The surface is then primed. After priming, the material can be adhered (6).

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 7. Instron 5500 Series Tabletop models for 450 lb to 11,250 lb capacities. New model updating the 1011.

Figure 8. Lap joint.

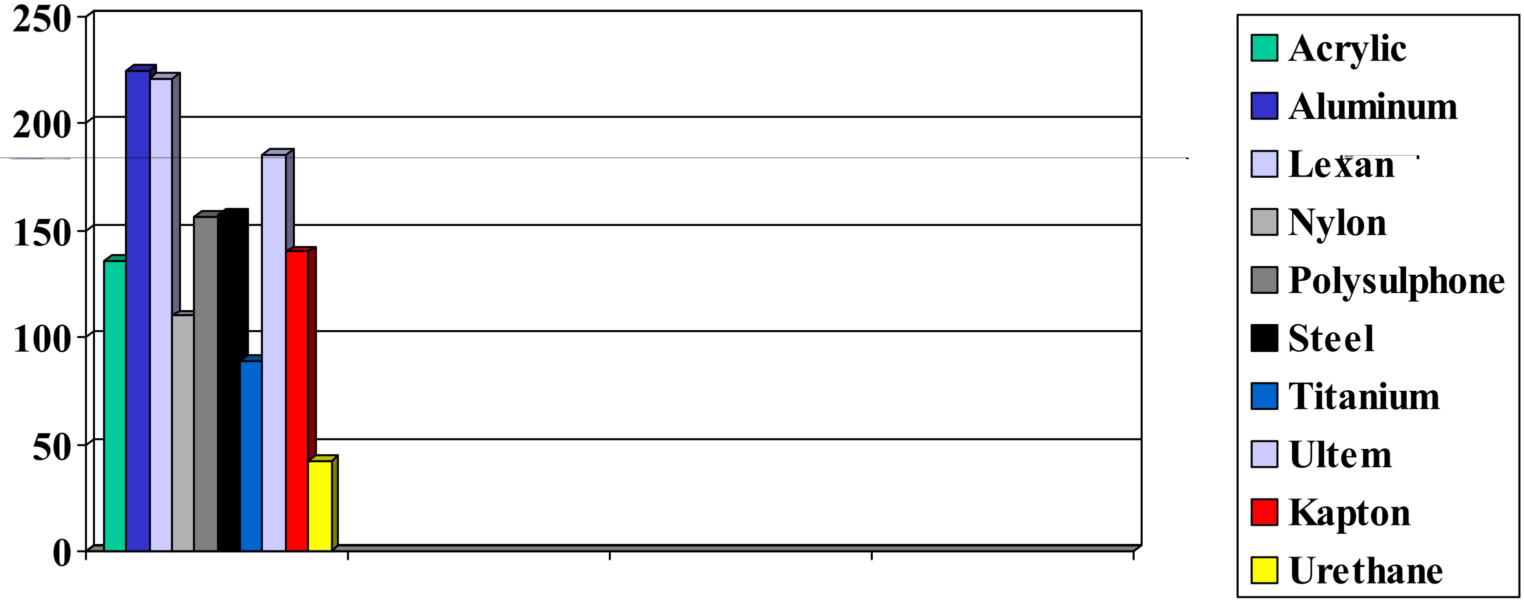


RESULTS

substrates	***low***	***medium***	***high***	***mean***	***median***	***st.dev. (s)***	***st.dev. (p)***	***c.o.v.***
Acrylic	101	147	161	136	147	31	26	23.02
Aluminum	156	256	262	225	256	60	49	26.50
Lexan Ж	185	223	254	221	223	35	28	15.66
Nylon	69	111	151	110	111	41	33	37.16
Polysulphone Ж	154	155	158	156	155	2	2	1.34
Stainless steel	82	168	220	157	168	70	57	44.49
Titanium	82	88	96	89	88	7	6	7.92
Ultem Ж	153	165	237	185	165	45	37	24.56
Kapton Ж	79	170	171	140	170	53	43	37.74
Urethane	28	30	69	42	30	23	19	54.60

Figure 9. All 100% cohesive failure. Flamed treated substrates denoted by the symbol Ж

Figure 10. Mean Lap-Shear Results



CONCLUSION

The two predominant mechanisms of failure in adhesively bonded joints are adhesive failure or cohesive failure. 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. This is the preferred goal of any adhesive, see Figure 11. 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).

Figure 11 Adhesive and cohesive failure of bonded joints. The adhesive is represented by the darker color .

For this adhesive/primer system to have 100% cohesive failure with all the substrates tried is fantastic. Although the lap-shear strength is not great with all substrates, such as Titanium and urethane, for applications requiring the most basic adhesion these materials would still work.

Given the breadth of substrates available, www.gepolymerland.com, provides information on over 30,000 thermoplastics and thermosets, and this doesn’t include the metals and various alloys, these adhesive/primer materials would make good starting points. NuSil Technology can also develop versions of these technologies for; healthcare, low outgassed space-grade material, optically clear, high temperature, fast-cure and fluoro silicone. 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. The automotive industry is one group specifically looking for these challenges (8).

(1) "Q&A Exchange", *Adhesives & Sealants Industry,* October/November 2001, Pg. 90.

(2) DuPont website, Dupont.com/kapton/

(3) "Product Focus", *Chemical Week,* February 2002, Pg. 48.

(4) "Accelerating Cure of Silicone Adhesives", SAMPE Technical Conference, November 2002, pg 1063-1077

(5) American Society for Testing and Materials (ASTM), D 1002-94, Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading.

(6) Adhesion Science ; John Comyn, Royal Society of Chemistry, Cambridge, UK; 1997.

(7) "Bonding Suggestions for the Piezoelectric Motor System", James Friend and Dan Stutts, University of Missouri-Rolla, Rolla, MO; 1995.

(8) "The Road More Traveled", *Adhesives Age,* March 2003, pgs12-13

Bill Riegler, is the Product Director for Engineering Materials for NuSil Technology, the largest privately owned silicone manufacturer in the United States. 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 Crompton.

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.

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Kyle Rhodes is the Senior Technical Sales contact for our Atlantic Coast & Canada Territory. Kyle has all adhesives background from his eight year career in both silicones and acrylates. Kyle has a Masters degree in Chemistry.