Silicone adhesives and primers on low surface energy plastics and high strength metals for medical devices

By Kyle Rhodes, European Sales Manager, Bill Riegler, Product Director-Engineering Materials, Rob Thomaier, Research Director, and Henry Sarria, R&D Technician
Presented by: Kyle Rhodes, NuSil Technology-Carpinteria, CA.

This paper will demonstrate the ability of silicone adhesives, with the aid of primers, flame treatment, or plasma treatment, to adhere to low surface energy plastics and to high strength metals.

WHITE PAPER

ABSTRACT

This paper will demonstrate the ability of silicone adhesives, with the aid of primers, flame treatment, or plasma treatment, 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, as well as with plasma treatment, 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.

1. INTRODUCTION

The medical device 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.

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

Table 1. Typical Surface Energy Dyne Levels (9)

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 to oxygenators to safety syringe needle hubs. 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.

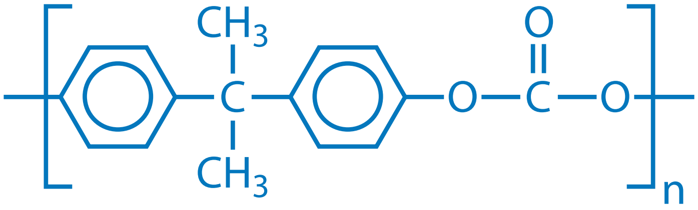


Figure 1. Polycarbonate Structure

Polyetherimides(PEI) are showing up in a number of industries including medical devices, 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/cm2 makes it difficult for an adhesive to wet out onto the surface. We looked at GE Plastic Ultem 1000.

Figure 2. Reservoir sealing. Silicone adhesives can be used to seal the various components. (Picture courtesy of Haemonetics)

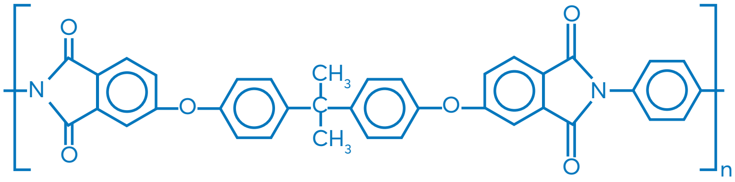
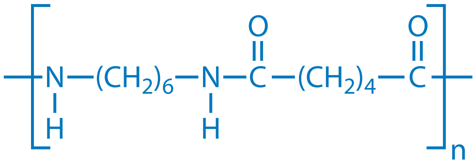


Figure 3. Polyetherimide Structure

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, wire harnesses, catheters, control knobs, and even cable ties. Nylons have great wear, chemical and thermal resistance, and are inexpensive. Nylon 6/6, 6, and 12 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.



$$\left[-\underset{\mathrm{H}}{\mathrm{N}}-(\mathrm{CH}_2)_6-\underset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-(\mathrm{CH}_2)_4-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}- \right]_n$$

Figure 4. Polyamide Structure (Nylon 6/6)

Titanium is often found in implantable devices, as pacemaker housings, and defibulators, to guidewires, to impeller blades in a minimally invasive device. 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 sealing or bonding metals such as stainless steel, aluminum, or titanium. 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 titanium pacemaker housing.

Figure 6. Staplers are often constructed from titanium or stainless steel, and internal components can be sealed with silicone adhesives. (Picture Courtesy of US Surgical)

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 210355D, a very common polyurethane, for these experiments.

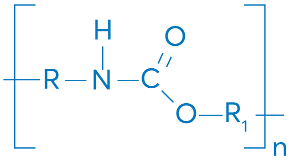


Figure 7. Polyurethane Structure

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 blood pump housing. We used CYRO Industries Cyrolite G20 100.

Figures 8. Acrylic Blood Pump/Filtering Units can be sealed with a silicone adhesive. (Picture courtesy of Haemonetics

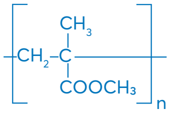


Figure 9. Acrylic Structure

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.

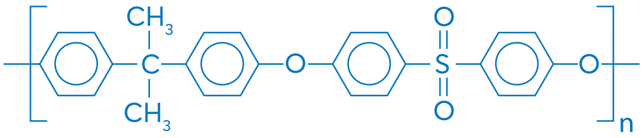


Figure 10. Polysulphone Structure

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, as well as catheter tubing.(3).

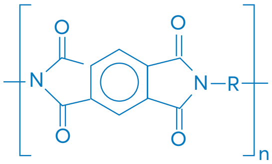


Figure 11. Polyimide Structure

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 1octenyl 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°C to 80°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. The flame may also burn off the adsorbed water on the surface which occupied the reactive groups on the 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. After treating and priming a substrate, the resulting bond is generally stronger.

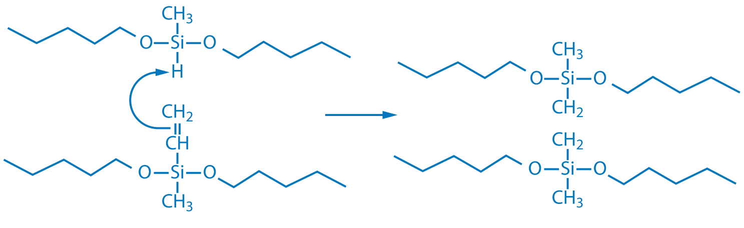
3.3 Adhesive

MED1-4013, a fast-cure addition-cure adhesive(4), was used with this primer.

Viscosity, 25oC	**80,000 mPa*s**
Work Time, 25oC	2 hours
Cure Time, 150oC	15 minutes
Mix Ratio	1:1
Specific Gravity	1.1
Durometer, Type A	A-15
Tensile	6.2 MPa
Elongation	6
Tear	11.3 kN/m

Table 2. MED1-4013 Typical Properties

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.



Polymer

Crosslinked Polymer Chain

Because this mechanism involves no leaving group, unlike 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). Materials to avoid are typically sulpher compounds, nitrile, and unreacted vinyl groups.

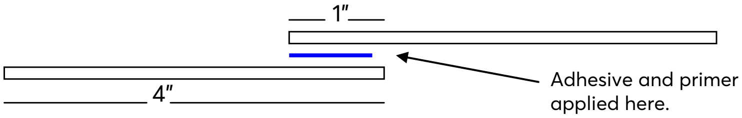
4. TESTING PARAMETERS

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 MED14013 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.

All substrates plasma treated were sent to Plasma Etch, Inc to be treated using their patented process. These panels were plasma treated at 38°C for 15 minutes at 350 Watts, using oxygen at 120 cm3/min as the plasma gas. These panels were then wrapped in plasma treated aluminum foil, vacuum-sealed in plastic and shipped back to NuSil Technology. Half of the surfaces of the plasma treated substrates were primed with NuSil Technology's SP-270 Silicone Primer, and half were left unprimed.

The equipment used to test for lap shear value was an ISTRON Model 1011 with MTS data acquisition and 454 kg (1000 lb) load cell installed.



Adhesive and primer applied here.

Figure 13. Lap joint Diagram.

5. 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	-	-

Table 3. Substrate Test Results

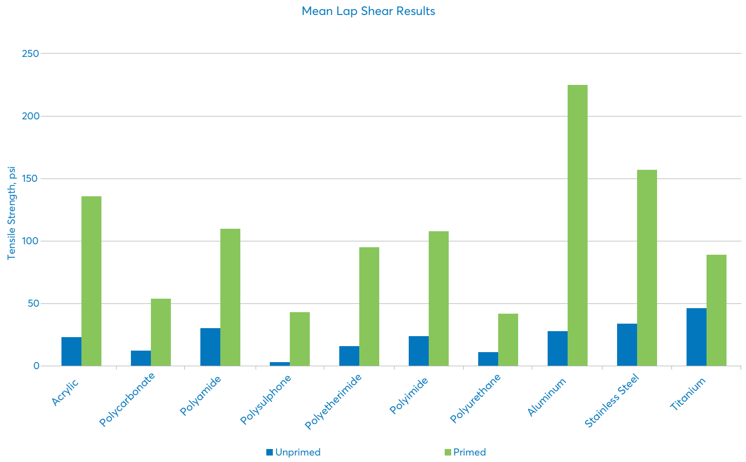


Chart 1. Mean Lap-Shear Results with Primed Results

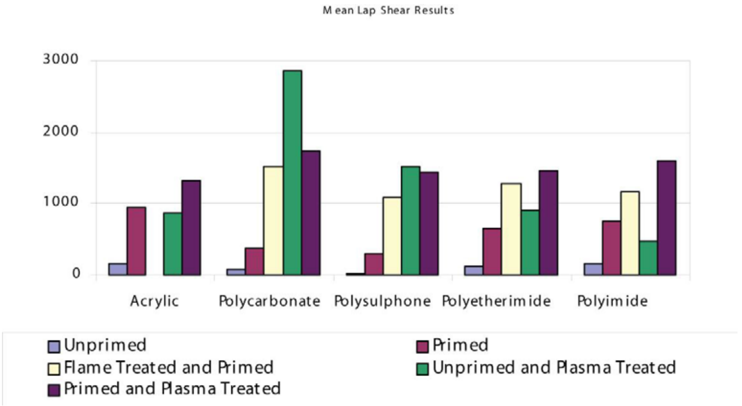


Chart 2. Mean Lap-Shear Results with Flame Treatment and Plasma Treatment Results

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.

The plasma treatment of a surface, when combined with a chemical primer, may provide the optimum tensile lap shear results on certain substrates, but as the data shows, there is no obvious way to develop a product without systematic bench testing to determine the best adhesive system and technology. Different variables, such as the type of gas used, temperature, and dwell time, may all have an impact on your process and results.

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.

7. References

(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) B. Riegler, "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) J. Comyn, Adhesion Science ; Royal Society of Chemistry, Cambridge, UK; 1997.
(7) J. Friend, D. Stutts, "Bonding Suggestions for the Piezoelectric Motor System", University of Missouri-Rolla, MO; 1995.
(8) "The Road More Traveled", Adhesives Age, March 2003, pgs12-13
(9) www.sabreen.com/surface_energies_of_polymers.html