

Choosing a silicone adhesive and treatment system

P. Peignot and K. Rhodes
Nusil Technology, Sophia Antipolis, France

As devices become smaller and bonds more critical, choosing the right adhesive system may be essential to the success of the device. This article investigates some adhesives and primers used to adhere difficult substrates

THE ADHESION PROCESS

The options are diverse for joining or sealing parts together. Because there are so many different substrates available, it is not possible for the supplier to test each adhesive on every substrate. However, by testing on some novel or difficult-to-adhere-to substrates, inferences can be made that can narrow the choices of adhesives and primers or other treatment systems. This article discusses some of the findings of a recent study.

Adhesion may be defined as the physical and chemical bonding of two substrates. Substrates that have reactive groups available for bonding such as hydroxyl groups (OH) or carbonyl groups (C=O) groups on glass, plastics and aluminium make this chemical attraction greater through van derWaals forces or weak hydrogen attraction. Substrates with limited available bonding sites such as acetal, Nylon 24 or polytetrafluoroethylene make adhesion difficult. Many other substrates fit somewhere in between.

Improving adhesion

Some plastics are difficult to adhere to because of their low surface energy. Typical surface energy dyne levels are shown in Table 1.^{1,2} Surface energy is a thermodynamic effect of how a liquid will “wet out” on a surface. Low surface energy materials such as polyethylene do not allow a liquid adhesive to easily wet out on its surface. Adhesion chemistry reveals that the better an adhesive can wet out on a substrate, the more surface area it can cover, which allows more reactive groups to interact and a stronger bond. Better wet out also provides a means for greater penetration into the substrate to fill in those peaks and valleys found on the surface of a metal or plastic, and allows better adhesion as a result of a mechanical interlock.

To improve adhesion to a specific substrate, silane adhesion promoters can be used to hydrolyse the surface of the plastic so that it readily accepts a silicone adhesive. The mechanism reacts in a similar way, whether the adhesion promoter is applied through a primer or contained within the adhesive as a self-priming adhesive. For example, with polycarbonate the most likely bonding site for the silane is through the reactive C=O group, which is proba-

bly stabilised by the aromatic phenyl groups (Figure 1). If this is compared with Nylon 6/6, the reaction is most likely through the carbonyl group only, but in this case the bonds may be slightly weaker because there are six carbon/hydrogen CH₂ groups between each carbonyl group (Figure 2). With Nylon 12 or Nylon 24, the number of bond sites within a given area would be spread to one bond site in every 12 groups or one bond site in every 24 groups, respectively, making the bonds more difficult to achieve.

Substrates	Dynes/cm 2
Polymethylmethacrylate	38
Polycarbonate	46
Polyamide	33- 46
Polysulphones	41
Polyetherimide	40-45
Polyimide	40-50
Polyurethane	43
Aluminium	45
Titanium	>250
Stainless steel	700-1100
Silicone elastomer	24

TABLE 1: Typical surface energy surface energy Dyne levels.

Primers

Primers have become a necessary evil in bonding. Although often required to aid adhesion, their use adds another step to the process. Silane primers are used to promote adhesion between two nonbonding surfaces. The primers usually consist of one or more reactive silanes, a condensation catalyst and some type of solvent carrier. The reactive silanes typically have two different reactive groups: one that is compatible with the substrate and the other that is compatible with the adhesive. Same types of groups may be hydrophilic such as a silanol (Si-OH) group or hydrophobic such as a 1-octenyl group. These different groups form a compatible interface between 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 the solvent in concentrations of 5-20%. The silanes and the condensation catalysts are deposited to form a thin polymeric film on the surface of the substrate. The silanes begin hydrolysing with atmospheric moisture and the condensation catalyst starts joining all the hydrolysed groups into a primer film on the substrate (Figure 3). Some condensation catalysts such as organotitanates are part of the primer film and help promote adhesion.

Theoretically, the best primer film is a monomolecular layer with the compatible groups facing the substrate and the organic groups facing the organic silicone adhesive surface. In reality, these monolayers do not 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.

Flame treatment for difficult substrates In tests, 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 and solvent etching have been evaluated, but modification of the bonding sites was more effective using flame treatment. Flame treatment of the substrate uses a propane flame from a torch to oxidise the surface of the substrate and results in a high-energy surface that is conducive to bonding. The flame generates excited species (radical oxygen molecules) that attack the polymer surface. The flame also burns off the adsorbed water on the surface that occupied the reactive groups located there. Care must be taken not to over heat the surface and cause damage; a cooler flame is the best 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 oxidise any hydrocarbon-type contaminant. Plasma treatment or the deposition of specific reactive groups on the surface of the substrate can also improve bonding and adhesion. After treating and priming a substrate, the resulting bond is generally stronger.

Curing systems

Typical silicone adhesive systems can generally be divided into two categories: one-part condensation (acetoxysilane) curing silicones

and two-part addition (platinum) curing silicones. The one-part condensation adhesives usually have good adhesion and rapidly skin over in thin band lines, but thick sections may take up to 3-5 days to achieve full cure. These systems cure in the presence of atmospheric moisture and release acetic acid on cure. This acetic acid byproduct helps increase adhesion in certain applications, but care must be taken with corrosion-sensitive substrates.

Some two-part addition-cure adhesives may need a primer to achieve the bond strength required for the application. One cures at room temperature in approximately 4-8 hours, but curing can be accelerated with heat to 3-5 minutes. Table 2 shows the typical properties of these two-part, platinum-cured adhesives.

The cure mechanism of this addition-cure two-part system involves the direct addition of the hydride functional crosslinker to the vinyl functional polymer forming an ethylene-bridge crosslink (Figure 4). Because this mechanism involves no leaving group, unlike the one-part curing silicones, these systems can cure in closed environments. Improving bond strength A study has been conducted into improving bonding strength with the use of a two-part platinum-cure silicone adhesive! The study compared the unprimed and primed substrates (Figure 5) and showed an increase of more than 250% in typical tensile strength when primed. The second phase of the study evaluated difficult-to-bond-to plastics. They were tested with no primer and a primer, flame-treated and primed, plasma treated, and plasma treated and primed. Acrylic, polyimide, polyamide, polyetherimide, and polysulphone materials were tested (Figure 6). The results showed that priming can give an increase of 250% or more in tensile strength, and the use of primer and plasma or primer and flame can often increase tensile strength by 600-2000%. On some plastics, using only plasma treatment gave a significant increase in tensile strength (polycarbonate achieved a 3000% increase), and with other plastics a moderate increase in tensile strength was seen (polyimide achieved 180% increase). The combination of priming and surface treatment showed a general increase from tensile strengths of <200 kPa (unprimed) to values over 1000 kPa.

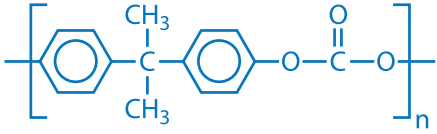


FIGURE 1: Polycarbonate structure.

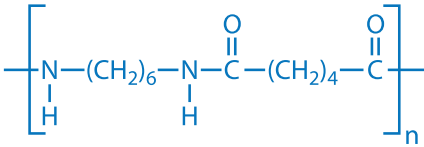


FIGURE 2: Polyamide structure (Nylon 6/6).

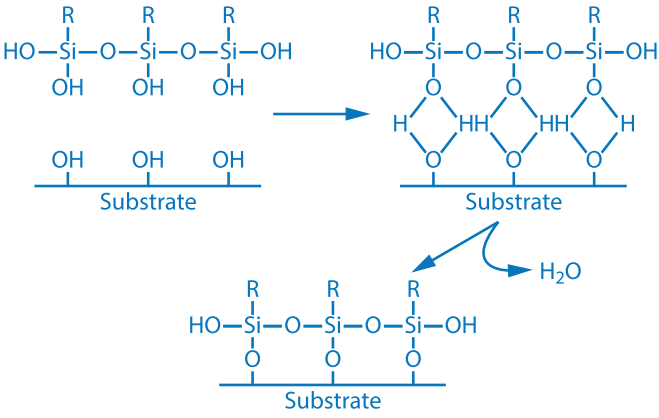


FIGURE 3: Primer mechanism showing condensation, hydrogen bonding and bond formation of a typical primer.

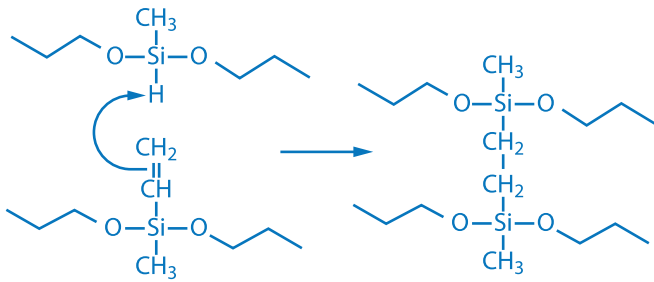


FIGURE 4: Platinum-cure mechanism.

	Adhesive I	Adhesive II
Viscosity 25 °C	80000 cP	80000 cP
Work time 25 °C	5 min	2 hours
Cure time	3-5 days at ambient conditions	3-10 min at 150 °C
Mix ratio	1 part	1:1
Speci gravity, density	1.07	1.10
Durometer Shore A	30	15
Tensile strength at break	3.8 MPa	6.2 MPa
Elongation at break	200 %	600 %
Tear strength at break	8.8 kN/m	11.3 kN/m

TABLE 2: Typical properties of two-part cure adhesives.

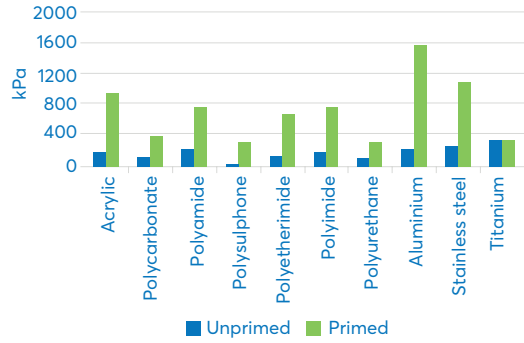


FIGURE 5: Mean lap-shear results of primed and unprimed substrates using an addition-cure adhesive.

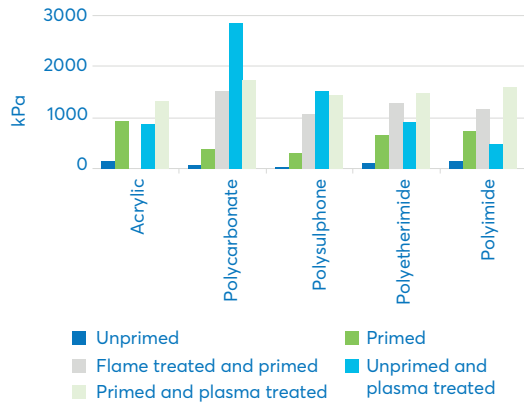


FIGURE 6: Mean lap-shear results for ame treatment and plasma treatment with an addition-cure adhesive.

CONCLUSION

Given the number of variables when developing a new medical device, selecting the best method of assembly requires a thorough understanding of the options that are available. Although priming or treating a substrate adds an extra step to the manufacturing process, it may be necessary when working with unusual or difficult substrates. Plasma treatment of a surface, when combined with a chemical primer, may provide the optimum tensile lap shear results on certain substrates, but 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 the process and results. Choosing the most effective adhesive system and process is the key to a winning project.

References

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