WHITE PAPER | September 2016

Advances in Adhesive Technology for Bonding Liquid Silicone Rubbers to Plastics and Metals

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ABSTRACT

LORD Corporation offers new adhesive solutions that effectively bond platinum-cured liquid silicone rubber (LSR) to various substrates directly in an injection or compression molding process. This technology does not require plasma treatment or other complicated and costly surface preparation steps. In this study, three new adhesive systems were tested to bond LSR to various substrates, including polycarbonate, thermoplastic elastomer, polyamide, and stainless steel. Parts were molded and peel tested. This process and product technology offers a number of benefits compared to existing technology, including enhanced design freedom, more robust processing, less surface preparation requirements, and environmental friendliness.

INTRODUCTION

Liquid silicone rubber (LSR) is used to produce a wide range of parts for many different markets. Some notable segments include medical devices, cookware, electronics, and personal electronic devices.[1] Silicone polymers exhibit many unique properties that other materials cannot achieve, combining rubbery flexibility with excellent thermal stability, durability, low surface energy, biocompatibility, soft feel, etc.[1,2] Because of its unique performance and relative ease of part manufacturing, the global LSR (silicone) market has seen rapid growth that is expected to continue.[3] As the market need for LSR expands, product designs are becoming more sophisticated and require bonding of silicone to other substrates, which can be challenging due to its ultra-low surface energy of around 20 mN/m and chemical resistance.[4]

Many different adhesives and primers for bonding silicones exist on the market today. Most of the commercial offerings are based on alkoxy silanes that contain functional groups that are appropriate for the curing mechanism used in the silicone. In this embodiment, solvated silane must be applied to the substrate followed by solvent evaporation and subsequent hydrolysis with atmospheric moisture to create silanols that bond to the substrate's surface. In order for bonding to occur, the substrate must contain hydroxyl groups.[5] The reaction kinetics of hydrolysis and bond formation are highly dependent on atmospheric moisture and temperature. This environment, especially in a manufacturing setting, can be very difficult to control. Furthermore, silanes must be applied as very thin coating (<1 micron) that is difficult to control and measure in a production environment. Most plastics require plasma treatment to create hydroxyl groups to promote silane bonding.

Because of all of the shortcomings with silane adhesive technology, there is a market need for silicone adhesives that are easier to use and more effective on various substrates. This study focuses on the evaluation of three adhesive technologies developed to improve upon existing silane technology. These adhesive were designed to bond a wide range of platinum-cured silicones to many substrates, eliminating the need for complicated surface pretreatment, precise environments, and difficult-to-control reaction kinetics.

EXPERIMENTAL SECTION

Materials

For this experiment, a representative spread of thermoplastic materials were gathered from various suppliers, and selected as substrates. These materials will be referred to by their generic designations: polycarbonate (PC), flame-retardant polycarbonate (PCFR), thermoplastic elastomer (TPE), and polyamide (PA). Stainless steel 304 with polished and grit blasted surface finishes was also included in this experiment.

Three LSRs were chosen, all of them were 70 durometer hardness silicones with very similar mechanical properties and curing profiles, and manufactured by three major silicone producers so that a range of commercial offerings could be evaluated. They are denoted as LSR 1, LSR 2, and LSR 3.

Three proprietary adhesives, developed by LORD Corporation, were included in this test and are denoted as LORD A, LORD B, and LORD C. LORD A is an aqueous hybrid whose primary solvent is water. LORD B and C are solvent-borne.

Plastic Molding

Plastic substrates were molded at LORD in a specially designed injection mold to produce plaques whose dimensions are 50 mm x 87 mm x 1.5 mm. Half of the plaque has a roughened surface texture that is defined as VDI-26, while the other half is a machined finish. Parts were injection molded on a Sumitomo SE100EV 100 ton electric injection-molding machine. Normal process conditions were chosen based on the mid points of the manufacturer's recommendation. No mold release was used. After molding, parts were stored in a typical lab environment (21°C / 50% RH).

Adhesive Application

The substrate was masked with Kapton tape such that only half of the test plaque would receive adhesive. In the case of the plastic substrates, adhesive was applied to the section with VDI-26 finish. Adhesives were applied with a Binks Model 95 siphon feed HVLP spray gun to a thickness of 10 to 15 microns. Immediately after spraying, parts were dried in a hot air convection oven at 50°C for 15 minutes. After removing from the oven, parts were stored at 21°C / 50% RH for up to 4 hours before overmolding with LSR.

LSR Molding

LSR silicones are supplied as two separate reactive components that are mixed before molding. Both sides of silicone were mixed in a Kitchen Aid mixer at low speed for five minutes. The substrate was overmolded with LSR in a Wabash MPI G30H-18-BX compression press that was heated to 125°C. In each cycle, three pieces of substrate were placed into a 150 mm x 150 mm x 5 mm mold, along with 150 grams of LSR. The parts were then molded at 20 tons of pressure for 5 minutes. Figure 1 shows an example of the test pieces used and the mold used to create LSR test specimens. After 5 minutes, parts were carefully removed and allowed to cool to room temperature before being separated with a utility knife. Strips 25 mm wide were cut into the LSR for peel testing.

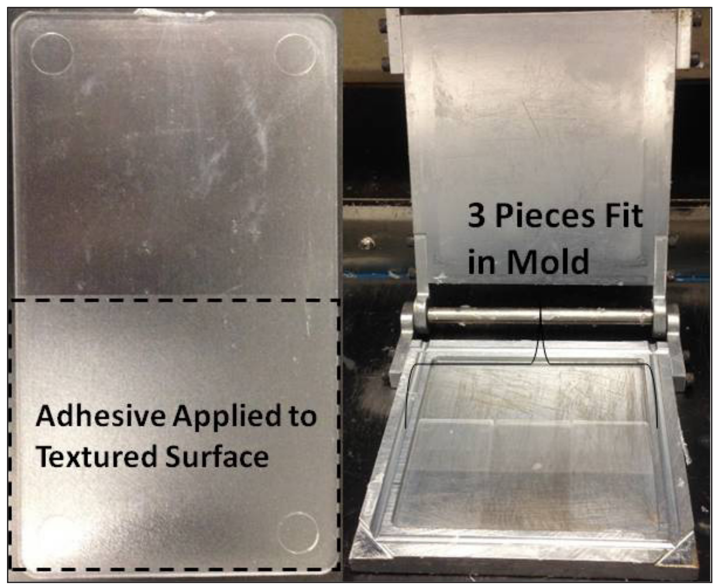

Figure 1: An example of a plastic test specimen is shown on the left, and the compression mold is shown on the right.

Peel Testing

After at least 24 hours after molding, parts were peel tested at 180 degrees at 300 mm/min in an Instron Model 3365 tensile tester utilizing a 1 kN load cell. Peel strength and failure modes were recorded. An example of a molded test specimen is shown in Figure 2.

DISCUSSION

Failure Modes

In addition to peel strength, failure mode analysis is key to understanding product performance and bonding mechanism. For the results reported in this paper, the test area is a 25 mm strip that is approximately 45 mm long. A schematic of the test specimen is shown in Figure 3. Failure mode is reported as a percentage of this area based on its state after testing is carried out. Failure modes were divided into four categories, each one is described below with depictions given in Figure 4.

Thick Rubber Retention: the entire thickness of the silicone rubber is intact. This is the most desirable failure mode and means that the strength of the adhesive exceeds the strength of the silicone.

Thin Rubber Retention: a thin layer of rubber is retained on the substrate. This means that the silicone rubber itself failed, but failed at a layer that is close to the adhesive interphase. This failure mode can be influenced by the performance of the adhesive, and can be caused, for example, if the adhesive retards or interrupts the silicone curing mechanism. A small amount (<20%) of thin rubber failure is normal and unavoidable in this test method.

Substrate-to-Adhesive Failure: the adhesive does not stick to the substrate, delaminating from it during testing and usually sticking to the silicone.

Rubber-to-Adhesive Failure: the adhesive does not stick to the silicone and remains on the substrate. This failure mode indicates that reaction between the adhesive and silicone did not occur.

Figure 2: The photo above shows a TPE test specimen that has been overmolded with LSR before testing for peel strength. The strip shown is 25 mm wide.

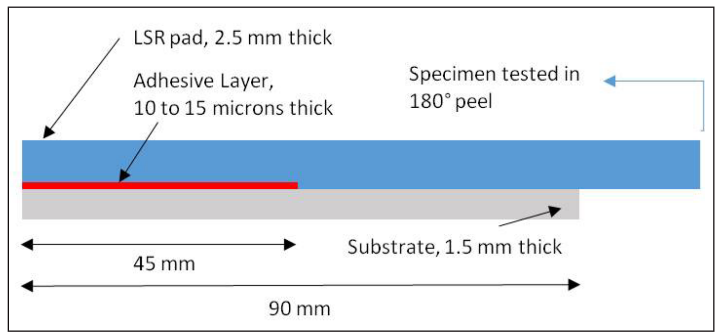

Figure 3: Schematic view of the cross section of a typical test specimen.

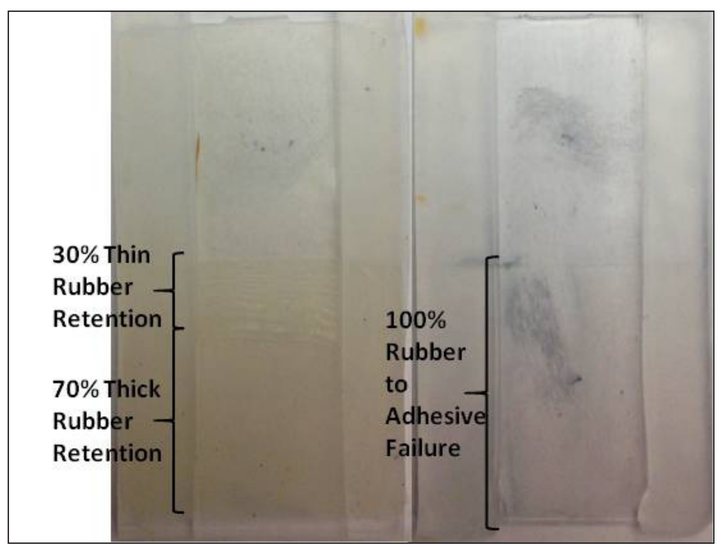

Figure 4: Examples of three failure modes are shown above. Failure mode is determined by the tested area and quantified based on a percentage of the test area.

Adhesive Bonding to Multiple LSRs

The first test evaluated the effectiveness of each adhesive on three different representative LSRs of similar durometer from three major silicone producers. Each LSR was mixed, per the manufacturer recommendation, at a 50:50 ratio of A to B and cured via addition reaction catalyzed by platinum. The same process conditions (125°C for 5 minutes) were also used for all three silicones. Bonding data is shown in Table 1 and charted in Figure 5.

The results show that all three adhesives bond completely to LSR 1 with high peel strength values of greater than 70 N/cm, at which point the silicone fails. This sample group did not show any evidence of failure to either the substrate or the silicone, indicating good adhesive performance. With LSR 2, excellent adhesion was achieved with adhesive A and C. However, adhesive B showed complete rubber-to-adhesive failure, indicating that no bonding occurred between the chemistry used in the adhesive and that of the silicone. Mixed results were achieved when bonding to LSR 3, with adhesive A and C continuing to achieve full bonding, but adhesive B showed relatively low peel strength and a large amount of thin rubber failure.

To help understand bonding mechanism and understand why LORD B adhesive failed to bond to LSR 2, LSR 1 and 2 were analyzed for chemical differences. Data is outlined in Table 2. It was discovered that LSR 2 contained around 4% of low molecular weight silicones, while none were detected in LSR 1. Also, LSR 1 contained more vinyl and silicon hydride functionality than LSR 2. Considering that the LSR adhesive technology utilizes functional groups on the LSR to create covalent bonds, a higher concentration of those groups should theoretically lead to stronger adhesion. During LSR molding, low molecular weight silicone constituents are well known to bloom to the surface, which can further interfere with adhesion. Both of these findings explain why LSR 2 is more difficult for LORD B to bond. Future work includes running this same analysis on LSR 3 to validate this theory.

Adhesive	Peel Strength (N/cm)	Thick Rubber Retention (%)	Thin Rubber Retention (%)	to Adhesive Failure (%)	Rubber to Adhesive Failure (%)
LSR 1					
LORD A	70	95	5	0	0
LORD B	77	98	2	0	0
LORD C	79	83	17	0	0
LSR 2					
LORD A	64	88	12	0	0
LORD B	0	0	0	0	100
LORD C	74	73	28	0	0
LSR 3					
LORD A	64	80	20	0	0
LORD B	49	20	75	0	5
LORD C	73	90	10	0	0

Table 1: Adhesion results and failure modes of three adhesive systems that were used to bond three LSRs to polycarbonate.

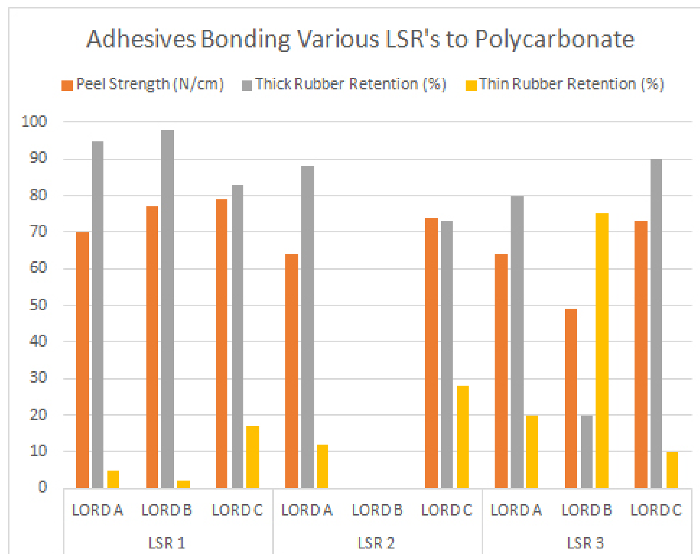

Figure 5: This chart shows peel strength and rubber retention of three adhesives with three silicones, all on polycarbonate.

Measurement/Component	LSR 1		LSR 2	
	Side A	Side B	Side A	Side B
High Molecular Weight Fraction (>25000 Mn)	100%	100%	95.7%	96.4%
Low Molecular Weight Fraction (<2000 Mn)	0%	0%	4.30%	3.60%
Main Polymer (PDMS)	98.0%	95.1%	98.9%	96.0%
Vinyl on Chain End	0.44%	0.55%	0.43%	0.49%
Vinyl in Backbone	1.56%	0.30%	0.72%	0.34%
Total Vinyl	2.00%	0.85%	1.15%	0.83%
Silicon Hydride	0%	4.10%	0%	3.20%
* All percentages expressed as weight - %				

Table 2: Molecular weight and functional analysis of LSRs.

Adhesive Bonding to Multiple Substrates

To further understand the applicability of these adhesive technologies, they were evaluated on multiple substrates, which included polycarbonate (PC), flame-retardant polycarbonate (PCFR), thermoplastic elastomer (TPE), 304 stainless steel (SUS) with polished and grit blasted surface finishes (25 to 50 micron blast profile), and polyamide. In this experiment, LSR 1 was used on all of the substrate and adhesive combinations and results are shown in Table 3 and Figure 6. A rubber retention of 100% is the best possible result, meaning that the adhesive bond exceeds the strength of the silicone. LORD A gave nearly 100% rubber retention to all substrates with the exception of a small amount of adhesive-substrate failure on polyamide.

Further unpublished experiments conducted at LORD have shown that residual moisture content in polyamide can cause this type of failure, so pre-drying the polyamide or applying the adhesive in a dry-as-molded state is critical to achieve a good bond. LORD B fully bonded to all substrates except for polished SUS. However, it had no problems bonding to grit-blasted SUS, which is a common method to prepare metals for adhesive bonding.[6] Grit blasting improves adhesion by increasing the surface area and creating areas for mechanically locking the adhesive onto the substrate.[6] LORD C provided complete adhesion to all substrates except for polished SUS and polyamide, in which case they completely failed to bond to the substrate.

Substrate	Peel Strength (N/cm)	Thick Rubber Retention (%)	Thin Rubber Retention (%)	Substrate to Adhesive Failure (%)	Rubber to Adhesive Failure (%)
LORD A					
PC	70	95	5	0	0
PCFR	78	70	25	0	5
TPE	67	100	0	0	0
304 SUS (grit blasted)	82	100	0	0	0
304 SUS (polished)	77	100	0	0	0
Polyamide	64	90	0	10	0
LORD B					
PC	77	98	2	0	0
PCFR	85	95	5	0	0
TPE	69	100	0	0	0
304 SUS (grit blasted)	71	100	0	0	0
304 SUS (polished)	74	75	0	25	0
Polyamide	67	100	0	0	0
LORD C					
PC	79	83	17	0	0
PCFR	80	85	15	0	0
TPE	83	85	15	0	0
304 SUS (grit blasted)	71	100	0	0	0
304 SUS (polished)	0	0	0	100	0
Polyamide	0	0	0	100	0

Table 3: Silicone adhesives were tested on multiple substrates.

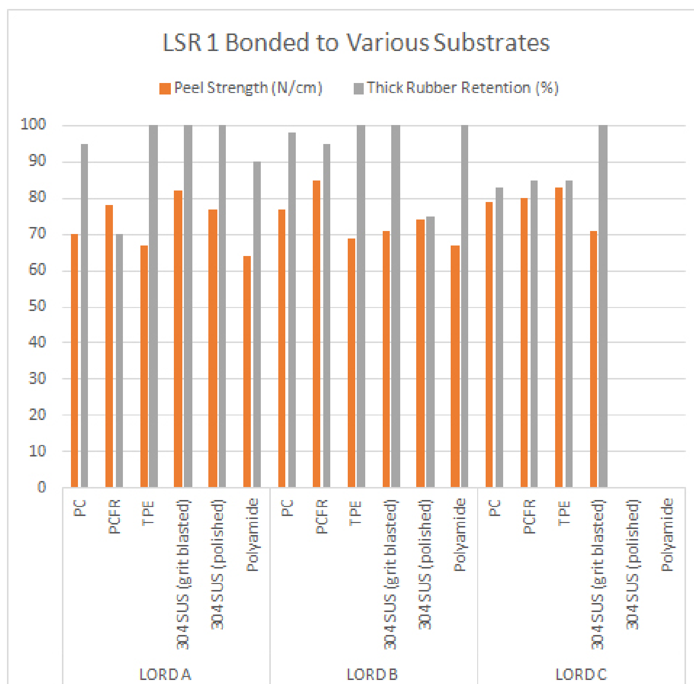

Figure 6: This chart details the bonding results on multiple substrates.

CONCLUSION

Three new adhesive technologies were tested for bonding platinum-cured liquid silicone rubber to multiple substrates. Common, off-the-shelf silicones of 70 durometer were chosen for this study. Of the three adhesives, LORD A and C bonded to all LSRs, while LORD B only bonded to two of them. Analysis of the LSRs concluded that low volatile content and high reactivity are important aspects to maximize bonding performance. Multiple substrates were also evaluated, including PC, PCFR, TPE, 304 SUS, and polyamide. All of the adhesives were effective on PC, PCFR, TPE, and grit blasted 304 SUS. Some of the adhesives had problems bonding to polished 304 SUS and polyamide.

We can conclude the three adhesive systems developed were successful in bonding multiple platinum-cured silicones to multiple substrates that do not require special surface preparation techniques such as plasma or flame treatment, and do not have the same application limitations as typical silane primers. Some of the limitations found are attributed to the composition of the different LSRs used. It is important to note one of the two options that were successful is water-based, and constitutes an environmentally friendly option.

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