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The Effects of Silicone Contamination on Bond Performance of Various Bond Systems

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The sensitivity to silicone contamination of a wide variety of adhesive bond systems is discussed. Generalizations regarding factors that make some bond systems more sensitive to contamination than others are inferred and discussed. The effect of silane adhesion-promoting primer on the contamination sensitivity of two epoxy/steel bond systems is also discussed.

Keywords: Contamination sensitivity; Epoxy; Fracture energy; Peel adhesion; Pressure sensitive adhesive; Silane adhesion promoter; Silicone contamination; Tensile adhesion; Vulcanizing agents

INTRODUCTION

Silicone contamination of bond surfaces has long been a concern in bonding operations. Although silicone-based adhesives and sealants are used in many bond applications, low-molecular-weight silicone oils on bond surfaces can inhibit or preclude adhesive-to-substrate contact required to achieve strong adhesion. The high lubricity and chemical and thermal stability of silicones make silicone oil or grease an outstanding lubricant in many production processes where they can be a significant source of bond contamination. An additional source of silicone contamination in many instances is processing and support materials that are often fabricated using processes where silicone is used extensively.

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Considerable effort has been made to investigate detection methods for silicone contamination [1–3] and cleaning of contamination [4,5] from bond surfaces. The open literature regarding sensitivity of adhesive bond systems to contamination is sparse [6,7]. The sensitivity of bond performance can change depending on the performance test employed to measure the sensitivity with fracture tests typically yielding greater sensitivity than strength tests [8]. The use of a silane adhesion-promoting primer has been shown to significantly reduce the sensitivity of an epoxy adhesive bond to steel substrates contaminated with low-level hydrocarbon grease [8]. There are also adhesive systems that are formulated to be insensitive to silicone contamination [9].

This manuscript details the test methods and equipment used to perform bond system contamination studies and the results of a program investigating the sensitivity of a wide variety of bond systems to silicone contamination. General conclusions regarding the sensitivity of various substrate/adhesive systems to silicone contamination are presented. A separate study is also discussed that significantly increased the understanding of the use of silane adhesion-promoting primer in reducing the sensitivity of the most sensitive bonds to silicone contamination.

EXPERIMENTAL

Bond System and Contamination Materials

A wide variety of bond systems was tested in the general study. The epoxy adhesives used for the study include three major types. Two commercially available fiber-filled epoxies with glass transition temperatures greater than ambient temperature were tested (referred to as Epoxy A and Epoxy B). A cork-filled epoxy (Epoxy C) and an in-house formulated fiber-filled epoxy with a room temperature glass transition were also tested (Epoxy D). The adhesion of an epoxy-polyamide paint used with an epoxy-polyamide primer (Paint A) and a polyurethane paint (Paint B) were also tested. Two vulcanized bond systems were tested for sensitivity to silicone contamination on steel substrate bond surfaces. Both systems contained a primer and an adhesive (VA-1 and VA-2). The second of the two systems contained a solvated natural rubber topcoat. Finally, a pressure sensitive adhesive was also tested.

The bond substrates to which the silicone contamination was applied were numerous. The tested metals included D6AC steel, 304 stainless steel, Inconel[®], and 7075 aluminum. Painted D6AC steel was also a tested substrate. Three different paints were tested in this manner: Paint A and Paint B previously described and a urethane paint system

(Paint C). The tested elastomeric insulation materials included cured silica fiber (SF)- and carbon fiber (CF)- filled ethylene propylene diene monomer (EPDM) rubber, asbestos fiber (AF)- and SF- filled nitrile butadiene rubber (NBR), and natural rubber (NR). Three non-elastomeric ablative insulation material substrates were also tested: graphite, carbon-cloth phenolic (CCP), and glass-cloth phenolic (GPC).

Not every adhesive/substrate system was tested. All combinations used in production bonds were considered, and testing was limited to systems where bond failure could have catastrophic consequences to the overall structure. The 21 combinations that were tested are shown in Table 1. The cleaning process used for each system was the baseline

TABLE 1 Bond Systems

Bondline (adhesive or paint/contaminated substrate)	Cure temperature (°C), time	Surface preparation
Epoxy D/CF-EPDM (cured)	21°C, 4 days min.	Abrade
Epoxy A/Paint A coated D6AC steel	21°C, 5 days min.	SOLV-2 wipe/abrade/ SOLV-2 wipe
Epoxy D/ASNBR (cured)	21°C, 4 days min.	SOLV-2 wipe
Epoxy C/SF-EPDM (cured)	21°C, 4 days min.	SOLV-2 wipe
Epoxy C/Paint C coated 7075 aluminum	21°C, 4 days min.	SOLV-2 wipe/abrade/ SOLV-2 wipe
D6AC steel/VA-1/SF-EPDM	143°C, 7 hr	Abrade/TCA wipe
Epoxy D/D6AC steel	21°C, 5 days min.	SOLV-1 wipe
Paint A/D6AC steel	21°C, 24 hr min. each	SOLV-2 wipe/abrade/ SOLV-2 wipe
Epoxy A/D6AC steel	21°C, 5 days min.	SOLV-2 wipe
Epoxy A/7075 aluminum	21°C, 5 days min.	SOLV-2 wipe
Epoxy A/Paint B coated aluminum	21°C, 5 days min.	SOLV-3 wipe/abrade/ SOLV-3 wipe
Epoxy B/graphite	41°C, 48 hr	IPA wipe
Epoxy B/SF-NBR (Cured)	41°C, 48 hr	MEK wipe/abrade/MEK wipe
CCP/PSA/D6AC steel	21°C at 34 psi, 1 day	Abrade/TCA wipe
PSA/ASNBR	21°C at 34 psi, 1 day	TCA wipe
Epoxy A/inconel steel	21°C, 5 days min.	SOLV-3 wipe/abrade/ SOLV-3 wipe
Epoxy C/stainless steel	21°C, 4 days min.	SOLV-3 wipe/abrade/ SOLV-3 wipe
Epoxy B/7075 aluminum	41°C, 48 hr	Detergent wash/SOLV-1 wipe/grit blast
Epoxy B/D6AC steel	41°C, 48 hr	Detergent wash/SOLV-1 wipe/grit blast
Epoxy B/high-ply-angle GCP NR/VA-2/D6AC steel	41°C, 48 hr 152°C, 2 hr	SOLV-1 SOLV-1

production surface preparation process. Thus, the post-clean bond performance is an indication of the effect of silicone contamination occurring prior to bond surface preparation. Also shown in Table 1 are the adhesive cure temperatures used in this study.

The surface preparations used were quite varied. Solvent wipes were accomplished by wiping the surface with solvent-dampened low-lint polyester knit cloth followed by a dry wipe using the same cloth. A 30-minute minimum dry time was instituted following all solvent wiping operations. Detergent washing was performed using commercially available industrial washers. The detergent used was a 10% aqueous solution of a commercially available mixture of detergents, sodium triphosphate (a corrosion inhibitor), and anti-foaming surfactants. The detergent solution is alkaline with pH between 9.5 to 10.5. The solution is heated to $77 \pm 5^\circ\text{C}$ prior to use, and the wash operation is followed by two separate deionized water rinses to remove all trace of surfactant from the bond surfaces. Sodium metasilicate is added to the final rinse water to inhibit corrosion of the steel substrates. Surface preparation by abrasion was performed by hand using 180-grit sandpaper or emery cloth. The grit blast operation was performed at 0.4 MPa (running pressure) and a stand-off distance of 3 cm. The grit medium used was staurolite sand.

Several solvents were used in the preparation of the various bond substrate surfaces. One is commercial solvent made up principally of 1-methyl-4-(1-methylethenyl)-cyclohexane, propanol, and 1-T-butoxy-2-propanol (SOLV-1). Another is a commercial solvent mixture of paraffin-based hydrocarbons and d-limonene (SOLV-2). A third consists mainly of mineral spirits (SOLV-3). Methyl ethyl ketone (MEK), trichloroethane (TCA), and isopropyl alcohol (IPA) were also used. The solvent used with any given material system coincides with that used in an equivalent production operation.

The silicone used as the contaminant for these experiments was a 1000-cs viscosity polydimethyl siloxane oil. In order to apply the contaminant at low levels for this testing the silicone oil was diluted in an n-propyl bromide-based solvent. The solvent was the best of five solvents tested in preliminary process development efforts for keeping the silicone in solution. The solution was constantly stirred until fed into the spray system.

The second study to investigate more fully the effect of cure temperature and the use of silane adhesion-promoting primers used the two commercially available epoxy adhesives, Epoxy A and Epoxy B, cured at a variety of temperatures. The silane primer used is a mixture of 40 weight percent cyclohexane, 40 weight percent absolute ethanol, and 5 weight percent each of n-butanol, 2-butoxyethanol,

distilled/deionized water, and γ -glycidoxy-propyltrimethoxy silane. To this mixture 0.3 weight percent acetic acid is added. The mixture is allowed a minimum of 7 days at $21 \pm 2^\circ\text{C}$ before use in order to allow the acidified solution to hydrolyze the methoxy end groups of the silane.

Application of Silicone Contamination

Silicone contamination was applied to the bond surfaces of the substrates following surface preparations representative of a given production process. The application was accomplished using a SonoFlux[®] 9500 ultrasonic spray system manufactured by Sono-Tek Corporation (Milton, NY, USA). The diluted silicone contaminant is supplied to the spray assembly from a closed reservoir by a positive displacement gear pump. The contaminant is atomized into a fine mist at the tip of the non-clogging, large-orifice ultrasonic nozzle where it is then dispersed horizontally to the correct width by low-pressure compressed air before being propelled onto the prepared bond surface by a turbulent stream of air.

The target level for the silicone contamination was $108 \pm 11 \text{ mg/m}^2$. This target level was selected to represent the high end of the amount of silicone that can transfer from processing materials to substrates during normal manufacturing operations. Measurement of the silicone level was performed using the average of gravimetric measurements from witness foils that preceded and followed each contamination application. The vast majority of the measured levels were in the 104 to 112 mg/m^2 range. Contamination uniformity has been shown visually by using the spray system to apply dye penetrant, then examining the coated surface under ultraviolet light. The reproducibility of the panel-to-panel test results and the low variability of the bond performance results from within a given bond system also evidence the uniformity of the contamination application.

Processes

The overall process flow was as follows:

1. The substrate bond surfaces were cleaned and prepared prior to spray application of the silicone contamination.
2. Silicone was applied at a level of 108 mg/m^2 for the general studies and a level of 22 mg/m^2 for the follow-up study.
3. The silicone was allowed to stage on the bond surface for 3 to 5 days at laboratory-ambient temperature ($21 \pm 2^\circ\text{C}$) prior to proceeding. In cases used as control samples in which no contamination was

applied, the bond substrates were staged for an equivalent amount of time in a clean environment held to approximately 50% relative humidity (RH).

4. Following the staging, half of the contaminated samples were cleaned using the same process as prior to contamination application.
5. The samples were bonded and tested.

Testing

The majority of the bond systems were tested for tensile adhesion strength using a tensile button-to-plate configuration (see Fig. 1). The plate (20×30 cm) in this configuration was the test surface serving as the control or contaminated surface as desired. The adhesive/plate bond was the desired test interface and is referred to hereafter as the primary bond.

In many instances, the plate was a composite of cured rubber or paint over the base metal plate. In all instances, the secondary bond of the composite plates (paint or rubber to the plate) was created in such a way (either by ensuring best practices in the bonding operations or geometrically increasing the bond area of the secondary bond in comparison with the primary or tested bond) to preclude secondary bond failures. The buttons bonded to the plates were all made of D6AC steel, and the button surfaces were also treated using best practices to preclude a secondary bond failure at the button/adhesive interface. In no case was secondary bond failure observed.

For statistical purposes, three separate plates were prepared per sample set, contaminated as appropriate and bonded using 12 buttons for each panel. Within plate bond performance, variation (as calculated by the standard deviation) was typically less than 10% of the median

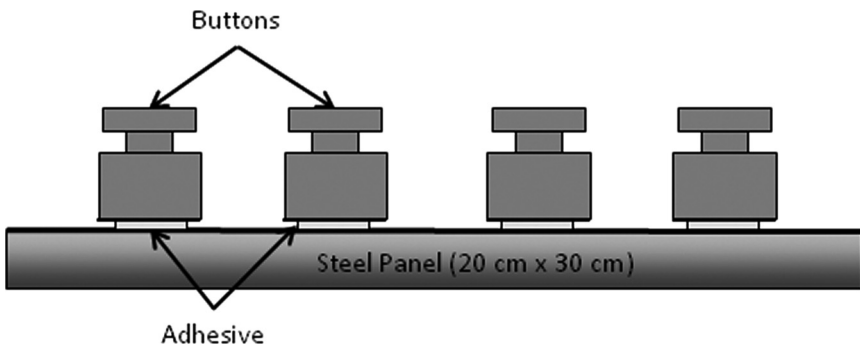


FIGURE 1 Schematic of tensile button-to-plate bond configuration.

tensile adhesion strength of the plate for control, contaminated, and contaminated and cleaned samples. The median tensile adhesion strength value for each plate was used as the value most representative of the plate bond performance. Each of the three plates was contaminated separately, although the bonding of all three plates was performed using the same adhesive mix. Thus, the variation of tensile adhesion strength among the three panels represents not only the test and process variation, but also minor differences in the silicone contamination level.

Four other specimen geometries were used for this testing: quadruple lap shear (also known as double strap lap shear), 90-degree peel, T-peel, and tapered double cantilever beam (TDCB). These specimens were used because each has been shown in previous testing to be more sensitive to material and process variation. This advantage is somewhat counteracted by the small dimensions of the specimens, which makes them significantly more difficult to clean and prepare for bonding in a way that would well represent much larger production hardware.

RESULTS

Many of the bond systems showed no effect in measured bond performance from 108 mg/m² silicone contamination on the bond surface. This statement is the result of performing analysis of variance using Tukey's Honest Significant Difference (HSD) test at a 95% confidence level. The results for these insensitive bond systems are shown in Table 2. Within the table, the coefficients of variation (CV) for the data set are the average of the individual CV for each panel. The CV data are included to determine if the variability in the bond performance results was affected by the silicone contamination even for the bond systems where the performance was unaffected.

In three cases, the variability of the bond performance was significantly greater for the contaminated samples *versus* the control samples even though the performance was equivalent. In all three of these cases, the failure was 100% cohesive within the substrate or the adhesive: Paint B, SF-NBR, and the pressure-sensitive adhesive (PSA). A possible cause of the increased variability is that the silicone may be negatively affecting the material in areas of inherent weakness near the surface to which silicone was applied. This could cause the variability to increase without affecting the median values of the performance.

It is of significant interest to identify commonalities among these bond systems, as those commonalities infer generalizations regarding

TABLE 2 Bond Performance of Systems Insensitive to 108 mg/m² of Silicone Contamination Applied to the Bond Surface Prior to Adhesive Application

Adhesive	Cure temp (°F)	Contaminated substrate	Test geometry	Bond performance (CV)			Failure mode
				Control	Contaminated	Failure mode	
Epoxy D	21	Cured CF-EPDM	B/P	0.55 MPa (14.0%)	0.49 MPa (10.6%)	100% coh CF-EPDM	
Epoxy D	21	Cured AF-NBR	B/P	5.61 MPa (5.5%)	5.23 MPa (6.5%)	100% coh AF-NBR	
Epoxy A	21	Painted steel (Paint A)	B/P	27.5 MPa (5.4%)	29.2 MPa (5.1%)	100% coh Paint	
Epoxy A	21	Painted aluminum (Paint B)	B/P	22.1 MPa (7.4%)	19.5 MPa (14.9%)	100% coh Paint	
Epoxy A	21	Inconel	B/B	12.8 MPa (21.2%)	12.1 MPa (15.4%)	85–100% adh	
Epoxy C	21	Painted aluminum (Paint C)	B/P	10.3 MPa (10.4%)	9.6 MPa (9.6%)	100% coh RT-455	
Epoxy C	21	304 stainless steel	B/B	3.0 MPa (20.3%)	3.2 MPa (24.4%)	>95% adh	
Epoxy A	41	Graphite	B/B	24.2 MPa (13.5%)	24.5 MPa (13.6%)	100% coh graphite	
Epoxy A	41	Cured SF-NBR	B/B	9.5 MPa (2.7%)	9.5 MPa (9.9%)	100% coh SF-NBR	
PSA	21	CCP	B/P	1.02 MPa (23.2%)	0.99 MPa (19.8%)	100% adh	
PSA	21	Cured AF-NBR	B/P T-peel	0.93 MPa (17.2%)	0.97 MPa (17.5%)	100% adh	
NR/VA-2	152	D6AC steel	QLS peel	4.96 pli (13.1%)	4.07 pli (23.4%)	100% adh	
SF-EPDM/ VA-1	143	D6AC steel	B/P peel	4.7 MPa (7.7%)	4.5 MPa (9.3%)	100% coh NBR	
				4.4 kN/m (12.1%)	4.6 kN/m (15.3%)	>80% coh NR	
				7.4 MPa (7.7%)	6.6 MPa (21.8%)	100% coh	
				16.6 kN/m (5.5%)	15.9 kN/m (9.3%)	SF-EPDM	
						100% coh SF-EPDM	

Test geometries: B/P is button-to-panel; B/B is button-to-button; QLS is quadruple lap shear.

Failure mode: coh is cohesive in the adhesive of substrate specified; adh is interfacial between the adhesive and the substrate.

silicone contamination sensitivity. Most of the substrates to which the silicone was applied prior to bonding for the insensitive bond systems allow diffusion of the silicone away from the bond surface. Because the substrates were given 3 to 5 days between application of the silicone and the bonding operation, this staging time may have allowed diffusion of the silicone into the substrate rather than remaining concentrated at the bond surface.

There are two exceptions to this in the results: Epoxy A bonded to Inconel and Epoxy C bonded to 304 stainless steel. In both of these instances, the failure mode of the control samples was almost entirely interfacial between the adhesive and the substrate, and the bond strength was relatively low, less than half the cohesive strength of the adhesive. These may be mitigating factors helping to explain these exceptions.

Eight bond systems demonstrated a statistically significant reduction in bond performance due to silicone contamination. In six of the cases, there was also a shift in the failure mode toward failure at the contaminated interface. In the other two cases, the failure mode of the control samples was already at the interface. Table 3 shows the results for these eight bond systems.

The two bond systems that did not experience a failure mode shift (Epoxy C/cured SF-EPDM and Epoxy B/high-ply-angle GCP) also experienced the smallest performance decreases on a percentage basis. The performance reductions of these two systems were in the mid-30% range. Two other commonalities of these bond systems were that they have a substrate that allows silicone diffusion from the surface and they experienced the lowest variability within the contaminated samples.

The cleaning methods attempted for these two bond systems were both solvent wipes using polyester cloths. The contaminated SF-EPDM surface was cleaned using SOLV-2 and the GCP surface was cleaned using SOLV-1. The results of the cleaning could not have been more different. The tensile adhesion strength of the Epoxy C/SF-EPDM bond showed no effect of the cleaning, remaining unchanged from the value of the uncleaned contaminated surface. On the other hand, the tensile adhesion strength of the Epoxy B/GCP bond returned to the baseline (control) value following cleaning.

The bond performance of the control samples of Epoxy A to steel and aluminum showed a large statistically significant difference in this study that was unexpected (see Fig. 2). The tensile adhesion strength of Epoxy A to uncontaminated aluminum was only 62% of the similar performance for uncontaminated steel (26.4 *versus* 42.3 MPa). The panel averaged coefficients of variation were low for both sets of samples: 5.4 and 6.7%, respectively. Consistent with the lower performance

TABLE 3 Bond Performance of Systems Sensitive to 108 mg/m² of Silicone Contamination Applied to the Bond Surface Prior to Adhesive Application

Adhesive	Cure temp (°C)	Contaminated substrate	Test geometry	Control			Contaminated			Cleaned		
				Bond performance (CV)	Failure mode	Bond performance (CV)	Failure mode	Bond performance (CV)	Failure mode	Bond performance (CV)	Failure mode	
Epoxy C	21	Cured SF-EPDM	B/P	2.6MPa (7.2%)	100% adh	1.7MPa (6.4%)	100% adh	1.7MPa (6.7%)	100% adh	1.7MPa (6.7%)	100% adh	
Epoxy D	21	D6AC steel	B/P	24.6MPa (2.1%)	95% coh Epoxy	0.81MPa (44.3%)	100% adh	10.9MPa (12.0%)	>95% adh	10.9MPa (12.0%)	>95% adh	
Paint A	21	D6AC steel	B/P	23.9MPa (6.8%)	100% coh Paint	7.7MPa (19.3%)	100% adh	14.1MPa (6.9%)	20% coh paint	14.1MPa (6.9%)	20% coh paint	
Epoxy A	21	D6AC steel	B/P	42.3MPa (6.7%)	>90% coh Epoxy	9.7MPa (15.3%)	100% adh	18.8MPa (9.3%)	100% adh	18.8MPa (9.3%)	100% adh	
Epoxy A	21	7075 aluminum	B/P	26.4MPa (5.4%)	>80% coh Epoxy	15.9MPa (12.6%)	>95% adh	18.7MPa (12.6%)	>95% adh	18.7MPa (12.6%)	>95% adh	
Epoxy B	41	D6AC steel	B/P TDCB	67.9MPa (2.4%) 3.54kJ/m ² (17.2%)	100% coh epoxy 70% coh epoxy	23.6MPa (15.4%) 0.09kJ/m ² (11.8%)	>95% adh	60.2MPa (6.2%) 1.75kJ/m ² (11.8%)	>95% coh epoxy 10% coh epoxy	60.2MPa (6.2%) 1.75kJ/m ² (11.8%)	>95% coh epoxy 10% coh epoxy	
Epoxy B	41	7075 aluminum	B/P TDCB	63.4MPa (5.3%) 3.01kJ/m ² (20.1%)	100% coh epoxy 50% coh epoxy	22.5MPa (9.7%) 0.67kJ/m ² (39.2%)	>95% adh	49.7MPa (4.9%) 1.52kJ/m ² (44.5%)	90% adh 100% coh epoxy 5% coh epoxy	49.7MPa (4.9%) 1.52kJ/m ² (44.5%)	90% adh 100% coh epoxy 5% coh epoxy	
Epoxy B	41	High-ply-angle GPC	B/B	50.3MPa (5.0%)	100% adh	33.1MPa (8.9%)	100% adh	52.1MPa (5.5%)	100% adh	52.1MPa (5.5%)	100% adh	

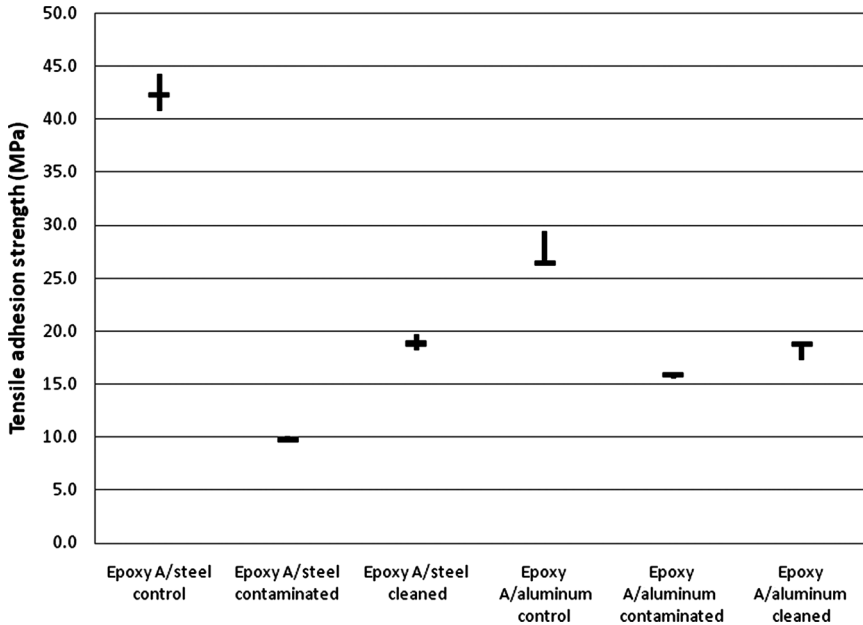


FIGURE 2 Effects of silicone contamination on Epoxy A tensile adhesion strength to steel and aluminum.

of the aluminum bond, the interfacial failure to the aluminum was marginally higher than that to the steel. A possible factor of the difference is the humidity level in the bond area, approximately 50% RH. Another possible factor could be the failure of grit-blast-induced asperities in the aluminum. This type of failure mode has been observed on other aluminum substrates experiencing multiple grit-blast operations without an etching operation in between. The effects of silicone contamination on bond performance for these systems also showed a statistically significant difference, only in the opposite direction. The contaminated aluminum samples exhibited tensile adhesion strength 63% greater than that of the contaminated steel. In both cases, the failure mode was nearly 100% adhesive between the Epoxy A and the metal substrate. Because of the significantly higher control performance and the significantly lower contaminated performance of the Epoxy A/steel system, the percent reduction in tensile adhesion strength for this system was nearly double that for the Epoxy A/aluminum system, 77 *versus* 40%.

The cleaning method used for the two Epoxy A contamination-sensitive bonds was a solvent wipe using polyester cloths dampened

with SOLV-2. Given the differences in Epoxy A/steel and Epoxy B/aluminum tensile adhesion strengths of the control and contaminated sample sets, it is interesting to note that the contaminated and cleaned samples exhibited virtually the same bond strengths at 18.7 to 18.8 MPa. This was an improvement of 94% over the contaminated steel substrate tensile adhesion strength and an 18% improvement for the aluminum bond.

The effects of silicone contamination on steel prior to priming and painting with the Paint A system or bonding with Epoxy D adhesive were large. As shown in Figure 3, the tensile adhesion strength reductions were 68 and 97%, respectively. Both systems also experienced a complete change in failure mode, from cohesive in the paint or adhesive to interfacial between the paint or adhesive and the contaminated steel substrate.

The Epoxy D bond strength was nearly nil after the contamination application, a 97% reduction for the control value. Cleaning the contaminated steel surface with a solvent wipe using SOLV-1 dampened polyester cloth prior to bonding with Epoxy D made a huge difference in the tensile adhesion strength in comparison with the contaminated

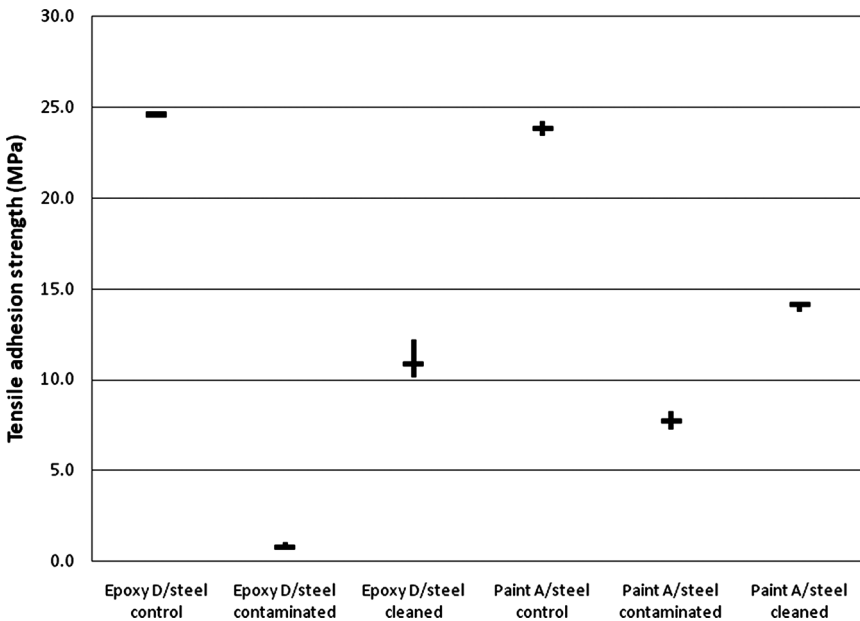


FIGURE 3 Effects of silicone contamination on Epoxy D and Paint A tensile adhesion strength to steel.

steel bond without cleaning. Where the contaminated surface yielded a strength of only 0.8 MPa, solvent wiping the contaminated surface prior to bonding increased the subsequent bond strength to 10.9 MPa. While this is still a 56% decrease in comparison with the control tensile adhesion strength, the order of magnitude improvement over the contaminated performance is impressive.

For the Paint A system, SOLV-2 was the solvent used to clean the silicone-contaminated steel in a solvent wipe. The post-cleaning tensile adhesion strength showed an 83% increase over the contaminated samples (14.1 *versus* 7.7 MPa), reducing the effect of the contamination from 68 to 41%.

The effects of contamination on Epoxy B bonds to steel and aluminum substrates were determined using buttons bonded to panels for tensile adhesion strength and TDCBs for bond fracture energy. The tensile adhesion strength and bond fracture energy results are shown graphically in Figs. 4 and 5, respectively. Consistent with the previous work of one of the authors [8], the fracture energy was affected more significantly than the bond strength. Where the bond strengths to steel and aluminum were both reduced 65%, the fracture energies

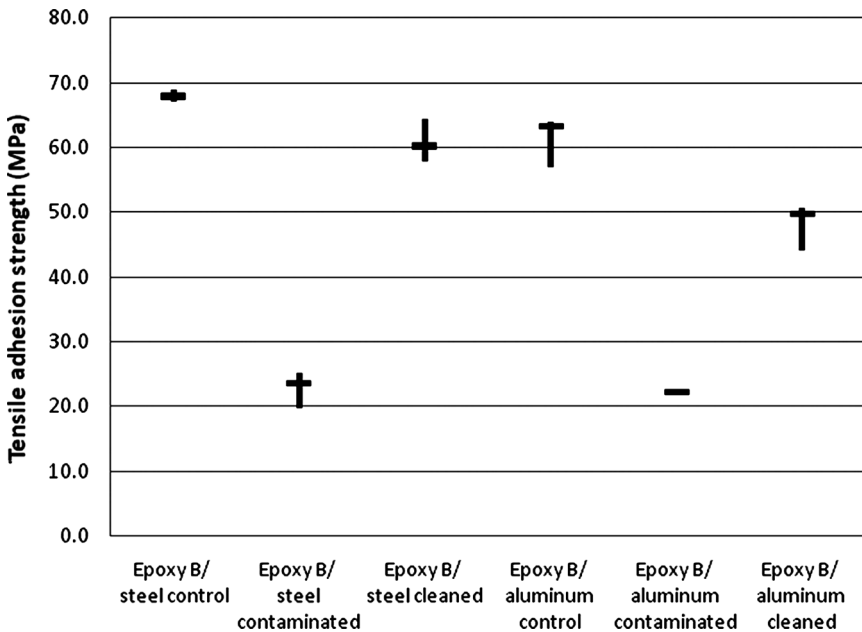


FIGURE 4 Effects of silicone contamination on Epoxy B tensile adhesion strength to steel and aluminum.

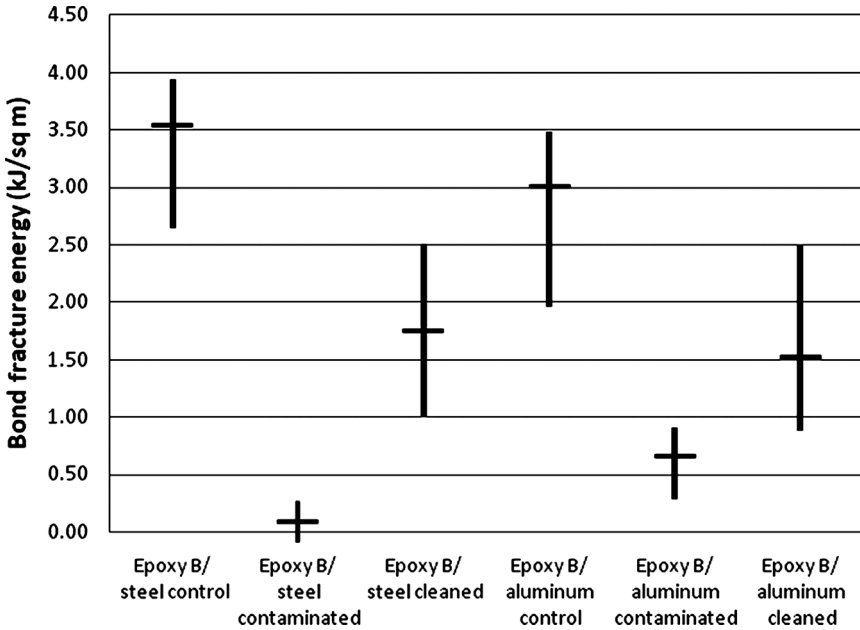


FIGURE 5 Effects of silicone contamination on Epoxy B bond fracture energy to steel and aluminum.

were reduced 98 and 78%, respectively. Unlike the Epoxy A results, the steel and aluminum control samples were statistically equivalent in the Epoxy B study.

A very rigorous cleaning method was used for the Epoxy B bonds to steel and aluminum. Contaminated samples were solvent wiped using polyester cloths dampened with SOLV-1, then grit blasted. Even with this extensive cleaning, bond performance as measured in terms of tensile adhesion strength and bond fracture energy was not returned to the baseline of the control samples. The tensile adhesion strength came closest to returning to baseline. The contaminated and cleaned samples decreased in strength only 11 and 22% for the steel and aluminum bonds, respectively. This compares favorably with the 65 % reduction without the cleaning. As measured by the bond fracture energy, the contaminated and cleaned samples still exhibited a performance decrease of 50 to 55% from the baseline. Although this is a huge improvement over the contaminated samples, the decrease is still quite large considering the cleaning method used. A possible cause of the continued bond performance reduction even after grit blasting is that a small fraction of the grit medium is embedded into the metal

surface during the blasting operation. The embedded grit medium likely entraps silicone beneath it that can spread over time onto the nearby bond surface. Another possible cause could be insufficiency of the grit blast duration ($0.3 \text{ cm}^2/\text{s}$) or pressure (550 kPa).

In looking at the silicone contamination sensitivities in general, it is important to note that six of the eight sensitive bond systems have surfaces through which the silicone cannot diffuse. The other two cases showed the smallest bond degradation of the eight systems exhibiting any effect. In contrast, nine of the 13 bond systems that showed no sensitivity to bond surface contamination at this level had substrates into which the silicone could diffuse. Two of the remaining insensitive bond systems had significantly elevated cure temperatures. The thermal energy of the silicone molecules at the higher temperature could be expected to overcome the secondary chemical forces attracting the silicone to the steel substrate. These thermally energetic silicone molecules would be more able to diffuse into the curing rubber during the 2 to 7 hour cure and bonding operation.

In an attempt to demonstrate further the effect of cure temperature on the silicone contamination sensitivity of a given bond system, a second set of experiments was carried out. In this set of tests, two bond systems were studied: Epoxy A and Epoxy B to D6AC steel. The contamination level for these tests was $22 \text{ mg}/\text{m}^2$ and the test geometry was the standard three panels with 24 buttons bonded to each. For both bond systems, the cure temperature was set at different levels: 21, 41, 57, and 82°C (for Epoxy B) and 93°C (for Epoxy A). Use of silane adhesion promoting primer was also a parameter examined in this testing. There were three conditions investigated for both adhesive systems: 1) no silane (contaminated control samples), 2) silane applied to the steel substrate prior to silicone contamination application, and 3) application of the silane to the silicone-contaminated steel bond surface. To accomplish this, each panel was divided into three sections, each with eight buttons bonded to each test section. The silane was applied using a paint brush, taking care to minimize the overlap between brush strokes. The silane was applied at ambient temperature ($21 \pm 2^\circ\text{C}$) at a minimum of 1 hour prior to silicone contamination application for one test section and prior to adhesive application for the other pertinent test section.

Another set of samples was created and tested under all three silane conditions in which the silane-treated substrates were subjected to elevated temperature ($110 \pm 5^\circ\text{C}$) for 1 hour. This staging at elevated temperature has been shown to drive to completion the condensation reaction between the silane and the hydrated metal oxide surface. This third set of samples was bonded using only the Epoxy B adhesive.

The results from the Epoxy A tests are shown in Fig. 6. The effect of cure temperature for the samples without silane was minimal with the tensile adhesion strength increasing only 22% as the cure temperature was increased from 21 to 82°C. The results were such that the only statistically significant difference (at the 95% confidence level) was between the two temperature extremes. The failure mode in these samples without silane was a mixture of adhesion failure to the panel at the contaminated interface and cohesive in the EPOXY A adhesive, with a trend of decreasing adhesion failure with increasing cure temperature. Because the failure mode was mixed, the cause of the increased performance with increasing cure temperature could have been due to additional curing of the EPOXY A at the higher cure temperatures, increased diffusion of the silicone from the bond surface into the adhesive, or a combination of the two causes.

The failure mode of the samples in which the silane was applied prior to the contamination exhibited nearly 100% cohesive failure within the Epoxy A. From these results, we observed that some additional curing of the adhesive occurs between the cure temperatures of 21 and 41°C. This is seen in the increase in the tensile adhesion strength between samples cured at these two temperatures. No

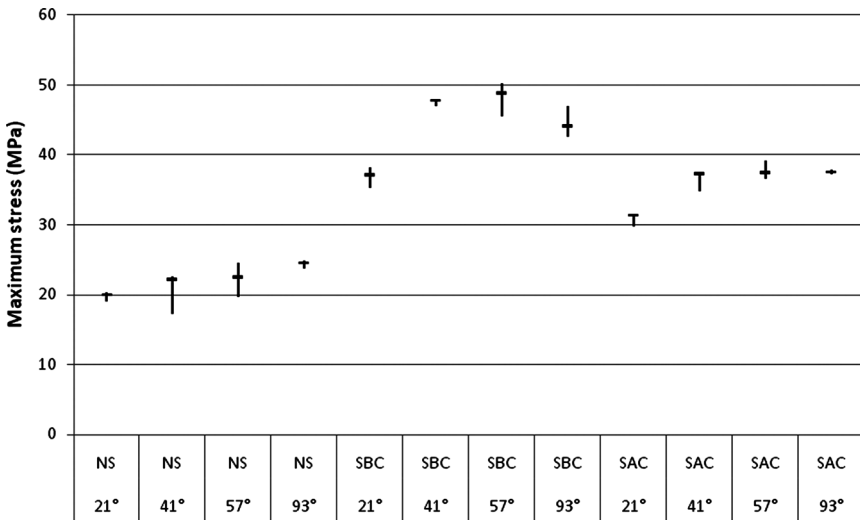


FIGURE 6 Effects of cure temperature and silane primer (21°C staging) on silicone contamination sensitivity of Epoxy A/steel. NS = no silane, SBC = silane applied prior to contamination, and SAC = silane applied after the contamination.

additional curing appears to occur at temperatures greater than 41°C. The results also show that low-level silicone contamination does not affect the steel/silane/Epoxy A bond system in cases where contamination of the substrate bond surface does not occur until after the silane application.

The application of the silane adhesion promoter reduced the sensitivity of the bond system to contamination whether the silane was applied before or after the contamination. The effect was significantly enhanced, however, in the case where the silane was applied before the silicone contamination. This can be explained when one considers that the silicone can create relatively strong hydrogen bonding to the metal oxide surface, resist displacement by the silane, and preclude the molecular contact between the silane and the metal oxide that is required for the desired condensation reaction between them.

Comparative results for the Epoxy B testing with the cure temperature and silane application parameters are shown in Fig. 7. The results lead to the same conclusions as the Epoxy A testing. Evidence of additional adhesive cure at temperatures above 21°C is seen in the data generated by samples treated with silane prior to contamination applications. These samples, like the Epoxy A samples, failed cohesively in the adhesive. Thus, as in the Epoxy A case, low-level silicone

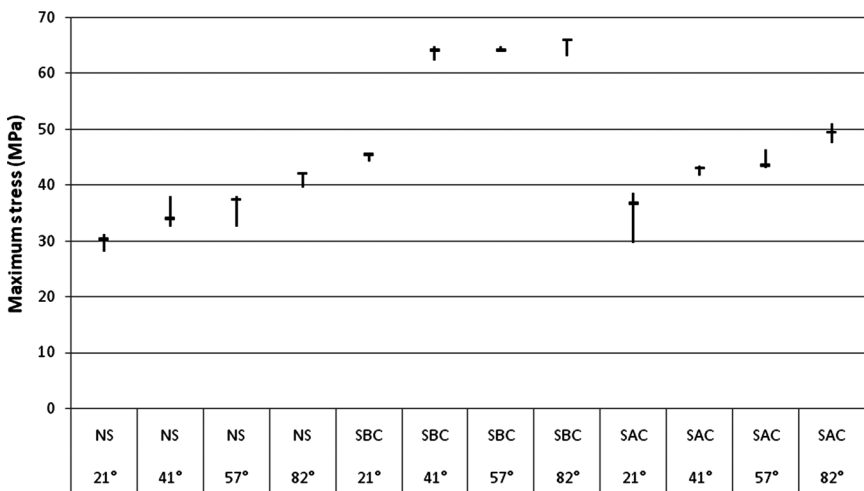


FIGURE 7 Effects of cure temperature and silane primer (21°C staging) on silicone contamination sensitivity of Epoxy B/steel. NS=no silane, SBC=silane applied prior to contamination, and SAC=silane applied after the contamination.

contamination does not affect the Epoxy B bond system as long as the silane can be applied before any contamination can take place. In the case where the silane was applied to a contaminated steel surface, the influence of the silane was much less with only a small increase in the tensile adhesion strength over contaminated samples that did not receive the silane application. The final set of tests shows a dramatic improvement in the effect of silane application to a contaminated steel substrate. These tests were generated from samples given a silane “cure” at 110°C following the silane application. The results, shown in Fig. 8, were equivalent to the silane results without the 110°C cure for the case where the contamination was applied to the silane-treated surface. For this case, the tensile adhesion strength improved to match the results from the samples treated with silane prior to contamination application. The failure mode also changed due to the silane cure. The failure mode shifted from approximately 10% adhesive failure at the contaminated interface to virtually complete failure within the adhesive at the baseline strength of the adhesive. It appears that the silane is able to displace the silicone contamination and react with the metal oxide substrate surface at the elevated temperature.

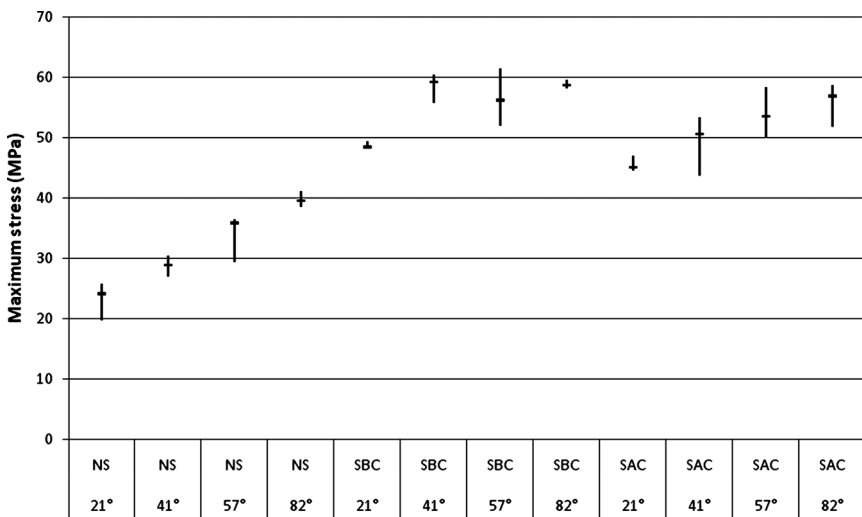


FIGURE 8 Effects of cure temperature and silane primer (110°C staging) on silicone contamination sensitivity of epoxy B/steel. NS=no silane, SBC=silane applied prior to contamination, and SAC=silane applied after the contamination.

CONCLUSIONS

Several general conclusions can be made from the results of this testing. The sensitivity of the strength of bond systems to silicone contamination on the substrate bond surface appears to be dependent on the substrate material and the adhesive or adhesion promoting primer cure temperature. In cases where the silicone is able to diffuse into the substrate, the bond system is generally insensitive to the contamination. The sensitivity to the contaminant also appears to decrease with increasing cure temperature.

Cleaning silicone-contaminated surfaces using a solvent wipe method generally improves the subsequent bond performance, but rarely brings that performance back to baseline. Even grit blasting contaminated metal substrates failed to restore subsequent bond strengths completely.

The bond systems that exhibited the greatest sensitivity to silicone contamination are high-strength bonds to metal surfaces where the baseline failure mode is cohesive within the adhesive. In such cases, the sensitivity can be reduced significantly or eliminated completely by the use of silane adhesion promoting primer. The beneficial effects of silane primer are magnified by exposing the silane-treated substrate to elevated temperature (110°C).

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