Henkel Adhesives & Enercon Plasma Treatment Case Study:
Surface Treatment Effects on Adhesive Bond Strength

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Abstract
In specialized industrial segments such as aerospace, automotive and medical fields, product performance applications demand not only materials with physical properties which meet performance requirements but also strong interfacial adhesive-based bonds between similar and dissimilar materials. Substrates such as silicone rubber, polytetrafluoroethylene (PTFE), acetals, and polyolefins have always presented challenges to product/process engineers, in part because of the low surface energy of these materials. Creating adequate surface wettability and functionalization of these substrates for adhesive adhesion plays a mission-critical role in optimizing bonds for long-term material and product performance. The purpose of this study was to clearly define the necessary alignments between 1) substrate type, 2) surface modification method, and 3) adhesive type to advise industrial protocols for engineers responsible for optimizing bonding specifically with silicone foam, PTFE and polyethylene substrates. A discussion of results and recommendations summarize the data from applied test methods.

Introduction
Although there are five major bonding mechanisms associated with adhesion promotion, there are two primary factors which predominately influence the adhesion of any type of polymer to another substrate - chemical surface-to-surface interaction at the molecular level, and the wettability of the adhesive so as to enable surface spreading. Adhesion values can also be influenced the matrix, or vehicle, which enables surface wet-out. For example, extrusion-coated, water-based, solvent-based, and energy-curable will all wet to a surface at different rates. Influencing this rate of wettability will be the surface condition, including the concentration of migrated or deposited contaminants, the concentration of oxides, surface tension level, etc. These will also directly or indirectly impact adhesion values.

When attempting to promote adhesion fluoropolymer, silicone and polyolefin surfaces, the modification of surface polarity becomes key. There are two primary mechanisms for changing surface polarity by discharge-based surface modification methods. One is a physical reaction mechanism which is performed by ionic activity. The other is a chemical reaction mechanism created by free radicals. With physical reactions, ionic species obtain charge and kinetic energy from a powered electrical field generated from an electrode. Molecules and atoms (and any trace contaminants) are dislodged from targeted surfaces as energy from the electrical field is transferred to these ions. This bombardment will also increase molecular surface roughness and promote interfacial adhesion of depositions. Chemical reaction mechanisms from plasma discharges rely on free radical effects which are generated at surfaces. These chemically active free radicals will actually decrease the activation potential of a chemical reaction, causing the atomic-scale removal of surface material. More polar substrates will have a positive or negative charge and will adhere well to polar adhesives or coatings. Non-polar substrates, such as PTFE, silicones and polyolefins, are charge-neutral and have to rely on other adhesion mechanisms, such as the physical (mechanical) and chemical reaction mechanisms described above, for bonding. A surface-diffusive bond may also be formed with a solvent based primer. The inherent or changed polarity of a substrate also directly related to its surface energy. The use of air plasma, flame plasma, chemical plasma (80% air-based) and priming techniques used in this study will modify surface polarity and surface energy to increase surface area (interfacial contact area), promote wetting, and improve adhesion.

Experimental
As stated above, the purpose of this study is to compare the effects of air plasma (blown ion) technology, flame plasma technology, variable chemistry plasma technology, and primer technology relative to respective changes in surface reaction mechanisms and their impact on bond strength using appropriate adhesives on various hard-to-bond substrates. Henkel partnered in this study, and therefore Loctite®-brand adhesives were applied to treated surfaces

for evaluation. Table 1, Table 2 and Table 3 below details the specific adhesives evaluated for this study, the dispensing/mixing equipment required, and the environmental/bond test tools required, respectively:

Table 1. Loctite Adhesive(s) Evaluated.

Product Number	Product Description
Loctite® 4011™ Prism® Medical Device Adhesive	100 cP, clear, ethyl cyanoacrylate adhesive. Low viscosity, one part, room temperature cure, surface insensitive instant adhesive.
Loctite® 3924™ Light Cure Adhesive	1,100 cP, transparent to hazy/fluorescent, UV/visible light cure acrylic adhesive.
Loctite® 3035 Acrylic Adhesive	5,000 cP (Part A), 40,000 cP, pale yellow, high strength, two component acrylic.
Loctite® E-30CL™ Hysol® Epoxy Adhesive	10,500 cP, ultra clear, 30 minute work life, two-part polyfunctional amine epoxy.
Loctite® U-05FL™ Hysol® Urethane Adhesive	640/35,000 cP, off white, 5 minute work life, two-part polyurethane adhesive.
Loctite® 7701™ Prism® Medical Device Adhesive Primer	3 cP, clear, polyolefin aliphatic amine primer.

Table 2. Henkel Equipment Used.

Picture	Description
	Loctite® 30 ml Manual Syringe Dispenser
	Loctite® 50 ml Dual Cartridge Manual Applicator, 1:1 & 2:1
	Loctite® 50 ml Mix Nozzle, Luer Slip End (Qty=10)
	50 ml Static Mix Nozzle; (10) pack; Stepped Tip; 6.18 inches long; 6.5 mm I.D.; 20 elements; 1:1, 2:1 mix ratios; B Cartridges.
	Radiometer Dosimeter for UV LED and UVA & UVB light sources
	Loctite® ZETA® 7215 UV Chamber (MPMA)
	Loctite Power Supply for Chamber

Table 3. Laboratory Equipment Used.

Manufacturer	Description
VWR	Thermohygrometer
VWR	Thermohygrometer
Loctite	Radiometer Dosimeter UV-AB
Mitutoyo	Digital Calipers

Instron	Model 4400R/4204 Universal Tester
Instron	10 kN Load Cell
Instron	100N Load Cell

The trial substrates of PTFE, silicone foam and polyethylene (Table 4) were configured to 1" x 4" x 0.125" dimensions to accommodate lap-shear adhesion testing.

Table 4. Trial Substrates

ID Number	Description
TS211	Polycarbonate, UV Trans. Gr.,1" x 4" x 0.125"
NA	Silicone lap-shears, 1" x 4" x 0.125", gray foam
NA	PTFE lap-shears, white, 1" x 4" x 0.125"
NA	PE lap-shears, white, 1" x 4" x 0.125"
TS021	Aluminum lap-shears (for support in bonding Silicone)

Laboratory conditions (Table 5) of temperature and humidity were established and maintained within the specified ranges for the duration of the project. In addition, a standardized test method (Table 6) was used for determining adhesive strength, surface preparation parameters, and adhesive environmental durability.

Table 5. Laboratory Experimental Conditions.

Ambient Conditions	Typical Range
Temperature	70 +/- 2° F
Relative Humidity	50 +/- 10 %

Table 6. Standard Test Methods, per ISO 17025.

Number	Title	Issue Date
STM-700	Shear Strength of Adhesives Using Lap-Shear Specimens	1/18/2008
Deviations	1. The cross head speed was increased to 4"/min instead of 0.05'/min for testing of the bonded silicone substrate. 2. The Hargrove No. 1 spring clamps were replaced with 2lb plastic cross clamps since the normal spring clamp completely deformed the silicone foam sandwiched between two aluminum lapshears. 3. Loctite® 3035 required a 72 hour cure instead of the 24 hour cure.	

An experimental matrix was developed (Table 7) to pair an adhesive and curing method to a control or surface-modified substrate. Surface treatments of all substrates were performed at Enercon and then express shipped to Henkel's Rocky Hill facility for bonding as soon as received. The window for bonding was managed as a critical factor, with the test plan requiring bonding with 48 hours of receipt of treated samples.

Table 7. Experimental Test Matrix.

Run	Adhesive	Substrate	Cure Method	Surface Treatment	Test/ STM	Replicates
1	401	PTFE	>24hr; RT	Control	700	5
2	3924	PTFE	UV/Vis	Control	700	5
3	E-30CL	PTFE	>24hr; RT	Control	700	5
4	U-05FL	PTFE	>24hr; RT	Control	700	5
5	3035	PTFE	>72hr; RT	Control	700	5
6	401	PE	>24hr; RT	Control	700	5
7	3924	PE	UV/Vis	Control	700	5

8	E-30CL	PE	>24hr; RT	Control	700	5
9	U-05FL	PE	>24hr; RT	Control	700	5
10	3035	PE	>72hr; RT	Control	700	5
11	401	Silicone	>24hr; RT	Control	700	5
12	3924	Silicone	UV/Vis	Control	700	5
13	E-30CL	Silicone	>24hr; RT	Control	700	5
14	U-05FL	Silicone	>24hr; RT	Control	700	5
15	3035	Silicone	>72hr; RT	Control	700	5
16	401	PTFE	>24hr; RT	Blown Ion Plasma	700	5
17	3924	PTFE	UV/Vis	Blown Ion Plasma	700	5
18	E-30CL	PTFE	>24hr; RT	Blown Ion Plasma	700	5
19	U-05FL	PTFE	>24hr; RT	Blown Ion Plasma	700	5
20	3035	PTFE	>72hr; RT	Blown Ion Plasma	700	5
21	401	PE	>24hr; RT	Blown Ion Plasma	700	5
22	3924	PE	UV/Vis	Blown Ion Plasma	700	5
23	E-30CL	PE	>24hr; RT	Blown Ion Plasma	700	5
24	U-05FL	PE	>24hr; RT	Blown Ion Plasma	700	5
25	3035	PE	>72hr; RT	Blown Ion Plasma	700	5
26	401	Silicone	>24hr; RT	Blown Ion Plasma	700	5
27	3924	Silicone	UV/Vis	Blown Ion Plasma	700	5
28	E-30CL	Silicone	>24hr; RT	Blown Ion Plasma	700	5
29	U-05FL	Silicone	>24hr; RT	Blown Ion Plasma	700	5
30	3035	Silicone	>72hr; RT	Blown Ion Plasma	700	5
31	401	PTFE	>24hr; RT	Variable Chemistry Plasma	700	5
32	3924	PTFE	UV/Vis	Variable Chemistry Plasma	700	5
33	E-30CL	PTFE	>24hr; RT	Variable Chemistry Plasma	700	5
34	U-05FL	PTFE	>24hr; RT	Variable Chemistry Plasma	700	5
35	3035	PTFE	>72hr; RT	Variable Chemistry Plasma	700	5
36	401	PE	>24hr; RT	Variable Chemistry Plasma	700	5
37	3924	PE	UV/Vis	Variable Chemistry Plasma	700	5
38	E-30CL	PE	>24hr; RT	Variable Chemistry Plasma	700	5
39	U-05FL	PE	>24hr; RT	Variable Chemistry Plasma	700	5
40	3035	PE	>72hr; RT	Variable Chemistry Plasma	700	5
41	401	Silicone	>24hr; RT	Variable Chemistry Plasma	700	5
42	3924	Silicone	UV/Vis	Variable Chemistry Plasma	700	5
43	E-30CL	Silicone	>24hr; RT	Variable Chemistry Plasma	700	5

44	U-05FL	Silicone	>24hr; RT	Variable Chemistry Plasma	700	5
45	3035	Silicone	>72hr; RT	Variable Chemistry Plasma	700	5
46	401	PTFE	>24hr; RT	Flame Plasma	700	5
47	3924	PTFE	UV/Vis	Flame Plasma	700	5
48	E-30CL	PTFE	>24hr; RT	Flame Plasma	700	5
49	U-05FL	PTFE	>24hr; RT	Flame Plasma	700	5
50	3035	PTFE	>72hr; RT	Flame Plasma	700	5
51	401	PE	>24hr; RT	Flame Plasma	700	5
52	3924	PE	UV/Vis	Flame Plasma	700	5
53	E-30CL	PE	>24hr; RT	Flame Plasma	700	5
54	U-05FL	PE	>24hr; RT	Flame Plasma	700	5
55	3035	PE	>72hr; RT	Flame Plasma	700	5
56	401	Silicone	>24hr; RT	Flame Plasma	700	5
57	3924	Silicone	UV/Vis	Flame Plasma	700	5
58	E-30CL	Silicone	>24hr; RT	Flame Plasma	700	5
59	U-05FL	Silicone	>24hr; RT	Flame Plasma	700	5
60	3035	Silicone	>72hr; RT	Flame Plasma	700	5
61	401	PTFE	>24hr; RT	7701 Primer	700	5
62	401	PE	>24hr; RT	7701 Primer	700	5
63	401	Silicone	>24hr; RT	7701 Primer	700	5

Following surface treatment and adhesive application, the lap-shear substrate plies were bonded according to standard method described in STM-700, section 9 for non-UV/visible light curing adhesives. A variation from standard method was required for the Loctite® 3035 adhesive, which required a 72 hour cure instead of the standard 24 hour cure.

Regarding the use of Loctite® 3924 and the UV-cured assemblies, a fixture was built to hold the two lap-shears in proper alignment. The substrate was placed on the bottom and the TS-213 was placed on top to allow for the UV cure through the PC. Both were IPA wiped and then the substrate was placed into the fixture. A bead of 3924 was dispensed with the 30ml manual syringe and a 22 Gauge green taper tip. One end of the prepared surface side of the PC lap-shear was placed onto the adhesive with the other end resting on the test lap-shear substrate and the mating lap-shear specimen was pressed gently until resistance from the lap-shears coming together was felt. A weight block was placed on top of the mating lap-shear specimen to achieve a final assembly, with verification of proper alignment of the lap-shear specimens (Figure 1). The block was placed behind the bond area so as not to block any of the light during exposure.

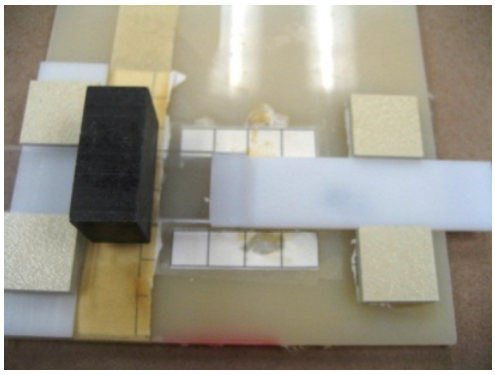

Figure 1. UV bonding fixture and alignment

Finally, the lap-shear specimen was cured in a Zeta® 7215 MPMA (Table 9). The Zeta® 7215 is a high intensity, benchtop light cure chamber used for curing Loctite Industrial "Light Cure" adhesives, and is particularly efficient for use in confined and exposed bond-line applications.

Table 9. UV Cure Irradiance

Light Source	Dosimeter (measured range)	Substrate	Distance	Cure Time	Dosimeter Exposure Time (s)	Energy (J/cm^2)		Peak Intensity (mW/cm^2)
Zeta 7215 MPMA	*UV A/B (280 – 405nm)*	*Through TS-213*	*7 in*	*30 sec*	*5 sec*	*362 (5 sec)*	*2167 (30 sec)*	*102*

The bonded lap-shears were tested per STM-700 by recording overlap, lbf, shear strength, and failure mode (Table 8 - PTFE, Table 9 - PE, Table 10). The cross head speed was increased to 4"/min when testing the bonded silicone assemblies and the manual grips were replaced with pneumatic grips. After initial testing of a set of the foam silicone substrate, the load cell was switched to the 100N load cell for increased accuracy, since the strengths were low.

Table 8: PTFE Substrate Test Results (Tested at 21°C, after 24 Hours (72hr for 3035) of Cure at 21°C)

Surface Treatment On PTFE	Summary	Adhesive				
		4011	**3924**	**E-30CL**	**U-05FL**	**3035**
Control	**Average Strength (psi)**	**27.7**	**43.2**	**32.3**	**3.6**	**1.8**
PTFE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**ADH**
	Stand. Dev.	12.5	6.1	9.5	4.7	1.8
Runs 1-5	**COV**	0.450	0.142	0.295	1.313	0.986
Blown Ion	**Average**	**5.1**	**42.1**	**35.8**	**12.3**	**8.9**
PTFE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**ADH**
	Stand. Dev.	7.1	1.8	3.9	10.7	6.6
Runs 16-20	**COV**	1.373	0.043	0.110	0.874	0.736
Variable Chemistry	**Average**	**3.1**	**34.1**	**31.6**	**10.4**	**9.4**
PTFE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**ADH**
	Stand. Dev.	6.9	19.2	2.3	9.8	5.7
Runs 31-35	**COV**	2.236	0.563	0.072	0.940	0.602
Flame Treatment	**Average**	**7.8**	**33.9**	**43.1**	**9.1**	**3.2**
PTFE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**ADH**

	Stand. Dev.	11.7	5.9	7.6	7.5	5.3
Runs 46-50	**COV**	1.507	0.174	0.175	0.828	1.651
Primer 7701	**Average**	**134.9**				
PTFE	**Failure Mode**	**ADH**				
	Stand. Dev.	37.1				
Run #61	**COV**	0.275				

Table 9. PE Substrate Test Results (Tested at 21°C, after 24 Hours (72hr for 3035) of Cure at 21°C)

	Adhesive					
Surface Treatment on PE	**Summary**	**4011**	**3924**	**E-30CL**	**U-05FL**	**3035**
Control	**Average**	**22.1**	**86.2**	**69.5**	**58.3**	**351.2**
PE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**COH/ADH**
	Stand. Dev.	15.5	26.3	10.6	13.0	184.8
Runs 6-10	**COV**	0.703	0.306	0.152	0.223	0.526
Blown Ion	**Average**	**214.0**	**314.8**	**627.6**	**407.0**	**436.3**
PE	**Failure Mode**	**COH/ADH**	**ADH**	**COH/ADH**	**COH/ADH**	**COH/ADH**
	Stand. Dev.	24.5	86.0	80.8	24.9	42.1
Runs 21-25	**COV**	0.114	0.273	0.129	0.061	0.096
Variable Chemistry	**Average**	**136.2**	**158.8**	**211.5**	**348.4**	**249.6**
PE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH/COH**	**ADH/COH**
	Stand. Dev.	4.1	69.0	7.9	41.7	196.6
Runs 36-40	**COV**	0.030	0.435	0.037	0.120	0.787
Flame Treatment	**Average**	**195.9**	**321.2**	**362.8**	**384.2**	**516.4**
PE	**Failure Mode**	**ADH**	**ADH**	**ADH**	**ADH**	**COH/ADH**
	Stand. Dev.	50.4	66.6	51.0	29.8	33.2
Runs 51-55	**COV**	0.257	0.207	0.141	0.078	0.064
Primer 7701	**Average**	**424.6**				
PE	**Failure Mode**	**ADH/COH**				
	Stand. Dev.	224.7				
Run #62	**COV**	0.529				

Table 10. Silicone Substrate Test Results (Tested at 21°C, after 24 Hours (72hr for 3035) of Cure at 21°C)

	Adhesive					
Surface Treatment On Silicone	**Summary**	**4011**	**3924**	**E-30CL**	**U-05FL**	**3035**
Control	**Average**	**1.3**	**5.1**	**6.6**	**5.7**	**1.2**
Silicone	**Failure Mode**	**ADH**	**ADH**	**SUBST**	**SUBST**	**ADH**
	Stand. Dev.	0.3	0.3	0.6	0.4	0.9

Runs 11-15	**COV**	0.240	0.065	0.089	0.064	0.743
Blown Ion	**Average**	**Run**	**4.5**	**5.9**	**Run**	**1.0**
Silicone	**Failure Mode**	**Eliminated**	**ADH**	**SUBST**	**Eliminated**	**ADH**
	Stand. Dev.		0.3	0.8		0.5
Runs 26-30	**COV**		0.061	0.131		0.561
Variable Chemistry	**Average**	**2.5**	**4.9**	**Run**	**7.1**	**2.6**
Silicone	**Failure Mode**	**ADH**	**ADH**		**SUBST**	**ADH**
	Stand. Dev.	0.2	0.7	**Eliminated**	0.9	1.3
Runs 41-45	**COV**	0.098	0.133		0.132	0.480
Flame Treatment	**Average**	**3.5**	**4.8**	**6.0**	**6.9**	**3.0**
Silicone	**Failure Mode**	**ADH**	**ADH**	**SUBST**	**SUBST**	**ADH**
	Stand. Dev.	0.4	0.4	0.3	0.5	0.8
Runs 56-60	**COV**	0.122	0.092	0.042	0.067	0.281
Primer 7701	**Average**	**5.2**				
Silicone	**Failure Mode**	**SUBST**				
	Stand. Dev.	0.4				
Run #63	**COV**	0.070				

Discussion of Results

The comparison of the effects of the surface treatments on the silicone foam substrate was minimal since above a certain strength substrate failure prevailed. Large differences in bond strengths were observed with the Loctite® 3035 on PE. The coefficient of variability (CoV) of the control was 0.526 and the CoV of the variable chemistry plasma was 0.787. However, blown ion (air plasma) and flame treatment had very small CoVs, 0.096 and 0.064 respectively.

Surface treatments had no statistically significant effect on the bond strength on the PTFE. This was the expected outcome, since all of the discharge technologies featured the ionization of air as the main process gas. This ionized air will have low electron density and low ionic surface bombardment. The most successful bonding system on PTFE was the Loctite® 4011 with the Primer 7701, followed by the Loctite® 3924 and the E-30CL.

Surface treatments of PE substrates resulted in statistically significant improvements in bond strength. The blown ion treatment had the most impact on bond strength with all of the adhesives. This surface treatment was also the only one where treatment resulted in visible surface etching due to positive ion velocities. Flame treatment also significantly impacted bond strength with all adhesives. The most successful bonding systems were the Loctite® E-30CL and Loctite® 3035. The 4011 with Primer 7701 also was successful except that one replicate (123.2 psi) brought down the average strength. The average strength, recalculated after removal of this run, was 500 psi.

Surface treatment and bonding of the foam silicone substrate resulted in generalized results. All successful bonding resulted in substrate failure during Instron testing. The strength readings were below the viable test range of the load cells. This was primarily due to the closed cell foam structure of the silicon lap-shear, having low inherent tensile strength. The Loctite® 4011 with Primer 7701, Loctite® E-30CL and Loctite® U-05FL successfully bonded the silicone foam following surface treatments.

Conclusions

Fluoropolymers posed the greatest bonding challenge for air-based plasma discharge pretreatment devices, strongly suggesting that higher density plasma discharges (those which exclude air as a process gas) which impart greater mechanical and chemical reaction mechanisms are required to increase surface polarity and bond strength. A follow-

up trial using this type of plasma device (existing Enercon Plasma3™ technology) with Loctite® 4011 (without Primer 7701), Loctite® 3924 and E-30CL is warranted. Polyethylene bond strength was significantly enhanced when pretreated with blown ion (air) plasma technology and bonded with either a two-part amine epoxy adhesive or two-component acrylic adhesive and imparted cohesive bond failure. Flame pretreatment also significantly enhanced polyethylene bond strength, particularly with two-component acrylic adhesives. Silicone foam surfaces experienced raised surface tension with all discharge treatment devices, with universal substrate failure theoretically caused by weak inherent substrate tensile strength. A follow-up trial incorporating solid (non-foam) silicone substrates with pretreatments using all plasma devices, and applying Loctite® 4011 with Primer 7701, Loctite® E-30CL and Loctite® U-05FL is recommended and will define appropriate adhesion protocols with silicone.