

Effects of Atmospheric Pressure Plasma on Adhesion

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Abstract:

Like any manufacturer, adhesive customers are constantly looking for ways to improve the reliability of their product while reducing cost. In order to increase bond reliability, there is typically a need for better surface preparation and more bond area which typically equates to higher cost. Cost reduction on the other hand can stem from many places such as switching to a less expensive substrate or material supplier or simply reducing adhesive usage. However, generally these types of changes can cause problems with the products performance and reliability. Through the use of atmospheric pressure plasma, APP, systems customers can clean their substrates, add functional groups to the surface, and increase its surface energy for improved adhesive wetting and performance in fractions of a second. Depending on how much strength is required for a given application, APP technology gives adhesive customers the option to seek less expensive substrates (which are traditionally difficult to bond) or reduce the amount of adhesive required to achieve desired bond strength.

The objective of this article is to educate the reader on the benefits of and relationship between APP systems and adhesives. Using APP treatment with adhesives can create potential for both cost reduction and improved part performance and reliability. Henkel has recently conducted a study on various difficult to bond substrates with a wide variety of adhesive chemistries to analyze the effects of APP on adhesion.

Outline:

1. General overview of APP technology
2. Brief description of alternative methods of improving adhesion
3. Cost comparison and surface energy of various plastics
4. Test Methodology
 - a. Selection of substrates
 - b. Selection of adhesives
 - c. Treatment and Test Methods
5. Discussion of results of testing

6. Conclusions and Future considerations for testing
 - a. Comparison versus vacuum plasma and corona treatment
 - b. Longevity of the treatment

Intro:

Like any manufacturer, adhesive customers are constantly looking for ways to improve the reliability of their product while reducing cost. In order to increase bond reliability, there is typically a need for better surface preparation (e.g. abrasion, solvent wipes, vacuum plasma, Corona discharge, flame treatment, etc.) and more bond area which equates to higher cost. Cost reduction on the other hand can stem from many places such as switching to a less expensive substrate or material supplier or simply reducing adhesive usage. However, these types of changes can cause problems with the products performance and reliability. Through the use of atmospheric pressure plasma (APP) systems customers can now feasibly reduce costs and improve bond reliability in fractions of a second. Depending on how much strength is required for a given application, APP technology gives adhesive customers the option to seek less expensive substrates (which are traditionally difficult to bond) or reduce the amount of adhesive required to achieve their desired bond strength.

Surface Treatment Background/Theory:

Plasma is the fourth and most abundant state of matter in the universe and its ionized nature provides very unique properties which can significantly enhance the bondability of a substrate's surface. Just a fraction of a second of exposure to an APP jet has been shown to improve the adhesion of some of the toughest to bond plastics, like HDPE, by over ten fold. The secret is the plasma treatment's ability to clean away soils, improve surface wetting, and activate a surface by adding functional groups to a substrate which help to anchor the adhesive. Any one of these attributes would enhance the reliability and performance of an adhesive but the combination of all three make for an ideal surface to bond for the following reasons:

1. Any type of surface contamination, including microscopic sized soils, can be considered a sacrificial layer which can cause an adhesive to delaminate or release from the surface. An adhesive can only be as strong as the surface that it is bonding. If the surface is sacrificial then so will be the adhesive. High velocity ionized plasma particles can break up and remove even microscopic sized surface contaminants to expose a stable bonding surface below.

2. A surface energy that is lower than the surface tension of a liquid adhesive (typically 30-40 dynes/cm) will cause beading and poor wetting. Therefore, improving a substrates surface energy will improve adhesive wetting and increase the bond area which will improve adhesion. Plasma treatment generally improves a substrates surface energy beyond 72 dynes/cm⁴ which means even water will wet the surface (see Table 1).

3. Even the cleanest and easily wetted surface can be difficult to bond if it is inert (i.e. polyolefin plastics). Therefore, activating the surface by adding favorable functional groups, such as carbonyl and hydroxyl groups, will enhance the interaction of the adhesive with the surface of the substrate and provide anchor sites for the glue.

Table 1: Surface Energy (dynes/cm)⁴

Substrate	Initial Surface Energy	Surface Energy Following Plasma
Polypropylene	29	>73
Polyethylene	31	>73
PTFE, FEP	22-37	72-73
Polycarbonate	46	>73
Polysulfone	41	>73
Silicone	24	>73
Polyurethane	38	>73

Source: GaSonics International Plasma Corp.

Traditionally, parts are plasma treated in a vacuum chamber in a batch process. Albeit this process is very effective at surface treatment given the reasons above, it is also time consuming, expensive and is not conducive to large parts and/or automated, in-line or high speed production processes. Depending on the chamber size required, the capital expenditures can well exceed \$50,000.

Alternatively, many customers will use Corona discharge to treat their parts to improve adhesion, which is similar to plasma treatment but not as effective. This process can generally treat many substrates up to 50 to 55 dynes/cm¹ in an automated, in-line, high speed (50ft/min¹) production process but this process is sensitive to moisture, generates hazardous ozone emissions, is poor at penetrating grooves or small cavities, and can be a safety concern given that it

generates a voltage on the substrate surface. The price of these units typically range anywhere between \$5,000 and \$15,000 depending on the size required.

APP treatment on the other hand combines the performance of a vacuum plasma unit with the process-ability of a Corona system with the use of shop air. Similar to vacuum plasma, APP bombards a substrates surface with ions (i.e. plasma) to provide a clean and active surface for enhanced bonding. However, APP is performed at atmospheric conditions so it does not require a vacuum chamber to operate, meaning an APP jet can be installed in-line with minimal to no process reorganization. Although Corona systems use a high voltage electrode to positively charge the surrounding air ion particles in an open air environment like an APP system, an APP system develops 100x more ion bombardment than a Corona system² at 3 times the line speed (150 ft/min¹). This is accomplished without producing any ozone or potential on the substrate surface. APP systems are also very inexpensive to operate, safe to use, compatible with metal substrates and insensitive to humidity¹.

Test Methodology:

In an effort to determine the effects of APP treatment on adhesion, Henkel completed a study comparing the adhesive shear strength of a wide variety of adhesive chemistries on various APP treated and untreated substrates (i.e. plastics, metals, and elastomers). The adhesives evaluated in this testing are detailed in Table 2. The substrates that were used are detailed in Table 3 along with their associated pricing/unit for comparison purposes only. The cost/unit of the plastic and elastomeric materials was calculated based on 12" by 12" sheets of medical/FDA grade material (if available) which were then cut to the sizes detailed in the Dimensions column.



Product	Product Description
Loctite® 401™ Prism® Instant Adhesive	100 cP, clear, ethyl cyanoacrylate adhesive. Medical version is Loctite® 4011™ Prism® Instant Adhesive
Loctite® 770™ Prism® Primer	1.25 cP, colorless, polyolefin aliphatic amine primer. Medical version is Loctite® 770™ Prism® Primer
Loctite® 3924™ Light Cure Adhesive	1,100 cP, transparent to hazy/fluorescent, medical grade UV/visible light cure acrylic adhesive.
Loctite® E- 30CL™ Hysol® Epoxy Adhesive	10,500 cP, ultra clear, 30 minute work life, two-part polyfunctional amine epoxy. Medical version is Loctite® M-31CL™ Hysol® Epoxy Adhesive
Loctite® U- 05FL™ Hysol® Urethane Adhesive	640/35,000 cP, off white, 5 minute work life, two-part polyurethane adhesive. Medical versions if Loctite® M-06FL™ Hysol® Urethane Adhesive
Loctite® H8110 Speedbonder™ Structural Adhesive	Methacrylate, Yellow Opaque Liquid, 2 components, 10:1 mix ratio



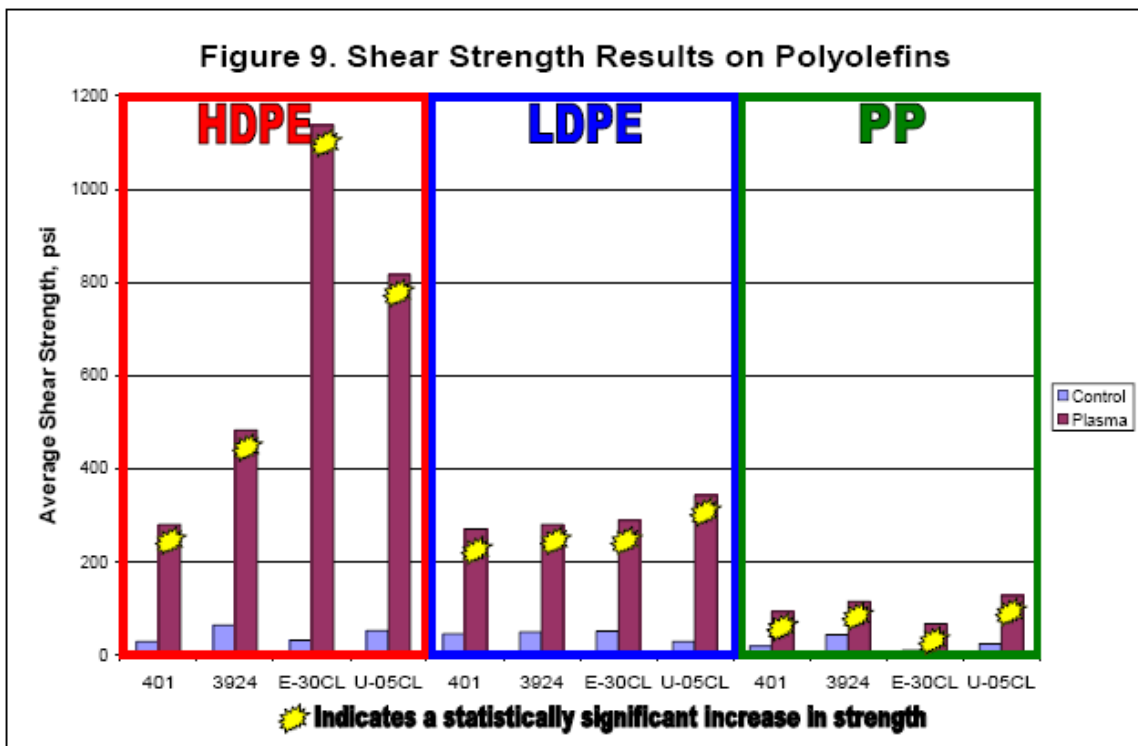
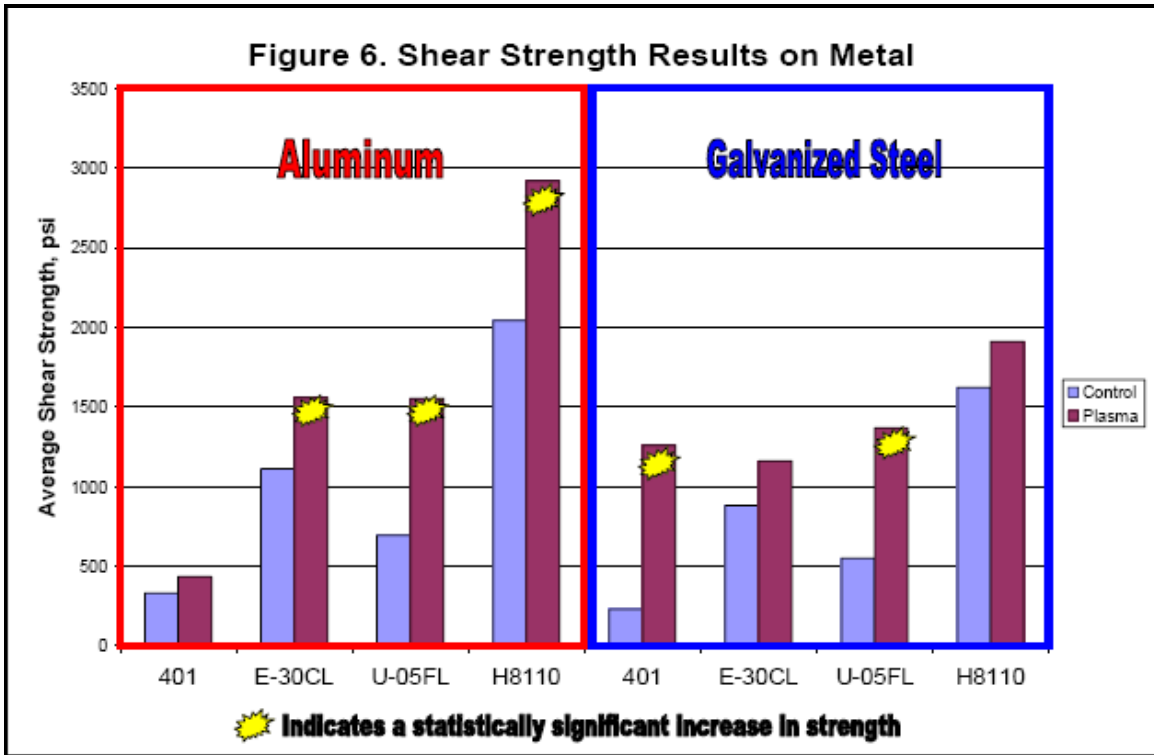
Dimensions	Description	Cost/Unit (\$)
1" x 4" x 1/16"	Galvanized Steel Lap-shears	\$0.92
1" x 4" x 1/16"	Aluminum Lap-shears	\$0.46
1" x 4" x 1/16"	Polycarbonate-Trans Lap-shears	\$0.35-0.48
1" x 4" 1/8"	Santoprene Lap-shears	\$0.47-0.52
1" x 4" 1/8"	Silicone Lap-shears	\$0.58-0.86
1" x 1" x 1/4"	Polyamide (Nylon) Blocks	\$0.15-0.20
1" x 1" x 1/4"	High Density Polyethylene Blocks	\$0.05-0.16
1" x 1" x 1/4"	Low Density Polyethylene Blocks	\$0.05-0.16
1" x 1" x 1/4"	Polypropylene Blocks	\$0.05-0.11
1" x 1" x 1/4"	Polybutylene Terephthalate (Valox) Blocks	\$1.63
1" x 1" x 1/4"	Polycarbonate-Trans Blocks	\$0.35-1.60
1" x 1" x 1/4"	Acetal Blocks	\$0.15-0.18
1" x 1" x 1/4"	Polyurethane Blocks	\$0.36-0.37

Source: McMaster Carr Inc.

All runs consisted of 5 replicates which were cleaned with isopropyl alcohol prior to being treated, bonded with a 1/2" overlap, and clamped for a minimum of 24 hours. The APP treated specimens were treated with a Plasmatreat Single Rotating Openair™ Plasma Jet RD1004 at a line speed of 20 ft/min from a distance of 8 mm away prior to being bonded within 10 seconds of treatment. All of the assemblies were tested with an Instron Mechanical Property Tester in compliance with ASTM D1002-05, D3163, and D4501-01.

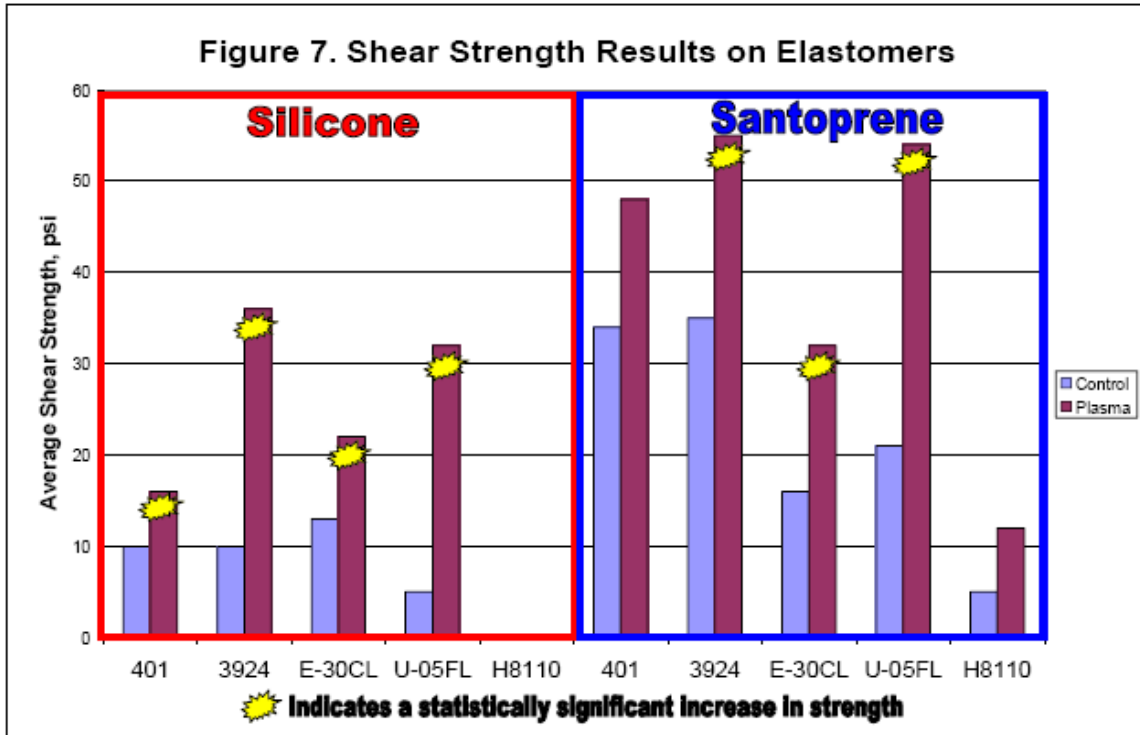
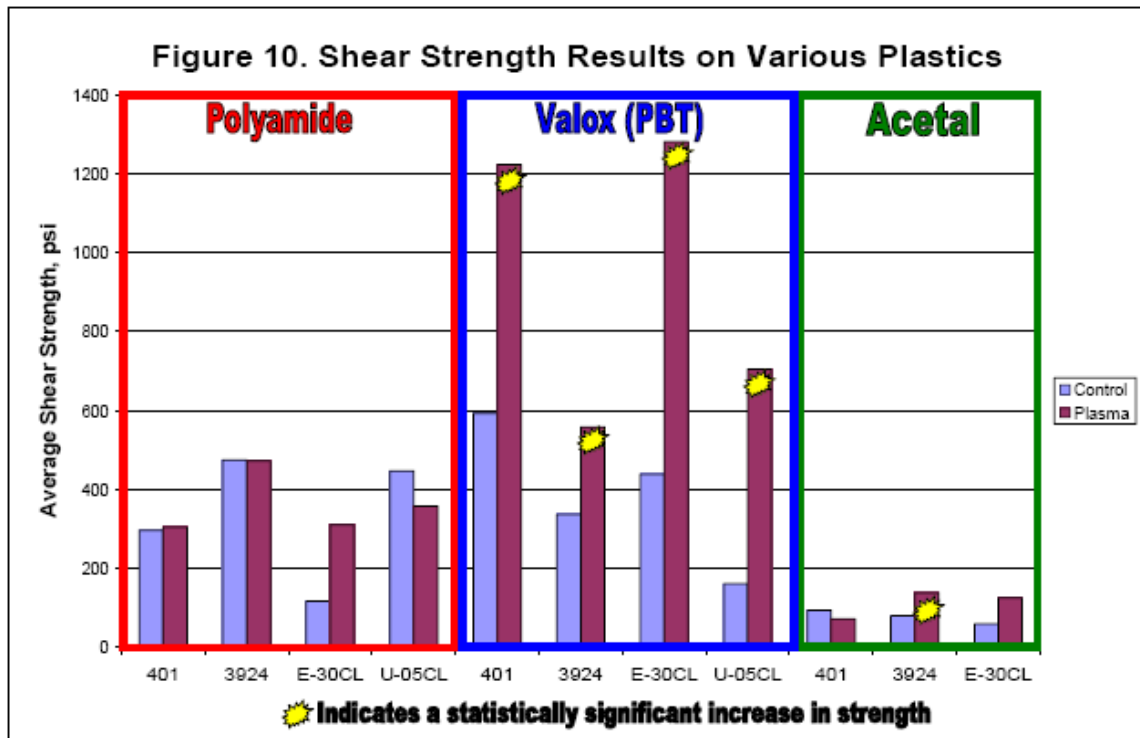


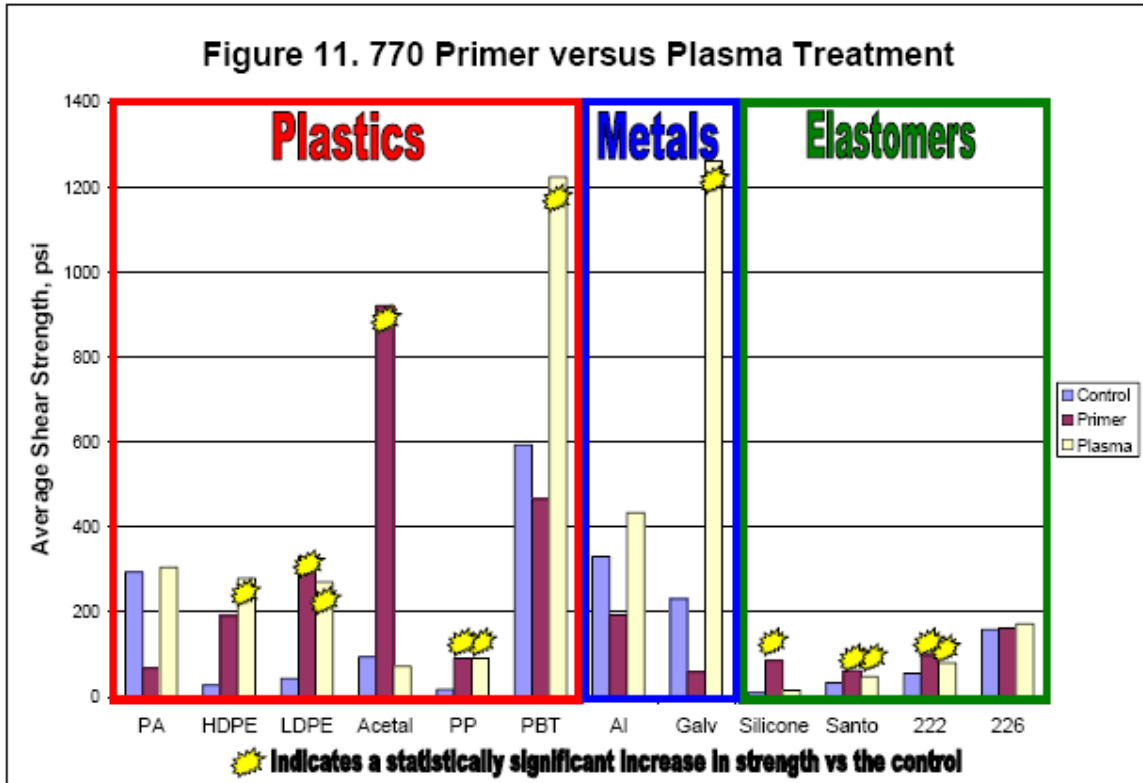
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Conclusions:

Aluminum oxidizes rapidly when introduced to oxygen and thus creates a barrier. Thus removal of this oxidation layer via APP treatment prior to bonding shows a significant improvement in adhesion APP treatment made a statistically significant improvement in adhesion with many of the adhesive/substrate combinations detailed above including all of the polyolefin runs. The polyolefin results are especially of interest given that they are quite inexpensive relative to the other materials tested and they offer favorable material properties that many customers have to pass on due to poor adhesion performance and bond reliability.