NEW ATMOSPHERIC PLASMA SURFACE TREATING TECHNOLOGY FOR IMPROVING ADHESION

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ABSTRACT

In-line atmospheric plasma surface treating is used to clean, etch and functionalize surfaces to improve bonding of adhesives, inks, paints, coatings and more. Treatment occurs in-line prior to bonding and effectively increases surface energy & wettability. A new Atmospheric Plasma Treatment system has been introduced to the market with expanded capabilities for treating composites, plastics, glass and metals. The technology offers uniform, high-density plasma treatment at higher processing speeds than previously possible. This presentation will share new laboratory data, which demonstrates how the industry can use this new technology to improve bonding in their operations.

INTRODUCTION

Surfaces with inherently low surface energy, contamination, or additives that bloom to the surface often require some type of surface preparation for successful bonding with adhesives. Atmospheric surface treatment technologies clean, micro-etch and functionalize surfaces to promote adhesion, improve quality and increase productivity. In the plastics industry, in-line plasma treating is growing in popularity for its ability to provide an automated and consistent surface preparation process. It has the ability to replace the need for mechanical surface preparations or specialty coating formulations.

For composites, two distinct applications can benefit from atmospheric plasma technology. The Aerospace industry is in need of surface treatment uniformity that can surpass results produced by manual methods. The Automotive industry is in need of effective surface treatment which can be automated to maintain manufacturing efficiencies.

The recent development of the Blown-ion™ 500 plasma treater with a MultiPort™ design offers such advantages.

2. SURFACE PREPARATION METHODS FOR IMPROVING ADHESION

2.1 Adhesion Mechanisms & Adhesion Requirements

One of the critical requirements for adhesive bond to perform well under mechanical loading is a well-prepared surface. Surface contamination, limited bonding sites and low surface free energy are the characteristics of a surface that will lead to the poor mechanical performance of an adhesive joint [1]. The following adhesion mechanisms explain how mechanical strength is directly correlated to these phenomena.

2.1.1 Mechanical Coupling

Mechanical Coupling is a mechanism based on the adhesive keying into the surface of the substrate. Some argue that mechanical interlocking provides higher adhesion strength; some believe it is increasing the surface area for more molecular bonding interactions. However, there is an argument that destruction of the surface may allow for the formation of macro-radials and hence an increase in chemical bonding sites [2].

Regardless of which statement is more accurate, it is commonly observed that roughening of surface prior to bonding enhances the strength of adhesive joints [2].

2.1.2 Molecular Bonding & Thermodynamic Mechanism of Adhesion

This is the most widely accepted mechanism for explaining adhesion between two surfaces in close contact. This mechanism describes the strength of the adhesive joints by interfacial forces and by the presence of polar groups [1].

2.1.3 Importance of a Clean Surface

The application on composite components of release agents such as FreKote® need to be removed prior to bond applications. Such contamination will result in poor bond strength [3], [4].

2.2 Surface Treatments for Composite Manufacturing

Peel ply, mechanical abrasion by grit blasting or with aluminum oxide paper along with the use of solvent cleaner are the most commonly used surface treatments in the manufacturing of composite materials.

2.2.1 Grit Blasting

Mechanical abrasion is a process considered to require a certain level of operator knowledge and experience. The cost of aluminum grit and solvent cleaners are quantifiable as a financial cost, along with the environmental impact of the production and disposal of such consumables [2]. Mechanical abrasion is perceived to remove loose contaminated layers and roughen the surface to provide some degree of mechanical interlocking or “keying” with the adhesive, it can be argued that the effect will increase the surface area of the component.

Surface Texture by the surface roughness has had mixed conclusions with respect to its effect on surface energy. It has been shown that smoother grit blasting has a greater effect on the surface energy than rougher grit. This has been suggested to occur because of droplets released by contact angle measurements which are affected by the barriers that peaks and ridges form with the spreading of the droplet. Capillary channeling has a counter effect and it occurs when the droplet seeks out areas of the surface where it can spread more easily [2].

A change in chemical composition has been attributed to a change in surface energy. Various types of grit blasting have shown to deposit various types of Na and/or Mg that correlate with the grit impurities [2].

2.2.2 Peel Ply

This consists of a single ply placed on one side of the composite material prior to the manufacturing process. Removing the peel ply at the beginning of the next process such as adhesive dispensing leads to a surface that has increased roughness and is free from contamination [3]. The application of peel ply can be a laborious and time-consuming process.

Surface roughness has increased dramatically 10 to 20 times higher than a mold-release agent [3]. Different peel ply will also deposit nitrogenous elements that lead to more polar surface characteristics. As discussed previously, this will cause the surface free energy to increase. There will also be no external contamination on the surface to assist in poorer mechanical strength.

2.2.3 Plasma Surface Treatment

Plasma Surface Treatment utilizes inert gas passed through an electrical discharge at high pressure to create an ionized gas mixture. When the ionized gas comes into contact with the material, it cleans contaminants from the surface and micro-etches the material to increase the surface roughness [1].

In the case of polymeric material, such as resin used in composite manufacture, plasma surface treatment adds highly energized functional groups to the surface of the material. Functional groups have polar or non-polar energy. These groups increase the surface energy of the material [1].

Compressed air is most commonly used as the inert gas. Along with the low power requirements of the equipment, it proves to have very low running costs and in terms of sustainability, produces no waste.

3. TYPES OF ATMOSPHERIC PLASMAS

Classification of air plasmas include blown arc [Figure 1] and blown ion [Figure 2] discharges. Blown-arc air plasma is formed by blowing atmospheric air past two high voltage power electrodes and is sometimes referred to as corona treatment. A typical blown arc treatment head can treat up to 2.5” wide. It has limitations in that it cannot treat conductive materials and it is generally capable of achieving treatment results at only low to moderate processing speeds less than 50fpm (feet per minute.)

Figure 1 Blown Arc Discharge

Blown ion air plasma systems push pressurized air past a single electrode, which unlike blown arc technology, discharges inside the treater head. The electrode creates positively charged ions in the surrounding air particles. The air pressure forces the air particles to accelerate out of the tip of the head as a high velocity stream of charged ions is directed toward the substrate surface. Through direct contact, these particles positively charge the object's surface increasing its surface energy and making it more receptive to inks and coatings.

Figure 2 Blown Ion Discharge

Blown ion technology can treat conductive and nonconductive surfaces and is effective at moderate processing speeds. A typical blown ion discharge can treat up to 3/8-5/8” in a single pass. Until recently, when wider blown ion treatment is required either multiple discharge heads are used, automation is required, or a rotating plasma discharge head is used.

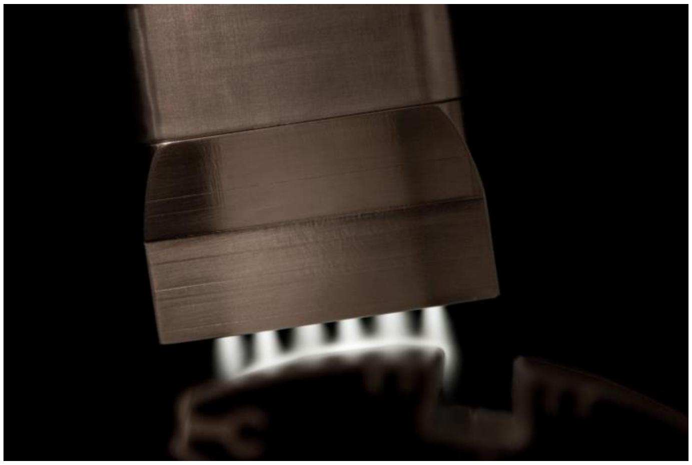

Figure 3 Blown-ion™ 500 with MultiPort™ Plasma Discharge

As seen in the experimental data below, rotating plasma heads have challenges in terms of their treatment level capacity and their ability to provide uniform treatment in a single pass.

The recent development of the Blown-Ion™ 500 with MultiPort™ design overcomes the limitations of existing blown ion plasma treating in terms of treatment levels, treatment uniformity and processing speeds.

4. MEASURING SURFACE ENERGY

Surface energy is key for successful adhesion. Think of how waxing an automobile’s surface affects how water droplets interact with the surface. After waxing, water droplets will bead up on the surface. This is an example of the forces of cohesion being greater than the forces of adhesion [Figure 4].

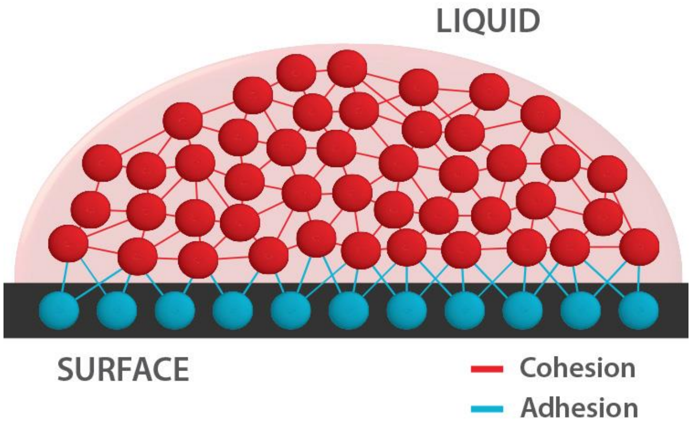

Figure 4 The forces of cohesion and adhesion

In order for a liquid to wet properly, the surface's energy must be substantially greater than the surface tension of the liquid.

4.1 Dyne Levels

Surface energy is measured in dynes per centimeter. One dyne is equal to 10 micronewtons.

Generally speaking, plastics and composites have chemically inert surfaces with low surface energy which inhibits bonding. Polyethylene and polypropylene, for example, have very low surface energy, in the 30-32 dyne range.

In order for a surface to be properly wet by a liquid, surface energy must be higher than the surface tension of the liquid. Ideally, the surface energy of the plastic or composite should be 7 to 10 dynes/cm higher than the surface tension of the solvent or liquid.

For example, a bonding liquid with a surface tension of 30 dynes/cm would not adequately wet or bond to a material having a surface energy less than 37 to 40 dynes/cm [5].

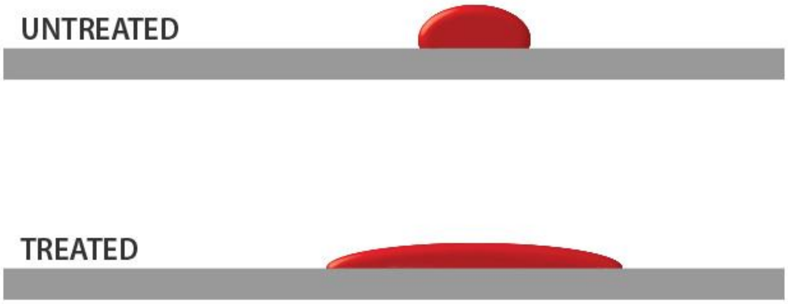

Figure 5 A liquid droplet beads up on a low energy surface while the same type of droplet will wetout on a surface with higher surface energy.

In general, higher dyne levels provide a greater chance for adhesion success than lower levels.

4.2 Experimentation #1 Dyne Levels Results

Initial laboratory experiments were conducted using the new Blown-ion™ 500 with MultiPort™ technology and rotary atmospheric plasma technology. Low Density Polyethylene [LDPE], Polyethylene [PE], Acrylonitrile Butadiene Styrene [ABS], Polypropylene [PP] and Aluminum surfaces were treated at speeds of 50, 100 and 150 fpm (feet per minute) processing speeds.

To determine the effectiveness of treatment, ACCU DYNE TEST™ solutions were used to compare post treatment dyne energy levels.

Figures 6-9 demonstrate how the new Blown-ion™ 500 plasma treater with MultiPort™ head design consistently exhibits higher treatment levels, and as processing speeds increased, the difference in the technologies became more significant.

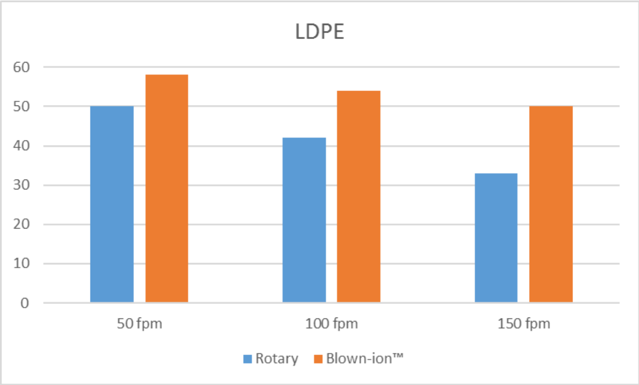

Figure 6 Post Treatment Dyne Levels LDPE

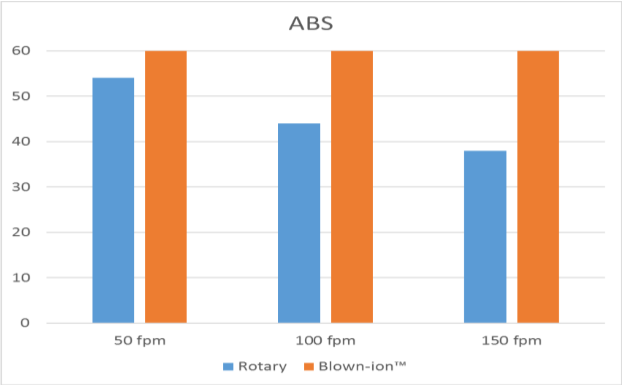

Figure 7 Post Treatment Dyne Levels ABS

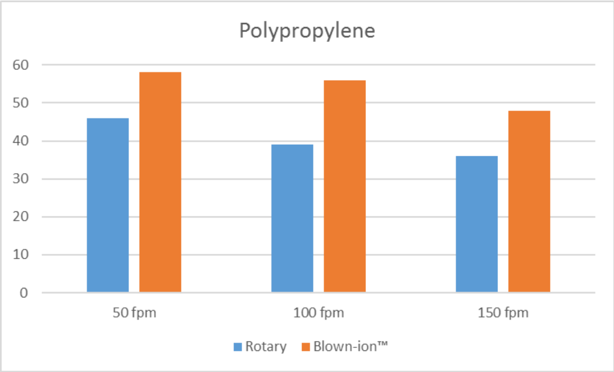

Figure 8 Post Treatment Dyne Levels PP

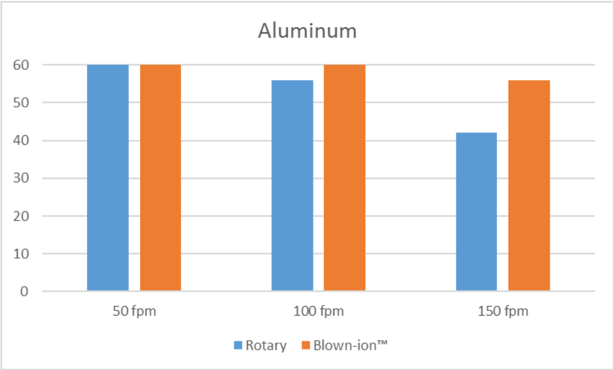

Figure 9 Post Treatment Dyne Levels Aluminum

4.3 Contact Angle Measurements

Dyne level testing is commonly used to measure surface energy because it is a simple and relatively inexpensive test to perform. Contact angle is a quantitative measurement of the wetting out of a liquid on a surface and requires sophisticated testing equipment. A lower contact angle indicates better wetting and conditions for successful adhesion.

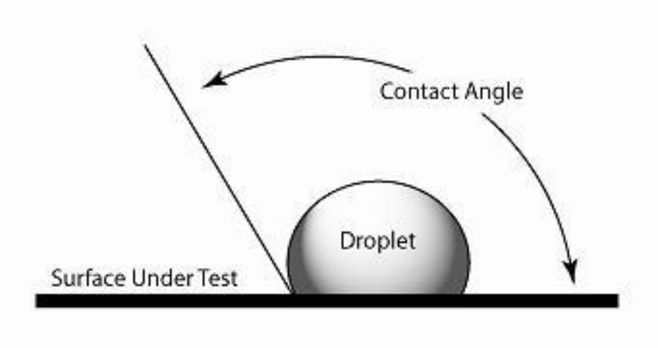

Figure 9 Contact angle measures the degree of wettability of a surface.

4.4 Experimentation #1 Contact Angle Results

A Kruss Mobil Surface Analyzer [MSA] was used to record contact angle measurements before and after treatment. MSA measures surface free energy by dosing two parallel drops, of different polarity, which are precisely measured and analyzed using a microscopic technique and sophisticated image analysis to determine wetting quality.

A lower contact angle indicates better wetting and conditions for successful adhesion. Figures 10-11 demonstrates the new Blown-ion™ 500 plasma treater with MulitPort™ technology produces lower average contact angles with less variation across the treated samples.

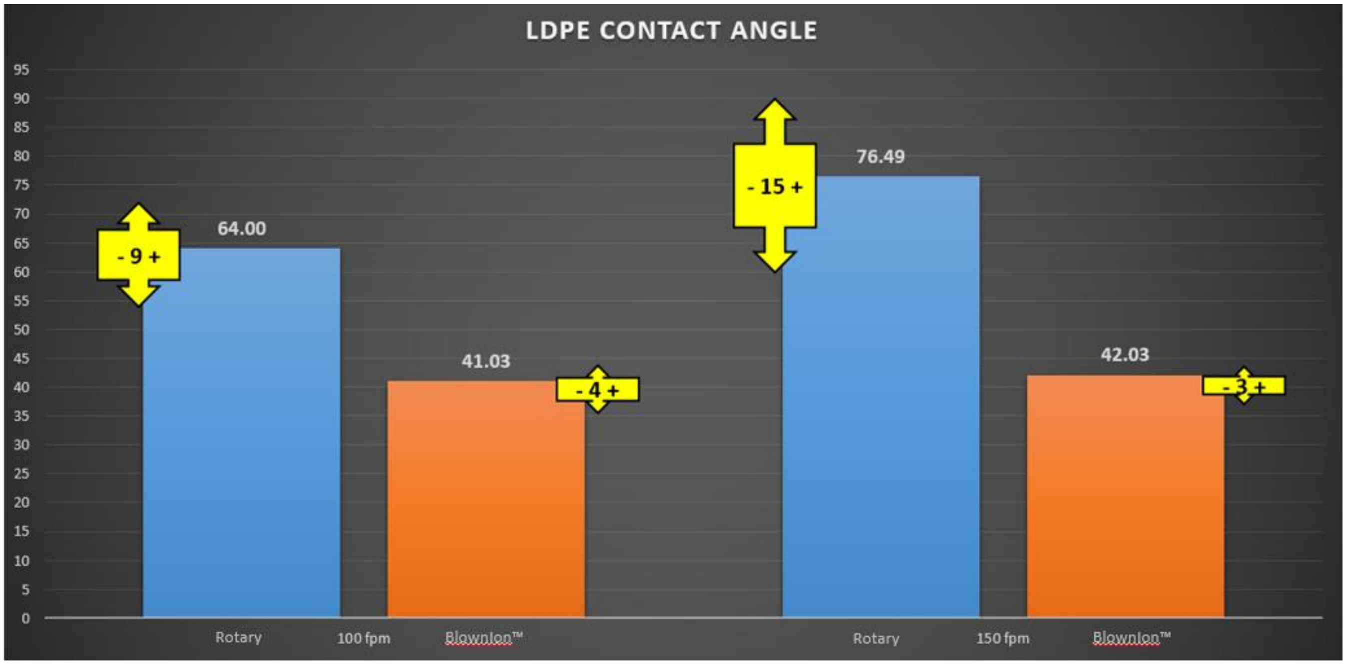

Figure 10 Post Treatment Contact Angle Average and Variation on Low Density Polyethylene (LDPE)

Figure 11 Post Treatment Contact Angle Average and Variation Aluminum

4.5 Experiment #2

In this experiment conducted at Abaris Training Resources, Inc. (Reno, NV USA), 350 degree CFRP (Carbon Fiber Reinforced Plastic) with peel ply were plasma treated with Blown-ion™ treatment immediately after removal of the peel ply. As described in section 2.2.2, peel ply is a surface preparation methodology commonly used to improve surface adhesion performance of composites.

A BTG Labs Surface Analyst™ was used to measure Contact Angle. Figure 12 shows the improvement in contact angle, key for surface adhesion and wettability, for plasma treated surfaces after removing peel ply.

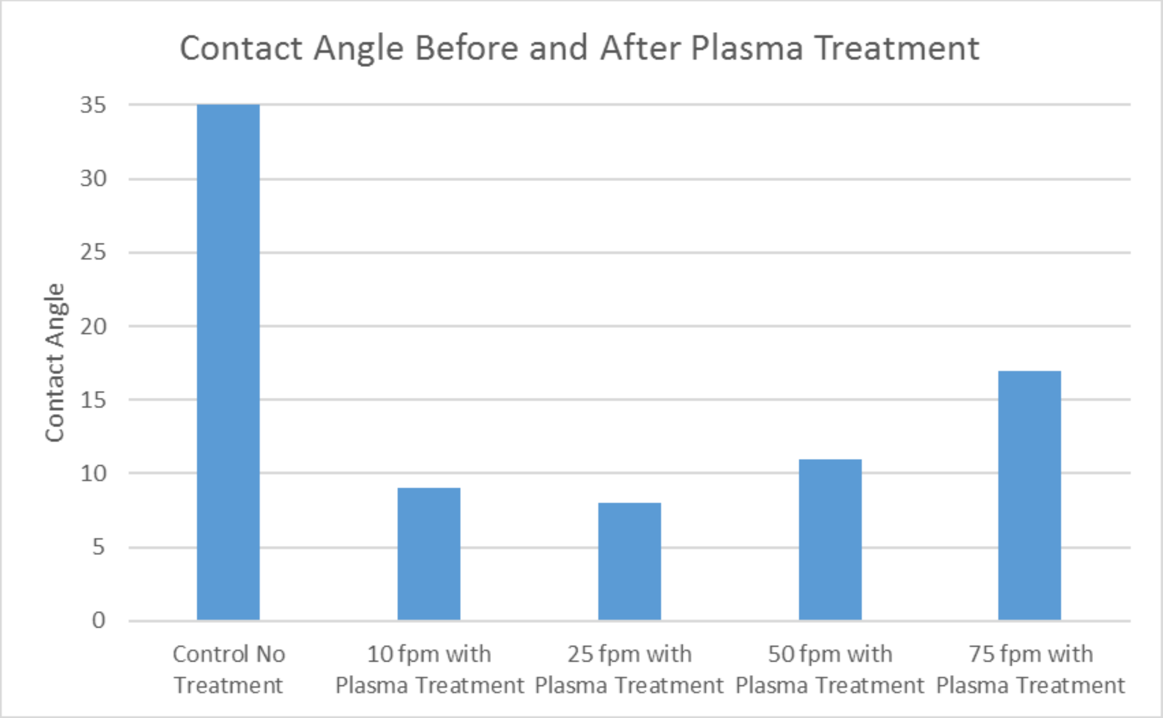

Figure 12 Contact Angle Comparisons of Peel Ply and Plasma Treatment at Various Line Speeds listed in fpm (feet per minute)

Lap sheer testing was conducted on surfaces with FM 123-5K 0.60 psf adhesive, 0.10 inch/min load rate with one inch grip from bond line, and 25 psi autoclave @ 250 degrees F for 60 min. Different combinations of peel ply, plasma treatment, acetone wipe, Scotch-Brite™ Pad roughening, and dry wipe treatments were tested.

Figure 13 shows the breaking pounds per square inch (psi) for each scenario. The combination of peel ply removal followed by Scotch-Brite™ Pad, Dry wipe and plasma yielded the strongest result. This result was slightly better than removing the peel ply, treating with plasma and then wiping with acetone, while eliminating the manual roughening step.

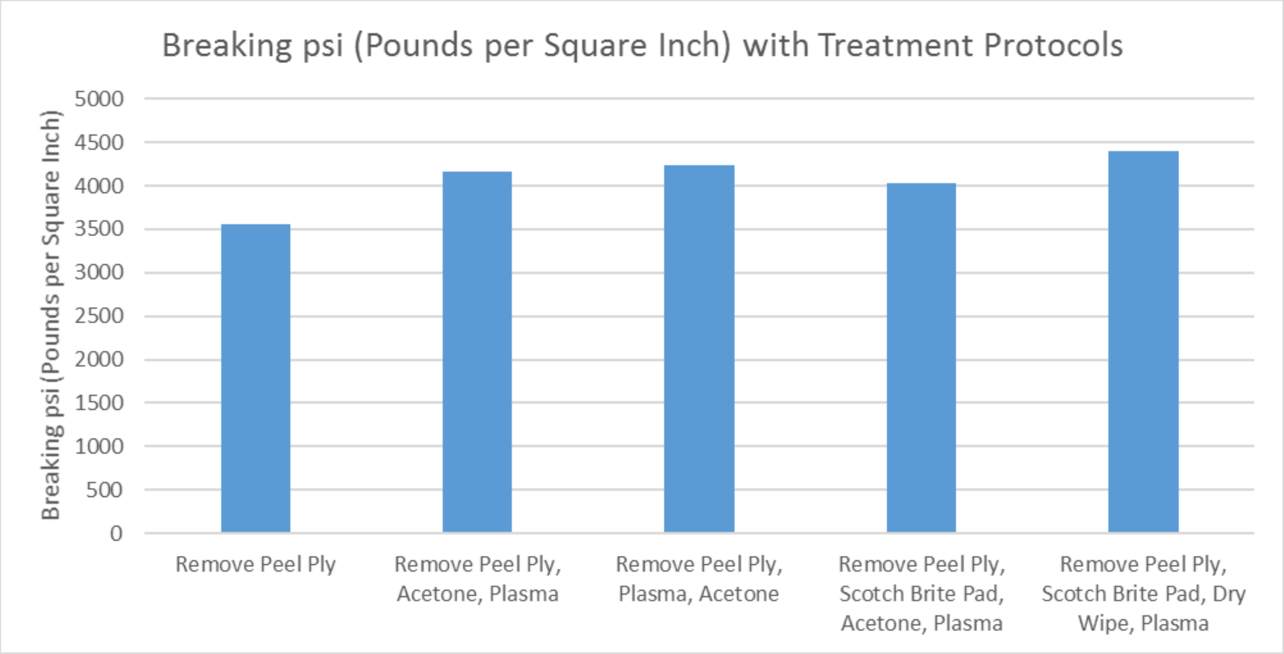

Figure 13 Breaking point psi (pound per square inch) comparisons of various combinations of surface preparation techniques.

4.6 Experiment #3

In this experiment, a composite surface was tested for bonding strength with peel ply and two secondary surface treatment procedures: "Hand Preparation" and Blown-ion™ plasma treating.

"Hand preparation" consisted of manual, mechanical roughing of the surface with a Scotch-Brite™ Pad, whereas Blown-ion™ plasma surface treatment was used to treat the surface automatically. Figure 14 shows a 16% increase in bond strength with peel ply and plasma as compared to peel ply and hand prep. It should be noted that manual hand preparation is subject to more variability as processing speeds and the size of the area to be treated increases due to the manual nature of the process.

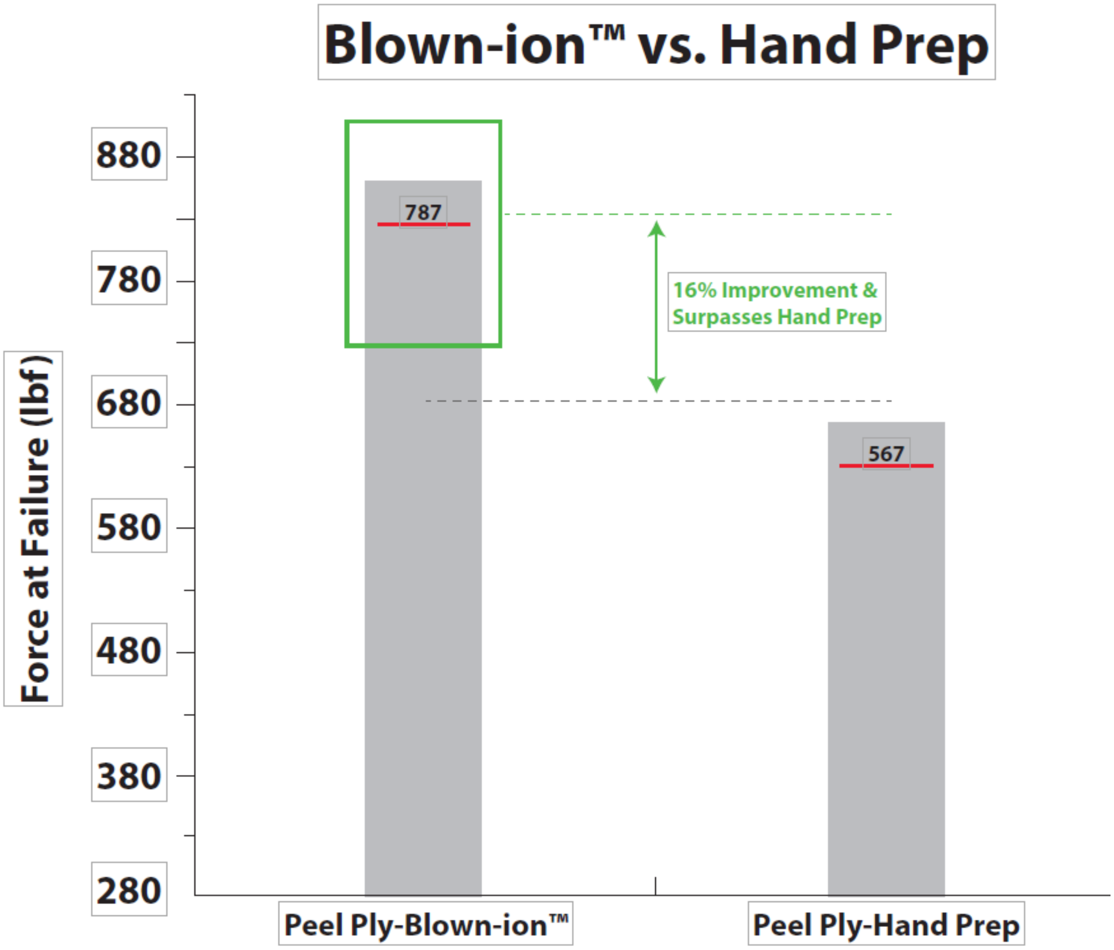

Figure 14. Post Treatment Contact Angle Average and Variation Aluminum

CONCLUSIONS

In laboratory experiments, the new Blown-ion™ 500 with MultiPort™ design has demonstrated an ability to increase surface wettability with uniform treatment levels at high processing speeds on a variety of materials.

- The combination of peel ply and plasma treatment show improvements in bonding strength with composites over peel ply and manual surface roughening.
- Contact angle results with new Blown-ion™ plasma treatment show favorable results even as line speeds increase.
- The use of plasma in specific orderly combination with other preparation technologies can maximize adhesion strength results.

These results show promise for industrial applications that require the benefits of uniform blown ion plasma treatment at wider widths and higher processing speeds. The technology may be integrated as a freestanding system mounted over a conveyor or indexing system, or part of a fully automated robotic installation.

Additional field and lab testing is recommended including, but not limited to:

- As many composite parts are quite large, it will be beneficial to understand the time degradation of surface effects after peel ply removal, and how plasma treatment can be used to offset this in a production environment.
- Combination treatments and processing recipes are needed to optimize the effectiveness of treatment for each application.
- Eliminating manual processes is key to realize product quality, efficiency and throughput goals.

Operations looking to evaluate the benefit of this new plasma technology should develop their own specific testing protocols to determine the optimal way to integrate plasma into their process for maximum results.

REFERENCES

1. [Awaja, F., Gilbert, M., Kelly, G., Fox, B., Pigram, P.J. [2009]. Adhesion of Polymers. Progress in Polymer Science, 34, 949-965.]

2. [Harris, A.F., Beevers, A., [1999]. The effects of grit blasting on surface properties for adhesion. International Journal of Adhesion & Adhesives, 19, 445-452.]

3. [Law, V.J., Mohan, J., O'Neill, F.T., Ivankovic, A., Dowling, D.P. [2014. Air based atmospheric pressure plasma jet removal of FreKote 710-NC prior to composite-to composite adhesive bonding, 54, 72-81.]

4. LOCTITE® FREKOTE Henkel Corporation

5. [Markgraf, D [1994] Corona Treatment: An Overview, TAPPI 1994 Polymers, Laminations & Coating Conference Proceedings, 3,4]