IMPLEMENTING PLASMA & FLAME SURFACE TREATING TECHNOLOGIES TO IMPROVE ADHESION WITH COMPOSITE MATERIALS

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Abstract

In-line surface treatment technologies are used to clean, micro-etch and functionalize surfaces to promote adhesion, improve quality and increase productivity. For some applications surface treatment is a requirement for adhesion success, for others it eliminates the need for expensive & specialty coating formulations, and in all cases it provides a safeguard against materials which may exhibit inconsistent surface energy. With the increased use of thermoset and thermoplastic composites in the automotive industry it is imperative for manufacturers to understand the capabilities of the various in-line surface treatment technologies available to them. This paper offers insights on how to select and implement treatment technologies to improve operations. Topics include; adhesion basics; the importance of properly defining your application; understanding surface energy & dyne levels; and how to apply the unique capabilities of blown arc plasma, blown ion plasma, variable chemistry plasma and high velocity flame plasma.

Introduction

After decades of automotive engineering optimization, traditional metals such as steel and aluminum are reaching their practical application limits. The need for decreased weight while maintaining structural properties have design engineers rapidly integrating plastics and composites into their latest products. Composites hold many functional advantages over their metal counter parts including superior mechanical performance, reduced weight, corrosion resistance, and the flexibility of part design. Automotive manufacturers are taking advantage of these benefits by incorporating plastics and composites into their designs and developing advanced manufacturing processes to improve production efficiencies.

With so many different types of composites available, design possibilities are nearly endless. Thermoplastics such as polypropylene (PP), polyethylene (PE) and polyamides (PA) offer fantastic corrosion and chemical resistance. With the addition of carbon, glass or natural fiber reinforcement, thermoplastics offer tensile strength comparable to steel, while weighing up to 75% less. [1] In addition to strength and weight characteristics, these materials can also be molded into complex shapes. This has allowed manufacturers to create parts from these materials such as covers, styling components, bezels and shrouds.

Thermosets such as polyester, vinylester and epoxy offer many of the same benefits as thermoplastics. Weight reductions and excellent mechanical performance make thermosets the ideal choice for body panels, shielding, and bracing. These composites are also beginning to be used in the core infrastructure of many automobiles. This has provided a drastic reduction in overall vehicle weight while maintaining the same safety standards as steel and aluminum. Meanwhile sheet molding, resin transfer molding and pre-pregnating fibers allows for the creation of complex curves in parts without compromising strength.

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[1] Lee S, Federation of Hong Kong Industries (2010)

Why surface treatment is often needed

New composite materials also present new production challenges. Bonding can be particularly challenging as advanced composite materials tend to have low surface energy and the surface tends to be very uniform on a nano level. There are multiple factors that can affect the bond strength of a material and an adhesive. Some of these factors include the presence of contaminants on the surface, the surface structure of the material, and the inherent surface energy of the material.

Having a clean surface is essential for proper bonding, and is the easiest way to improve adhesion. Layers of contaminants form a barrier between the material and the adhesive, reducing the bond strength. Possible contaminants include dust, oil and release agents.

The surface structure of the material affects bond strength in multiple ways. Ridges of nano fissures increase the bond energy, as a material that is inhomogeneous on the nanoscale inherently has a higher potential energy than a material that is uniform. Micro fissures on the surface effectively increase the surface area of an object allowing for bonding sites per unit area.

Surface energy is defined as the excess energy at the edge of an object compared to the bonding energy of the bulk material. If the surface energy is less than the bonding energy, the bulk material will sublime away. When a bond is formed the excess surface energy is transferred to the bond, resulting in a stronger bond. With a high enough surface energy is possible to bond two like materials together without thermal welding or adhesive, as seen with Silicone.

Surface energy is not a scalar unit. It has both a polar and non-polar part. When bonding, it important to consider not just the surface energy of the materials, but the polarity of both the surface energy of the material and the adhesive.[2] A highly polar water based adhesive will have a limited ability to bond with a material with a non-polar surface energy such as most thermoplastics and thermosets.

How in-line atmospheric plasma surface treatment improves adhesion

For this paper we conducted experiments with in-line atmospheric blown-ion plasma with compressed air, and in-line flame plasma with a high velocity drilled port burner. Each technology is well known to improve the adhesion properties of a variety of surfaces. All samples were wiped down three times with acetone before initial peel testing. The samples were treated at 100 feet per minute.

Plasma treatment increases surface adhesion through cleaning, nano and micro etching and by adding high energy functional groups. The most direct way that plasma improves adhesion is by cleaning the surface and removing surface contaminants. Dust, oils and other contaminants that are not bonded to surface are vaporized by the plasma. Plasma treatment has an advantage over traditional cleaning methods in that it in addition to removing environmental contaminants it removes low bond strength impurities that form on the surface. These often include oxides and additives that bloom to the surface of the material. These impurities while useful in the bulk material tend to have lower bond strength to both the bulk

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[2] Paul C. W, Journal of Adhesion Science and Technology 22 31-45, (2008)

material and the adhesive. Removing these impurities from the surface allows nano and micro fissures to form. These fissures increase surface area and surface energy of the material.

In addition to removing contaminants and micro etching, plasma treatment adds highly energized functional groups to the surface of the material.[3] Functional groups can have polar or non-polar energy. These functional groups increase the surface energy of the material

The purpose of this testing is to measure the surface energy and bond strength before and after various plasma treatment methods. The surface energy of a material is measured by comparing the contact angle of a polar and non-polar liquid. Bond strength will be measured with a peel tester. A list of samples used during testing is shown in Table I.

Table I - Test Material

Material	**Type**
Polypropylene (PP)	Thermoplastic
Polyethylene (PE)	Thermoplastic
Polystyrene (PS)	Thermoplastic
Nylon 6 (PA6)	Thermoplastic
Nylon 6, 6 (PA66)	Thermoplastic
Polyester (PET)	Thermoset
Epoxy Resin (CF)	Thermoset

Figure 1 and Figure 2 show examples of the water contact angle of epoxy resin before and after the surface has been treated with flame. The contact angle for polar liquids has gone from roughly 90 degrees to 40 degrees. This corresponds with an increase in polar surface energy from 2.2 mN/mm to 24.5 mN/mm.

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[3] Wolf R,SPE ANTEC, (2006)

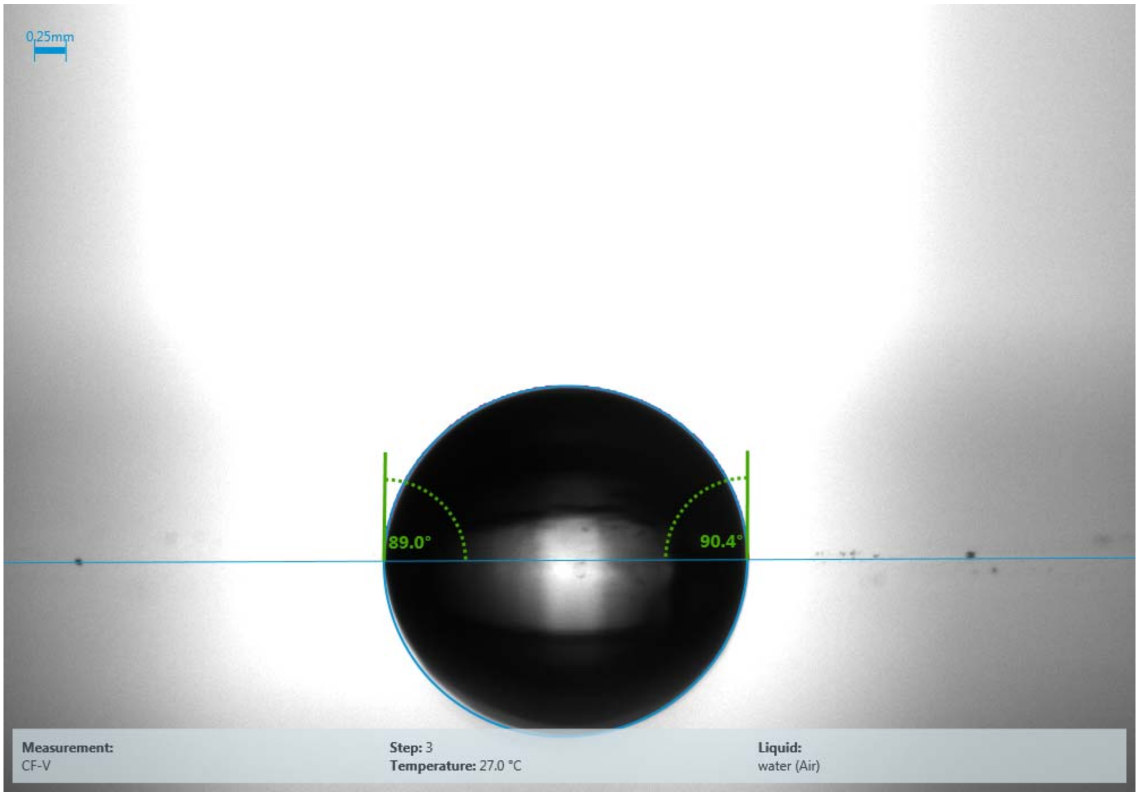

Figure 1 - Water Contact Angle of Epoxy Resin before treatment

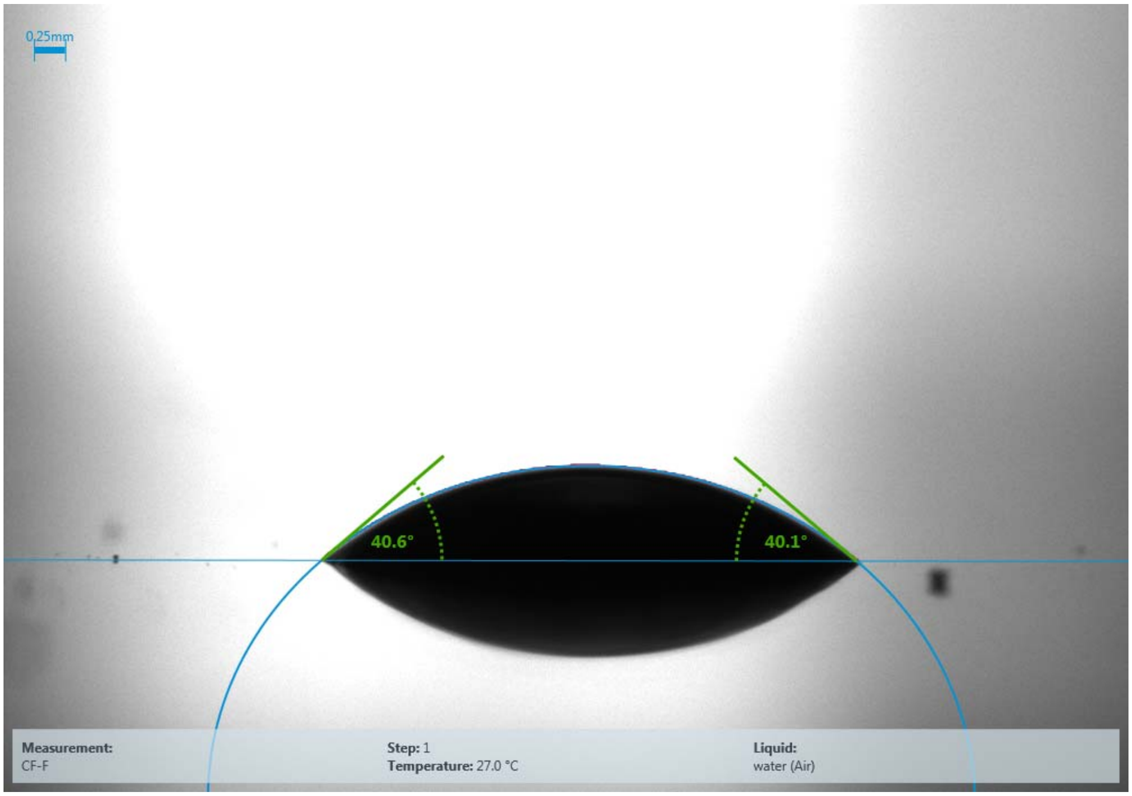

Figure 2 - Water Contact Angle of Epoxy Resin after flame treatment

Comparing Atmospheric Plasma and Flame Technologies

Blown ion plasma and flame treatment increased the surface energy in all tested materials with the majority of the increase in the polar component. Treatment improved the peel strength of all material with the noted exception of polystyrene. The results of flame treatment are shown in Table II. A comparison of surface energy and peel strength before and after flame treatment is shown in Figure 3 and Figure 4.

Table II - Flame Treatment Results

Material	Initial Surface Energy			Final Surface Energy			Peel Test	
	Polar	**Non-Polar**	**Total**	**Polar**	**Non-Polar**	**Total**	**Initial**	**Final**
Polypropylene (PP)	1.5	28.1	29.7	9.5	35.1	44.6	0.22	0.37
Polyethylene (PE)	0.3	28.4	28.7	16.9	39.4	56.3	0.02	0.16
Polystyrene (PS)	0.6	40.8	41.4	7.7	40.2	47.9	0.41	0.27
Nylon 6 (PA6)	6.9	34.8	41.7	15.8	37.8	53.5	0.25	0.20
Nylon 6/6 (PA66)	8.1	41.2	49.2	17.8	38.2	56.0	0.38	0.35
Polyester (PET)	0.3	28.4	28.7	5.2	30.7	35.9	0.16	0.18
Epoxy Resin (CF)	2.2	35.4	37.6	24.5	36.0	60.5	0.27	0.26

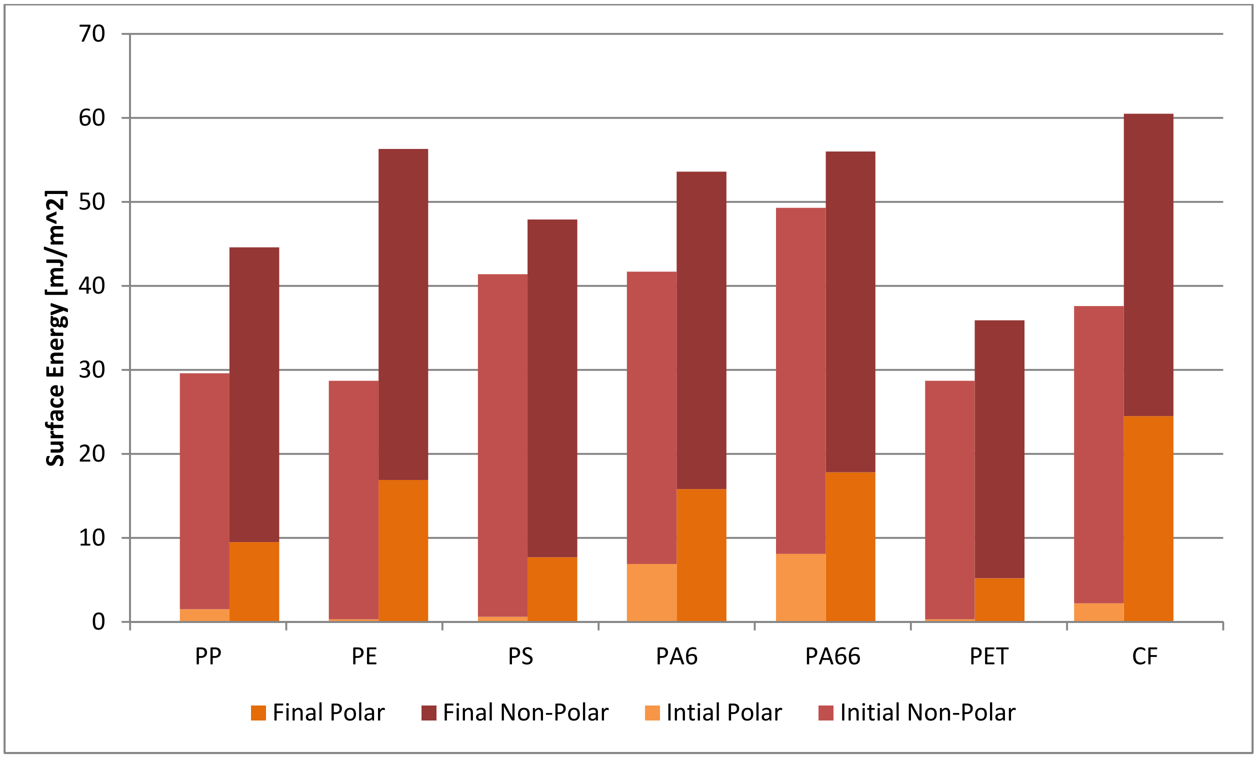

Figure 3 - Flame Treatment Surface Energy Results

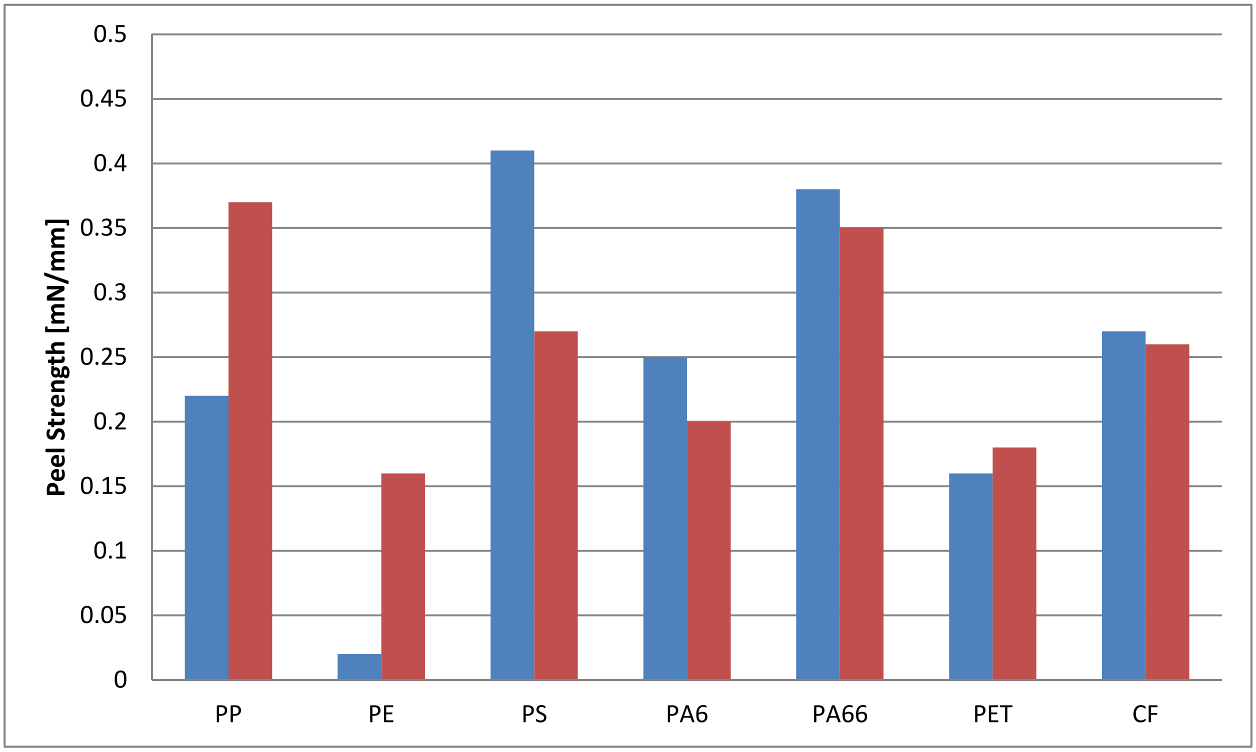

Figure 4 - Flame Treatment Peel Test Results

The test results of blown ion atmospheric plasma with compressed air are shown in Table III. A comparison of surface energy and peel strength before and after plasma treatment is shown in Figure 5 and Figure 6. The blown ion treatment increased the polar component of the surface energy on average 120% more than flame treatment with the exception of epoxy resin, which dropped by 20%.

Table III – Blown Ion (Air) Treatment Results

	Initial Surface Energy			**Final Surface Energy**			**Peel Test**	
Material	**Polar**	**Non-Polar**	**Total**	**Polar**	**Non-Polar**	**Total**	**Initial**	**Final**
Polypropylene (PP)	1.5	28.1	29.7	14.3	35.4	49.6	0.22	0.45
Polyethylene (PE)	0.3	28.4	28.7	21.4	38.5	59.9	0.02	0.16
Polystyrene (PS)	0.6	40.8	41.4	27.7	37.8	65.4	0.41	0.31
Nylon 6 (PA6)	6.9	34.8	41.7	22.1	38.3	60.3	0.25	0.27
Nylon 6, 6 (PA66)	8.1	41.2	49.2	27.7	36.9	64.6	0.38	0.36
Polyester (PET)	0.3	28.4	28.7	27.7	34.6	62.3	0.16	0.21
Epoxy Resin (CF)	2.2	35.4	37.6	20.1	37.7	57.2	0.27	0.31

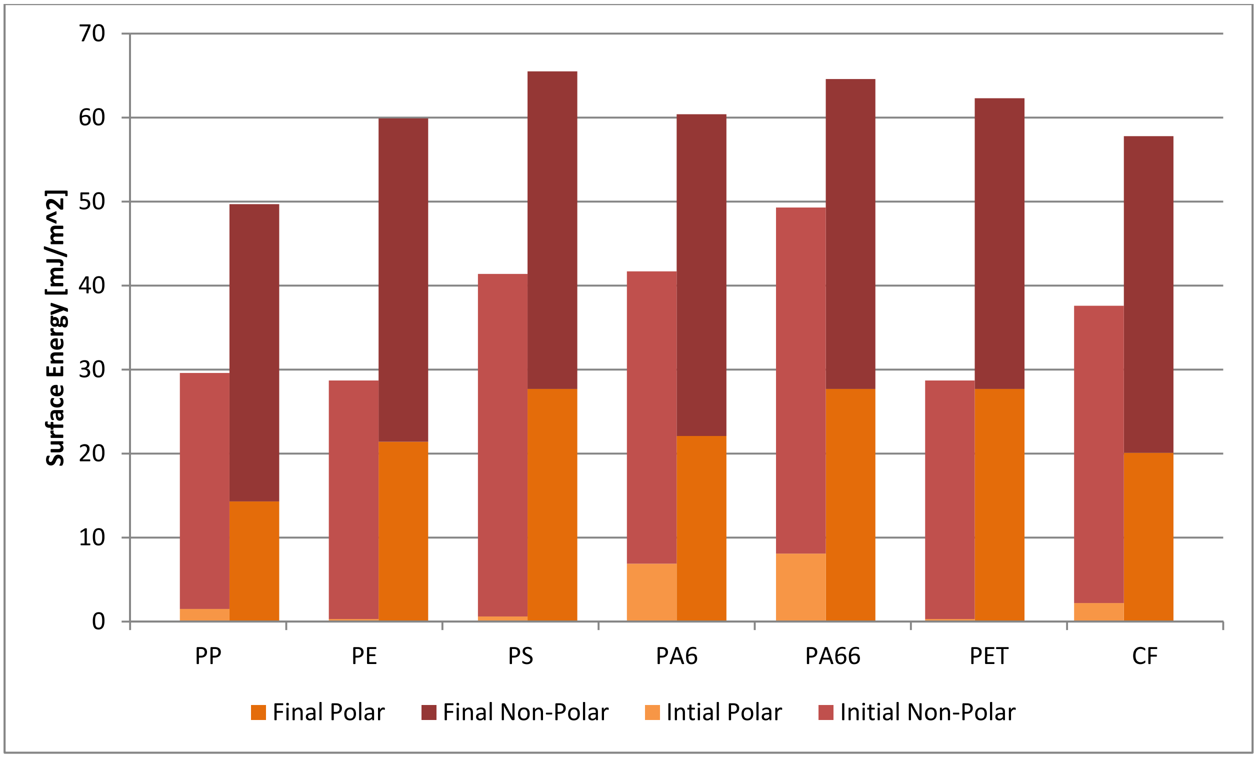

Figure 5 - Blown Ion (Air) Surface Energy Results

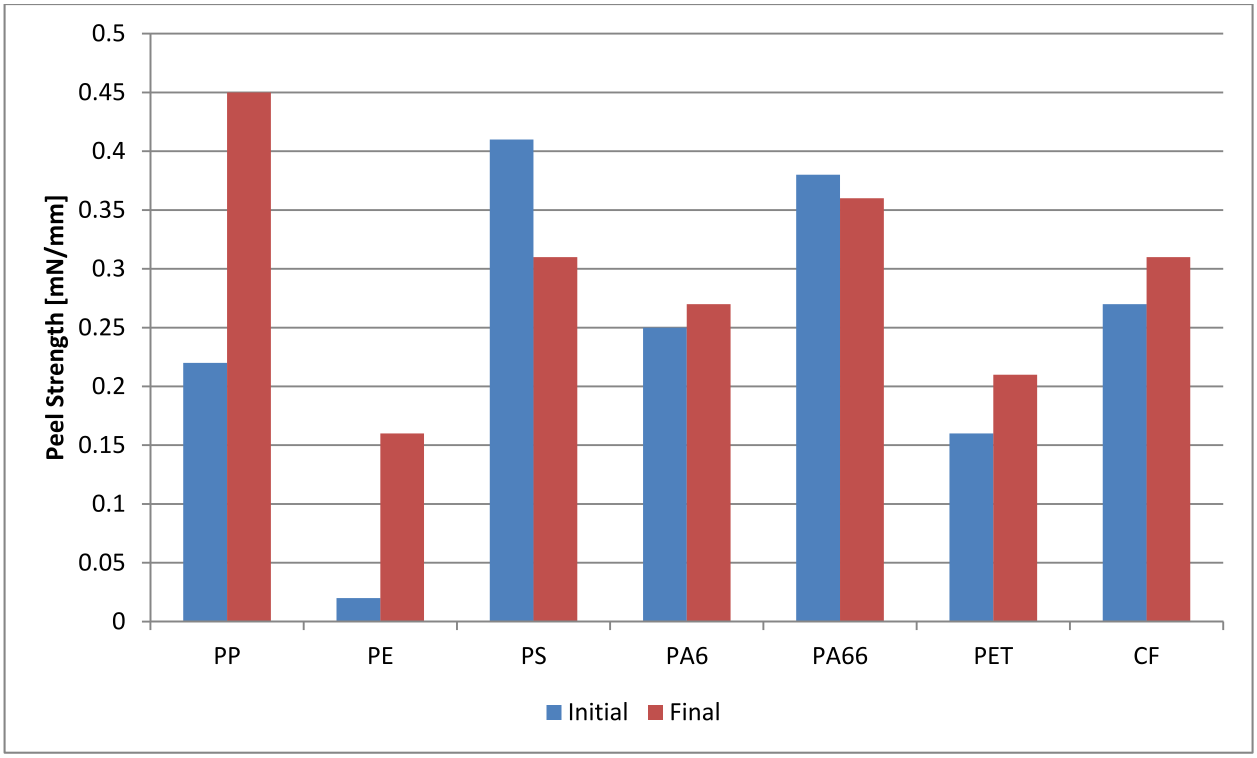

Figure 6 - Blown Ion (Air) Peel Test Results

Blown ion plasma can use specific gasses in addition to compressed air. Further testing was done with CO2 and nitrogen. Peel testing showed little difference between compressed air, CO2 and N2, with the exception of using CO2 to treat PA6/6 which saw a slight increase in peel strength rather than a slight decrease which is shown in Figure .

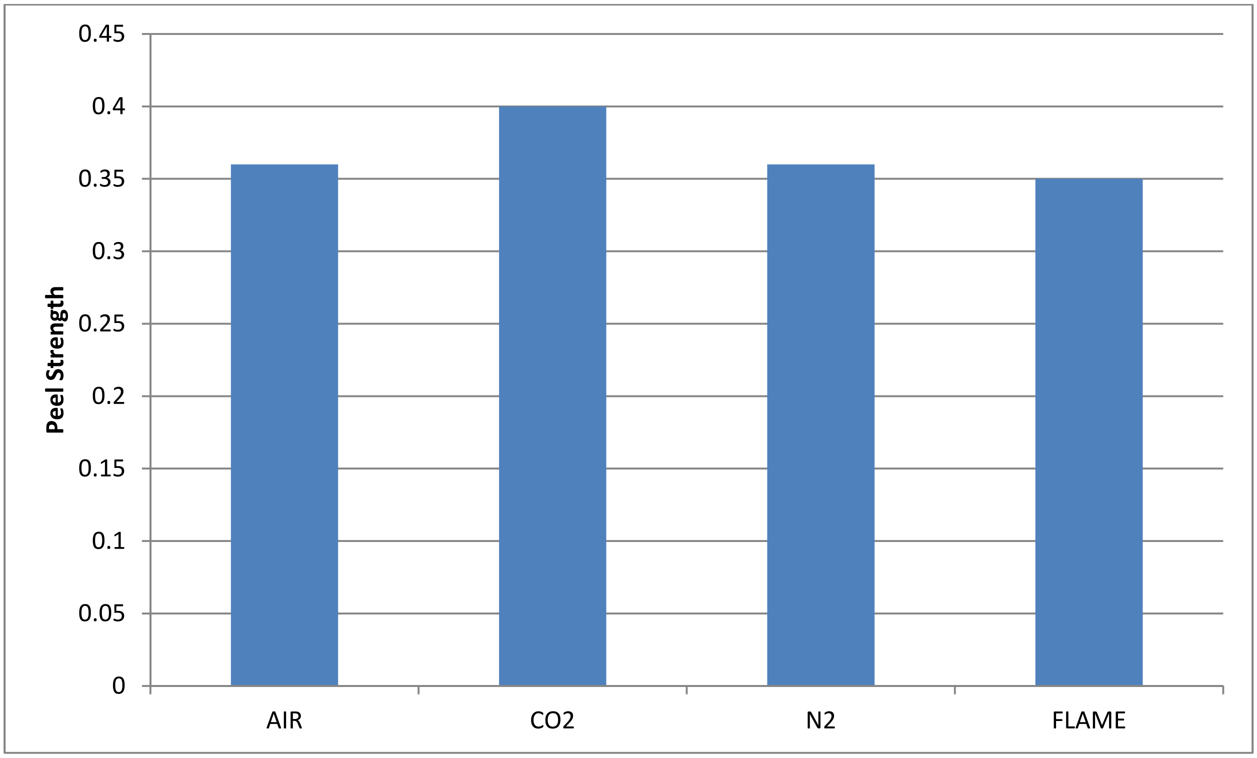

Figure 7 - Nylon 6, 6 Peel Test Results

The change in surface energy and peel strength before and after treatment represented by delta and is shown in Table IV. Testing showed no correlation between peel strength and total surface energy. However test results indicated a very strong positive correlation (0.82) between the change in non-polar surface energy and the increase in peel strength. The correlation between change in peel strength and change in non-polar surface energy is shown in Figure 8. This should not be interpreted as showing that non-polar surface energy is the only factor to consider when bonding. This shows the limitations of the peel test, and that the tape used in the peel test has a mostly non-polar component. An adhesive with a higher polar component would most likely have stronger effects from the plasma treatment.

Table IV – Delta Surface Energy and Peel Strength after flame treatment

Material	**Polar**	**Non-Polar**	**Total**	**Peel**
Polypropylene (PP)	7.95	7.07	15	0.15
Polyethylene (PE)	16.7	10.98	27.7	0.14
Polystyrene (PS)	7.07	-0.57	6.5	-0.14
Nylon 6 (PA6)	8.83	3.05	11.9	-0.05
Nylon 6, 6 (PA66)	9.7	-2.99	6.71	-0.03
Polyester (PET)	4.87	2.35	7.22	0.02
Epoxy Resin (CF)	22.3	0.64	22.9	-0.01

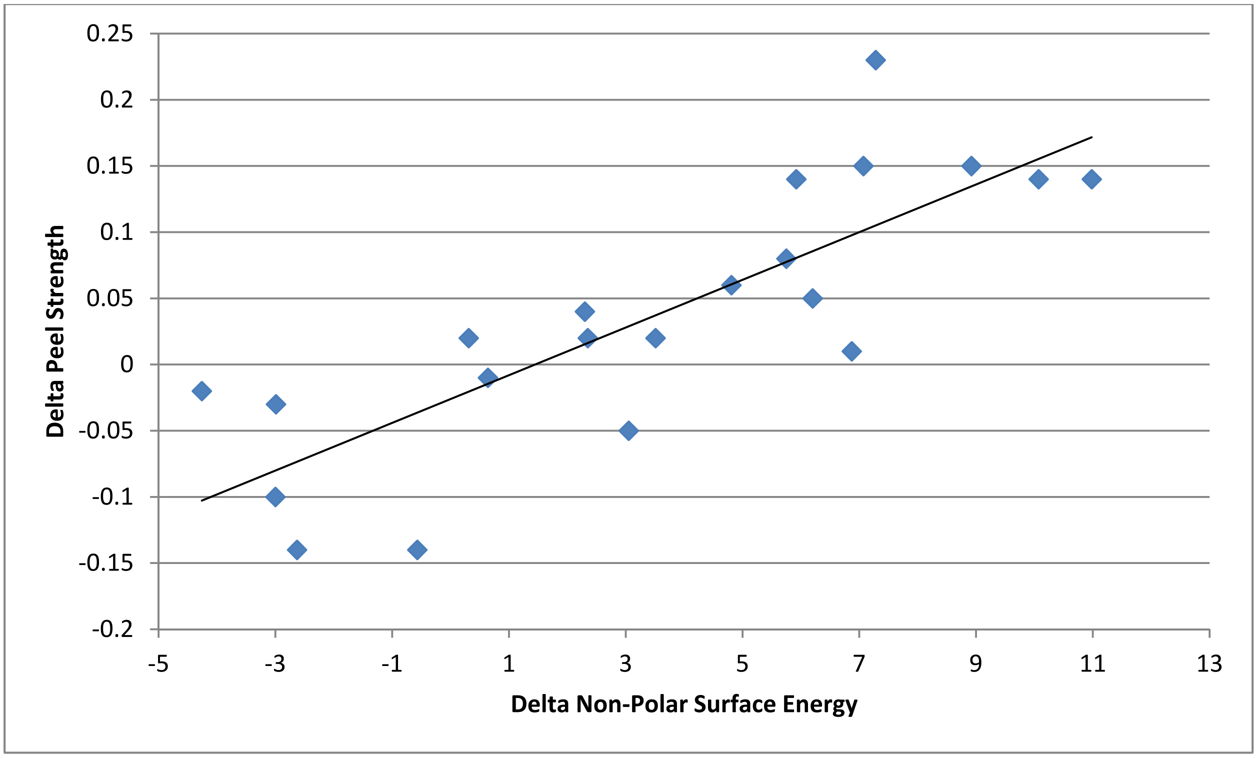

Figure 8 - Delta Non-Polar Surface Energy versus Delta Peel Strength

Integration

Plasma and flame surface treatment offers great versatility for manufacturers when it comes to integration. These system help eliminate slower and less efficient manual surface preparations, and unlike batch vacuum plasma treatments, atmospheric flame and plasma are integrated in-line.

Eliminating the need to remove parts from a production line to undergo an entirely separate process prevents disruptions in work flow, decreases production time, and reduces cost to the final product. By treating parts as they're conveyed, carried, and transferred from one process to the next, manufactures can ensure a precise reliable bond will be made without adding extra processing time and space.

Plasma and flame surface treaters may be integrated in a fixed stationary position with parts moving past them. For composite applications that involve complex shapes the part can remain stationary and the treatment head can be made mobile. Surface treaters have relatively small treatment heads and are connected to control cabinets via flexible cables. This makes them well suited for pairing with robotics. Any machine from a two axis bench top robot, to six axis robotic arms can be fitted to treat even the most complex shapes.

Blown ion air plasma offers a precise treatment ideal for shallow glue channels, and spot treating direct glue bead paths. This type of treatment is capable of increasing the surface energy of materials at a wide range of line speeds and is often applied simultaneously with glue dispersion. Parts can be treated and glued in the same process. This creates a high performance, reliable bond with zero added processing time.

Flame surface treatment, like blown ion plasma has the ability to treat composites at a wide range of line speeds and offers virtually unlimited processing widths. This enables treatment of small, intricate parts with complex shapes as well as the largest components found throughout automobiles like frames and cosmetic panels. An additional benefit of flame treatment is the ability to treat materials at a wide range of distances. Components can be located anywhere from one to six inches away from the treatment head depending on the application. This wide range minimizes the need to create long, slow robotic paths to ensure treatment of complex shapes and curvature, ultimately reducing cycle time.

Practical Application Consideration When Implementing a Surface Treatment Solution

Application parameters that must be taken into consideration when evaluating flame and plasma technologies also include:

Dwell Time: The experiments for this paper were conducted at 100 feet per minute. Typically longer dwell times will result in higher treatment levels. However dwell time may be limited by the surface's ability to maintain its integrity when exposed to higher levels of heat that are often present with longer dwell times.

Surface Geometry: Flame treatment burners can be designed in widths much wider than blown-ion plasma discharge heads. This makes flame treatment a preferable choice when treating large surface areas or objects with irregular surfaces; for example an automotive dashboard or bumper. Blown-ion air plasma offers a smaller, but more direct treatment area and may be a preferred method when treatment is required in very specific areas, particularly those with deeper recesses such as a with an automotive head lamp assembly.

Integration: Both flame and blown ion plasma systems are equally well suited for fixed mounting or robotic integration. Areas identified as hazardous require specific examination to determine if flame and plasma are suitable for the environment.

Consumables: Blown ion air plasma requires compressed air, while flame requires both compressed air and natural gas or propane.

Surface Energy Degradation: Many factors can affect how long surface energy is retained after treatment. Storage conditions such as temperature, humidity, external contaminants and time itself can reduce the effects of treatment. In addition, material additives can also rise to the surface and reduce the effects of surface treatment. While acceptable treatment levels may last for hours, days, or even weeks, is a best practice to perform the next bonding process as soon after treatment as possible.

Conclusion

In-line surface treatment technologies will play an important role in the efficient and economic assimilation of composite materials in the automotive manufacturing process. In-line blown ion atmospheric plasma and flame surface treatment technologies are proven to increase the wettability and surface energy of a variety of materials which improves bonding characteristics. In addition to surface energy, changes in surface polarity imparted by each of these technologies can be advantageous for bonding. Additional considerations for integrating plasma and flame surface treatment include application parameters including line speeds and surface geometries.