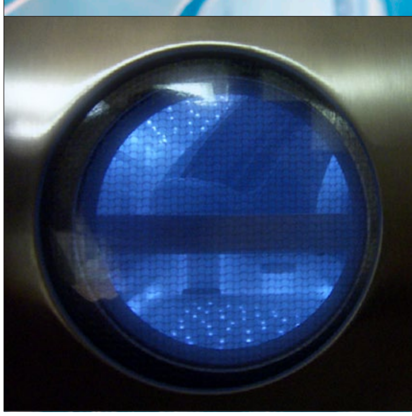
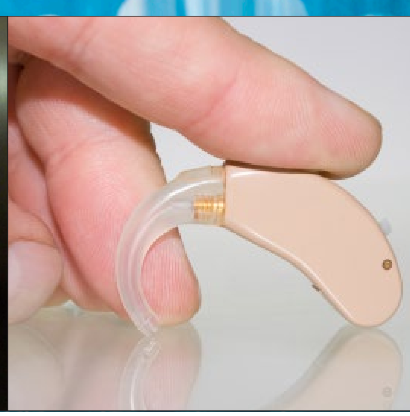
TriStar

Engineered Plastic Solutions™

Surface Modification:

How low-pressure plasma treatments can benefit your manufacturing process





surface modification

Surface modification is growing exponentially as industrial engineers and manufacturers realize the potential benefits of altering their polymer and elastomer materials. Simply stated, surface modification involves altering the physical, chemical, mechanical or biological properties of a surface in order to better control the interactions and responses of a specific application.

Industries ranging from medical and biotech, to aerospace, electronics and even consumer goods are realizing that altering the surface of their materials can yield significant benefits. Surface modification can solve many manufacturing challenges, such as improving adhesion, micro-cleaning, functionalizing, biocompatibility, hydrophobicity, or creating a moisture barrier.

While there are several surface modification techniques, perhaps the preferred method is low-pressure plasma processing. Plasma delivers exceptional results for manufacturers in many fields.

Plasma surface modification can improve adhesion, micro-clean, functionalize and produce biocompatibility, hydrophobic or hydrophilic characteristics.

On the Cover:

Top: A microtiter plate — a flat plate with multiple "wells" used as small test tubes. Low-pressure plasma treatments are used to alter the chemistry of the polymer components. This promotes fluid enzyme binding and keeps the testing fluid stable.

Bottom Left: Close-up of a plasma chamber window showing parts being treated.

Bottom Middle: Manufacturers use potting and encapsulation to protect sensitive assemblies (such as those used in hearing aids) from moisture, dust, and vibration. Plasma pre-treatment is a vital step in preparing the components for these treatments.

Bottom Right: Testing the bond strength on an overmolding application. Plasma treatment is used to "ultra clean" materials prior to bonding, which significantly increases the strength of such bonds.

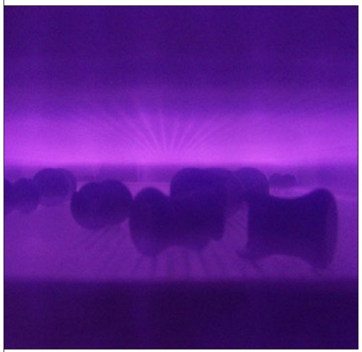
What is plasma treatment?

Plasma can be described as a low-pressure gas with electricity running through it. It can be observed as a glowing cloud that contains ions, free radicals, excited molecules and UV light. Fluorescent lights and neon signs are good examples, since each utilize the visible light released by plasma discharge.

When a gas under partial pressure is exposed to a high-voltage energy source (such as microwave), it becomes a mixture of ions, radicals, free-electrons and other types of molecular "fragments." The resultant plasma treatment can completely remove virtually all organic contamination to promote better adhesion.

When properly applied, plasma can accomplish multiple goals:

- Microscopically etch the surface of a polymer substrate to improve mechanical bond strength without altering the haze, transmittance, or clarity
- Clean the surface to improve the surface wetting of the adhesive, paint, marking, or coating
- Functionalize groups (carboxyl (HOOC-), carbonyl (-C=O-), hydroxyl (HO- and others) to the polymer substrate to significantly increase the surface energy for bonding, particularly in applications where aqueous-based adhesives require a bond strength that cannot be obtained with conventional cleaning techniques.



Plasma is a low-pressure gas process that removes all traces of organic contamination for improved acceptance of secondary manufacturing processes.

The Plasma/Bonding Connection

Plasma is frequently used to treat the surface of metals, polymers, glass, elastomers and ceramics to clean and improve "bonding." Bonding refers to either the adhesive of one part to another or the thin coatings/thick layers of lacquers, overmoldings, or potting resins to the substrate.

To ensure the best bond possible, the surface of a substrate must be prepared properly — this is true whether the polymer is commodity-grade (polystyrene, polypropylene, PVC, ABS, etc.) or high-performance (PSU, polycarbonate, Delrin®, Teflon®, UHMW, etc.).

How is a surface prepared for bonding? There are two common methods; conventional mechanical abrasion (followed by wiping with a wet-chemical agent or solvent), or acid etching, which is the most-common method, particularly with fluoropolymers. While effective, these methods usually require significant labor and/or cost. Another downside is that they may leave a thin layer of contamination on the surface of the substrate.

For sensitive bonding applications, virtually any contamination can reduce bond strength. A monolayer of contamination (about 0.1 microgram/cm2) can be residually formed from the evaporation of only 0.2 drops/cm2 of liquid containing 10ppm of non-volatile organic material. The majority of water or solvents contain significantly more than 10 ppm of dissolved organic matter. Therefore, any cleaning process using a liquid rinse or solvent vapor will leave the parts with a coating of organic contamination residue that can interfere with bonding.

Low-pressure plasma (or vacuum plasma) process takes the cleaning and surface preparation of materials to the next level.

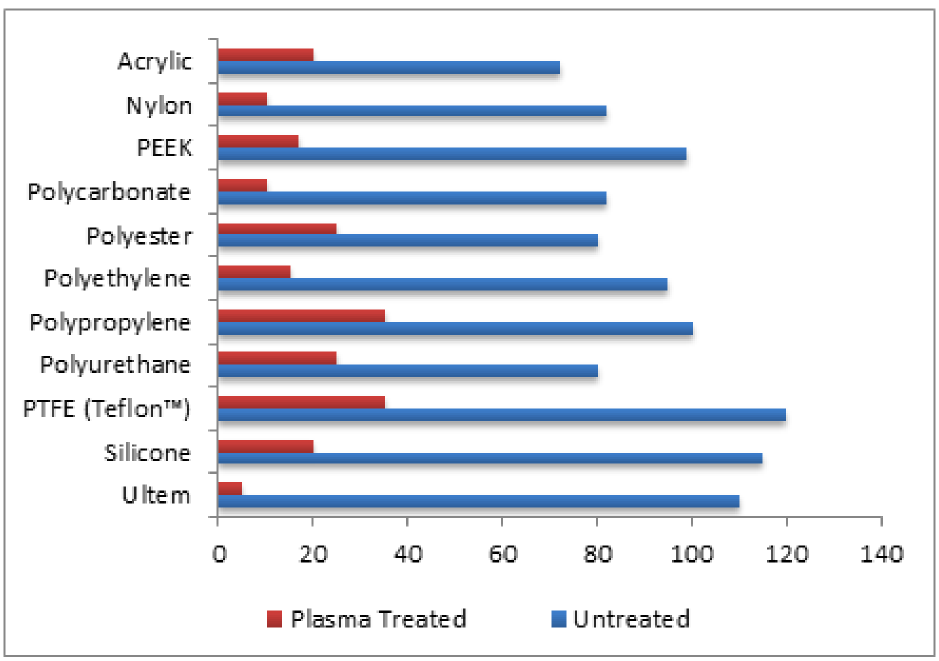
Many materials including metals, polymers, glass, elastomers and ceramics can achieve better bonding results after plasma cleaning.

Which devices can benefit from plasma cleaning?

Essentially, any device that requires a secondary treatment such as assembly, painting, overmolding, printing or coating can benefit from plasma cleaning.

Devices that are injection-molded and machined devices are good candidates for plasma cleaning since they are often contaminated during the manufacturing process. They may contain residuals of mold-release, flow-agents, UV stabilizers, plasticizers, or other low-molecular weight compounds that migrate (or “bloom”) to the surface of the molded device.

Beyond manufactured devices, some materials simply do not have surface properties that are agreeable to bonding. They may be too hydrophobic (non-wettable) or too hydrophilic (wettable) for the intended application. Or materials may be too tacky; requiring they be wetted with silicone oil to prevent clumping during a secondary manufacturing process. One example is in the treatment of small elastomeric devices that are bowl-fed into an automated assembly system. A detack treatment will retard the ability of the devices sticking together during the process.



The graph (left) illustrates the difference in contact angle between an untreated material and the same material after plasma treatment.

The following applications have a very good success rate with plasma treatments:

Medical:

- Syringe barrels prior to printing and/or to minimize bubble formation or retention
- Syringe plungers to minimize stick/slip properties
- Molded hubs (cannula / luer) for increase adhesion to needles or peripherals
- Catheter devices prior to printing, bonding or coating

Optics:

- Cleaning of optical devices prior to coating or assembly
- Intraocular lens cartridges to promote the adhesion of lubricous coatings

Diagnostic:

- Microtiter (multi-well) plates to promote hydrophilicity and/or specific functionality
- Glass slides for silane deposition
- Glass or polymer array devices for cleanliness and facilitating the flow and/or dot patterning
- Filter media to promote hydrophilicity without the need for surfactants

Injection-molded devices:

- Removal mold-release residue and/or other surface contamination
- Increasing the adhesion of overmolded materials
- Containers and/or lids to promote the adhesion of labels or gaskets

Printing:

- Improving the adhesion of water-based inks in pad printing or screen printing applications on materials/devices

Potting & Encapsulation Applications:

- Cleaning and functionalizing components and housings to induce resin flow
- Minimizing and/or eliminating bubbles in potted enclosures

Detack:

- Removal of “tackiness” or replacing silicone oils and/or specialty coatings such as parylene

Conventional cleaning vs. plasma cleaning

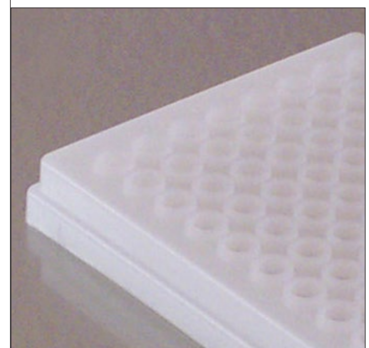
To select the best cleaning process prior to bonding, consider the type of surface treatment being performed, the material being treated and the objective of the treatment. Cleaning methods include:

Sanding and grit-blasting:

Plastic devices:
If the part is plastic and is only being abraded to increase the surface area to promote a better mechanical bonding of paint or adhesive, this process can usually be eliminated by plasma treatment. Not only will plasma clean the surface and make it more hydrophilic, the surface functionality provided by the plasma treatment will assure significantly increased bonding of the paint or adhesive.

Metal devices:
If the part is being surface abraded to remove burrs or gross oxidation, a plasma treatment cannot be effectively applied. Plasma treatments will not remove inorganic contamination (like dirt or metal burrs), so a grit blasting process is recommended. However, since it is common practice to wash grit-blasted devices to remove residual blasting media, a plasma process done after washing will assure that the surface of the metal device is truly clean.

Washing & degreasing (ultrasonic and/or vapor):
Washing and/or degreasing processes will leave a residual layer of contamination which will prohibit or retard effective bonding to the cleaned surface. It is still recommended that a wash and/or degreasing process be performed to remove all gross contamination, and that a plasma process be added to remove residuals and functionalize the surface of the part.



Plasma cleaning renders materials “ultra-clean” and better prepared for bonding when compared to conventional cleaning methods.

What are the different methods of plasma treatment?

Surface modification treatments are generally separated into two categories: atmospheric and low-pressure (or vacuum). Both use energy to ionize gas and are very effective at altering the surface properties of materials — but that is where the similarities end.

Atmospheric plasma processes or corona treatment

These methods work by forcing a gas (usually air) at a high rate of speed between two high-powered electrodes. As the air passes through the electrical discharge, it becomes ionized and, in the presence of the ambient oxygen, can form various chemically functional groups on the surface of the substrate. The functional groups resulting from this "oxidizing" process can effectively increase the surface energy on a wide range of polymers.

However, the only controls available to a user of corona treatment are the distance at which the material is held away from the electrical discharge and the speed at which the material is passed through the active plasma region. For a long residency time in the plasma region, material is passed slowly.

Corona treatments are most-commonly applied to in-line applications where rolls of material, or thin films, are conveyed or passed through the discharge. Corona treatments are frequently used in packaging and printing applications.

Advantages:

> Corona treatments rapidly treat large substrates, and are effective at making many commodity-grade polymers wettable to facilitate the application of adhesives, paints, inks and tape.

Both atmospheric (corona) and low-pressure plasma treatments offer unique advantages and considerations for altering surface properties.

Considerations:

Functionality is limited due to the ratio of ambient oxygen in the air. Treatment lifetime can be relatively short; minutes, hours or days depending on the substrate and the effectiveness of the treatment. For in-line applications where the adhesive or paint is being applied immediately after the treatment, the lifetime of the treatment becomes moot.

Heat: because the electrical discharge is quite hot, it is important to calibrate the speed at which the substrate passes through the plasma region and the distance between the substrate and the discharge. Thermal distortion may occur if the speed is too slow or the distance too short.

Line-of-sight: because only the area of the substrate that is passed through the plasma region is treated, there may be areas of the substrate that do not receive uniform treatment. This is particularly true when treating parts with complicated geometries.

Uniformity: because the plasma region is relatively small, getting uniform treatment over the entire surface of the material can be difficult unless the corona “wand” is robotically controlled. Automation is also required to maintain part-to-part repeatability of the treatment.

Environmental and health: many corona treatments generate high levels of ozone and NOx. This gas should be treated as a serious respiratory hazard.

Low-pressure plasma treatments

Low-pressure plasma is different from atmospheric treatments in that materials to be treated are placed inside a vacuum chamber instead of being passed below, or in front of, an open electrical discharge.

Advantages:

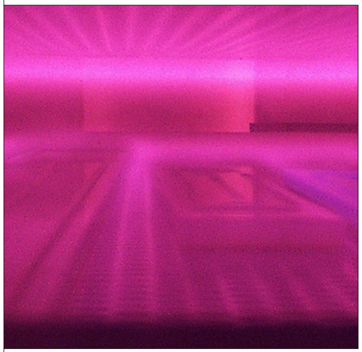
Low heat: because the pressure inside the plasma chamber is maintained well below 500mT, there is a low possibility of thermal deformation of the substrate. Although some deformation is possible with polymers that have very low melt temperatures, deformation can be avoided by special fixturing.

Minimal surface ablation can be achieved, when desired, to eliminate concerns about altering the optical properties (haze, transmittance, and clarity) of treated parts.

Uniform and three-dimensional treatment: because the active plasma field is uniform throughout the chamber, all areas of the device(s) are treated. Low-pressure plasma treatments are not line-of-sight.

Repeatable lot-to-lot batches: because all aspects of the plasma process (gas flow, chamber pressure, power, and time) are computer controlled, low-pressure plasma offers the highest level of repeatability.

Environmental and health concerns are essentially non-existent with low-pressure plasma treatments. All processing takes place in a vacuum chamber and exhausted gases (trace amounts of water vapor, CO, and CO2) can be vented to the open air or passed through a carbon scrubber.



Plasma surface modification appeals to many manufacturers since it provides superior cleaning without the use of harmful solvents

Considerations:

Lot size and throughput issues can sometimes become a factor since parts cannot be treated "in-line," but must be treated in batches according to size and quantity.

Substrate size can sometimes be limited based on the size, shape and configuration of the vacuum chamber.

I**ncreased part handling** because the parts are loaded onto trays, in baskets, or on racks.

Plasma Processing: Is it right for my application?

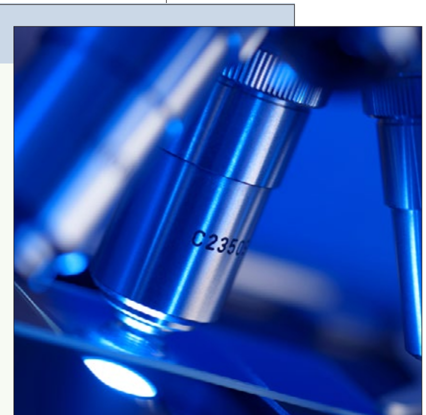
If you've asked any of the questions below, then plasma surface modification may be the right fit for your application:

- **Is there a more effective and less labor-intensive method of assuring that my parts are as clean as possible?**
  - Example: "I have to sand-blast my parts to increase the surface area to enhance mechanical bonding; but then I have to aggressively wash the part to remove blast media residue. Can I forego the blasting process and just plasma-treat my part?"
- **Do I really need all of these chemicals in my facility?**
  - Example: "The cost of continuously purchasing, storing, using, and disposing of wet chemicals and solvents (acetone, MEK, alcohols, acids, etc.) is just too high and I am under pressure to 'clean up' my operation by management and/or local environmental authorities."
- **Am I dissatisfied with the level of adhesion that I am getting from my paints, inks, or coatings; do I have an unacceptable delamination issue?**
  - Example: "Since I am unable to mold the part in the color that my customer requires, I have to paint the part but I cannot get the paint to wet-out on the part and – once the paint cures – it just delaminates with little effort. Since I don't want to abrade the surface of the part, will plasma treatment make the part paintable and give me the adhesion that I need?"
- **The material that I am using is just not giving me the surface properties that I need for my application to be successful, but I cannot change the material type.**
  - Example: "I have to use PEEK for my part, but I just cannot achieve the bond-strength required with the adhesive that I am using. Do I have to change adhesive or can I just plasma-treat the PEEK part to increase adhesion to my epoxy?"

The TriStar Advantage for Surface Modification and Low-Pressure Plasma Treatment

TriStar Plastics is a leader in the field of Surface Modification. We have a complete, in-house lab to help you solve your toughest surface issues. From enhancing cell culture trays to bonding dissimilar materials, our scientists have access to the latest advancements to deliver a superior application outcome. We provide complete surface analysis, surface treatments, plasma services plus custom adhesives and specialty coatings.

The TriStar Advantage for the Medical Industry



Cleaning Medical Substrates for Material Vapor Deposition

Challenge:

A manufacturer of protein microarray devices contacted TriStar to provide a solution for improving the cleanliness of glass slides in preparation for a silane deposition process. Their method of cleaning the slides with solvent-based chemicals was laborious and ineffective at assuring maximum cleanliness.

Solution:

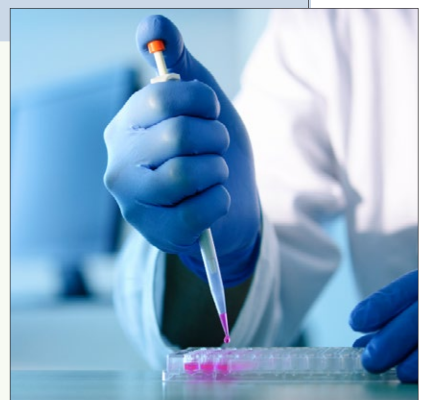
An inert-gas low-pressure plasma process was performed on the slides with no additional cleaning processes needed.

Result:

The plasma process uniformly and effectively cleaned the slides to a level previously unachievable with wet-chemical processes. The higher level of cleanliness resulted in consistently uniform deposition of the silane material.

Note: the silane deposition was also conducted by TriStar in a heated and pressure-controlled chamber immediately following the plasma-cleaning process.

The TriStar Advantage for Medical Diagnostics



Modifying Diagnostic Plates and PCR Strip Wells

Challenge:

Because of the chemical inertness of many of the polymers used in the molding of microtiter plates (and PCR strips), a global provider of PCR array devices was having difficulty achieving the desired level of hydrophilicity in the wells of the microtiter plates that they purchase from a supplier.

Solution:

After experimenting with several different low-pressure plasma process parameters, we developed an effective, optimized and validated process. The plasma process was able to consistently and uniformly increase the surface energy inside the wells to a degree specified by the customer.

Result:

The optimized plasma treatment not only delivered the desired surface energy properties, but it may also alter the (-/+) charge potential that resides on the surface of the substrate.

The TriStar Advantage for Surgical Devices

Increasing Adhesion of Grips

Challenge:

Because many injection-molded devices are overmolded with an elastomer material (for use as a comfort or non-slip grip) many manufacturers of medical/surgical devices experience delamination – or “peeling away” – of the overmolded elastomer material from the base polymer.

Solution:

Plasma treatment of the injection-molded device was conducted prior to the overmolding process. The plasma process cleaned and functionalized the surface to increase the bond-strength of the overmolded material.

Result:

Peel tests conducted on finished devices have proven that the overmolded material – whether silicone, urethane, or other – adheres significantly better to plasma-treated base substrates without the need for any other pretreatment method (blasting, washing, priming, other) to the injection-molded device.

The TriStar Advantage for Textiles

Increasing the Hydrophobicity of Polymer

Challenge:

It is often the case that a manufacturer of a device would like to increase – rather than decrease – the natural hydrophobicity of a material. This is particularly true in cases where a plastic part may be exposed to harsh chemicals or used in an application where ambient materials (such as inks or adhesives) have a tendency to stick to, and build up on, plastic devices. Generally, the material of the part is simply changed (example: from acrylic to Teflon®), but this can be cost prohibitive.

Solution:

A simple, efficient and economical solution is to expose the material/device to a plasma-assisted surface fluorination process. This process has been used for many years by the textile industry to enhance water-repellent properties on fabrics. It works equally as well on most rigid polymer and elastomer materials.

Result:

As with all other types of plasma processing, treating the surface of the device with a fluorination process does not change the bulk properties of the material. However, once treated with a fluorination process, the increased hydrophobicity of the surface renders the part significantly less wettable by liquid media.

TriStar Plastics is at the Forefront of Surface Modification Treatments

When you are ready to explore the benefits of surface modification — from increasing bond strength and adhesion, to promoting hydrophobic or hydrophilic properties, look to the experts at TriStar for a solution.

Beyond Plasma – TriStar's Enhanced Materials Division

Plasma treatment is highly effective for improving the performance of materials, but it's only one option. Our Enhanced Materials Division (EMD) has been established to provide a comprehensive approach.

Our Enhanced Materials Division has multiple product and service offerings collected in three key categories:

- **Surface Enhancements** - We offer multiple techniques and processes to amplify adhesion, inhibit corrosion, reduce/enhance protein binding, and promote many other effects or properties. Learn more.
- **Engineering Services** - TriStar engineering services is an integrated design, process, and material consulting department that will support projects and companies as they work through engineering challenges. Learn more.
- **Innovative Product Offerings** - We are rolling out a suite of cutting-edge products to achieve specific technical outcomes. We have primers, adhesives, and innovative materials specially engineered for the most demanding applications. Learn more.

Our expert engineers can help you identity the ideal approach based on your exact application requirements. Let us know how we can help.

Look to TriStar's Enhanced Materials Division (EMD) for in-house services, including surface analysis, plasma treatment, process engineering, plus custom adhesive and specialty coating applications.