EMPHASIS Automotive

Plasma and adhesion to rubber, plastics substrates

By Shaun Glogauer
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Plasma is based on a simple physical principle. As a result of input of energy, the states of matter change: solid becomes liquid and liquid turns to gas.

If further energy is now supplied to a gas it becomes ionized, i.e. the electrons are given more kinetic energy and leave

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their atomic shells.

Free electrons, ions and molecular fragments are produced, and the gas changes into the plasma state (**Fig. 2**). Because of its instability, however, this "fourth state of matter" can scarcely be used at normal atmospheric pressure.

The "Openair" atmospheric-pressure plasma process patented by Plasmatreat GmbH of Steinhagen, Germany, in 1995 opened up new opportunities. By developing and using plasma jets, it became possible to integrate this scarcely used state of matter into industrial production processes.

Executive summary

World-class, fully automated manufacturing processes rely more and more on advanced, environmentally friendly surface treatment technologies. An innovative atmospheric pressure plasma technique (**Fig.1**) allows inline rubber and plastic manufacturing processes to become fully automated with total process control.

A thorough pretreatment must produce surfaces with reliable and repeatable characteristics to achieve optimal adhesive bonding, coating and printing results. In addition, pretreatment must be delivered in a cost-effective and safe manner.

The new process uses the high effectiveness of plasma for microfine cleaning, high-surface activation and nanocoating. In most cases the plasma application takes the place of environmentally unfriendly and costly solvent cleaning or chemical adhesion promoters and primers.

The innovative technology enabled the use of plasma "in-line" under normal atmospheric conditions for the pretreatment of material surfaces on a large industrial scale.

On contact with the surfaces of materials the additional energy supplied is transferred to them and is available for subsequent reactions on the materials.

In this way surfaces are produced which have ideal properties for coating, printing, adhesive bonding or foaming.

Electrically neutral plasma beam

The process is based on a jet principle.

Fig. 1. Atmospheric plasma jets pretreating an EPDM profile.

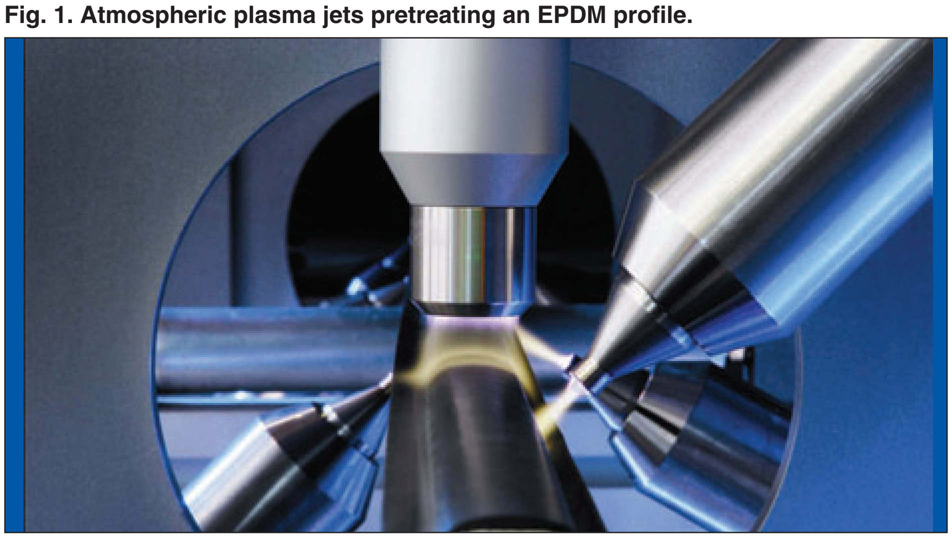

Fig. 2. States of matter.

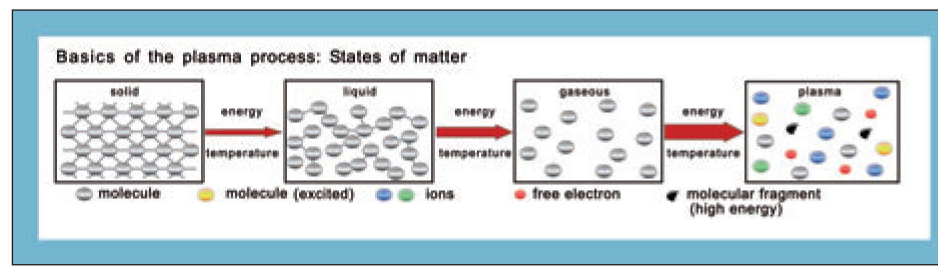

Fig. 3. Openair plasma system.

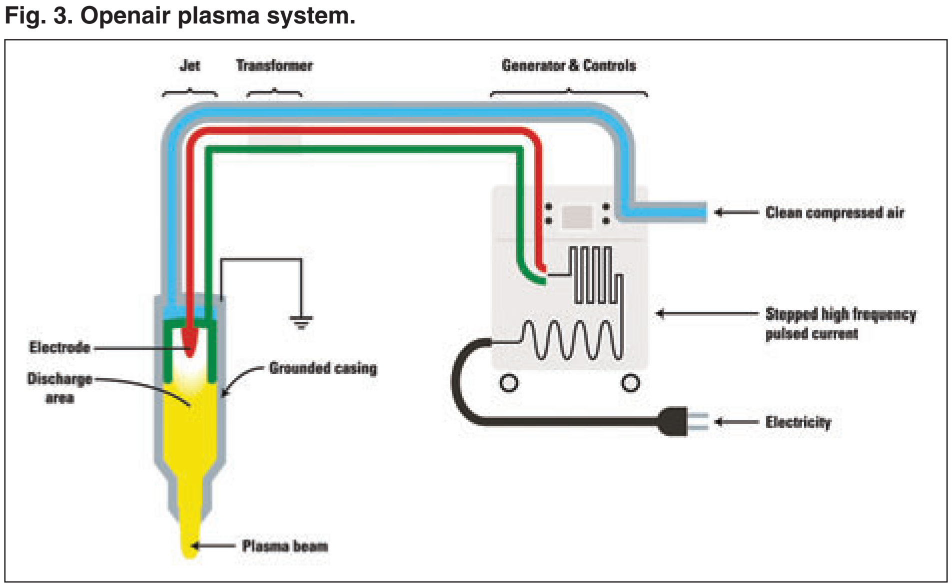

Fig. 4. In-line application inside the injection mold. The plasma nozzle can be injected directly into the user's process.

Fig. 5. Pretreatment with plasma allows for optimal bonding of the EPDM profile located in the door frame.

In contrast with high-cost low-pressure plasma systems (vacuum chamber) the jets here operate in-line at atmospheric pressure, that is to say under normal atmospheric conditions. They are driven solely by air and high voltage.

A particular feature is that the emergent plasma beam is electrically neutral, and as a result the range of possible applications are greatly extended and simplified.

Its intensity is so high that treatment speeds up to several hundred m/min can be achieved.

The typical rise in temperature of a plastic surface during treatment results in this case to $\Delta T < 20°C$.

The plasma system is characterized by a threefold action: it activates surfaces by selective oxidation processes, discharges them at the same time and brings about microfine cleaning of the surfaces of metals, plastics, ceramics and glass.

In addition, the plasma energy of this system is utilized for depositing coatings. By adding a precursor, the technique has also been developed further for purposes of providing nanocoatings.

Microfine cleaning, high activation

Atmospheric plasma technology is increasingly being employed in applications that are environmentally sensitive and require highly effective pretreatment.

The plasma generated by an intense pulsed arc discharge in the interior of plasma jets is conditioned at the jet outlet and gives up its energy on contact with the surface.

The most important components of this plasma system are the plasma jets and generators (**Fig. 3**).

Inside the plasma jet, an atmospheric-pressure plasma is generated by means of a high-voltage discharge.

A directed stream of air flowing along the discharge segment separates off parts of the plasma and carries these through the jet head to the surface of the material to be treated.

The jet head holds back any parts of the plasma stream carrying electric potential and additionally determines the geometry of the emergent beam.

The working gas in this process is usually clean, dry compressed air at 30 to 50 psi, although other gases and gas blends can be used to impart specific functionality.

The charged particles of ions and electrons in the plasma possess a great deal of kinetic energy as well as thermal energy.

When they encounter organic material on the surface, the particles tend to sever covalent bonds, breaking these contaminants up into smaller, more volatile molecules.

Some of these simply vaporize; the balance are oxidized to carbon dioxide and water vapor.

At the same time, functional groups (e.g. hydroxyl, carbonyl) are added to the surface.

These increase the surface energy of the treated substrate, allowing for highly improved wettability as well as more bond sites for the adhesive or coating to be applied.

This improves the adhesion properties of the substrate, allowing for novel applications with difficult-to-bond materials.

Fig. 6. Various geometries can be treated by Openair plasma rotation jets.

The need for plasma

In general, molded or extruded technically clean engineering materials derived from an industrial production process have in reality a contaminated surface. This is true for metals, glass, ceramics and all types of polymers.

Polymers, especially, tend to contain a high amount of additives and fillers. Their purpose is to engineer the performance of the polymer, including processability.

The low-molecular-weight additives, like flow agents and plasticizers, usually migrate to the surface of molded or extruded engineering components.

In addition, external agents can be applied to the mold or extruders as lubricants to facilitate release of the molded or extruded part, and in the process often may be deposited as contaminants on the polymer surface.

The contaminants on polymers and other engineering materials act as a barrier to adhesives, coatings and inks on the material surface. In other words, good surface preparation is required.

The best adhesion results always occur when the adhesive, coating or ink is directly applied to the actual structural backbone of the material, not on top of a layer of surface contamination.

Inline atmospheric plasma surface treatment (**Fig. 4**) is enabling manufacturers to clean and activate substrates on a molecular level, resulting in this process in most cases outperforming competing and older surface treatment technologies.

The EPDM rubber market

Most rubber compounds like EPDM, and thermoplastic elastomers, have very low inherent surface energies. This low surface energy results in difficulty in bonding or coating materials onto these surfaces.

With the plasma system described here, these difficulties can be easily overcome. The pretreatment with atmospheric plasma allows for optimal bonding of the EPDM, such as profiles located in the door frame (**Fig. 5**). Various geometries also can be treated by using patented Openair rotation jets (**Fig. 6**).

In particular, weatherstrip door and window seal manufacturers identified new surface treatment possibilities shortly after the introduction of this plasma technology.

Automotive weatherstrip seals are typically extruded and coated or flocked to provide slip, anti-squeak and UV resistance properties.

This is generally performed in-line, either directly after the extruder or after the vulcanization process.

See **Plasma,** *page 18*

The author

Shaun Glogauer is sales and marketing manager of Plasmatreat North America.

In this role, he is responsible for market penetration and growth of plasma applications as they relate to automotive rubber and plastics manufacturing.

He is a member of SAE International and the Automotive Parts Manufacturing Association, and attends exhibitions at key trade shows primarily within the automotive industry.

Most recently, Glogauer authored and presented a technical paper at the SAE 2009 World Congress in April.

As part of an up and coming worldwide corporation, Glogauer is excited at the prospect of furthering plasma technology as a truly revolutionary, environmentally friendly technology that enables improved quality and lower-cost automotive processing.

He graduated from York University in Toronto in 1994 with an Honors Bachelor of Science degree majoring in biology, with a minor in chemistry.

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Plasma

Continued from page 17

The slip-coat and flock application must comply with stringent mechanical and environmental testing as specified by the OEMs.

Achieving a robust bond between the extruded material and the flock or coating has historically been a major constraint in this market.

In general, the surface to be coated or flocked has traditionally required either an abrasive surface preparation or a primer to achieve OEM specifications, often resulting in uneven and inconsistent results.

Abrasive surface treatment of weatherstrip profiles typically involves the use of a rotating metal sanding wheel.

This process results in several issues of concern: the sanding wheel becomes clogged on a regular basis requiring cleaning and/or changing the wheel; contaminated material already removed from the surface is often redeposited on the bonding surface.

This process results in the creation of dirt and dust that can cause equipment and sensors to malfunction and produce toxic dust that can be inhaled by operators in the area.

Treatment with a primer can also lead to problems: the primer may not wet out completely on the low-surface energy material resulting in uneven application.

Primers in general attempt to dissolve surface contamination and form mechanical linkages (as opposed to true chemical bonds) with the surface, resulting in less robust adhesion properties.

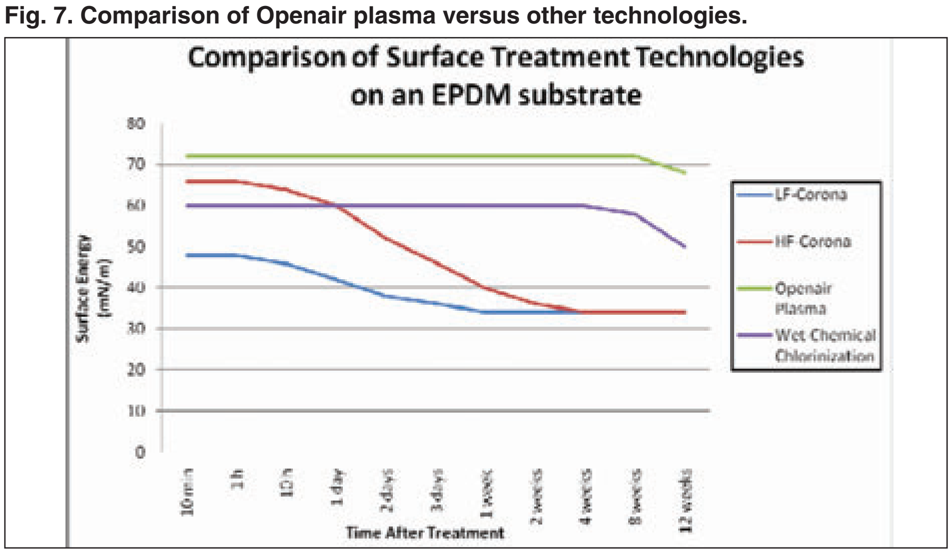
Most primers contain aggressive solvents that create toxic fumes requiring an enclosure and operators to wear personal protective equipment in their presence.

As a result of these issues, rubber manufacturers have long sought an alternate process for treating bonding surfaces.

Plasma treatment resolves bonding issues

Because of the very high effectiveness of plasma treatment, providing for activation of the surface energy levels beyond 72 mN/m (dynes – the unit of surface energy measurement), primers and abrasive surface treatments can be eliminated from the manufacturing process.

Fig. 7. Comparison of Openair plasma versus other technologies.



This allows for surface treatment that increases surface energy far beyond competing technologies while maintaining that surface energy for a longer period of time (**Fig. 7**).

As a result of the initial success in pre-treating extruded EPDM profiles, manufacturers were then able to expand the use of plasma processes to enable the application of tape, textured materials and inkjet printing.

Plasmatreat responded to these successes by developing an industry first, compact weatherstrip extrusion plasma station, which can be seen in its latest rendition below (**Fig. 8**).

This type of treatment station can house up to 16 plasma jets allowing for complete and thorough treatment of the most complex extruded profiles.

This has become the industry standard for pre-treatment of extruded profiles to enable enhanced adhesion on bonding surfaces.

For process control, a spectral evaluation of the plasma was developed for continuous verification of the presence of plasma.

In addition, positioning arcs for the plasma jets allow for fully reproducible and repeatable positioning of the jets for various profile geometries.

Both of these allow manufacturing companies to maintain a process that is compliant with stringent automotive auditing requirements.

Changing to atmospheric plasma treatment has afforded manufacturers numerous advantages compared to previous techniques. The following list is a summary of these advantages:

- Outstanding and reliable adhesion to extruded profiles
- No effect of ambient humidity and pressure conditions on the treatment
- Reduced coatings and adhesives consumption—20- to 30-percent reduction reported
- Process is not disrupted by metal core and carbon black as it is a voltage free process
- No fire risk
- Environmentally friendly
- Increased line speed and productivity
- Significant reduction in scrap due to variations created by previous treatment methods.
- There is now the possibility to optimize bulk properties of the extrusion material (e.g. performance, processability, cost) while achieving reliable adhesion
- No ozone emission
- Small footprint—only four feet of line space required
- Ease of operation with a wide production window (**Fig. 9**)

As evidenced in the above chart, plasma treatment can obtain surface energy levels in excess of 72 mN/m over a large spectrum of treatment speeds and distances to the substrate. This makes the process forgiving and allows for processing variations not previously allowable with traditional treatment methods.

Environmental and human health benefits

As environmental and workplace safety standards continue to place more stringent demands on manufacturers, the following benefits in these areas are listed below:

- Elimination of volatile organic compounds as a result of elimination of adhesion promoters or primers
- Reduction of VOCs by changing from solvent-based to water-based adhesives
- Reduced energy consumption as a result of the elimination of steps and equipment in the adhesive process
- Less non-degrading scrap material sent to landfills as a result of higher quality finished parts

Elimination or reduction of health risks as a result of inhalation of VOCs

Fig. 8. Latest C-frame plasma treatment station. This particular model houses eight plasma jets.

from exposure to hazardous chemicals and fumes/vapors associated with these chemicals, spills or fire hazards during material handling of volatile materials, as well as health risks from exposure to toxic airborne dust from excessive abrasive sanding operations.

Other related applications

As the weatherstrip industry adapted atmospheric plasma technology, the same principles were being adapted to related applications.

The following are two examples of applications currently utilizing Openair plasma treatment in large-scale production:

Encapsulation of automotive side window glass with TPE has in the past, resulted in the need for harsh chemical treatments. In order to obtain reliable adhesion between the glass and TPE, the glass is normally treated by wiping with solvent and then applying a primer.

Plasma treatment eliminates these costly and environmentally unfriendly applications.

In addition, the subsequent application of one- or two-component polyurethane foam is enabled with plasma pretreatment.

In a similar manner to slipcoat application on extruded weatherstrip profiles, windshield wiper manufacturers are now using plasma treatment to obtain adhesion on EPDM wiper blades (**Fig. 10**). This eliminates solvent wiping and/or primers traditionally used by these manufacturers.

Ongoing R&D

In its quest to remain at the forefront of surface treatment technology, Plasmatreat's R&D scientists continually strive to increase the effects of plasma treatment and also to uncover new potential applications.

Recent cooperative work (2007) with the German Institute of Rubber Technology (DIK, Hannover, Germany), has shown excellent results using this technology and the company's new atmospheric plasma polymerization process called PlasmaPlus.

Materials tested include NBR, EPDM and SBR elastomers with plasma using nitrogen as a process gas.

Plasma polymerization was accomplished using different precursor materials (e.g. toluene, decaflouropentane).

Results of this testing show enormous changes on the surface of the test materials, in particular for increasing bond strength and the functionalization of the surface.

For example, it was possible to realize huge increases in bond strength of EPDM to EPDM bonding surfaces.

Also, plasma polymerization on SBR was found to decrease the coefficient of friction, while at the same time improving barrier properties (e.g. permeation of aromatic compounds was delayed by 50 percent).

Conclusion

Atmospheric pressure plasma used inline is now validated as a highly effective surface preparation method within high-volume manufacturing processes.

The Openair plasma process provides reliable, cost effective and environmentally friendly surface treatment of not only rubber materials, but also metals, ceramics, glass, plastics and other polymers to enable the highest quality bonding, coating and printing results possible.

The ease of use, workplace safety and broad production window make it a process that can easily be utilized in many industrial applications.

The technology is currently revolutionizing automotive and other industrial processes by eliminating or reducing solvents, adhesion promoters, primers, VOC emissions, waste water streams, non-degrading parts from landfills, and energy-intensive equipment and processes.

In an age of ever increasing consumable and processing equipment costs coupled with acute environmental awareness, Openair plasma can be the solution for sustainability in manufacturing as an enabling technology for product and process innovation.

References

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2. A. Wildberger, H. Geisler, R.H. Schuster, DIK (German Institute of Rubber Technology), Hannover, Germany.
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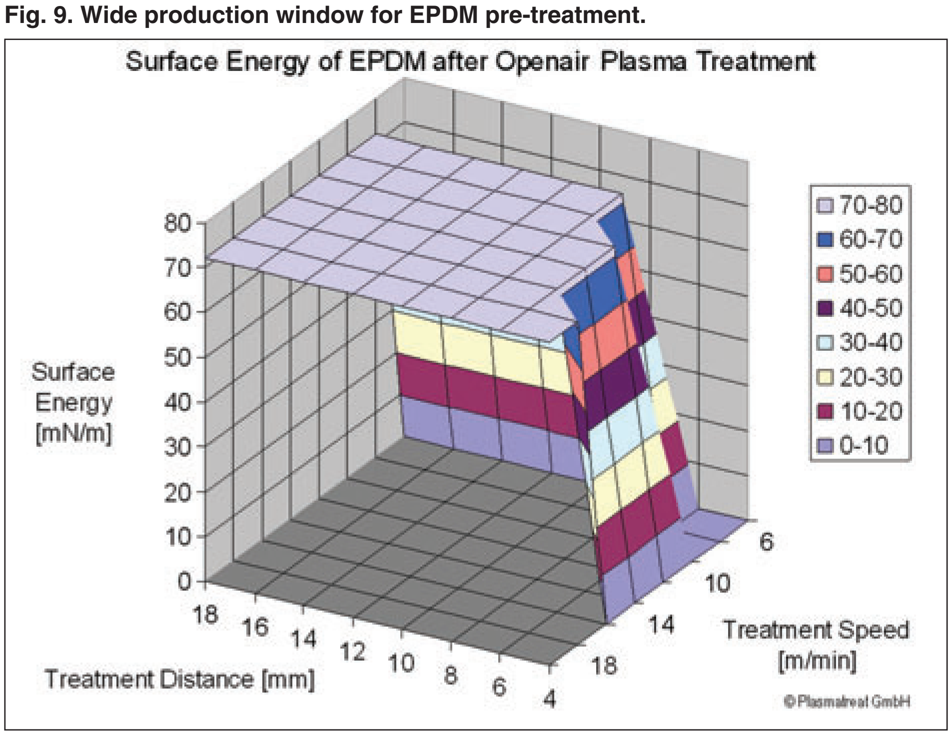
Fig. 10. Plasma enabled slipcoat application on wiper blades.

Fig. 9. Wide production window for EPDM pre-treatment.



Products

DSM Thermoplastic Elastomers Inc. has improved and expanded its Sarlink 6100 series of thermoplastic vulcanizates that are based on dynamically vulcanized rubber in a polypropylene matrix.

Sarlink 6100 series grades provide a solution to a number of application related issues, such as corrosion problems during processing or paint staining problems for architectural profile applications, according to the company.

Available in hardnesses ranging from 35 Shore A to 90 Shore A with very high lot-to-lot consistency, Sarlink 6100 products can be processed through standard thermoplastic techniques, but is particularly suited for injection molding. Because of its lower crystallization temperature, cycle times may be reduced by as much as 30 percent when compared to conventional technology, the firm said.

For more information, call 800-524-0129 or visit www.sarlink.com

Momentive Performance Materials Inc. has introduced Element 14 polydimethylsiloxane fluids. Available worldwide under brand name Element 14, these fluids replace current regional low-viscosity fluids, providing customers with standard global specifications, improved surety of supply, standardized containers and weights, and uniform label information.

Call 800-295-2392 or visit www.momentive.com for details.