PLASMA AS A CHEMISTRY DELIVERY METHOD

Marc Jacobs and Stuart Jackman
Materials World magazine
6 Jan 2020

An opened aircraft engine in the hangar. Credit: Ferenc Szelepcsenyi/Shutterstock

Molecular Plasma Group CEO, Marc Jacobs, and Jackweld Ltd Director Stuart Jackman, explain how a molecular plasma technology can help multiple materials to bond.

The quest for ever lighter and stronger structures is a key innovation driver in multiple industries. Advanced composite structures that are affordable and have a low environmental impact can contribute significantly towards this goal.

Currently, there are several technical challenges that limit the use of advanced composite materials. For instance, the need for high-temperature and low-pressure autoclaving is costly, time consuming, and very energy intensive. Therefore, out-of-autoclave technology development is high on the priority list of many companies. Various physical and chemical priming technologies exist that change the surface roughness or energy, or provide chemical anchors such as amine groups or hydroxyl groups to surface.

Examples of conventional etching techniques are liquid oxidative processes in nitric acid (HNO_3) or sodium hypochloride (NaClO), gamma or laser irradiation, and rare earth treatment with lanthanum chloride ($LaCl_3$), neodymium nitrate ($Pr[NO_3]_3$), ytterbium fluoride, (YbF_3) dissolved in suitable solvents, such as alcohols. Depending on the requirements, they can be used on their own, or in combination.

One technology that is widely used to increase the surface energy and wettability of surfaces is activation by plasma, i.e. ionised gas.

This can be done under vacuum or atmospheric pressure. Some drawbacks of vacuum plasma are its limited scalability as well as its high capital and operating costs.

Commercially available corona-like atmospheric plasma systems successfully increase surface energy, however, the treatment is not stable over time and decreases quickly. Also, treatment of temperature-sensitive materials is limited because of the high energy level and corresponding high temperature –

more than 80°C – of the plasma. This limits the ability of this technology to introduce chemistry in the plasma stream to only certain precursors such as hexamethyldisiloxane.

Wet-chemical priming technologies are widely used on their own or in combination with a plasma pretreatment. There is a strong trend towards water-based primers to minimise environmental impact but, because of the required drying, even these are energy and time consuming.

Especially in slow-moving, highly regulated industries such as aviation, toxic chemical legacy priming continues to exist, for which there is an urgent need to find alternative solutions.

To resolve this, the company created a technology called MolecularGrip to combine the advantages of atmospheric plasma surface activation with the ability to graft specifically chosen functional groups to any surface in one single process step, while preserving the functionality of the chemistry. In effect, the plasma is no longer a solution in itself, but becomes the delivery system that transports and bonds the preferred chemistry to the surface.

Surface preparation

The key features of the process are that it must prepare a surface for bonding, for example, activate the substrate by creating free radicals and at the same time activate the organic molecules introduced into the plasma while maintaining the desired chemical functionality of the molecules.

The plasma is blown onto a surface and, regardless of the material, surface radicals will be formed. These will react with other species in the vicinity to become stable again.

The key elements required to be able to introduce molecules into the plasma and keep its functionality are precise control over the energy level in the plasma, no arcing between the electrodes, room temperature operation and the absence of oxygen.

Using a proprietary direct barrier discharge (DBD) reactor design, the technology fulfills these requirements. It enables arc-free ionisation of any inert gas such as nitrogen (N_2), helium (He), argon (Ar), carbon dioxide (CO_2) and reactive gases such as air and ammonia into a plasma state at a controlled energy level. This can be achieved by using an electromagnetic field generated by a high-frequency AC power source. The energy level in the plasma can be precisely controlled so the treated surface remains at room temperature. The energy distribution in a DBD reactor follows that of a Boltzmann, which has a clear peak and a high energy tail. This means there are very few high-energy species that can break any bond, and a lot of low-energy species at the desired power level.

Each type of chemical bond has its own specific binding energy. Because it is possible to control peak energy level in the plasma, certain double or triple bonds can be preferentially opened. Radicals are also formed on the surface and in the precursor molecules.

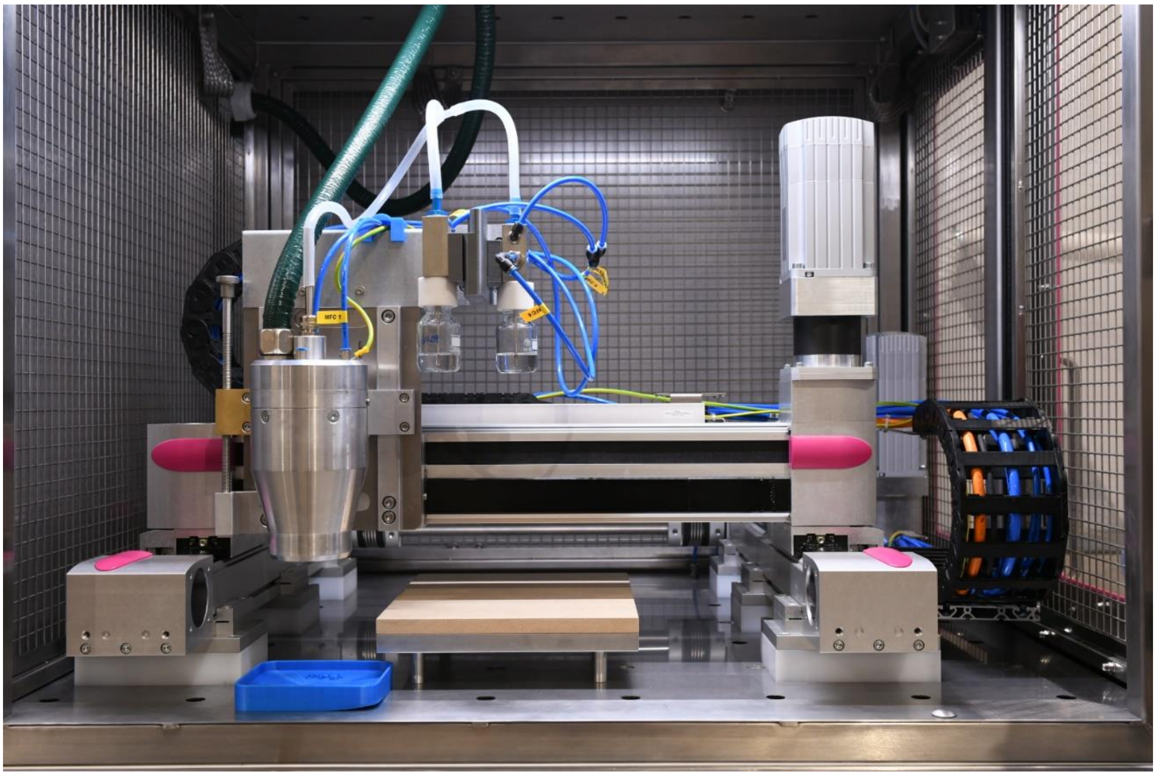
Working out how to recombine it all and obtain a desired surface functionality lies in finding the balance between the choice of chemistry and the various process parameters.

The result is that the activated molecules will react between themselves as well as covalently bind with the activated surface through radical recombination reactions and thus permanently change the chemical functionality of that surface.

These reaction processes have a probabilistic nature and are hard to predict or simulate. Therefore, every application development starts with a design of experiments, in which multiple chemical precursors and a range of process settings are evaluated. Testing has shown that the new technology is capable of sufficiently controlling the probabilistic nature of the recombination reactions to create a desired chemical surface functionality.

Adhesion applications

An example application for which the technology can be used is adhesive bonding of a highly inert Teflon film onto a substrate, using a 2K epoxy glue system. The new technology is used to graft a molecule that reacts with a glue system onto the desired substrate. When working with a 2K epoxy glue system, precursor molecules such as primary amines or epoxy-functional groups are introduced into the plasma stream and grafted onto the Teflon. The chemical functionality of its surface is permanently changed and is now compatible with the 2K poxy.



The technology can also be used to improve adhesion of carbon-fibre to a polymer matrix. Carbon-fibre is notoriously difficult to properly bond to a polymer matrix. Improving the wettability will help and is performy by treating unsized carbon-fibre with oxygen-containing precursor chemistry such as hydroxyl or carboxyl groups.

Furthermore, the carbon-fibre can also be treated with more specific chemistry that will participate in the reaction with the polymer matrix such as amino, epoxy, isocyanate or hydroxyl groups. Using these strategies, the strength of the bond between the carbon-fibre and the polymer matrix can be increased up to 10 times over sizing.

Other areas in which the technology can be applied include improvement of polyurethane adhesion on glass, replacement of recorcinol-formaldehyde-latex adhesive systems, and reduction of the environmental impact of fabric dying processes.

Multiple substrates and chemistries

Radicalisation of the surface is a purely physical process and operates at room temperature, therefore it can be used on materials ranging from very sensitive cellulose-based ones and natural proteins such as silk, to inerts like Teflon, polyether ether ketone and gold.

The uniqueness of molecular plasma technology is that a wide range of highly sensitive organic chemistry can be used. Also, the technology can be used to graft biomolecules such as antibodies, peptides, proteins and DNA, onto any substrate.

Biomolecule immobilisation

In partnership with the University of Leuven, Belgium, the company has demonstrated that its technology, antibodies can be grafted onto a substrate at less than 10 seconds, while maintaining full bio-functionality. This is possible due to the soft process conditions and the extremely high degree of control over the energy in the plasma process.

Since this proof of concept, the company has demonstrated instantaneous immobilisation of other biomolecules such as peptides, proteins, enzymes and DNA onto any substrate while preserving full bio-functionality. The ability to graft highly sensitive organic chemistry to any surface in a single step, scalable atmospheric process at room temperature opens up many new opportunities for surface functionalisation that can bring a lot of value to multiple industries.