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Pretreating non-polar materials

Pioneering – Atmospheric Pressure Plasma for Medical Engineering

Plasma processes provide an effective solution wherever there is a need to fine-clean, modify and functionalize surfaces. In medical engineering it is particularly important to be able to selectively alter the surface characteristics of plastic components. Atmospheric plasma jet technology enables pretreatments to be applied to precisely defined areas.

◄ The Openair-Plasma technology enables highly effective pretreatments to be applied to predefined areas. Due to the high activation force of the plasma, plastic surfaces intended for medical applications can be printed immediately after treatment to produce long-time stable results.

Image source: Plasmatreat

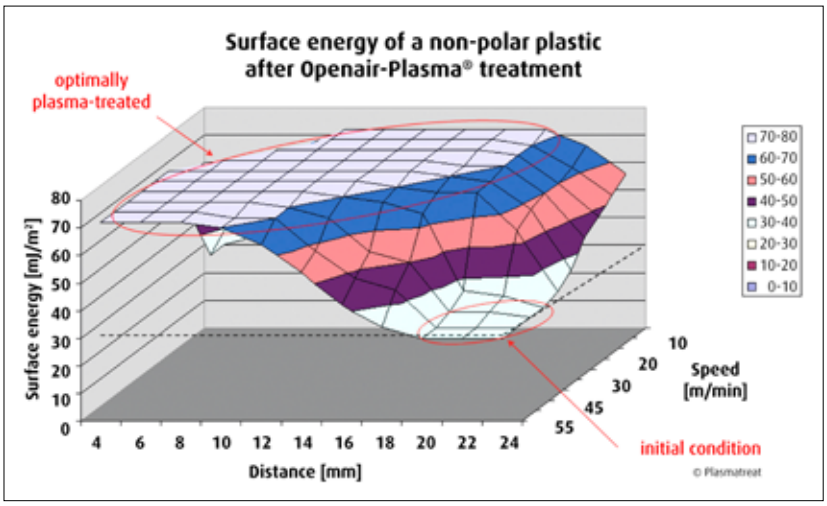

Image source: Plasmatreat

The diagram shows a non-polar plastic surface which was pretreated with plasma as a function of distance and speed. Treatment renders the surface polar and with some plastics the surface energy rises to >72 dyne with a large process window.

Plasma is based on a simple, physical principle. States of matter change when energy is applied; solids become liquids and liquids become gases. If even more energy is applied to a gas, it becomes ionized, giving rise to free electrons, ions and molecular fragments which transform the excited gas into a plasma.

It's all about surface energy

Since the non-polar plastics such as polyethylene (PA), polypropylene (PP) and polyetheretherketone (PEEK) used in medical engineering have low surface energy, activation is essential to increase their wettability.

Atmospheric pressure plasma jet processes (AP) use a pulsed, arc-like high-voltage discharge in the kilohertz range to generate plasma. The process gas consisting mainly of air travels through this arc, where it is ionized before impinging on the surface to be treated. When applied to plastics, it brings about the fine-cleaning, static discharging and simultaneous activation of the material surface in a single operation. Activation enables the surface wettability to be adjusted and modified to suit different media. This is achieved by influencing the polar and dispersible fractions of the substrate's surface energy. Good wettability occurs when the surface energy of the solid material is ideally higher than the surface tension of the liquid medium, or the two are very similar at least. This can be attained by adjusting the plasma treatment parameters as required.

Surface interface

The surfaces of components are invariably the first point of contact with their environment. This interface varies depending on the risk class of the medical device. In implants, for example, the surface forms the interface with the biological system, in medical equipment it is the external point of attachment to the patient, in Petri dishes or microfluidic diagnostic tools it is the contact with analytical media. Manufacturers must make substantial regulatory efforts and comply with strict requirements concerning the biocompatibility of the materials and production resources used in order to satisfy the varying demands placed on the performance of these surfaces. The pretreatment methods are also tightly regulated. Pretreatments and coatings with atmospheric pressure plasma can ensure the long-time stability of adhesive bonds while at the same time satisfying requirements for biocompatibility. Plasma processes are suitable for medical devices in all risk classes.

As in electromobility or the aerospace industry, lightweight materials have long been used in medical engineering applications. These materials frequently have difficult-to-bond surfaces which require a pretreatment. Electronic components often require hermetic encapsulation, which in some instances can be achieved only with a surface treatment, possibly combined with a coating. Both issues are becoming increasingly important in medical engineering, whether for lightweight fiber composite prosthetics or to protect the electronic components of active implants. Material pretreatments for modern laboratory analysis and diagnostics are equally important.

Various surface pretreatment processes are used in the production of medical devices. The pretreatment of components with low-pressure plasma is already a well-established practice in medical engineering. However, this process is technically complex and expensive since it requires a vacuum chamber and furthermore, it cannot be used for partial pretreatments without additional masking. In contrast, AP nozzle plasma is always area-selective, in other words it is applied to precisely defined areas, so there is no need to mask the remaining surface.

Adhesive bonds

In addition to adhesion promoters, conventional methods of preparing adhesive bonds also involve the use of mechanical processes such as blasting, which roughen the surface of the substrate. The adhesive mechanically anchors to the surface crevices created by abrasion to produce a stronger adhesive bond. An additional cleaning step is often performed after this process.

Web-Tipp
www.plastverarbeiter.de/07210

Image source: Plasmatreat

Image source: Plasmatreat

Selective wettability: Super-hydrophobic surface after plasma coating.

Applying a water-repellent Plasma-Plus coating to battery contacts in the plastic housing of a medical wristband.

The Openair-Plasma technology developed by Plasmatreat facilitates the use of optimal material combinations favored in medical engineering applications. Plasma treatment even allows substrates previously regarded as incompatible to be bonded to one another without using primers, whereby water-based and often even UV adhesives provide long-time stable adhesion once the surfaces have been activated. The temperature of the plastic surfaces typically rises by just $\Delta T < 30°C$.

In special cases, an additional adhesion-promoting plasma coating is needed to attain a reliable and durable material bond without mechanical surface preparation.

Printing and painting

In printing and painting processes many medical engineering requirements necessitate homogenous wetting of the components with ink or paint. This is an increasingly topical issue in view of the implementation of the new Medical Devices Regulation (MDR), which comes into force on 26 May 2020. Among other things, it requires medical devices to have a globally valid product label which is both machine-readable (a barcode, for example) and human-readable (in plain text). This label is designed to improve traceability in the event of a claim and to ensure that the medical device can be matched to a manufacturer. [1] Laser marking is the state-of-the-art method, but this requires a matrix material that is correspondingly receptive or the use of laser-activated additives. These additives often fail to comply with regulatory requirements regarding food contact testing or biocompatibility, for example.

Due to the activation effect of plasma, a wide variety of substrates – such as PVC catheter bags – can be printed with long-time stable results without the need for special additives.

Plasma coating under normal pressure

The Plasma-Plus process can be used to coat a range of different substrates. This process involves introducing chemicals or metallic particles such as copper into the plasma stream which are then deposited on the activated surface. The chemical precursors may be liquid in the form of a sol, or gas. The wide range of precursors available makes it possible to tailor component functionalization to the respective application. [2] The thin films deposited in this process specifically target wettability. The surface can be functionalized to make it hydrophilic, hydrophobic, biocompatible or even antimicrobial. Furthermore, coatings can act as a barrier or anticorrosion layer, reduce friction or ensure the molecular bonding of hybrid components.

Antimicrobial functionalization

With antibiotic resistance on the rise, infections in hospitals, and especially associated with implants, are now a global problem. As a result, there is a growing and significant interest in the antimicrobial functionalization of medical devices. Plasma-Plus technology can be used to deposit metal oxide coatings with a photocatalytic and therefore antimicrobial effect on a very wide range of substrates. The metal oxide layer is activated by light in the ultraviolet

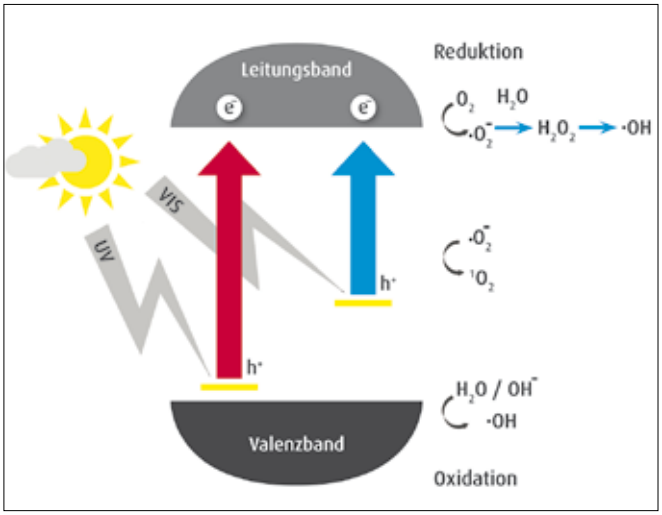

Image source: Plasmatreat

Visible and ultraviolet light excites the electrons in the metal oxide layers, which jump up from the valence to the conduction band. Hydroxyl radicals form in a moist environment.

and visible range, thereby exciting the electrons. In a moist environment, water splitting leads to the formation of reactive species such as hydroxyl radicals, which are directly antimicrobial. The exact mechanism behind the reactive species' antibacterial effect is not yet fully understood, but it is thought to mainly involve oxidative damage to the bacterial cell membrane. Plasmatreat is currently looking into the antimicrobial and self-cleaning features of surfaces in the "Auto Protect" project (D-NL-Interreg Projekt, Förderkennzeichen: 144131)

When applied to plastics or metals, the non-cytotoxic antimicrobial plasma coatings offer scope for a wide range of applications as self-cleaning surfaces or for disinfecting air or water. They are likely to become of great importance on implant surfaces as a means of preventing implant-associated infections during or shortly after operations.

Positive impact on bone cells

In medical engineering, the aim it to tailor implants optimally to the patients' needs. Personalized implants based on data from diagnostic imaging can now be produced using additive manufacturing processes. Polyetheretherketone (PEEK) has proved to be an ideal material for this purpose. It is chemically inert, non-toxic, biocompatible and unlike metal implants, does not produce artifacts in imaging processes such as radiography. Additive manufacturing processes allow structurally compatible, load-bearing implants to be created which have mechanical properties similar to those of bone [3]. However, the poor wettability of PEEK surfaces adversely affects their ability to be colonized by osteoblasts – the cells that form new bone.

The Munich-based medtech startup Kumovis specializes in the production of 3D printing systems for processing high-performance polymers for personalized implants. In collaboration with Plasmatreat, colonization tests with osteoblasts (bone cells) have been conducted on different plasma-treated PEEK and reference samples. The tests showed that, compared with an untreated PEEK surface, a pure plasma activation did indeed bring about osteoblast colonization of the surfaces, although the effect was not particularly pronounced. However, very positive results were obtained when the atmospheric plasma coating was added to the pretreatment process: there was a significant improvement in bone cell growth. PEEK implant surfaces with good osseointegrative properties which promote bone growth have been created with the aid of Plasma-Plus technology.

Pioneering

The atmospheric plasma jet technologies described here are regarded as pioneering processes in medical engineering. They can effectively support the manufacture of medical devices in diverse ways. Apart from the area-selective applicability and simple systems integration, other factors which make them particularly worthwhile in medical engineering include high process speed, high process reliability, robot compatibility and accurate process reproducibility. The atmospheric pressure plasma processes can be integrated easily into digitally controlled production processes and furthermore, they are more cost-effective than conventional pretreatment methods. ■

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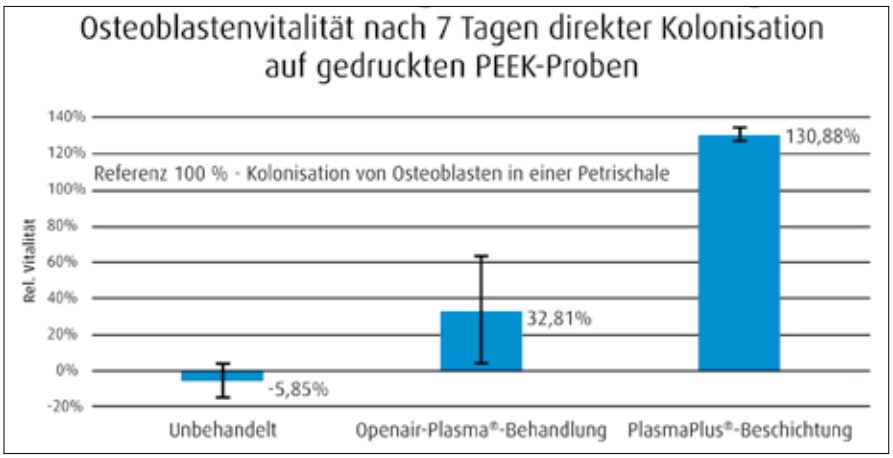

Image source: Kumovis

Proof on a PEEK surface: The Plasma-Plus coating leads to a significant growth in bone cells.

Literature:

[1] Verordnung (EU) 2017/745 des Europäischen Parlaments und des Rates vom 5. April 2017 über Medizinprodukte, zur Änderung der Richtlinie 2001/83/EG, der Verordnung (EG) Nr. 178/2002 und der Verordnung (EG) Nr. 1223/2009 und zur Aufhebung der Richtlinien 90/385/EWG und 93/42/EWG des Rates. Europäische Union, 2017

[2] Verfahren und Vorrichtung zur Plasmabeschichtung von Oberflächen, Patentnummer EP 1 230 414 B1

[3] S.-W. Ha, E. Wintermantel. Medizintechnik Life Science Engineering, 5. Auflage, Springer-Verlag Berlin Heidelberg, 2009