Evaluating the Activation Capacity of Atmospheric Plasma Systems

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This article shows that a comparative evaluation of different methods of surface treatment can be carried out using simple means. The outcomes can be directly extrapolated to practice and yield, as a measurable result, the area (per time unit) whose surface energy can be increased to a desired level.

Introduction

The surface energy \( \gamma \) is the energy per area unit in J/m\(^2\) which is necessary to increase the surface of a solid body or a liquid.

The equivalent mechanical interpretation speaks of the surface tension in N/m, defining the surface tension as the work to be invested in order to enlarge the surface of a liquid film.

When a drop of liquid is applied to the surface of a solid body which additional attracting forces between solid body and liquid are acting on (adhesion), the drop deviates from its spherical shape and wets the surface of the solid body. This deviation, and therefore the wetting effect, becomes more pronounced the stronger the adhesion between solid body and liquid is.

This fact makes it possible to calculate the solid body’s surface energy from the contact angle using Young’s equation (Good, 1993).

\[
\sigma_s - \sigma_{SL} = \cos(\theta) \cdot \sigma_{LS}
\]

The solid body’s surface energy is an important property which determines the usability, the adhesive qualities and the homogeneous coatability of a surface. Any deviation from values typical of the materials used may point to (possibly invisible) contamination such as a greasy film.

A particularly simple system for evaluating surface energy is to make a qualitative assessment of how well a number of differently colored test inks spread. This method makes do without a detailed analysis of the droplet geometry. If the liquid’s surface energy equals that of the wetted solid body, the contact angle approaches zero and the liquid can form a thin stable film on the surface. In the first approximation, the solid body’s surface energy lies between the surface energy of the test ink whose wetting properties are just about good and the ink whose wetting properties are not quite good enough.
Atmospheric plasma treatment is a common and established method for fine cleaning and activating surfaces. One of the desired effects is an increase in surface energy (Liebermann & Lichtenberg, 2005).

For polymers and composite materials, this kind of activation using atmospheric pressure plasma can be the most efficient method as well as the most cost-effective one when operated with compressed air. Moreover, it is compatible with virtually any serial process.

No wet-chemical primers are necessary, which makes atmospheric plasma functionalization particularly eco-friendly and gentle on material. Fine-cleaning and functionalization are achieved and static surface charges are neutralized in only one single process step.

Naturally, it is in the users’ interest to be able to compare the efficiency of the different systems available for plasma, flame or corona treatment in order to choose the application, which is optimally suited for achieving the desired result when treating a specific surface. In the following, a simple method is defined which makes it possible to objectively determine the activation performance. The process is exemplified by a practical comparison of two different atmospheric plasma systems.

Atmospheric plasma nozzles for surface treatment

The widespread method of generating a highly reactive plasma jet under atmospheric pressure, and typically using air, is successful when a concentrated jet is emitted from a hot discharge zone, with said jet containing all relevant surface-active species and being electrically neutral if possible.

Figure 1: plasmabrush® plasma system, consisting of high voltage source (PS2000) and plasma generator (PB3). Optimized for high outputs and for integration into production plants with high throughput.

The effects of plasma treatment on a given surface are of a thermal, chemical and electrical nature and depend on the setting of the process parameters. Working distance, type of process gas used, preset excitation power and processing speed play just as important a role as the substrate properties.

Piezoelectric plasma generator

With piezoelectric direct discharge (PDD®), a plasma is ignited directly at a piezoelectric crystal. Similarly, as with a dielectric barrier discharge (DBD), a cold atmospheric discharge occurs along with an ionization of the surrounding gas, provided the oscillating field strengths are sufficiently high.

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Plasma generators using piezo technology are among the most efficient methods of generating surface-active species.

Figure 2: burning behavior of the Piezobrush® PZ2 used with different nozzle inserts. For the measurement described here, the first nozzle variant (picture far left) was chosen.

Measuring method

The activation power is here defined as the change in surface energy of a given object after a known time (exposure). If a plasma jet or a flame is applied to a surface, there is a spatial distribution of surface energy. The activation power can therefore be understood as a kind of fingerprint of a surface activation process.

When measuring the activation capacity, a number of problems arise in practice, as saturation effects may occur as the duration of the treatment is increased, and spatial distribution may be inhomogeneous.

In order to record the “fingerprint” of the surface activation, it is for instance possible to choose three test liquids with differing surface energies (E1, E2, E3). The surface is exposed to static plasma activation for a defined period of time, just long enough for the test liquid with the lowest wettability (i.e. the highest surface energy) to already have wet a small part of the surface.

The evaluation is now performed through a simple surface assessment, in which two values are correlated: how much has the surface energy changed compared to the substrate’s initial surface energy, and how big a portion of the surface has each liquid been able to wet?

\[ \Delta E_{of} = (\gamma_1-\gamma_0) A_1 + (\gamma_1-\gamma_0) (A_2-A_1) + (\gamma_1-\gamma_0) (A_3-A_2) + \ldots \] (in Joule)
The activation capacity (in watt) is now simply a result of taking into account the duration of treatment.

\[ \Delta P_{off} = E_{off}/\Delta t \text{ (in Watt)} \]

**Result**

A typical plastic substrate received exemplary treatment with an atmospheric plasma system of the 1KW performance class (Plasmabrush® rotating light arc in PAA® technology) and with a cold plasma system of the 10W class (Piezobrush® in PDD® technology).

The substrate (ABS plastic) with an initial surface energy of 41mJ/m² (correspondingly 41mN/m) was treated with plasma, then brushed with three different test inks. The wetted surface areas were then measured.

![Figure 4: test body (50mmx50mm ABS), wetted with different test inks. The wetted areas are specified for each picture. The picture series above illustrates the result after a 0.5s treatment (pulsed) using the high-performance Plasmabrush® system. The pictures below show the wetting behavior of the different inks after a 0.25s period of exposure (pulsed).](image)

![Figure 5: “Fingerprint” of the Piezobrush® PZ2 handheld plasma device on a 50mmx50mm ABS test body after 3s of treatment. The test inks used had the specified surface tensions.](image)

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For the ABS substrate, plasma treatment using the Plasmabrush® PB3 effected a change in surface energy of 6.2 µJ after 0.25s and of 6.9 µJ after 0.5s of exposure. These values show that the activation capacity is about 25µW for the first 0.25s and then decreases. For an exposure time of 0.5s, the average activation capacity is only about 15µJ. A first rough estimate allows the conclusion that ca. 10^{13} surface groups per square centimeter are chemically functionalized.

For similar ABS test bodies, the handheld plasma device Piezobrush® PZ2 achieved an equal effect after about 3s of exposure. Its average activation capacity of 2µW is only about one order of magnitude smaller, although the power supplied is about two orders of magnitude less.

These results might not seem sensational on paper at first glance - surface activation effects are by nature hard to evaluate, and the effects of atmospheric processes on a surface are energetically rather inefficient. A plasma system with an input power of 1kW may possibly only have an activation capacity of a few microwatt. For practical applications, however, the achieved effects can make a substantial difference, as the relative change in surface energy may be absolutely decisive for the quality of an adhesive bond.

**Conclusion**

Through a simple measurement of the surface energy, the activation capacity of a surface treatment may be evaluated and quantified. This allows for a quantitative comparison of the performance and efficiency of various methods of surface treatment using a physically defined quantity (activation capacity in watt).

**References**
