

Successful Use of Plasma Jets in Production Lines

The pre-treatment of polymers and metals with plasma jets at atmospheric pressure can yield high adhesive bonding strengths. For reliable operation, it is necessary to know the time stability of the pre-treatment effect, the influence of the process parameters and the principles of the activation mechanism.

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Polymers and metals can be pre-treated (activated) by mechanical, chemical or physical methods [1]. Plasma pre-treatment is a common technique within the group of physical methods. Plasmas can be categorized according to their operational pressure range, Table. Low-pressure plasmas operate at pressures of between 10^{-2} and 10^{-6} bar and can be generated with a variety of different electrical excitation methods. Their main advantage is the treatment of the whole surface that is exposed to the plasma zone. Their main disadvantage is the need to generate a vacuum. In contrast, atmospheric-pressure plasmas need no vacuum but often have a high consumption of process gas.

Corona discharges and dielectric barrier discharges, both of which are atmospheric-pressure plasmas, have been in industrial use for many years. In recent years, atmospheric-pressure plasma jets have been added to these methods. The plasma is generated inside a nozzle and expelled through the nozzle orifice onto the substrate surface, Figure 1. The different commercially available plasma jet systems differ for the most part in the gases needed for operation (air, nitrogen or inert gases), as well as in the plasma temperature and the electrical excitation (power). Several aspects should be considered when plasma jets are installed in a production line. Of special practical importance is the ease of integration into an existing production line, as well as a suffi-

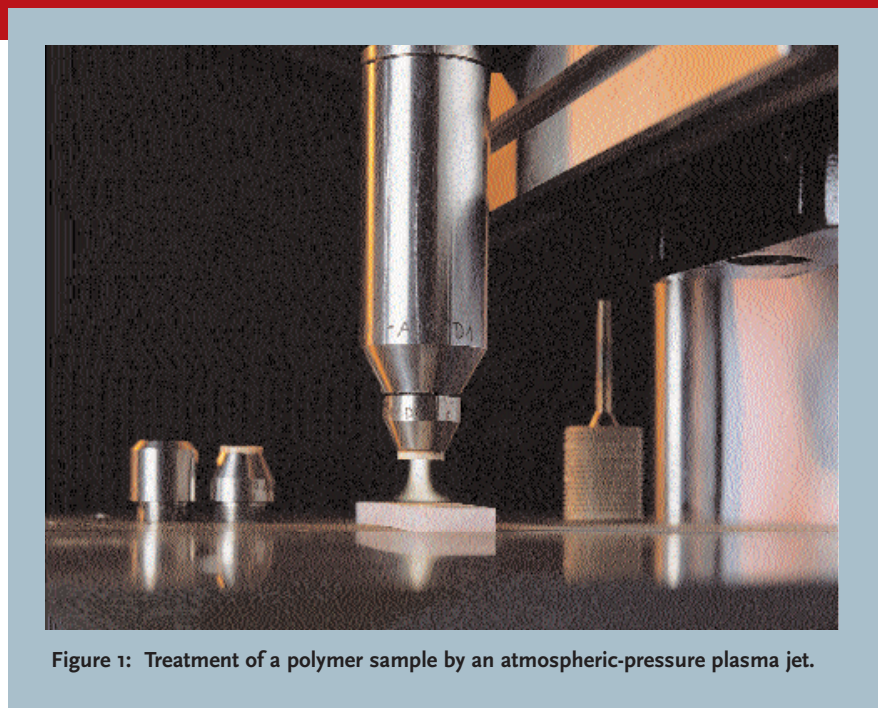


Figure 1: Treatment of a polymer sample by an atmospheric-pressure plasma jet.

cient time stability of the pre-treatment effect and the tolerance of the pre-treatment to changes in the process parameters. For this purpose, a thorough knowledge of the pre-treatment mechanism and the influence of process parameters is of great interest [2-3].

Plasma Treatment and Adhesive Bonding

The polymers PP, PVDF, PA6 and the aluminium alloy AlMgSi1 were studied. The substances are likely to contain typical additives (such as internal release agents or stabilizers) since industrial grade materials were used. Prior to the plasma treatment,

the samples were ultrasonically cleaned for 30 seconds in iso-propanol. For the plasma treatment, a commercially available system manufactured by Plasmamatreat GmbH was used. The thermal non-equilibrium plasma is generated using dry air as the process gas. The samples are moved through the plasma jet at speeds of between 10 and 200 m/min. The special design of the plasma jet causes only a weak electric field outside the nozzle, also allowing the treatment of metals as well as polymers. For adhesive bonding, a two-component polyurethane resin was used for the polymers, and a two-component epoxy resin for the aluminium alloy. The thickness of the adhesive layer

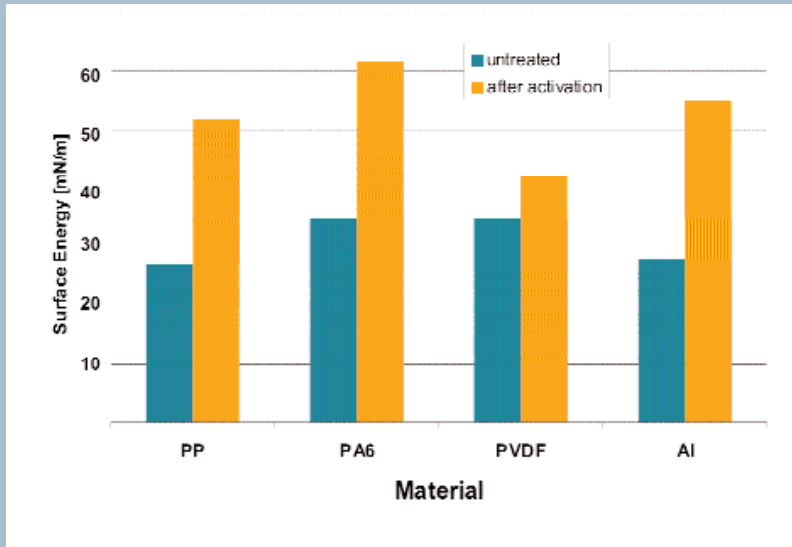


Figure 2: Surface energy before and after plasma treatment.

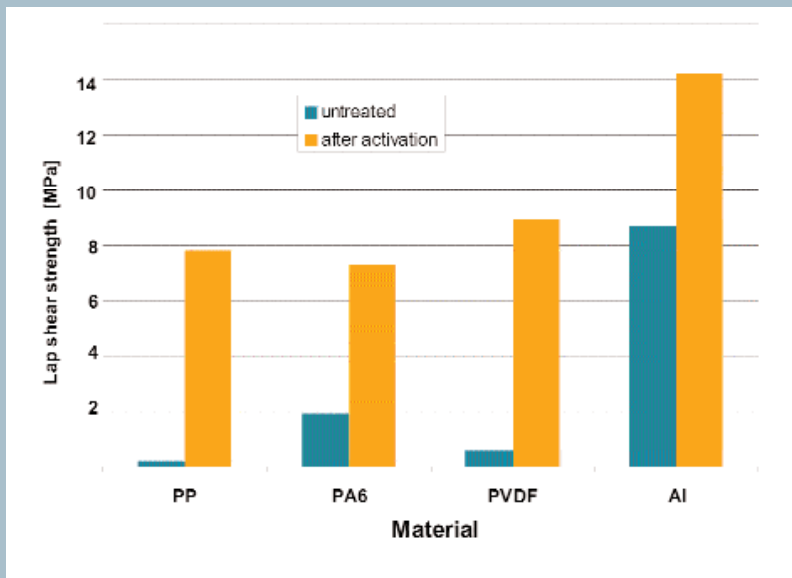


Figure 3: Lap shear strength with and without plasma treatment. All activated samples exhibit substrate or cohesive failure modes.

was 0.1 mm. The adhesive bonding strength was determined by lap shear measurements in accordance with DIN EN 1465. The surface energies were calculated from dynamic contact angle measurements using water, glycerine and diiodomethane. The chemical surface composition was determined by photoelectron spectroscopy (XPS), and the surface topology was mapped by atomic force microscopy (AFM).

Adhesive Bonding Strength

The efficiency of the plasma pre-treatment was determined by measuring the surface energy and the lap shear strength. Figure 2 presents the surface energies before and after pre-treatment for all materials studied. In all instances, a strong increase in surface energy can be observed, resulting in improved wettability of the substrate surface by an adhesive. The improvement in adhesion itself was studied by comparing the bondability of the samples with and without pre-treatment. As Figure 3 shows, all materials that have been pre-treated exhibit a strong improvement in lap shear strength. Especially noteworthy is the change in the bonding failure mode. All untreated samples show an adhesive failure mode. In contrast, all samples that received a plasma jet treatment show substrate failure modes (the aluminium sample showed a cohesive failure mode). Thus, plasma jet treatment allows the full structural strength of the adhesive joint to be used. This is the ideal result for a pre-treatment method.

Ageing and the Influence of Process Parameters

An important characteristic of any pre-treatment method is the maximum time between pre-treatment and adhesive bonding

	Technical Design	Features
Low-Pressure Plasma $p \approx 10^{-2} \dots 10^{-6} \text{ bar}$	Typical excitation frequencies: <ul style="list-style-type: none"> • Low-frequency plasma (10 – 80 kHz) • Microwave plasma (13.56 MHz) • Microwave plasma (2.45 GHz) 	<ul style="list-style-type: none"> • Whole surface is treated • Usually batch operation • Capital invest higher than for atmospheric-pressure plasma
Atmospheric-Pressure Plasma $p \approx 1 \text{ bar}$	Typical configuration: <ul style="list-style-type: none"> • Corona • Dielectric Barrier Discharge (DBD) • Plasma Jet 	<ul style="list-style-type: none"> • In-line operation possible • High treatment speed • Gas consumption higher than for low- pressure plasmas

Classification of technical plasmas for pre-treatment

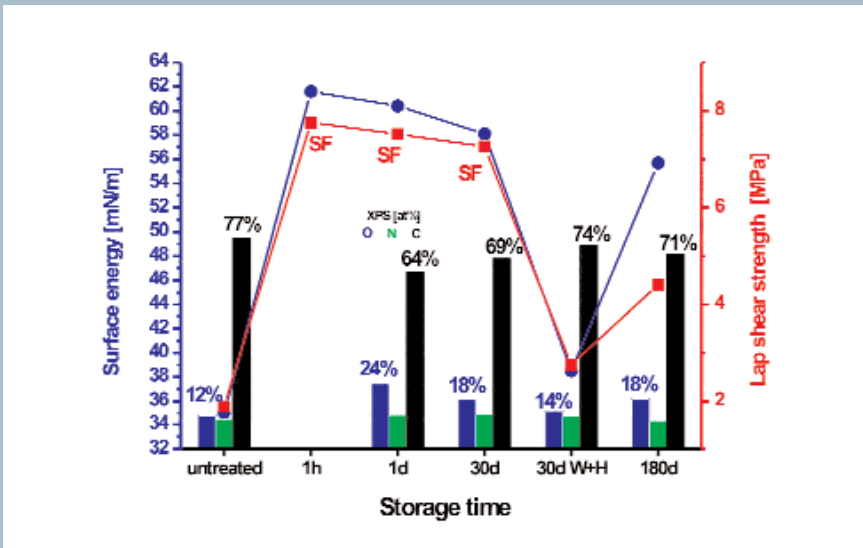


Figure 4: Time stability of the pre-treatment effect for PA6 (with surface energy and lap shear strength displayed in blue and red, respectively; the chemical composition is displayed as columns). The failure mode is adhesive for all samples, except where substrate failure mode (SF) is indicated. The sample 30d W+H was stored for 30 days at 100 % humidity.

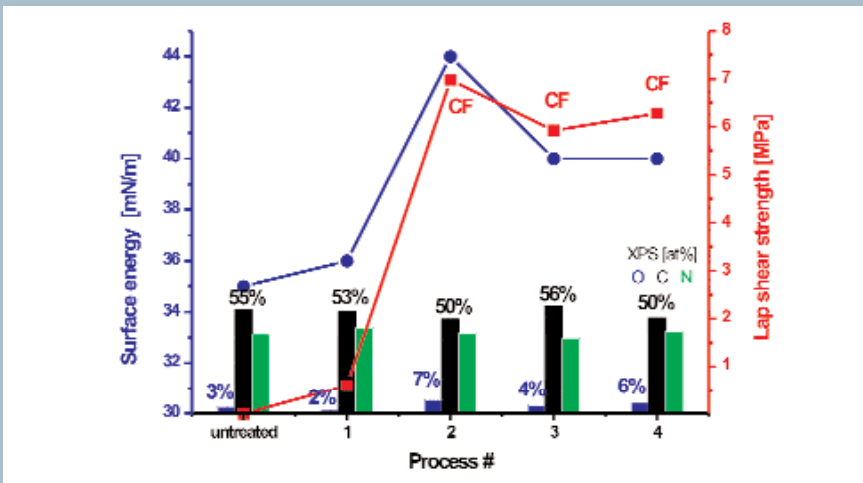


Figure 5: Pre-treatment of PVDF with different process parameters. All samples show an adhesive failure mode, except where a cohesive failure mode (CF) is indicated.

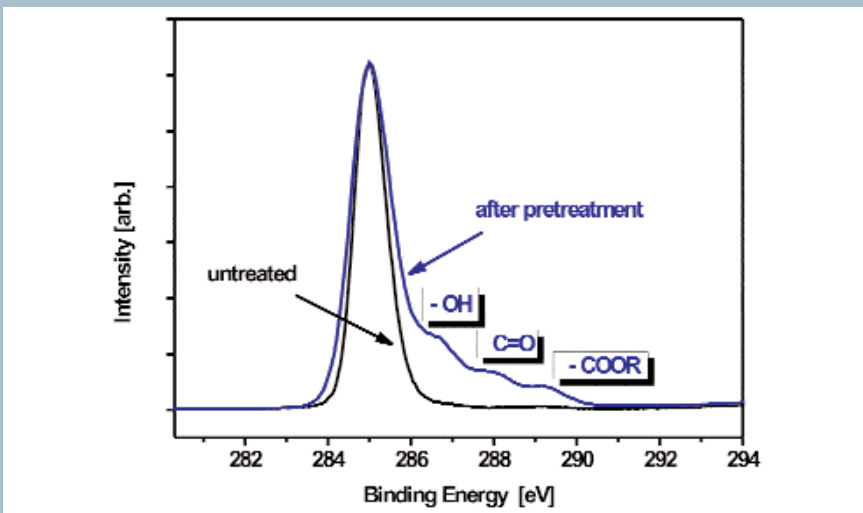


Figure 6: Photoelectron spectrum (C1s region) of PP before and after plasma treatment.

without a significant decrease in the pre-treatment effect. A loss of the pre-treatment effect can be caused by molecular reorientation on the substrate surface, diffusion processes or the adsorption of molecules to the surface. Figure 4 shows the loss of activation for PA6 by measuring the surface energy and the lap shear bonding strength over time. Within the first 30 days, only a slight decay in the activation effect is observed. Even after six months, the surface energy and the adhesive bonding strength are on a high level (although a substrate failure mode is no longer observed). In contrast, storing the activated samples for 30 days at 100 % humidity gives rise to a strong loss of activation. But in spite of the harsh conditions, the level of surface energy and bonding strength is still improved compared to the initial values without pre-treatment. Figure 4 also shows the surface oxygen concentration. The oxygen concentration shows a very similar time dependence to that of the surface energy and the bonding strength. This correlation indicates that the number of oxygen atoms plays an important role for the adhesive bonding strength (see also below).

The effect of parameter changes for the pre-treatment is shown in Figure 5. Four different sets of process parameters (1 – 4) were used for the treatment of PVDF. After each treatment, the surface energies, bonding strengths and chemical compositions were determined. The most significant difference between parameter sets 1 to 4 is the decreasing distance between the plasma jet and the substrate surface (distances = 20, 10, 5 and 3 mm for sets 1 to 4, respectively). A good correlation between the adhesive bonding strength and the oxygen concentration can again be observed. As Figure 5 also shows, the dependence of the activation effect on the process parameters is complex. A similar complex behaviour is observed when the dependence on the process time is studied (not shown). An adequate explanation still needs to be established. It has to be noted that, in general, the optimum process parameters are different for different materials. Therefore, the process parameters need to

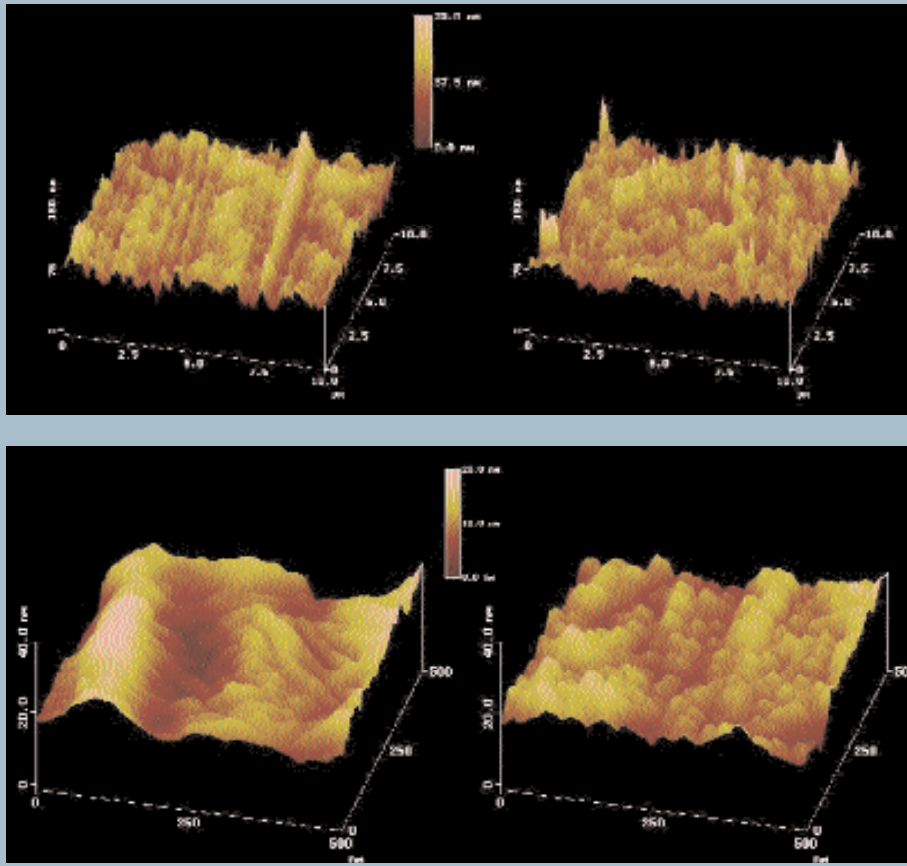


Figure 7: Surface topology of PVDF before (left) and after (right) plasma treatment on two different scales a) and b).

be established for each material before pre-treatment.

Pre-Treatment Mechanism

The pre-treatment effect is a result of the chemical and physical interaction of the plasma with the substrate. Of special importance for improving adhesion are the modifications of the chemical composition and the topology of the substrate surface. The changes in chemical composition of PP after plasma jet treatment are presented in Figure 6. The quantitative analysis of the XPS spectrum indicates an increase in the oxygen concentration from 3 at% to approximately 17 at%. The spectral features at 286.6, 287.9 and 289 eV indicate the formation of alkoxy, carbonyl and acidic/ester groups. These different functional groups allow the formation of a stable chemical bond between the adhesive and the substrate material, resulting in high bonding strengths.

Figure 7 shows the modification of the surface topology of PVDF from the plasma jet treatment. At each of the two different

scales (magnifications), the loss of the initial surface topology can be seen. On the 500 x 500 nm scale, the formation of a regular patterned surface is observed. The sur-

face roughness (RMS value) remains approximately constant. The changes in surface topology can be the consequences of the thermal component of the plasma or the outcome of chemical reactions. The relevance of the topology modification for adhesive bondability is difficult to judge, since a chemical modification that is difficult to separate from the topological changes occurs simultaneously.

Summary

Adhesion properties were strongly improved by using an atmospheric-pressure plasma jet for the pre-treatment of four different materials. The improvement in adhesion can be related to the incorporation of oxygen-containing functional groups and probably to changes in the surface topology. The surface activation remains stable for several weeks and does not disappear completely even after storage at elevated temperatures and high humidity. These features are a significant advantage over corona treatments.

Different materials can be treated with the plasma jet when the process parameters are adjusted specifically for the particular material. ■

Quellenverweis Autoren & Vita

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