Hydrophobic Polymers – Better Bonding and Painting by Atmospheric Pressure Plasma Treatment

English translation of "Hydrophobe Polymere – besser Verkleben und Lackieren durch Atmosphärendruckplasmabehandlung"

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The interfacial area between plastic and adhesive or plastic and varnish is decisive for the adhesive bond or the adhesion of the varnish. Coatings as well as adhesives are polymers, therefore several observations are transferable between both domains. The presentation focusses on adhesive bonds, also attendants may take along ideas and check transferability to their own applications. This conference handout is intended to present some core ideas, only. Further detailed information can be found in the two publications[1,2] by the same authors of TH Lübeck and on the TH Lübeck homepage "Labor für Oberflächentechnik"[3]. The referenced publications can also be downloaded there. Other publications and papers will follow (see TH Lübeck homepage).

Plastic components are often bonded, while the respective properties such as strength or transparency in the bonded interface area need to retain. Usually, the weak point is the contact point between plastic and adhesive, i.e., the interface.
If the adhesive, varnish, or a previously used adhesion promoter (precursor) is able to dissolve the surfaces and allows better penetration of the adhesive, then in addition to adhesion as the bonding mechanism, mechanical clamping of the surface molecules can also be expected and one can assume very good adhesion. Some adhesion promoters also create contact points for chemical bonds.
When dissolving, the surfaces of the joining partners are strongly altered, so that properties are impaired. For example, transparency, which is particularly desirable in the case of plastic foils. Several very effective adhesion promoters are also harmful to health, so that they need to be omitted.

A possible solution is to use atmospheric plasmas for interface activation. Often, a considerable improvement in the bondability is already archived by a single targeted and beam-overlapping atmospheric plasma treatment on the surfaces of the parts to be joined. The plasma treatment removes organic and inorganic contaminations from the parts to be joined, increases the surface energy, and usually achieves a change in the surface roughness.

The available amount of surface energy is of great importance, especially for plastic surfaces. In particular, Polyethylene (PE) and Polypropylene (PP) have a low surface energy, which becomes clear when looking at a drop of water on a surface. The drop does not spreads, but contracts and rolls off easily. Water is polar and plastic surfaces are less polar, precisely, non-polar. Therefore, PE and PP are difficult to wet with water and thus, also difficult to wet with adhesives and in conclusion difficult to glue, print, or paint.

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[1] A. Bender, S. Fricke, L. Dethlefsen, **Polyethylen besser kleben**, Kunststoffe 04/2021, Seite 48 – 51, Carl Hanser Verlag
[2] A. Bender, S. Fricke, **Die richtige Rauheit für das Kleben von Polymeren**, Kunststoffe 09/2021, Seite 78 – 79, Carl Hanser Verlag
[3] https://www.th-luebeck.de/hochschule/fachbereich-maschinenbau-und-wirtschaft/labore/oberflaechentechnik/forschung/

For successful bonding and painting of plastics, it is necessary to increase the surface energy of the plastic surface. The surface energy should reach a value close to that of the adhesive or paint. Atmospheric plasma treatment allows this.

The total surface energy of the substrate can be determined with test inks in a simple way, but this is often not sufficient. More sufficient is the determination of the disperse part (van der Waales interactions) and the polar part (e.g., interactions through polar hydrogen bonds). Their sum represents the total energy of the surface.
Good bonding of two composite partners with the same total energy can only be expected if the disperse and polar part of the partners, i.e., plastic and adhesive, are also approximately equal.

Two atmospheric plasma devices are used to pre-treat the samples, both devices belong to the so-called cold plasmas and blow the plasma jet (so-called afterglow) out of the nozzle by an increased gas pressure:
First, the *Plasma Beam* (generator frequency 29 kHz) from *Diener electronic GmbH und Co. KG* with a power of 300 watts (process gas: air) and second, the *KinPen 11* (generator frequency 1 MHz) from *Neoplas tools Gm*bH with a power of 10 watts (process gas: argon).

In order to investigate the quality of a bond with regard to pre-treatment with plasma, tensile shear specimens (referred to as Zugstab in Figure 1 and 2) are manufactured by means of injection molding, which are then bonded untreated and plasma-treated.
These tensile shear specimens are tested for their tensile shear strength. The maximum error for all measurements is 0.1 MPa.

The surface energies of the tensile specimens with their disperse and polar parts are determined using the *FM 40 Easy Drop* device from *Krüss GmbH*.
Thereby, 5 drops of diiodomethane and deionised water each are applied to the plastic surfaces. In the process, the drop shapes are measured, the contact angles are determined, and mean values are formed. Using the model calculations by Owens, Wendt, Rabel and Kaelble (OWRK), the disperse and polar parts of the total surface energy are determined. The maximum error is less than 0.5 mJ/m^2.
A good method for the initial assessment of the bondability is the measurement of the surface energies of the adhesive partners involved.

The used adhesive is a solvent-free two-component epoxy resin-based adhesive from UHU (*UHU Plus Endfest 300,* producer *UHU GmbH &Co. KG, Bühl*). In the cured state, the surface energy is 45 mJ/m^2 (disperse part 33mJ/m^2 and polar part 12 mJ/m^2).
Furthermore, a one-component cyanoacrylate-based adhesive from Pattex (*Pattex Sekundenkleber Plastix Flüssig*, producer *Henkel AG &Co. KGaA, Düsseldorf*) is used. In the cured state, the surface energy is 33 mJ/m^2 (disperse part 33 mJ/m^2 and polar part 0 mJ/m^2).
Thus, the Pattex adhesive can be considered as non-polar and the UHU adhesive as polar.

Selection of some results on PE (PP – results and discussion will be published on the TH-Lübeck homepage at a later date).

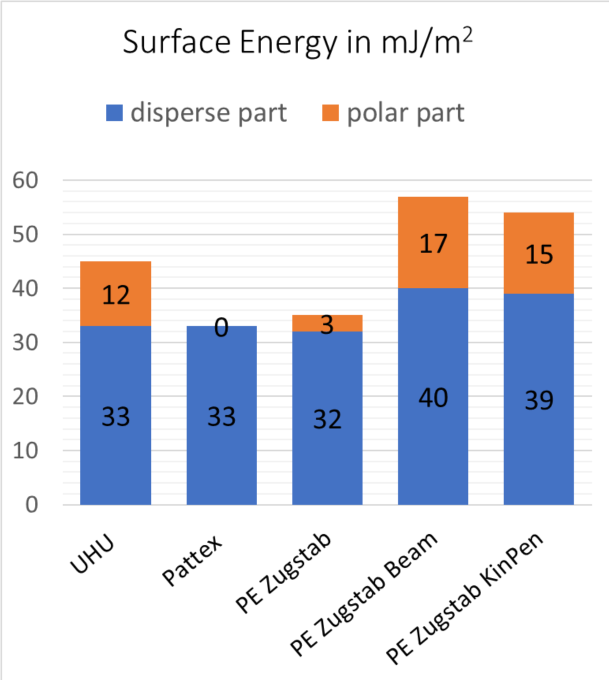

Figure 1: Surface energies of the PE samples before and after plasma treatment. Besides the cured adhesives UHU and Pattex.

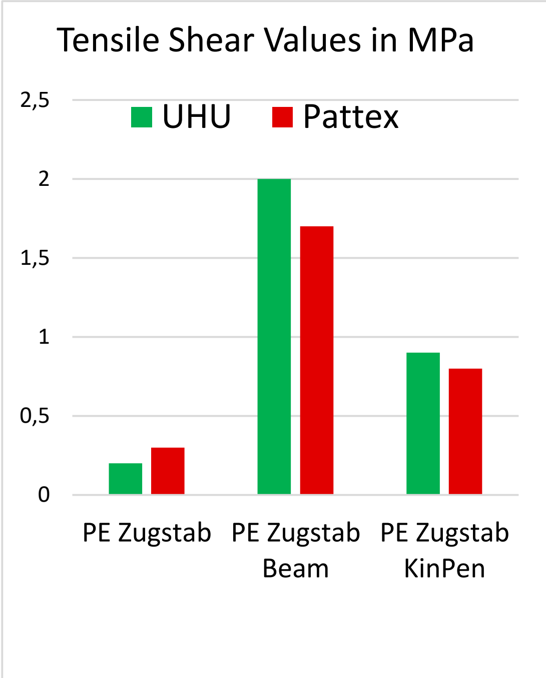

Figure 2: Tensile shear strength values of the bonded PE samples before and after plasma treatment.

Figure 1 clearly shows that the disperse surface energy part of PE and both adhesives differ only slightly. After plasma treatment, the polar surface energy part of the PE samples increases and reaches values similar to the UHU adhesive. It is interesting to note that the disperse part also increases.

In Figure 2, the tensile shear strength values show that the untreated PE samples can be bonded better with Pattex than with UHU.
An explanation would be that the values of surface energies are close together and especially the differences in the polar surface energy part are small. UHU is much more polar than PE and sticks worse. Plasma treatment improves the bondability of PE with both adhesives. The best values are achieved with UHU and plasma treatment using the *Plasma Beam*.

Plausibly, this can be explained by the incorporation of oxygen into the surface and the resulting functional groups, which increase the polar part of the total surface energy.
In addition to this surface functionalization, plasma treatment can increase the surface roughness and can cause the surface to melt.
Using the *KinPen*, no melted surface and no change in roughness was detected even after multiple plasma treatments. In difference to the *KinPen*, the *Plasma Beam* produces a higher energy input and the surface melts slightly. The roughness showed an increase in the maximum values. It is interesting to note, that larger microscale roughness peaks became larger and smaller peaks decreased or disappeared completely on the flanks of the larger peaks. The samples treated with the *Plasma Beam* show a glassy, mirror-like surface.

Coming back to the results of Figure 2, the samples treated with the *Plasma Beam* show the best tensile shear values. The values using the *KinPen* are lower, however, significantly higher than the values without plasma treatment. In addition to the functionalization achieved with both plasma sources, the roughness discussed above leads to even better bonding.

The model in Figure 3 describes the influence of different roughnesses on the bond. Here, the adhesive has the usual processing properties.

Figure 3: Illustration and model taken from[2].

In Figure 3, the upper samples have a coarse microscale roughness with many fine and long roughness peaks (like needles). The adhesive hangs mostly on the needles only and when pressing on, even bending the needles and shielding the adhesive can occur. After the adhesive has cured, the bent and possibly weakened fine needles have to absorb the tensile and shear forces.
The lower samples again have a coarse microscale, but smoother roughness resulting from surface heating. The adhesive penetrates better and the coarser smoother roughness peaks can even form caverns (a kind of push button) when pressed on, thus, can better withstand tensile shear loads.

Atmospheric pressure plasma treatment activates the surface by generating functional groups and by fine cleaning the surface. An appropriately selected energy input influences the roughness. By optimizing the roughness, an improvement in the adhesion of adhesives and varnishes can be achieved.

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