

# More than Hot Air

## *Structural Gluing of Semi-Crystalline Plastics through Atmospheric Plasma Treatment*

Many thermoplastic materials are very difficult to glue. Activation with atmospheric plasma significantly increases the adhesive force of the joint in just one process step. The search for the cause harbors some surprises.

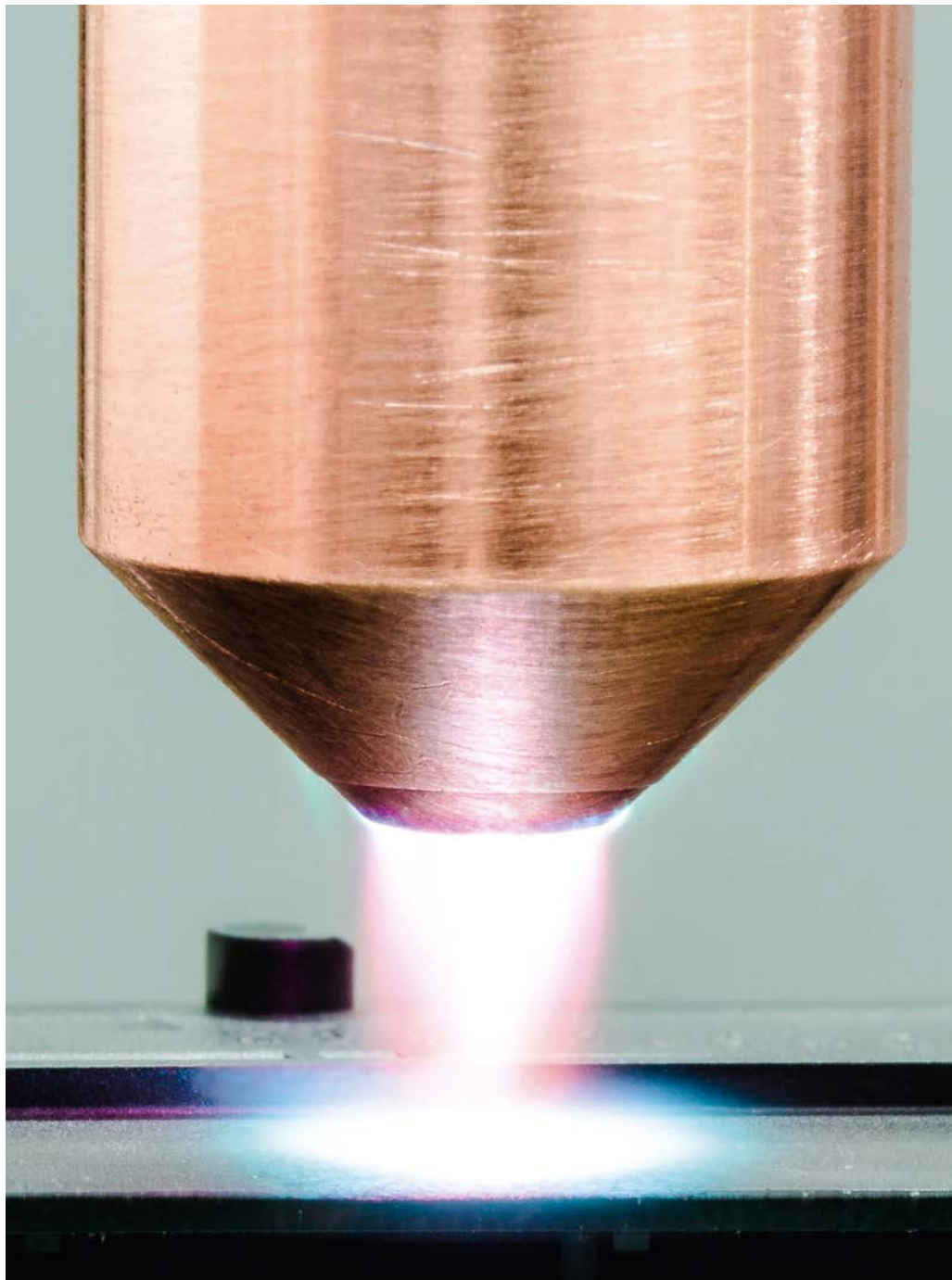
The effect of plasma treatment on a surface is of a thermal, chemical, and micromechanical nature, and depends on the chosen process parameters. Factors that play an important role include the working distance, type of process gas, excitation power level, and processing speed, but also the properties of the material. Semi-crystalline plastics have some characteristics that make them especially well suited for plasma pre-treatment so that the adhesive force of a bonded joint can be significantly increased. Interesting effects are revealed when the reasons are investigated in greater detail.

### *Model System and Tests*

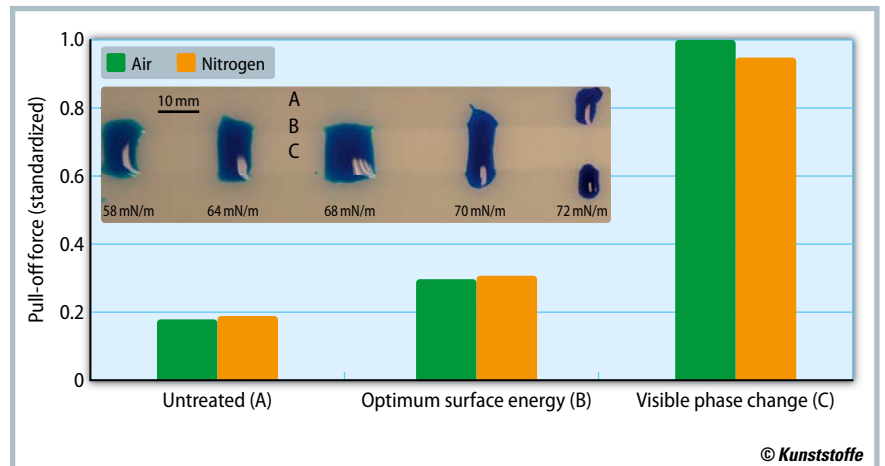
As the model system for testing a polyoxymethylene homopolymer (POM-H) was chosen. With a degree of crystallization up to 90%, it is opaque white in color due to its high crystallinity and remains unchanged up to the melting temperature of approximately 175–178°C. POM starts to thermally decompose at around 220°C and releases formaldehyde.

All tests were conducted with an integrated atmospheric plasma system (type: Plasmacell 300, manufacturer: Relyon Plasma GmbH, Regensburg, Germany). A typical two-component epoxy resin adhesive system was used for the gluing tests (ESK-50 fast-acting epoxy resin adhesive from Würth, Künzelsau, Germany).

Tensile/shear tests confirmed a significant difference with the adhesive force being several times greater (Fig. 1). Two main reasons are usually given for this improvement in the quality of bonded joints after plasma activation: Better wettability of the surface and the removal of residual contaminants (changed chemical compo- »



Atmospheric plasma burner aimed at a plastic surface (© Relyon Plasma)



**Fig. 1.** Plasma effect on a POM surface: The wetting behavior, gloss, and adhesive force have changed significantly after a pass at a constant speed within a track width of about 10 mm (C) by contrast with an untreated surface (A) (source: Relyon Plasma)

## The Authors

**Dr. Stefan Nettesheim** has been the Managing Director of Relyon Plasma GmbH in Regensburg, Germany, since 2011, and is involved in technology development as a physicist; [s.nettesheim@relyon-plasma.com](mailto:s.nettesheim@relyon-plasma.com)

**Dipl.-Ing.(FH), MBA Stefan Reichlmaier** has been the Managing Director of Physical Electronics GmbH in Ismaning near Munich, Germany, since 2004 and is also responsible for the analysis laboratory; [reichlmaier@phi-europe.com](mailto:reichlmaier@phi-europe.com)

## The Examination Method

A combination of light microscopy, time-of-flight secondary ion mass spectrometry (TOF-SIMS) [9] and atomic force microscopy (AFM) [10] was used in order to determine the topography and chemical properties on the surface of the specimen as accurately as possible. The specimens were analyzed using instruments of the company Physical Electronics in Ismaning, Germany (PHI TRIFT II and Anasys nano-IR20). High-resolution images deliver a precise "fingerprint" of the polymer surface and react with great sensitivity to any change caused by intentional or unintentional treatment.

## Service

### References & Digital Version

- You can find the list of references and a PDF file of the article at [www.kunststoffe-international.com/3342044](http://www.kunststoffe-international.com/3342044)

### German Version

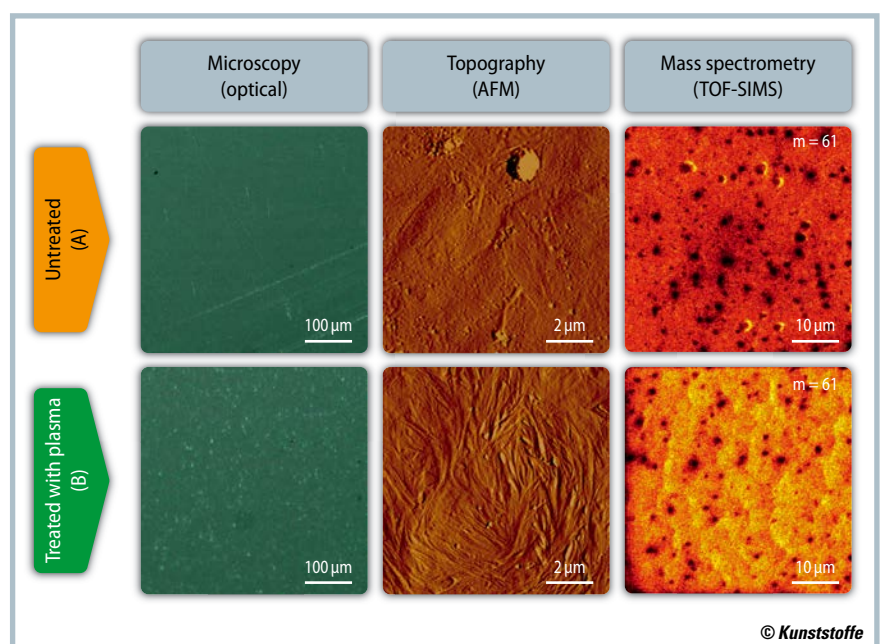
- Read the German version of the article in our magazine *Kunststoffe* or at [www.kunststoffe.de](http://www.kunststoffe.de)

sition of the surface). This makes it all the more astounding that a third aspect appears to play the most important role for thermoplastic polymers: The temperature increase during treatment.

### Wettability of the Surface Is Increased

The wettability of the surface gives an initial indication of the surface treatment effect. It can be easily made visible by applying a liquid test ink [1]. One can clearly see the increased wettability of the line swept by the plasma flame with a certain

width (**Fig. 1, brown Box**). Here a striking aspect is that, starting from the untreated surface (area A) by approximately 40 mN/m, the highest surface energy is found directly at the edge of the visible trail (area B). A more detailed analysis by means of contact angle measurements shows that the maximum surface energy with atmospheric plasma treatment at approximately 58 mN/m is reached prior to visible clouding of the surface. However, the maximum adhesive force with the two-component adhesive being used is not reached in this state of maximum surface



**Fig. 2.** Optical microscopy, non-contact AFM, and a secondary ion raster image on the mass characteristic for POM ( $m=61$ ). The brightness corresponds to the intensity standardized for total counts at  $m=61$  (source: Relyon Plasma)

energy, but at a processing intensity where the surface has already changed visibly and the surface energy has decreased again to approximately 52 mN/m (area C). Thus, simply examining the surface energy is not sufficient for specific optimization of the bonded joint.

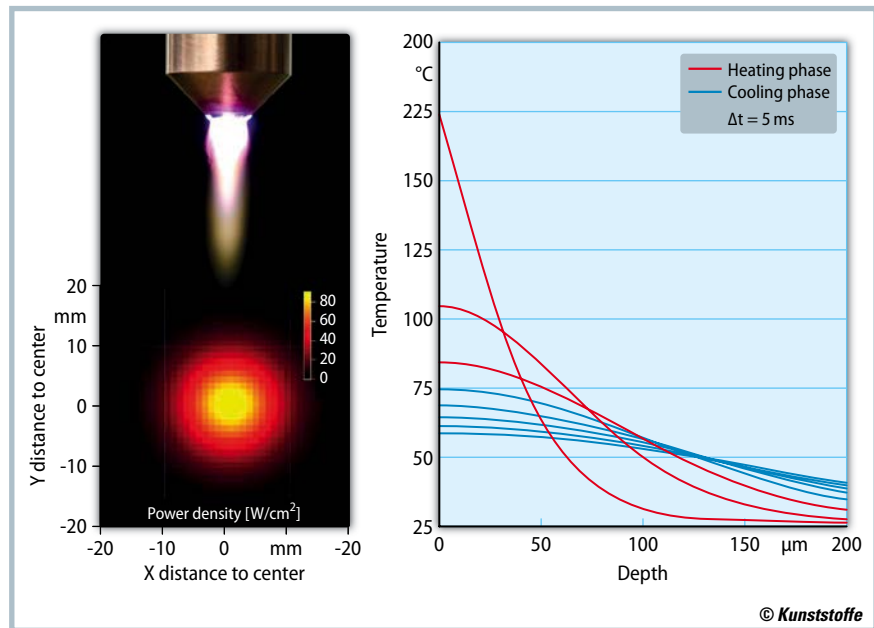
### Contamination Is Reduced

Even small traces of contaminants can significantly decrease the joining quality in the gluing process. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) with secondary ions released from the surface was used for a chemical analysis of the surface with high sensitivity and spatial resolution.

In addition to the mass signals characteristic for POM (for instance  $m = 31, 61, 98$ ), some contaminants such as sodium ( $m=23$ ), silicon ( $m=28$ ) and traces of a silicon material (PDMS;  $m = 147, 221$  and  $281$ ) are found on the untreated specimen. The intensity of the mass signals characteristic for POM increases after plasma treatment and the signals interpreted as contaminants decrease. This effect is shown in **Figure 2** using mass 61 as an example; presenting the complete mass spectra is omitted. One thing is for certain: Plasma treatment has effectively cleaned the surface. However, specimens carefully cleaned with solvents did not do better in tensile/shear tests than the untreated surfaces in this case. It therefore seems likely that removing residual contaminants alone cannot be the central factor explaining the improved adhesive force after plasma treatment.

A look at the literature shows that the contribution of functional chemical surface groups for the joining of various polymer materials in principle is well known [2]. It is often assumed that the functional groups on the surface make the greatest contribution to the adhesive force between the substrate and adhesive. That these functional groups can be specifically integrated on the surface through atmospheric plasma treatment [3] and thus among other things change the surface energy is known. The quantitative contribution to the technically relevant quality of the joint is certainly often debatable and difficult to quantify.

However, we observe very little difference in the practical effect on the quality of the bonded joint when the



**Fig. 3.** Plasma effect close to the surface: On the left, the spatial distribution of the power density, on the right, the simulated depth profile for temperature development in the heating and cooling phase (source: Relyon Plasma)

plasma process is converted from air (containing 21% oxygen) to nitrogen (see **Fig. 1**). Changing the adhesive to a modified methyl methacrylate adhesive also changes little. It is therefore questionable whether the quality of the bonded joint is dominated by chemical surface groups in this case.

### Optimized Cross-Linking of Polymer Chains

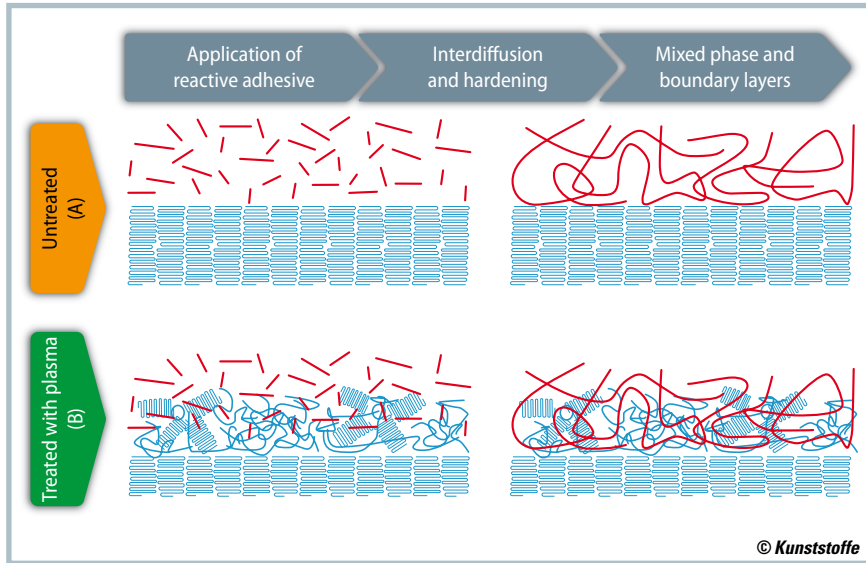
Examining the temperature development during application is particularly revealing for answering the question of where the improved adhesive force for bonded joints of crystalline thermoplastic materials after plasma treatment comes from (**Fig. 3**). Given the typical power densities and travel speeds of atmospheric plasma treatment, the temperature of the substrate surface and layers close to the surface is briefly increased [4]. Here the great dynamics of heating the surface followed by very rapid cooling are especially interesting. The heating/cooling rates can exceed 5000 K/s at travel speeds of 100 mm/s.

Beyond a certain threshold, the phase change temperature of the polymer is exceeded in this layer. However, both the heating and the cooling phases are limited to this thin layer and to a short time. Therefore this dynamic temperature effect determines the melting and crystallization

behavior of the polymer material in this layer. In contrast to a thermoplastic that solidified after bulk melting, new phase mixtures are now created on the surface and down to a depth of a few μm.

Starting at a certain thermal surface load, visible clouding of the POM specimen can be seen even with the naked eye (see **Fig. 2**). However, this is not due to roughening of the surface as one might assume. In fact, small irregularities such as scratches or point defects tend to be smoothed out by plasma treatment. The fine granular structures indicate a mixed phase of amorphous and crystalline zones that have frozen due to rapid cooling and therefore coexist in a thin layer [5, 6]. A change in the refraction of light and the resulting diffuse scattering accounts for the matte visual appearance. A structural change is clearly discernible in the AFM images (**Fig. 2**). However, the images confirm that the filament structures occurring after the intensive plasma treatment correspond to only negligible roughening of less than 0.2 μm. The granular structure is indicative of spherulites close to the surface that typically develop during melting and incomplete crystallization processes [6].

It is known from the literature that the diffusion of components with a low molecular weight is much higher in the amorphous phase than in the crystal- »



**Fig. 4.** Gluing process sequence: On the untreated POM surface (top), the oriented crystalline structures (blue) act as a diffusion barrier for the applied components of the adhesive (red). A sharply defined interface has developed after hardening (right). In the treated specimen, the surface structure is greatly disrupted and partly amorphous so that the components of the adhesive diffuse into the loose structure and harden there. A highly cross-linked and therefore strong joint forms (source: Relyon Plasma)

line phase [7, 8]. When an adhesive that hardens through polyaddition is now applied to an amorphous polymer structure, the monomers can diffuse very well into the open structures of the amorphous polymer prior to complete hardening. The better adhesion achieved with reactive adhesives is therefore based on optimized cross-linking of the adhesive's polymer chains with the polymer chains of the substrate (Fig. 4).

### Summary

Through a combination of various methods, it was possible to show that a thermally induced phase change from crystalline to amorphous can be observed for surface treatment with an atmospheric plasma burner using the thermoplastic polymer POM as an example. This plays a crucial role in improving the joining properties with reactive two-component adhesive systems. ■

## Individually Controlled Demolding of Five Female Threads Proceeds Quickly and Gently with High Precision Servo-Electric Unscrewing Units

Servo-electric unscrewing units developed by **Servomold** and sold by its sister company **i-mold** support precision-controlled, gentle demolding of threads in injection molded parts. Krallmann, a German toolmaker, has integrated five such systems into a mold which Festo Polymer uses to produce the complex housing for the DB Mini pneumatic maintenance unit for its parent company, Festo.

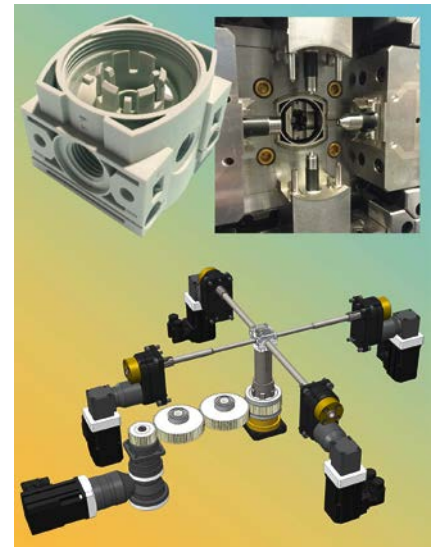
Hendrik Sanio, project manager at Krallmann, cites the reasons why servo-electric unscrewing devices were given preference over their hydraulic counterparts: "The respective unscrewing torques can be individually monitored and controlled, and the threads can be demolded at the optimum speed in each case. The servo-electric unit requires less mounting space and yields shorter cycle times than a hydraulic solution. In addition, there is no risk of contamination by leaking oil."

Festo Polymer produces the cube-shaped housing with an edge length of some 40mm from a high-strength, high-modulus glass-fiber-reinforced polyamide (PA66-GF50). Its five female threads have diameters of 1/8", 1/4" and 36mm and are

between 12 and 22mm long. In line with the positions of these threads, four of the associated unscrewing spindles are arranged at 90° angles to each other, in parallel with the parting surface, on the ejector side of the single-cavity mold. A fifth spindle moves parallel with the ejector set in the central machine axis.

Servomold selected and dimensioned the five unscrewing units to match the torques which were found to range from 6 to 33Nm. They are controlled by a mobile SRS-8.6 rack-type controller which is capable of handling up to six servo motors. This adapts the individual speeds so that all five liquid-cooled threaded cores reach their respective limit positions simultaneously when they are screwed in. The SRS also monitors the torque of each servo unit and emits corresponding signals when preset threshold values are reached.

The servo motors are equipped with resolver-type encoders whose zero positions are individually referenced on the clamped, preheated mold in each case. The mold is thus protected from possible damage during closing, because in everyday operation the control unit of the mold-



Five female threads and multiple undercuts make demolding of the housing for a pneumatic maintenance device (top) a challenge. Servo-electric unscrewing units (bottom) provided an elegant solution for this task

(© Servomold)

ing machine will issue start clearance only when the SRS reports that these reference points have been reached.

To the manufacturer's product presentation:  
[www.kunststoffe-international.com/3436141](http://www.kunststoffe-international.com/3436141)