Five times stronger

By pre-treatment of polymer surfaces in low-pressure plasma, a respectable increase in tensile strength of adhesive bonds can be reached in comparison to untreated samples. It is crucial to choose the right plasma parameters and adhesives. Tests were conducted on Polypropylene (PP), Polyether ether ketone (PEEK) and Polyamide (PA) 6.6.

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For every adhesive joint, the whole system, consisting of the two surfaces to be joined, the adhesive, and the handling and curing conditions, are responsible for the result. Numerous polymer substrates are hardly wettable in their original state after injection molding. Therefore, adhesives cannot readily bond to them. Applying aggressive chemicals or organic solvents is no longer state-of-the-art due to environmental, health and work safety concerns.

Low-pressure plasma is available as a state-of-the-art manufacturing technology for activation of polymer surfaces which is of no or low impact on the environment. As a huge variety of surface properties may be exhibited by the actual workpieces due to different production steps undergone, the effectiveness of plasma treatment needs to be shown for every single case, developing a suitable plasma process. The present study covers such an example using rectangular block specimens consisting of PP, PEEK and Polyamide, bonded with two-component epoxy adhesives from Epoxy Technology Inc. *(Figure 1)*

Procedure

Treatment of the polymer substrate samples was conducted as follows:

- Manual pre-cleaning using a cloth soaked in isopropanol (IPA).
- Treatment in low-pressure plasma (s. Info Box 1). This step was skipped for the reference samples.
- Immediate bonding applying the adhesives Epo-Tek 301, Epo-Tek 301-2 and Epo-Tek 353ND and curing inside a curing oven.

The bonding area was 25 mm wide and 10 mm long for all samples (for more details concerning the test objects cf. *Figure 2)*. The plasma processes were developed individually for each of the three polymer substrate types and are therefore not the same for all of them *(cf. Info Box 1)*. The adhesives were chosen by manufacturer's advice and curing was conducted according to the manufacturer's recommendations *(cf. Info Box 2)*. Every combination of polymer substrate and adhesive was represented by five individual samples tested. The given tensile strength in *Table 1* is the mean value of the five samples. The bonded samples were stored for four months at room temperature and subsequently underwent tensile testing *(cf. Info Box 3)*.

Material	**PP**		**PEEK**		**PA 6.6**		
Adhesive	301	301-2	301	353ND	301	301-2	353ND
With Plasma [kN]	1.05	0.48	4.91*	5.68*	1.19	1.58	1.73
[MPa]	4.2	1.9	19.6*	22.7*	4.8	6.3	6.9
Reference [kN]	0.20	0.21	1.09	1.24	0.61	0.81	0.86
[MPa]	0.8	0.8	4.4	5.0	2.4	3.2	3.4

Table 1 > Results of the tensile test for different polymer substrate-adhesive-combinations; MPa value: recalculation regarding the bonded area. *Value does not fully represent bond strength as material broke.

Condition \ Material	**PP**	**PEEK**	**PA 6.6**
After treatment	54°	18°	33°
Reference	91°	80°	66°

Table 2 > Water contact angle before (reference) and after plasma treatment for the polymers PP, PEEK and PA 6.6.

Figure 1 > PEEK samples after tensile tests: without pre-treatment (l.), after insufficient plasma treatment (m.) and after treatment with optimized plasma parameters (r.).

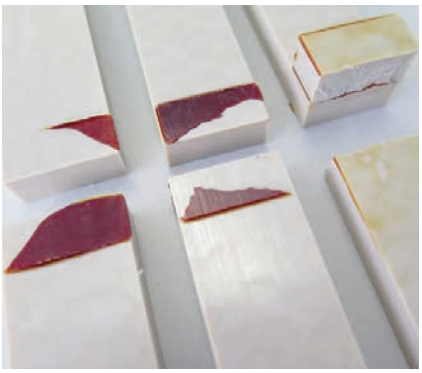


Figure 2 > Setup of the test objects manufactured and tested in the test series. For PEEK, material thickness was 10mm.

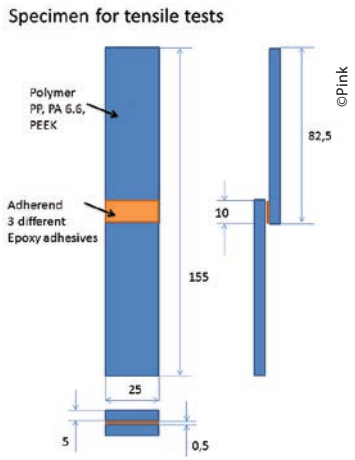
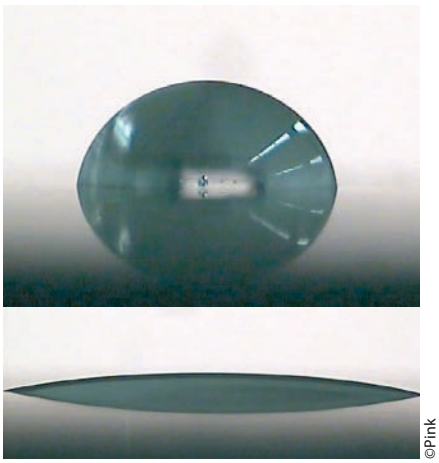


Figure 3 > Behaviour of water on PEEK before (above) and after plasma treatment (below)



Plasma makes the difference

The tensile forces needed to break the bonds were by far higher for the plasma treated samples than for the reference samples *(Table 1)*.
For PA 6.6 the strength increased by a factor of about 2 and for PP – depending on the adhesive – in between 2.3 and 5.2 was achieved. For all untreated samples (as well as plasma treated PA 6.6) all failure modes were adhesive or mixed-mode fractures. Some of the plasma treated PP samples broke in the bulk material (thickness 5 mm). For all plasma treated PEEK samples the bond strength was higher than the substrate material's internal strength, even after the substrate material's thickness had been doubled to 10 mm. Therefore, measuring the real bond strength was not possible. The given numbers (mean forces up to 5.7 kN, i.e. 23 MPa) only represent aminimum value.

Measuring surface tension and contact angle

For a better understanding of the plasma effect, similar samples were treated in the same way and their surface tension and water contact angle have been measured before and after. Surface tension increased for all polymers mentioned from below 38 mN/m to above 66 mN/m. Water contact angles decreased significantly due to the plasma treatment *(Table 2)*. Again, plasma treatment on PEEK was exceptionally effective *(Figure 3)*.

Figure 4 > Plasma System, suitable for cleaning and activation of polymers and many more materials

Evaluation of every single case is required

Within the test series it could be shown that pre-treatment in low-pressure plasma may significantly increase bond strength, for which certain exemplary combinations of polymer substrates and adhesives have been used. But even though these results are in agreement with former tests, it is impossible to predict the behaviour of any – even similar – other case. These results stress the potential which is available by implementing low-pressure plasma into bonding processes *(Figure 4)*. To obtain the best results possible from the necessary tests, it is recommended to acquire advice from both plasma and adhesive experts. //

Info Box 1

Parameters of Plasma Treatment
Plasma System: PINK V15-G
Process Gas: Oxygen
Energy Source: Microwave
Power: 500 W
Treatment Time: 5 Minutes. (For PEEK another treatment of five minutes using a mixture of oxygen and CF4 preceded.)

Info Box 2

Curing Conditions
Epo-Tek 301: 2 h at 65 °C
Epo-Tek 301-2: 3 h at 80 °C
Epo-Tek 353ND: 3 h at 80 °C

Info Box 3

Tensile Tests
Tensile tester: TIRAtest 2710
Load sensor: 10 kN
Tensile speed: 5 mm/min

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