The Effect of a Plasma Pre-treatment on the Quality of Flock Coatings on Polymer Substrates

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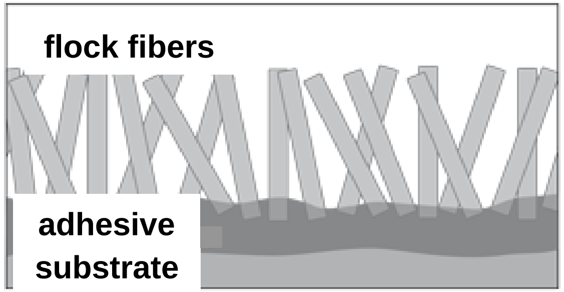
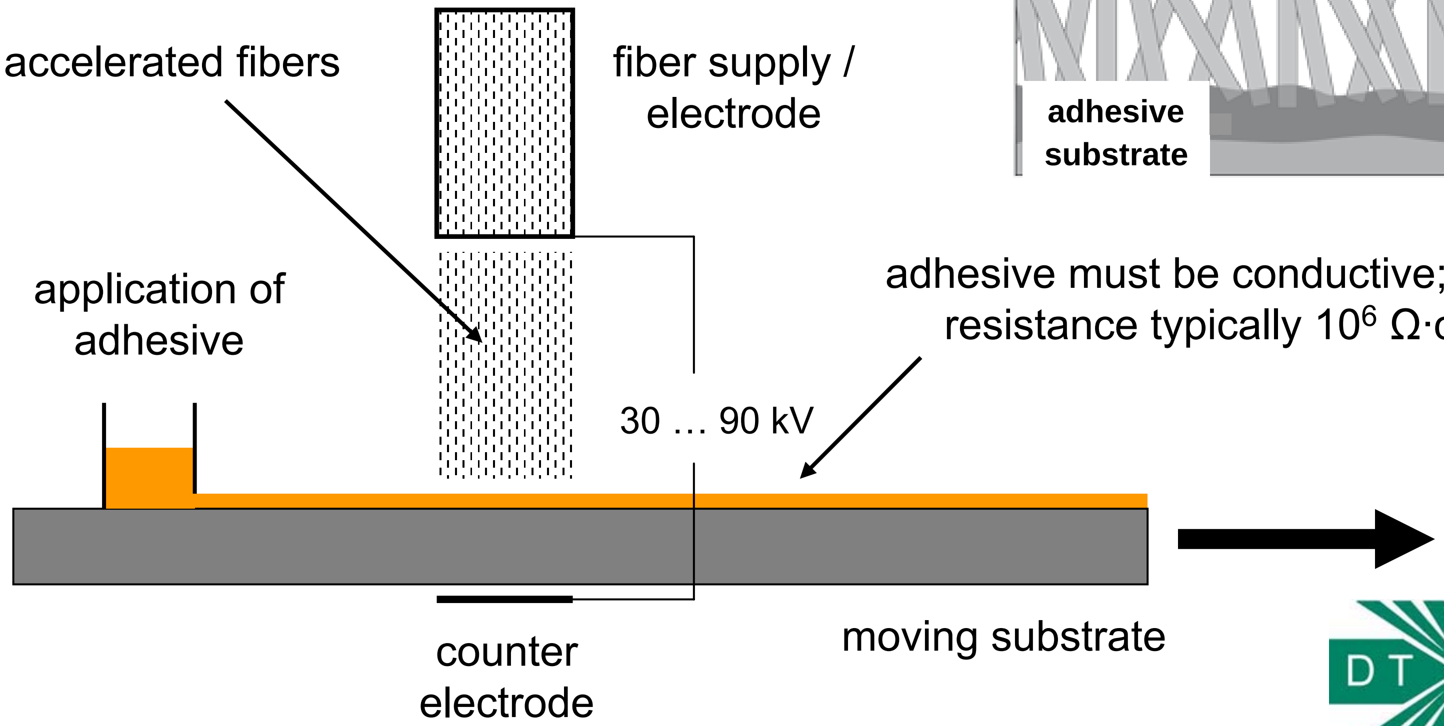
Flock coating

- In the process, flock fibers - short fibers typically 1 to 3 mm long – are oriented and accelerated towards the substrate by means of an electric field. Impacting fibers are stuck to the substrate surface by an appropriate adhesive.

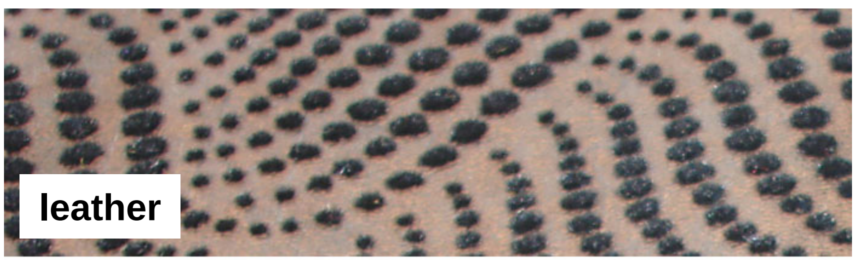




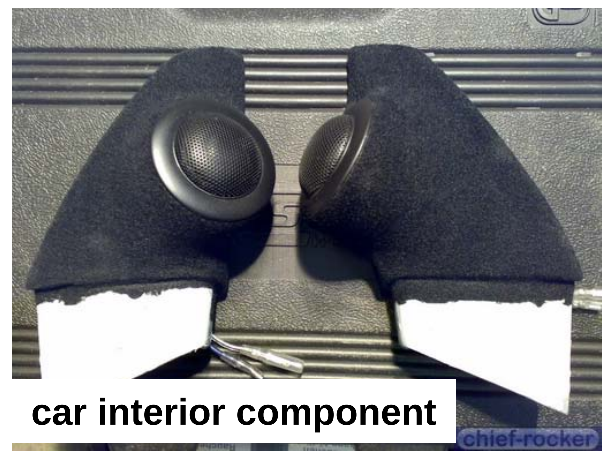
Flock coating

- A widely used process to create a textile-like texture on substrates of arbitrary shape and material (polymers, metal, ceramics).

- The technique is applied to textiles, car interior components, floor coverings or furniture with the objectives being decorative, but also functional effects, e.g., with regard to friction.


leather


textile



car interior component

Flock coating

- Present developments, especially with regard to car parts, aim at easy to recycle single-material systems, i.e. substrate, adhesive and flock fibers based on identical polymer chemistry.

- A system presently under investigation is comprised of a molded car component, hot-melt adhesive, and flock fiber based on aliphatic polyamides (PA).

- The adhesive, e.g. co-polymer of PA6 and PA12, is modified with black carbon or with ions, e.g. Li^+, solvated in a polyethyleneoxide (PEO) matrix.

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- The adhesive, e.g. co-polymer of PA6 and PA12, is modified with black carbon or with ions, e.g. Li^+, solvated in a polyethyleneoxide (PEO) matrix.

- One aspect in this study was the application of an air plasma pre-treatment of the PA substrate in order to increase hot-melt adhesion and interface conductivity.

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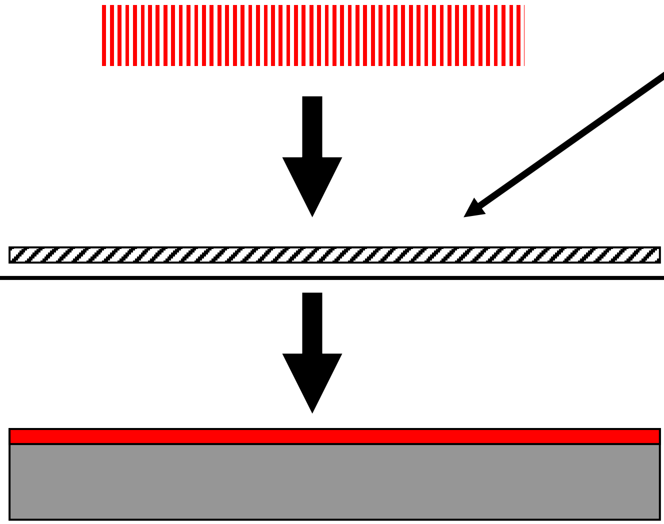
Experiment

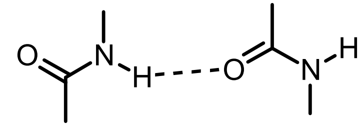
flock fibers



hot melt coating with adhesive, e.g. PA copolymer

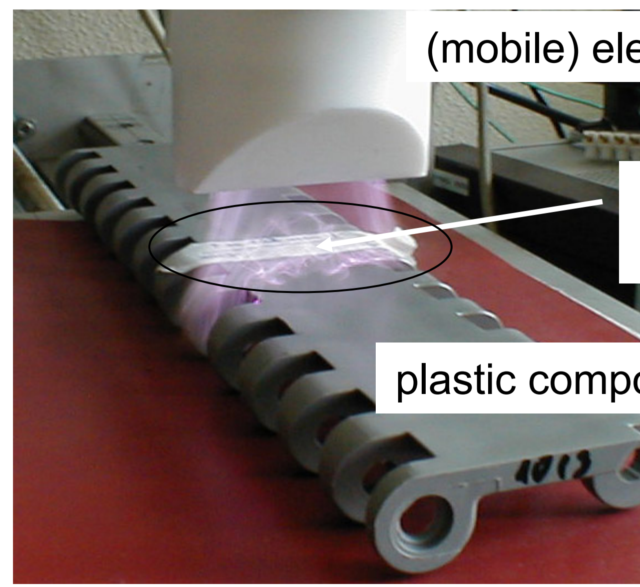
Griltex 1500A (EMS Chemie);

T_m = 80°C, T_g = 60°C, $\eta_{130°C}$ = 300 Pa·s



modified interface

PA-plate



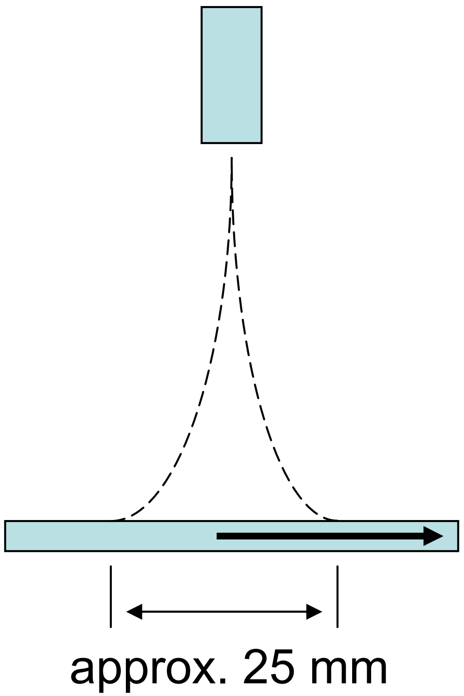
Characterization:

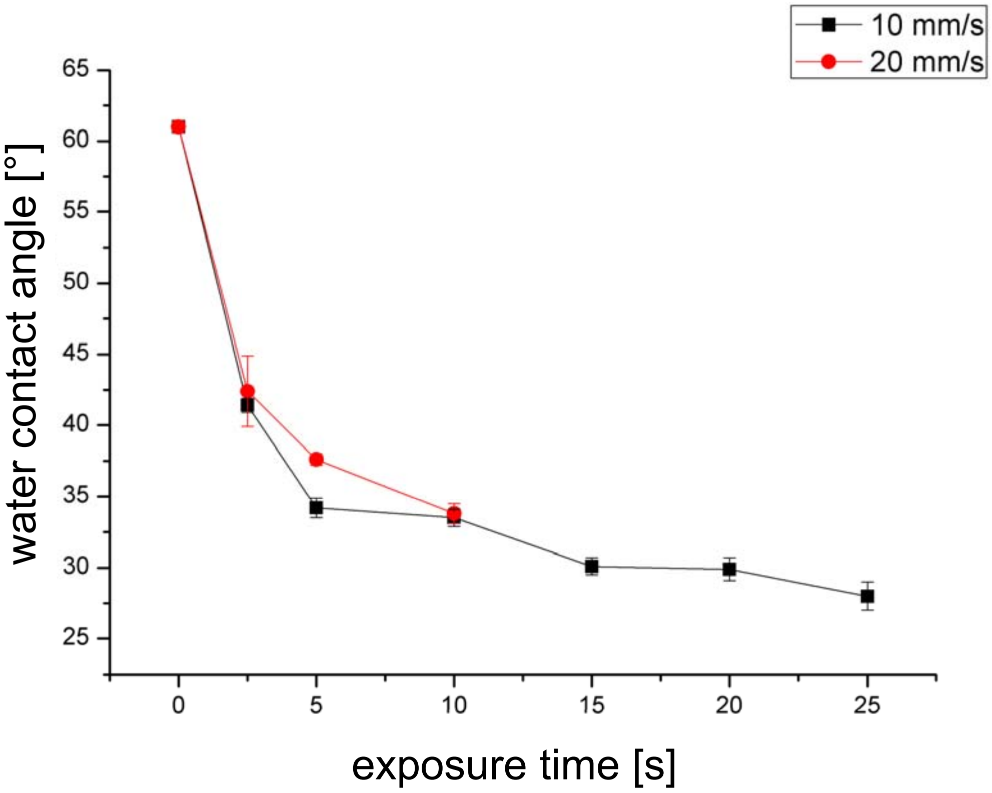
a) Contact angle, surface tension, XPS, AFM, adhesion of hot melt

b) Flock fiber adhesion, flock density

Wettability / Surface Energy

exposure time = number of runs x length of plasma zone / sample displacement per s





The length of the plasma zone can only be estimated, the stated value shall be assumed in the following.

Wettability / Surface Energy

Neumann's equation is a simple formula based on the contact angle measurement with only *one* liquid.

$$\cos\theta = -1 + 2\sqrt{\frac{\sigma_s}{\sigma_l}} \cdot e^{-\beta(\sigma_l - \sigma_s)^2}$$

with β = 0,0001247 [m²/mJ²]

⇒ Polar and dispersive components of the surface tension cannot be determined by Neumann's equation.

Alternatively, contact angles were determined using water and methylene iodide and the data evaluated by

a) **Owens and Wendt equation**

(σ described as geometric mean)

$$\sigma_l(1+\cos\theta) = 2(\sqrt{(\sigma_l^d \sigma_s^d)} + \sqrt{\sigma_l^p \sigma_s^p})$$

b) **Wu equation**

(σ described as harmonic mean)

$$\sigma_l(1+\cos\theta) = 4\left(\frac{\sigma_l^d \sigma_s^d}{\sigma_l^d + \sigma_s^d} + \frac{\sigma_l^p \sigma_s^p}{\sigma_l^p + \sigma_s^p}\right)$$

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Wettability / Surface Energy

Surface tensions as calculated after Owens und Wendt equation

	water		methylene iodide		
τ [s]	θ [°]	σ_s^p [mN/m]	θ [°]	σ_s^d [mN/m]	σ_s [mN/m]
0	62.0 ±0.9	**9.8**	29.2 ± 1.3	**46.3**	56.1
5	36.1 ± 2.8	**23.9**	33.8 ± 1.2	**44.2**	68.1
10	33.0 ±1.4	**25.9**	31.9 ± 1.8	**45.1**	71.0
15	37.1 ± 3.6	**23.4**	32.3 ± 1.7	**44.9**	68.3
20	44.9 ± 2.9	**19.3**	30.1 ± 1.7	**45.9**	65.2
25	38.4 ± 3.7	**22.7**	32.5 ±1.4	**44.8**	67.5
reference data for PA 6	σ_s^p [mN/m]		σ_s^d [mN/m]		σ_s [mN/m]
	10.7		36.8		47.5

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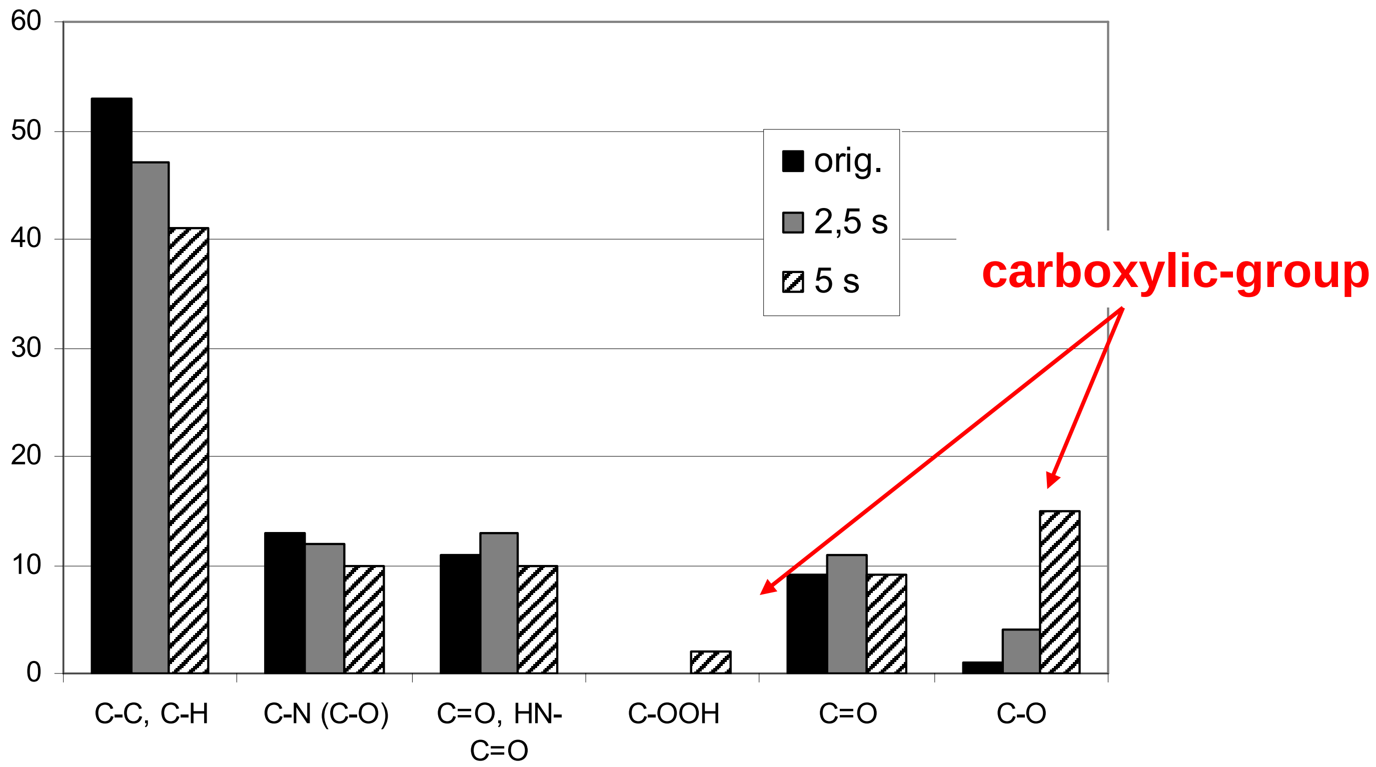
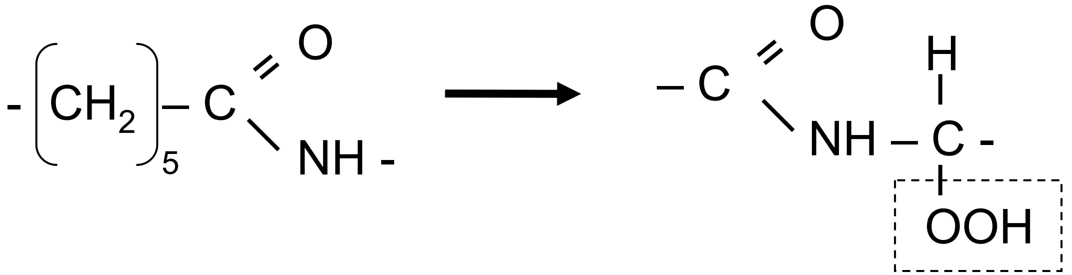
Analysis of chemical composition by X-ray photoelectron spectroscopy (XPS)





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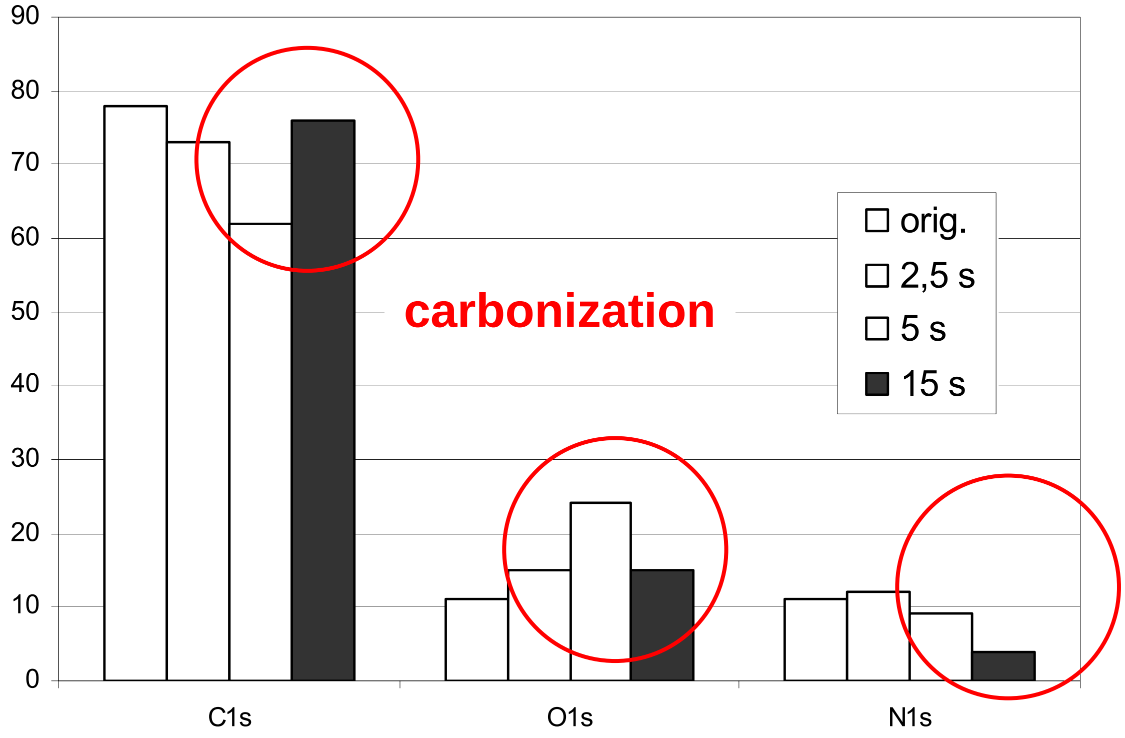
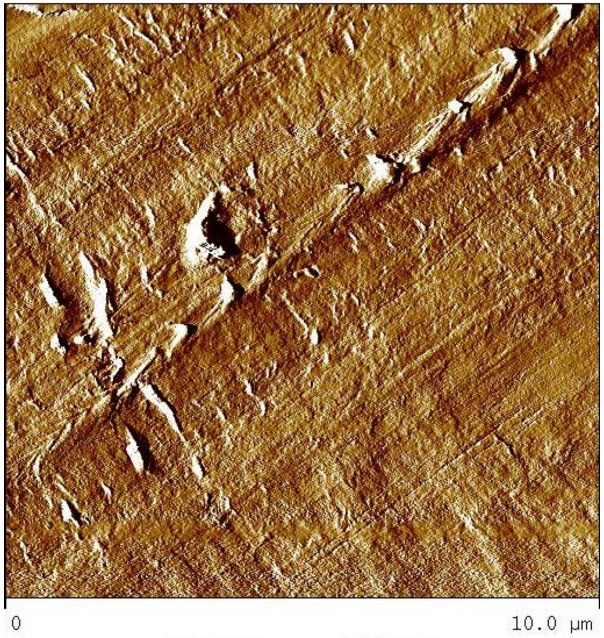


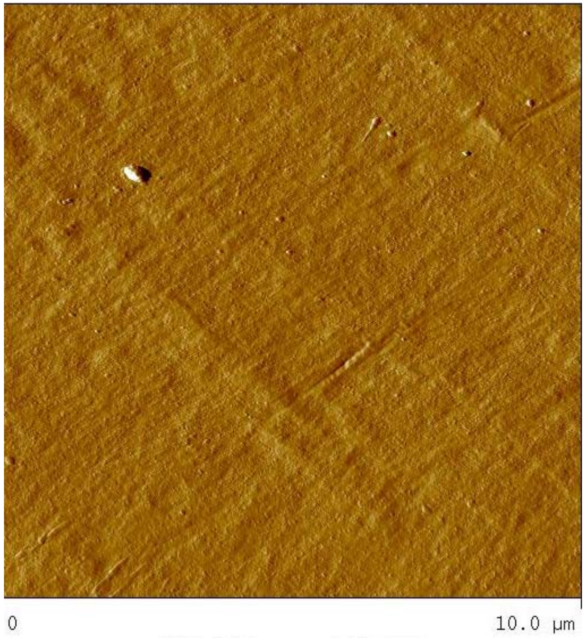
carbonization indicates damage following longer exposure

AFM - Topography



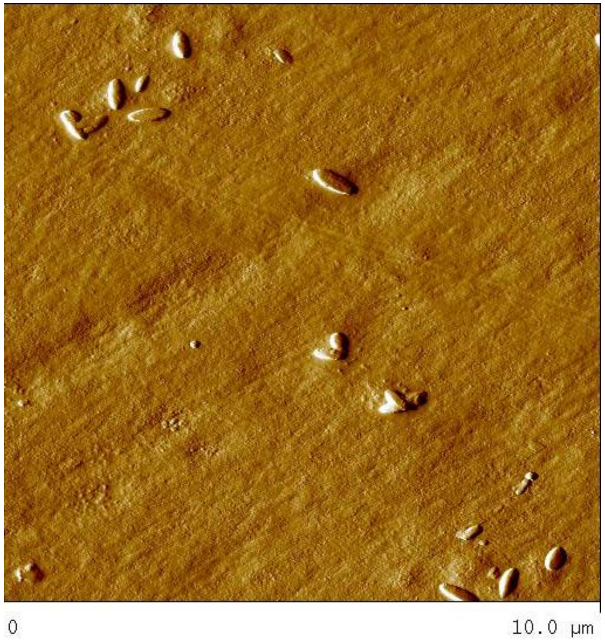
untreated

R_q = 36,9 nm
R_a = 23,4 nm
A/A_0 = 1,031



plasma treated 5 s

R_q = 15,7 nm
R_a = 12,6 nm
A/A_0 = 1,008



plasma treated 15 s

R_q = 23,0 nm
R_a = 16,8 nm
A/A_0 = 1,014

Indication of damage following longer exposure

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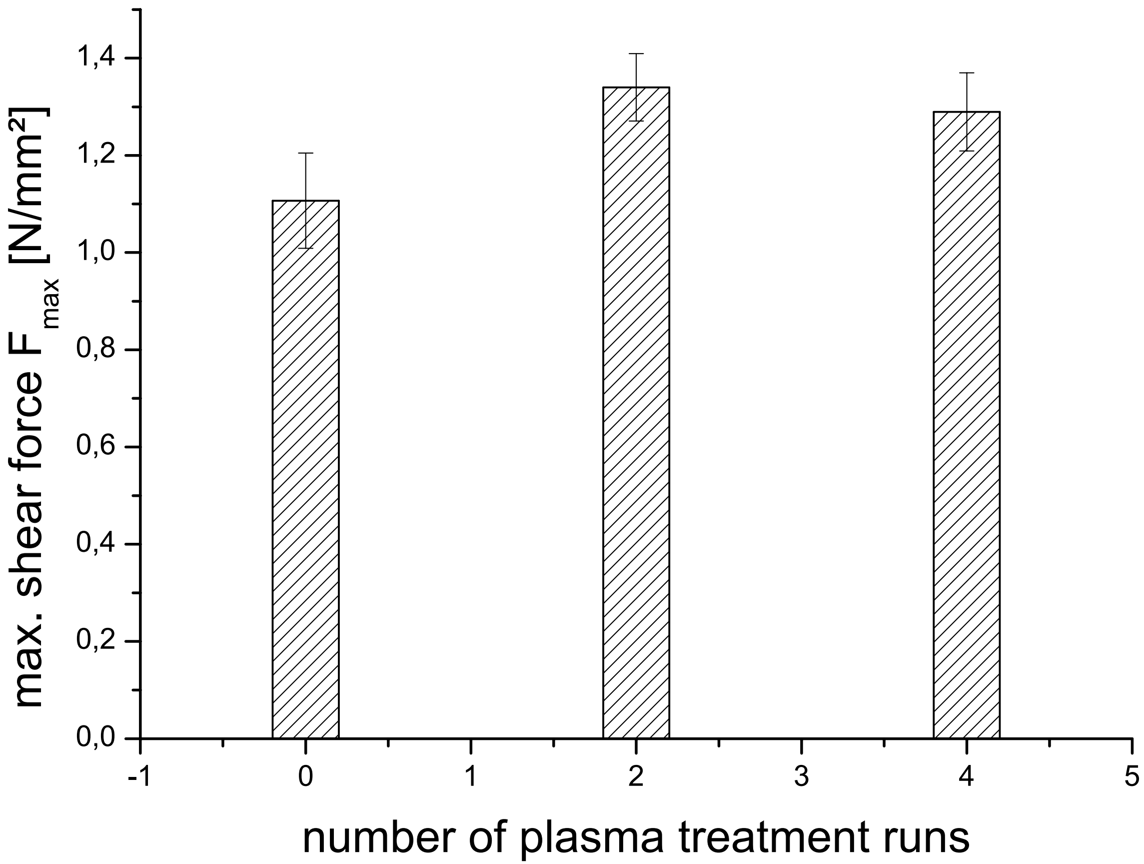
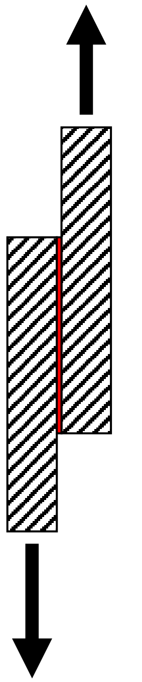
Measurement of (shear) strength of an adhesive bond of PA plates



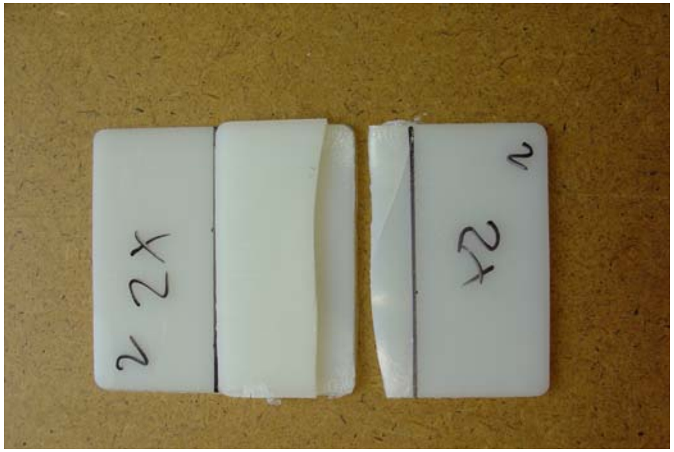


→ Pre-cleaning with EtOH
→ plasma treatment at 10 mm/s; distance 25 mm
→ **<u>no post-cleaning</u>**
→ bonding of plates using Griltex 1500A (EMS Chemie, Domat, Switzerland); bonding at 120°C and 300 kPa for 4 min

Measurement of (shear) strength of an adhesive bond of PA plates

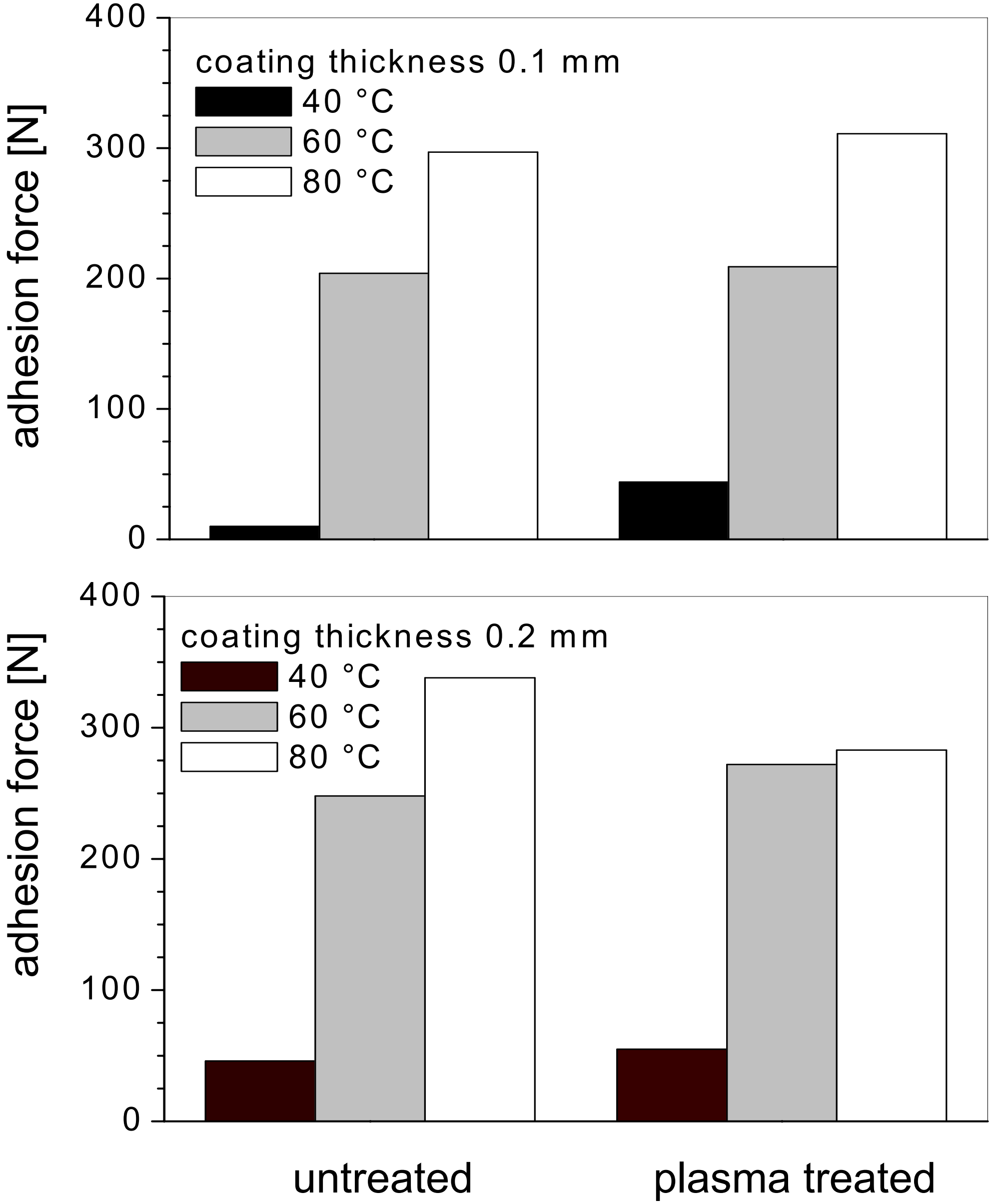
number of runs	**$\langle F^{max} \rangle$ [N/mm²]**	+/-Δ [N/mm²]	min. value [N/mm²]	max. value [N/mm²]	no. samples	note
0	**1.107**	0.098	0.750	1.563	9	8 of 9 sheared
2	**1.340**	0.069	1.069	1.581	8	4 of 8 sheared
4	**1.289**	0.0803	0.975	1.62	8	2 of 8 sheared

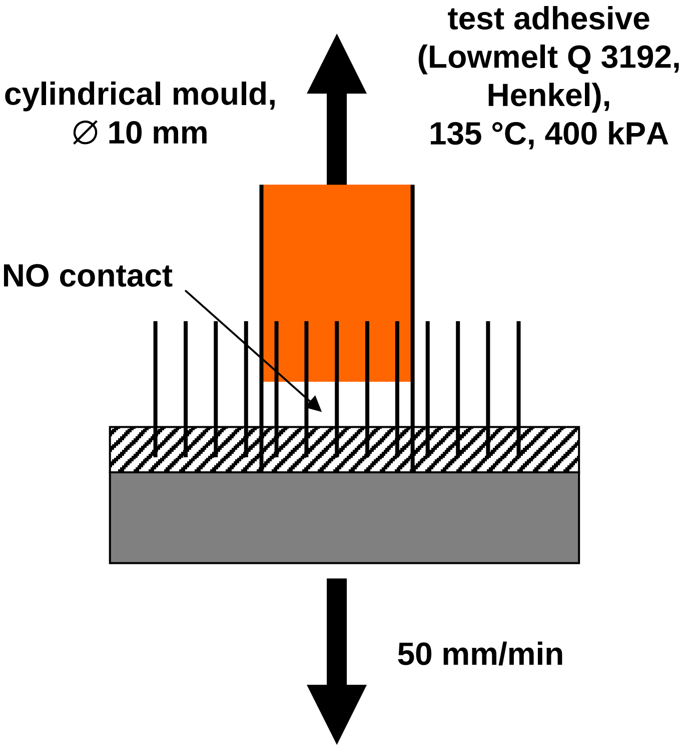
failure through adhesive cohesion of adhesion

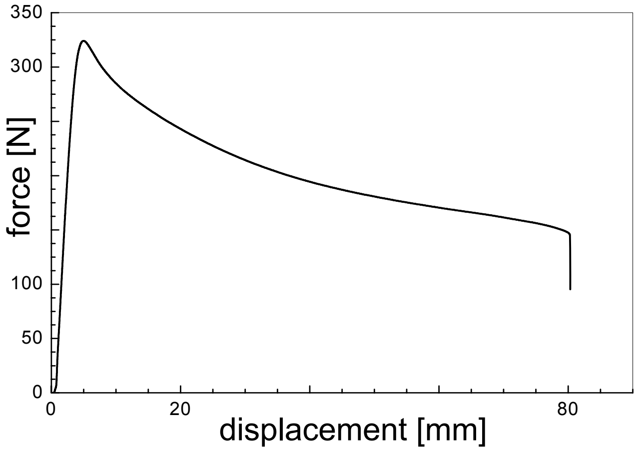


failure through substrate cohesion

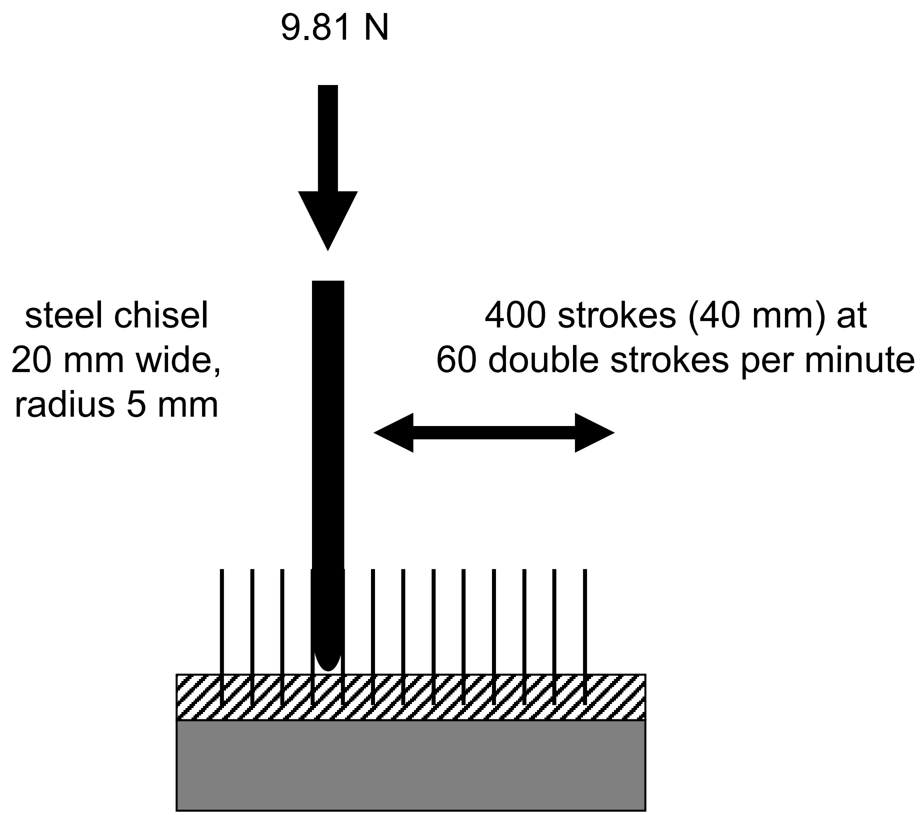
Effect on flock coating – I. flock fiber adhesion

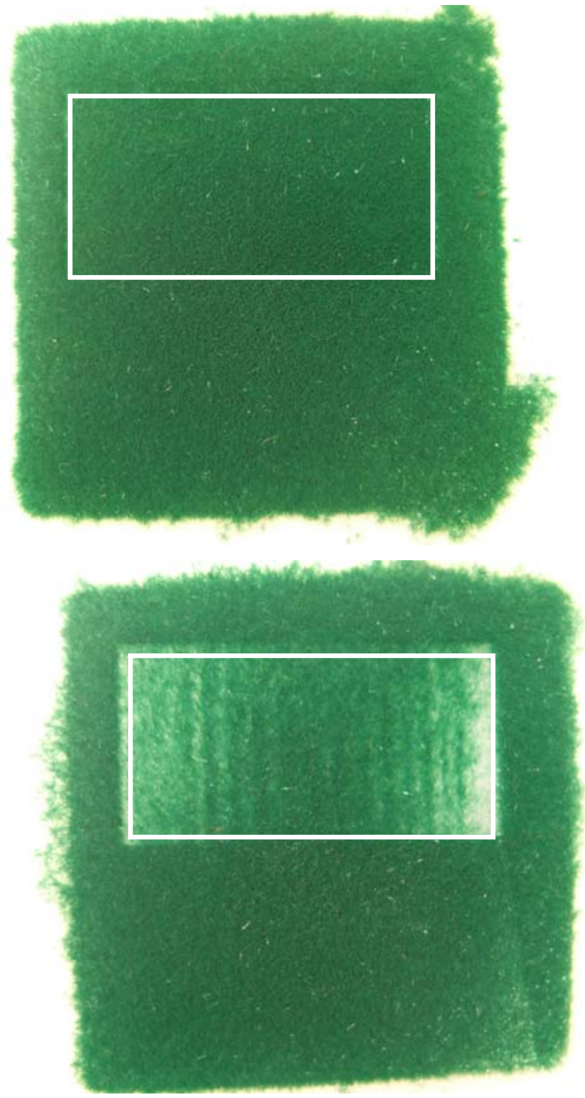






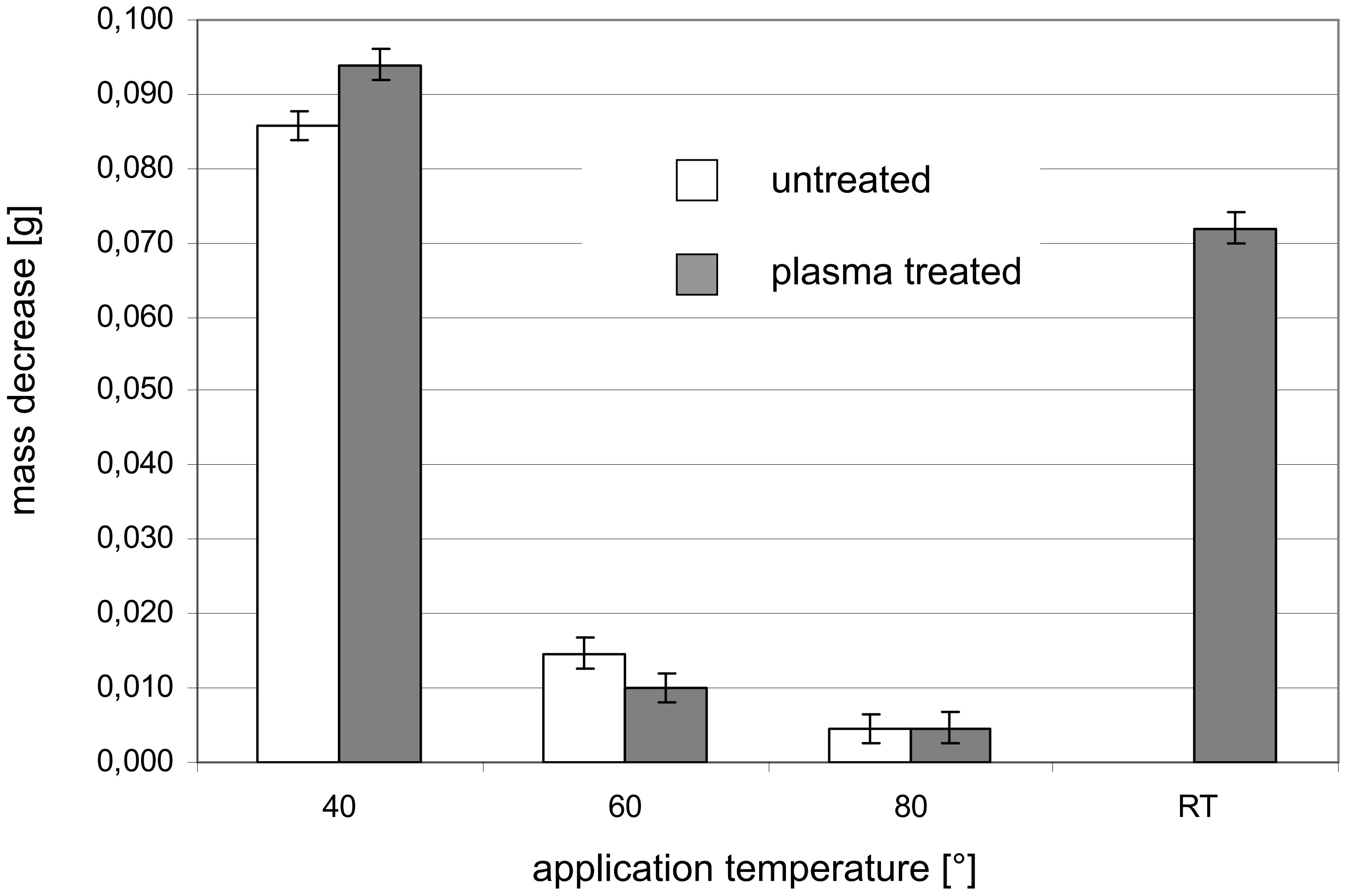
Effect on flock coating – II. abrasion





test based on a modified Volkswagen procedure

Effect on flock coating – II. abrasion



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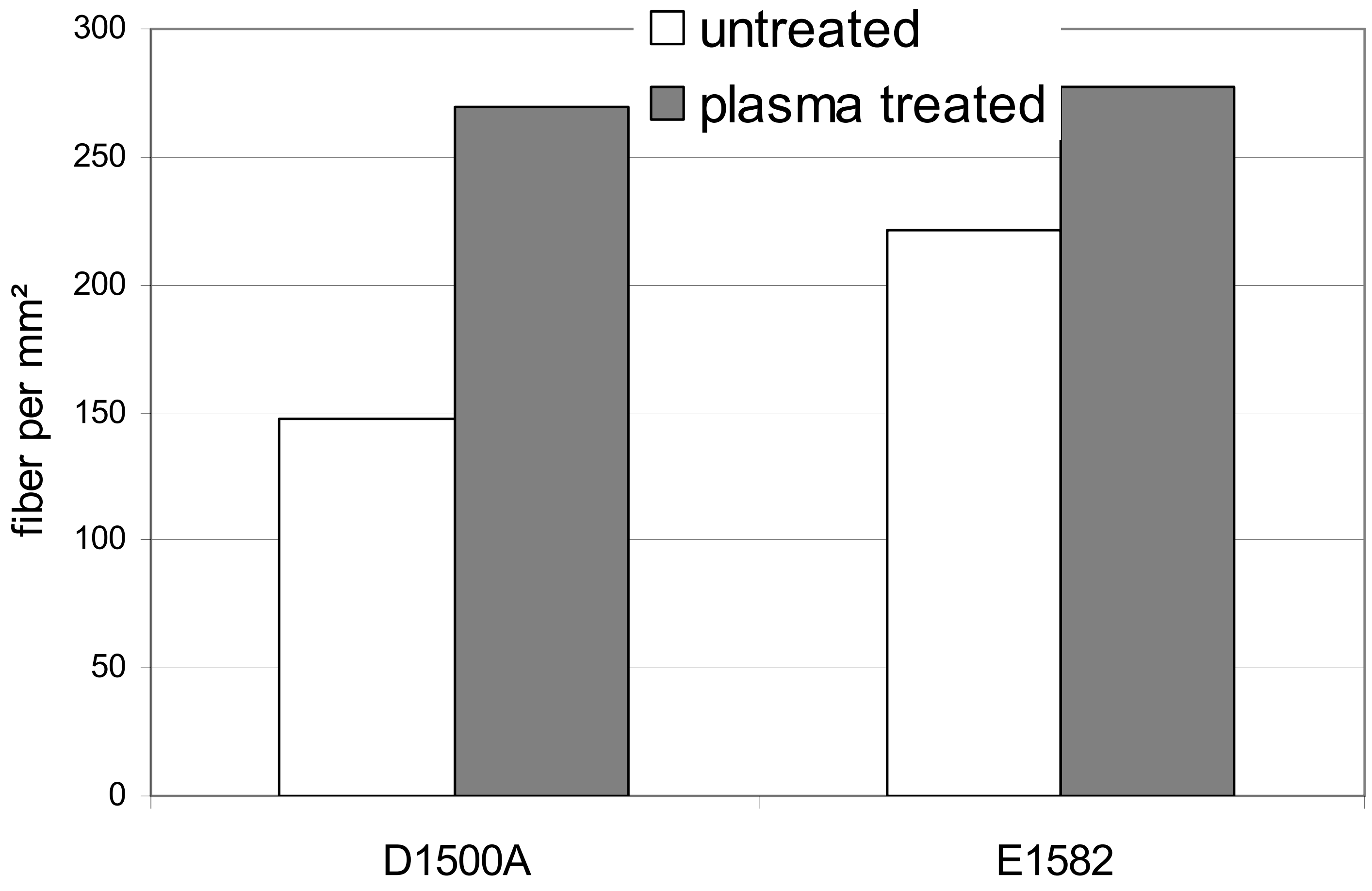
Effect on flock coating – III. flock fiber density



Flock fiber ‚density‘ is quantified by the number of fibers per unit area, which can be determined from mass increase after flocking and fiber geometry and density.

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Lessons learned from flock coating experiments

- The plasma treatment has no effect on flock fiber adhesion in pull out and abrasion simulation. These properties are determined by the choice and application parameters of the hot melt.

- A (potential) effect on hot melt application, e.g. enhanced wetting, cannot be proven. NB: A thicker coating on an untreated substrate has stronger effects.

- The plasma treatment has a significant effect on flock density. This could be due to **enhanced dissemination of charges**, which otherwise would reduce the effective field strength.

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Charge dissemination, wettability and water take-up

- PA has a water take-up of up to 10 %!

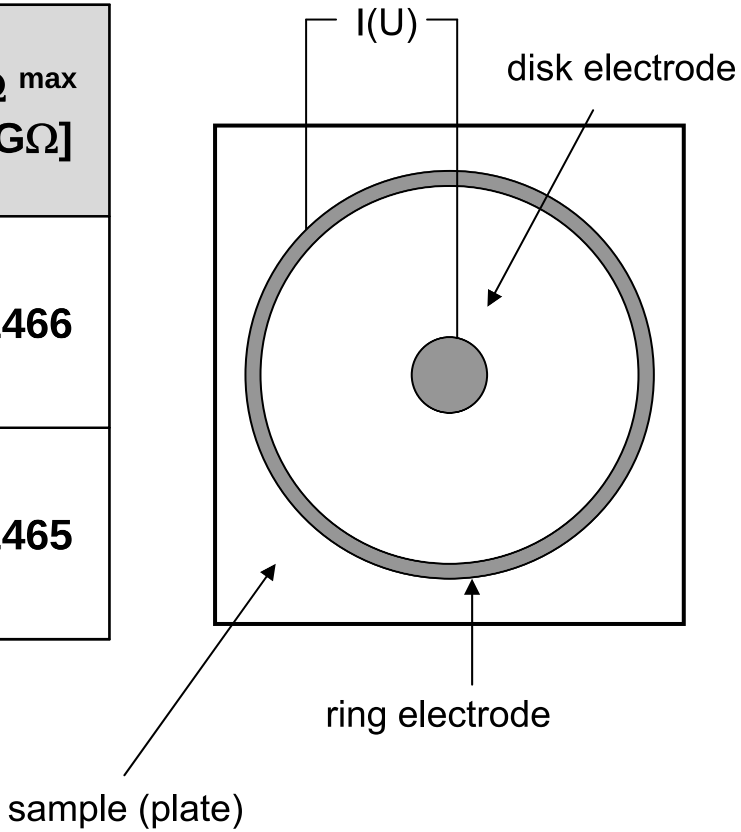
- Water is adsorbed during storage from the atmosphere and forms a conductive layer on the surface.

- It could be assuemd that the plasma treatment enhances water take-up (cf. contact angles) and thus increases charge dissemination.

$\Rightarrow$ **Study of surface conductivity and charge relaxation.**

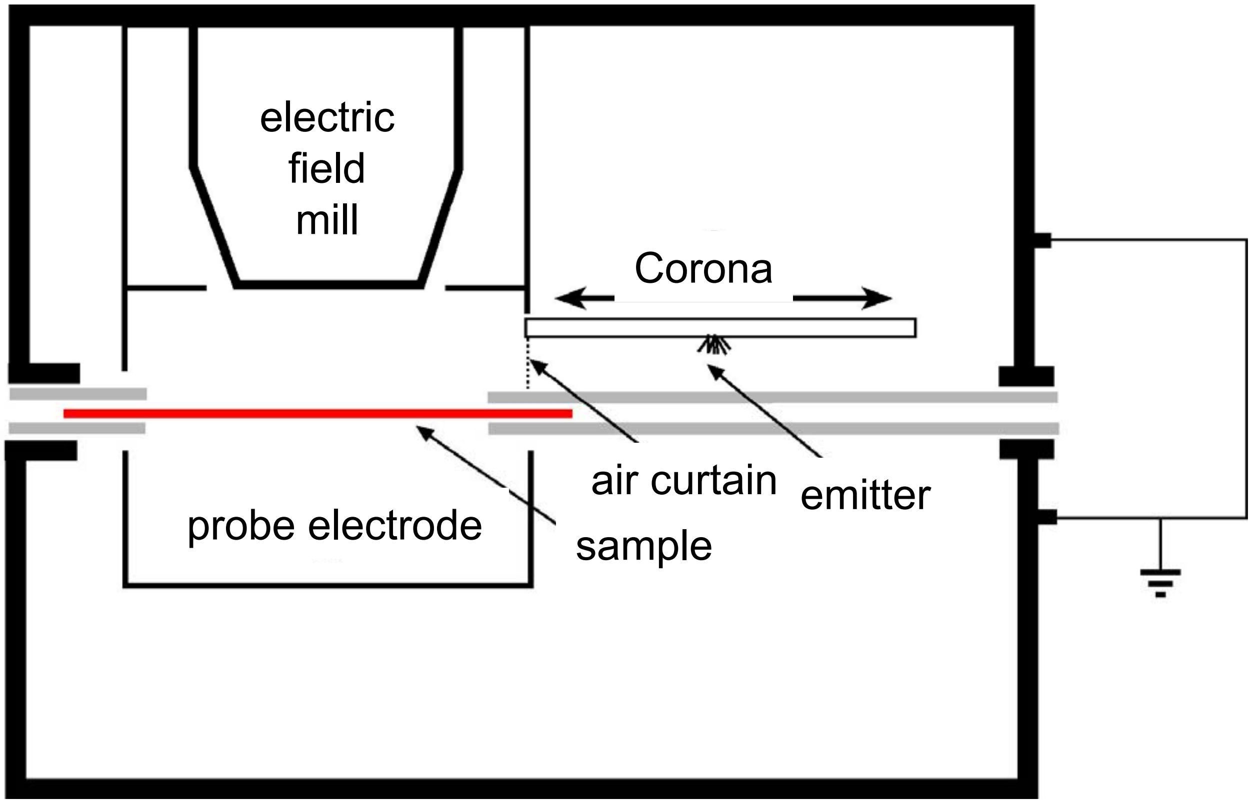
Measurement of electric conductivity (surface resistance)

	Ω mean [GΩ]	+/-SD [GΩ]	+/- SEM [GΩ]	**Ω min [GΩ]**	**Ω max [GΩ]**
untreated	666	452	91	**116**	**1466**
plasma treated	515	442	74	**155**	**1465**



PA6 plates 130 mm x 130 mm
exposure to plasma 5 s
samples wiped with EtOH

Measurement of charge relaxation (artificial charging)



Measurement of charge relaxation (artificial charging)

sample	t to 1/e [s]	t to 10% [s]	Q [nc]	CL	Cond [nc]	Ind [nc]
untreated	**4.17** +/- 0.88	**15.00** +/- 4.00	**4.20** +/- 0.2	**1.83** +/- 0.07	**1.15** +/- 0.13	**1.40** +/- 0.03
plasma 5 s	**1.06** +/- 0.06	**3.44** +/- 0.21	**4.39** +/- 0.12	**1.95** +/- 0.06	**1.68** +/- 0.14	**1.23** +/- 0.02
plasma 15 s	**0.92** +/-0.16	**2.95** +/- 0.53	**4.09** +/- 0.08	**1.93** +/- 0.02	**1.65** +/- 0.15	**1.11** +/- 0.07

Increased water take-up by the polymer enhances charge transport

NB: Sample handling was identical to the plates which were shipped to ITB for flock coating, i.e.

- pre-cleaning
- plasma treatment
- storage for 3 days in a normal laboratory
- measurement

(NB: for the measurement, the samples were taken into a standard climate of 21 °C and 76 % RH.

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Thank you for your attention!

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