Plasma and Dry Micro/Nanotechnologies
7. Plasma Treatment

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Outline

7.1 Introduction to Plasma Treatment

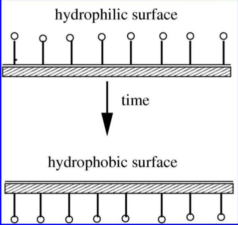
Plasma Treatment

combination of various processes (chemistry, ions, UV) results in:

- removal of material
- modification of original material (especially important for polymers)
- grafting of new functional groups

In contrary to depositions the changes are limited to a very thin surface layer (in the order of nm) but please note that the term "surface" is a matter of definition!

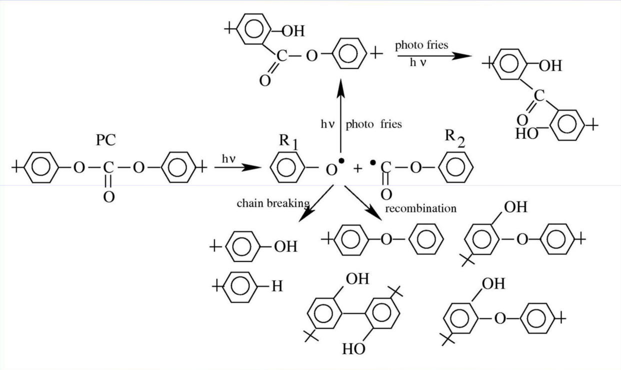
ageing of treated surfaces



important issue of any surface treatment processes

Effect of UV Radiation on Polycarbonate

suggested mechanism of carbonate bond breakage
due to UV radiation:



Plasma generates also UV photons and this effect is often forgotten!

Plasma modifications of polymers in inert gas

➢ discharge in argon, helium:

chemical bonds, such as C-H, C-C, C=C, are broken
☞ generation of free radicals at or near the surface
☞ radicals react with each other either directly (if polymer chain is flexible enough) or due to migration along polymer chain („chain-transfer“)
☞ **cross-linking, branching, removal of low molecular weight material or its conversion into high molecular weight one (no new functional groups)**

CASING

(cross-linking by activated species of inert gas)

R. H. Hansen, H. Schonhorn, J. Polym. Sci. B 4 (1966) 203
H. Schonhorn, R. H. Hansen, J. Appl. Polym. Sci. 11 (1967) 1461

increase of surface hardness, improvement of adhesive forces at the interface

Additionally, changes of surface roughness

Plasma treatment in reactive gases gases

➢ plasma containing oxygen (O_2, H_2O, CO_2 …)

- etching of surface carbon radicals by atomic oxygen
- new functional groups, e.g. C-O, C=O, O-C=O, C-O-O, CO_3, OH

hydrophilic surface, change of roughness

➢ plasma containing nitrogen (N_2, NH_3 …)

- new functional groups such amine (N-C), imine (N=C), nitrile (N≡C), amide (N-C=O)
- incorporation of oxygen and its functional groups
- grafting of amine groups $-NH_2$

hydrophilization, biocompatibility, imobilization of biomolecules

➢ plasma containing fluorine (SF_6, CF_4, C_2F_6 …)

F and CF_x radicals react with surface and two different processes compete:

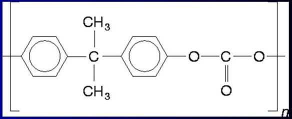
- etching
- grafting and deposition

hydrophobization, change of roughness

7.2 Low Pressure Plasma Treatment

Why Plasma Modification of Polycarbonate?

Polycarbonates are attractive business article, the most important PCs are based on on bisphenol A (Diflon®, Macrolon®, Lexan®)



Properties

- excellent breakage resistance (15-20x than acrylate, 250x than glass)
- good transparency (3 mm thick – 90 %)
- low inflammability, good workability, lighter than glass

replace glass and metals in:

- automobile headlamps, stoplight lenses,
- corrective lenses,
- safety shields in windows, architectural glazing

can be applied to:

- plastics vessels, parts of machines
- in optical grades for compact discs (CDs, CD-ROMs and DVDs), optical fibers

- low hardness (0.2 GPa)
- low scratch resistance
- degradation by ultraviolet light

modification of PC surface properties is necessary

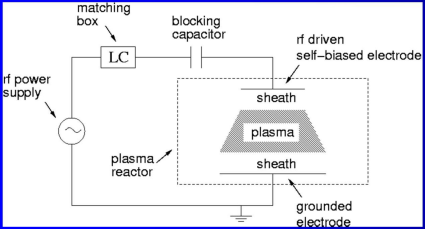
deposition of functional films (scratch resistant, reflective, ...)

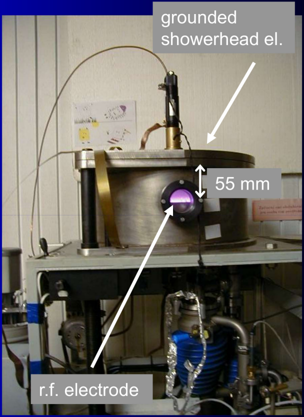
surface treatment for improved film adhesion

Plasma treatment of polycarbonate in Ar or O_2 discharges (CCP)

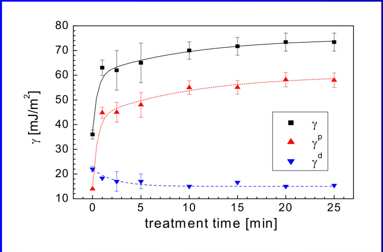
External plasma parameters:

- f = 13.56 MHz
- inner diameter of reactor 490 mm
- r.f. driven bottom electrode (420 mm)
- Ar, O_2: Q = 5.7 sccm , p = 1.5 Pa
- r.f. power P = 100 and 400 W

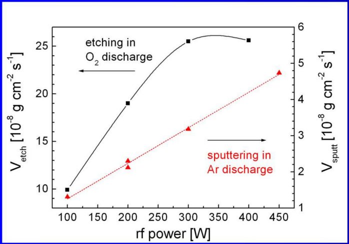


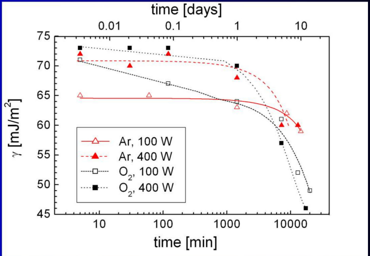


Plasma treatment of polycarbonate – etching rate and surface free energy

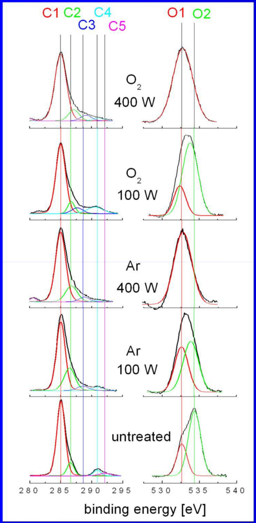


P = 100 W, U_{bias} = -115 V, Q_{ar} = 5.7 sccm, p = 1.5 Pa





Plasma treatment of polycarbonate – surface chemistry by XPS



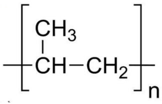
	position [eV]	assigment
C1	285.0	C-C, C-H
C2	286.6	C-O
C3	288/289	C-C(=O)-C / O-C(=O)-O
C4	290.9	C-C(=O)-O
C5	292.1	shake up

gas	power [W]	C [at. %]	O [at. %]	Si [at. %]	N [at. %]
untreated		84.3	15.7	0	0
Ar	100	76.4	20.3	0.4	2.2
Ar	400	76.0	19.9	1.3	2.8
O_2	100	74.0	24.0	0.4	1.7
O_2	400	72.6	24.7	1.6	1.2

7.3 Atmospheric Pressure Plasma Treatment for Adhesive Joints

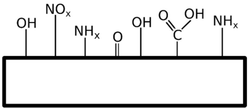
Case study: Polypropylene (PP) adhesive joints with aluminium

General problem of PP (and other syntetic polymers):
low free surface energy, chemical inertness



$\Rightarrow$

- Surface modification is required
- Added value is low, i. e. atmospheric pressure plasma treatment

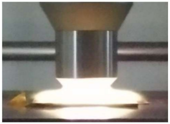


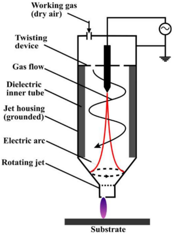
Experiments: comparison of different atmospheric pressure plasma jets, water contact angle, surface chemistry and topography, adhesive joint between PP and Al strips created with the epoxide adhesive DP 190 (3M)

7.3 PT & AFS Atm. Pressure Plasma Jets

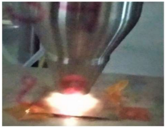
Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area ø [mm]
Plasmatreat rotating plasma jet (PT)	Electrical arc	Dry air	30	–	1000	21 kHz	33
AFS Plasmajet® (AFS)	Electrical arc	Dry air	5–10	–	200–500	16–31 kHz	8
SurfaceTreat gliding arc (GA)	Electrical arc	Dry air	11.8	Ar	550	50 Hz	27–36
RF plasma slit jet (RF)	CCP/ICP	Ar	50–100	N_2	300–600	13.56 MHz	150–300

plasmatreat





AFS®
PLASMA CORONA PERFORATORS



7.3 SurfaceTreat Atm. Pressure Plasma Jet

Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area ø [mm]
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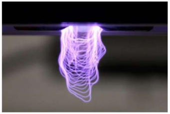
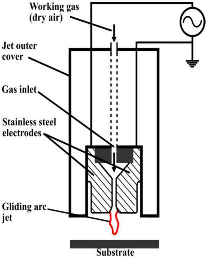
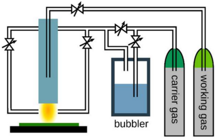
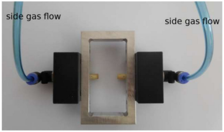




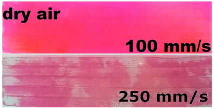
SurfaceTreat

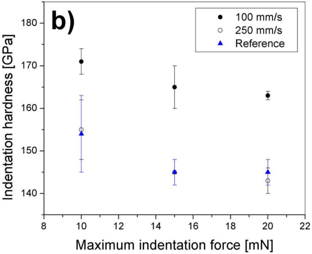


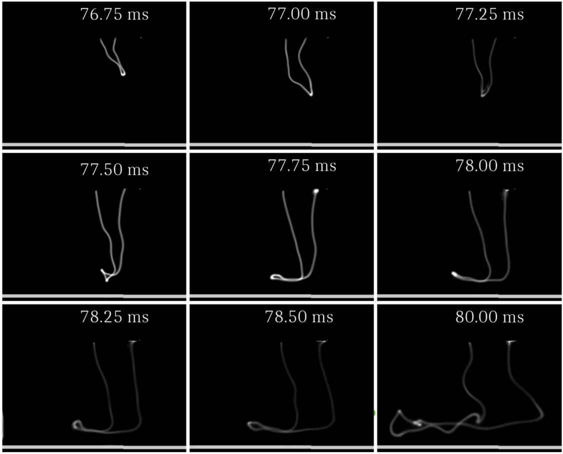


Modification of SurfaceTreat Plasma Jet

- without a cross flow







7.3 “Cold“ RF Plasma Slit Jet

Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area ø [mm]
Plasmatreat rotating plasma jet (PT)	Electrical arc	Dry air	30	–	1000	21 kHz	33
AFS Plasmajet® (AFS)	Electrical arc	Dry air	5–10	–	200–500	16–31 kHz	8
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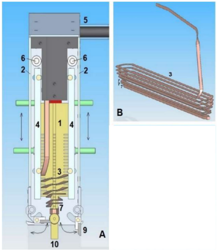
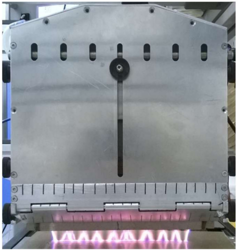
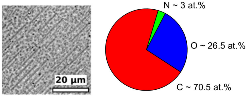


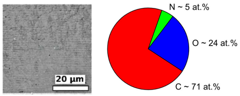


7.3 Results

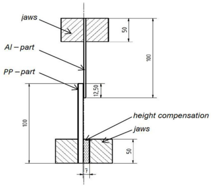
PP/Al joint's strength

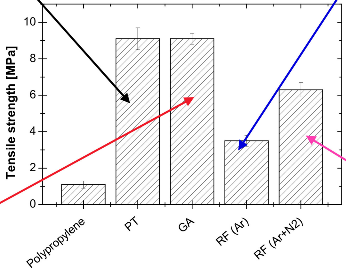


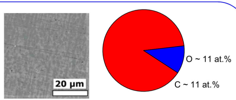
WCA = 28 ± 6°
1000 W, dry air 30 slm, 0.26 s, *h* = 5 mm



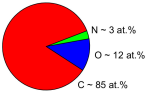
WCA = 56 ± 2°
550 W, dry air 11.8 slm + Ar 3.5 slm, 1 s, *h* = 10 mm







WCA = 74 ± 4°
500 W, Ar 50 slm, 0.6 s, h = 10 mm



WCA = 67 ± 4°
600 W, Ar 100 slm + N_2 3.5 slm, 0.12 s, h = 10 mm

The best adhesion ~ higher discharge gas temperature + presence of NH_x/NO_x groups