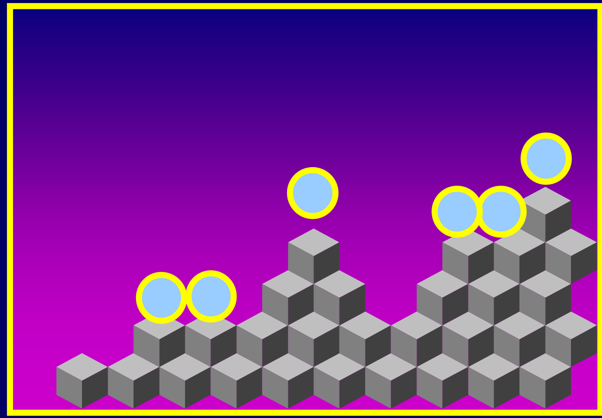
Bundesanstalt für Materialforschung und –prüfung,
Federal Institute of Materials Research and Testing

Fachgruppe VI.5: „Polymeroberflächen“
Department VI.5: „Polymer surfaces“



Einführung von haftvermittelnden Molekülen an plasmabehandelte Polymeroberflächen

Renate Mix, Joerg Friedrich

Introduction

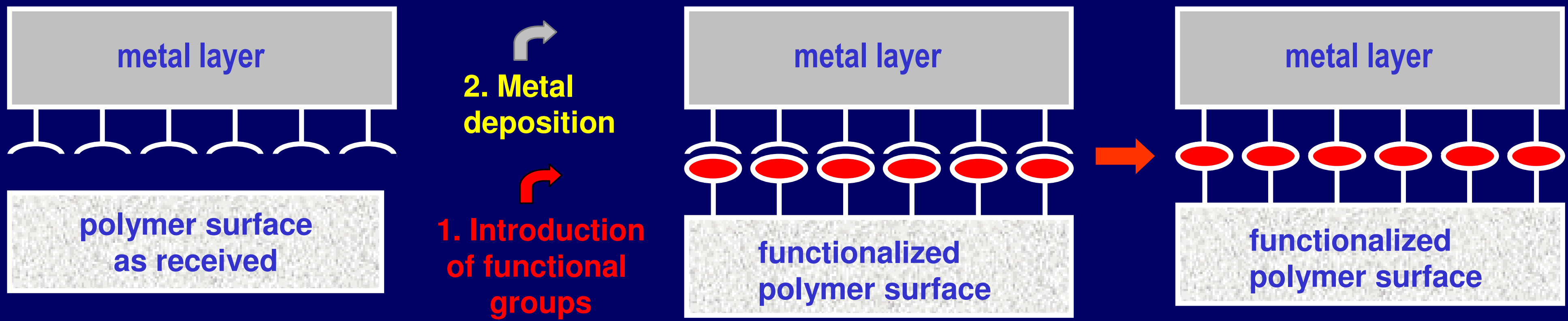
General problem of metal-polymer composites:

Poor adhesion between metal and polymer

Reason: Absence of functional groups at polymer surfaces

unmodified polymer | plasma-modified (functionalized) polymer

no adhesion | strong adhesion



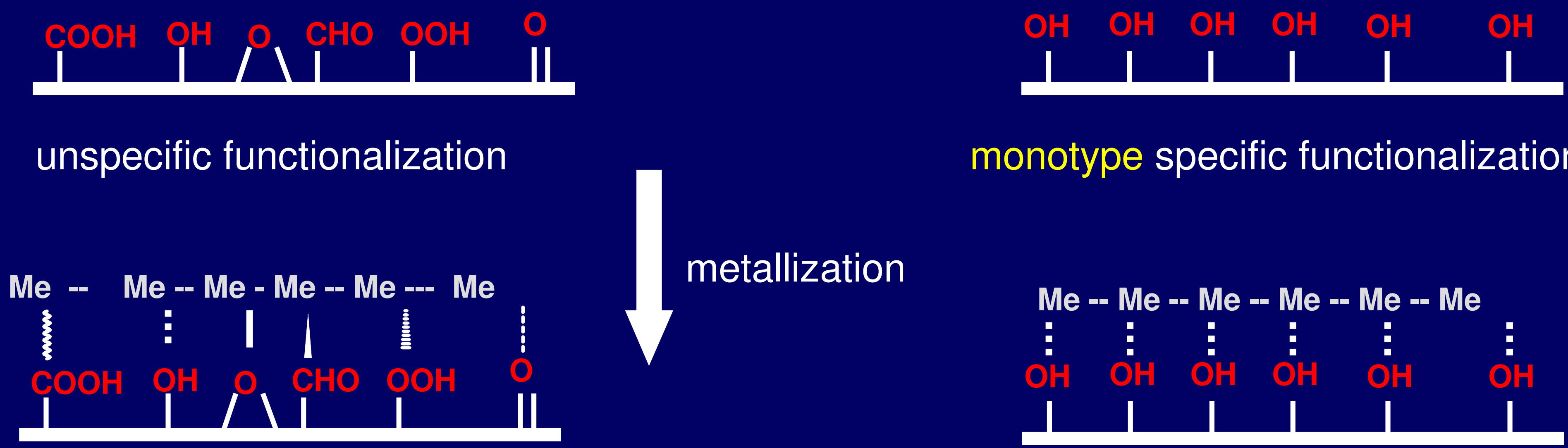
Solution of the problem in two ways:

Plasma functionalization of polymer surfaces

Deposition of adhesion-promoting functional group-carrying plasma polymer layers

Result: Improvement of adhesion in metal-polymer composites

Types of surface functionalization for improving the adhesion to metals



The adhesion strength is the sum

of all products of the concentration c_i and the bond strength ω_i of every type of functional group i

$$W = A * L * \sum_{i=1}^{i=n} (c_i * \omega_i)$$

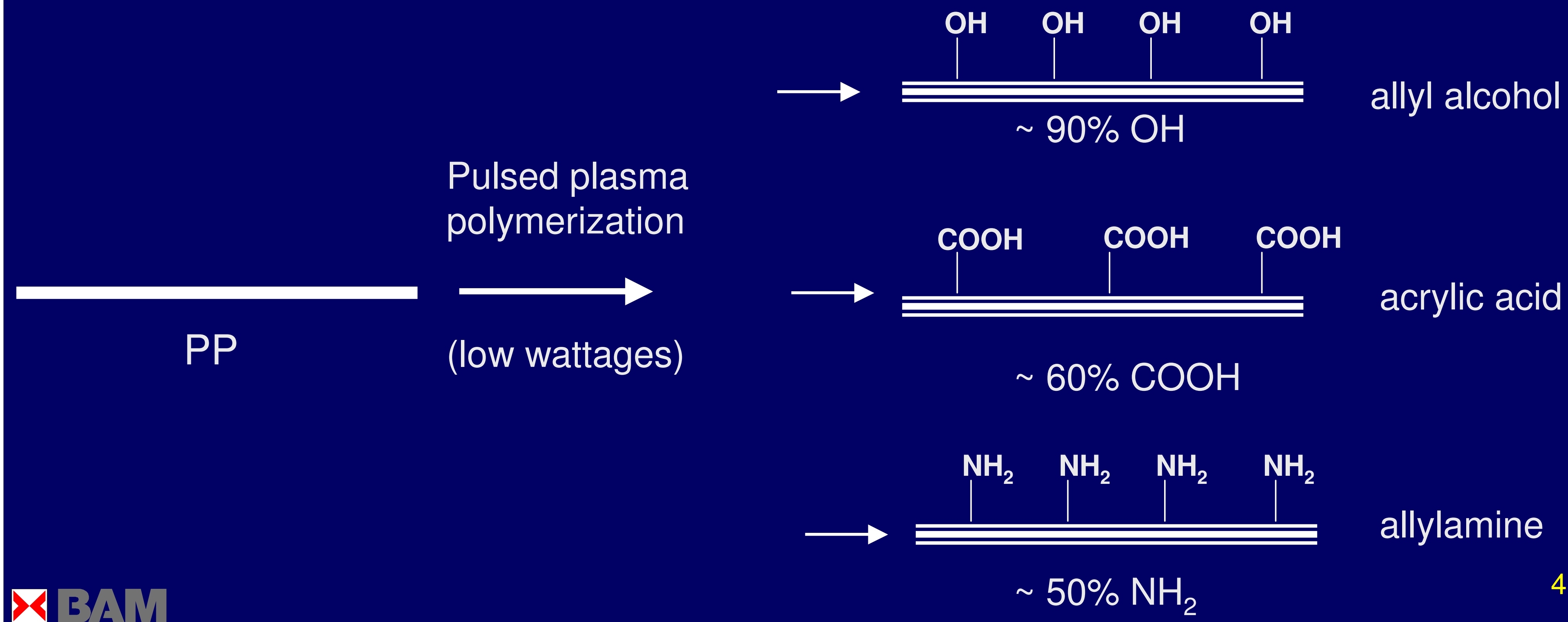
the product of the bond strength ω_x and the concentration c_x of the functional group

$$W = A * L * \Sigma c_x * \omega_x$$

Pulsed plasma deposition of functional groups carrying monomers

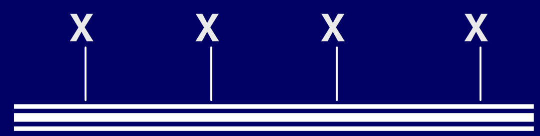
Advantage: High retention of functional groups of the used monomers in plasma polymer films

Disadvantage: Low degree of crosslinking → problems in contact with solvents

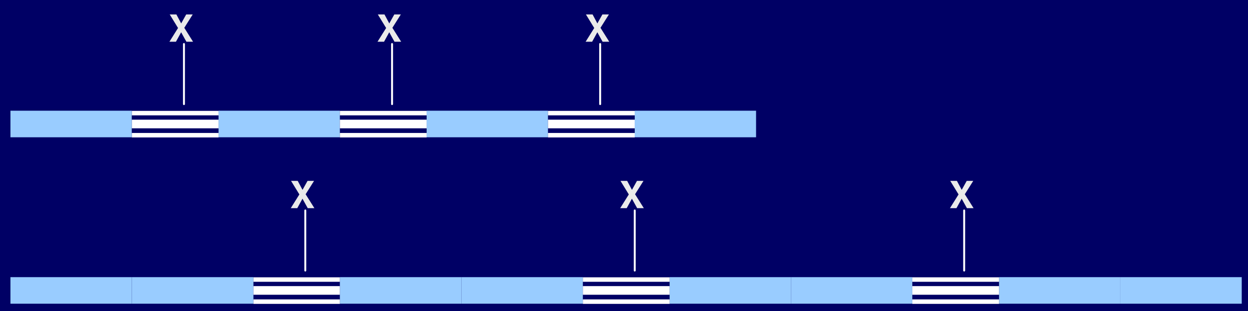


Plasma Initiated Chemical Copolymerization - Variation of the Concentration of Functional groups

Structure of homopolymers:



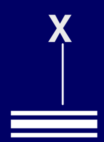
Structure of copolymers:



1:1 copolymer

1:2 copolymer

neutral monomers:
ethylene, butadiene, acetylene,…

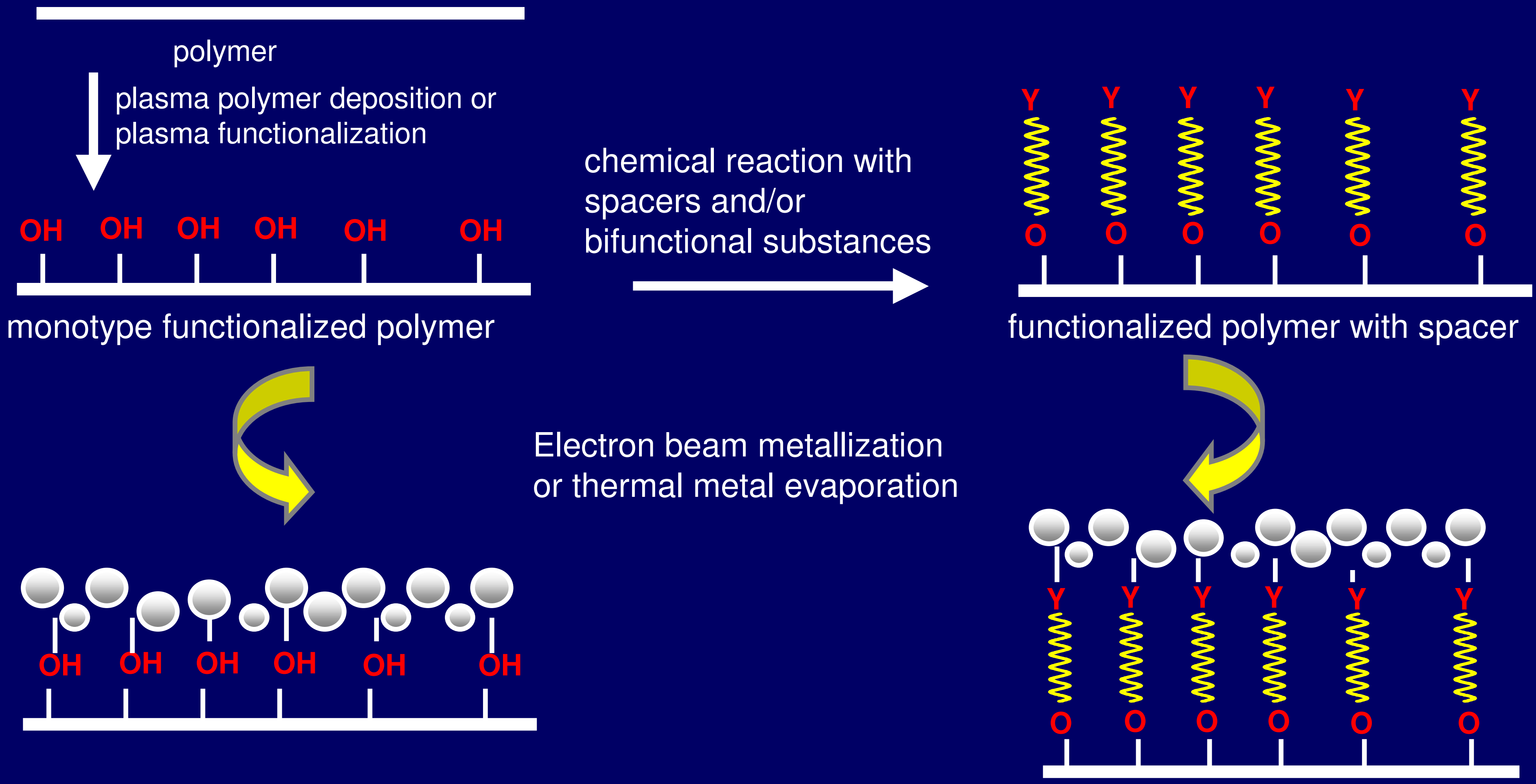


functional group carrying monomer,
X = COOH, OH, NH_2, ..

Influence of the number of functional groups on the deposition of aluminium? Islands?

Manufacturing of metal-polymer composites

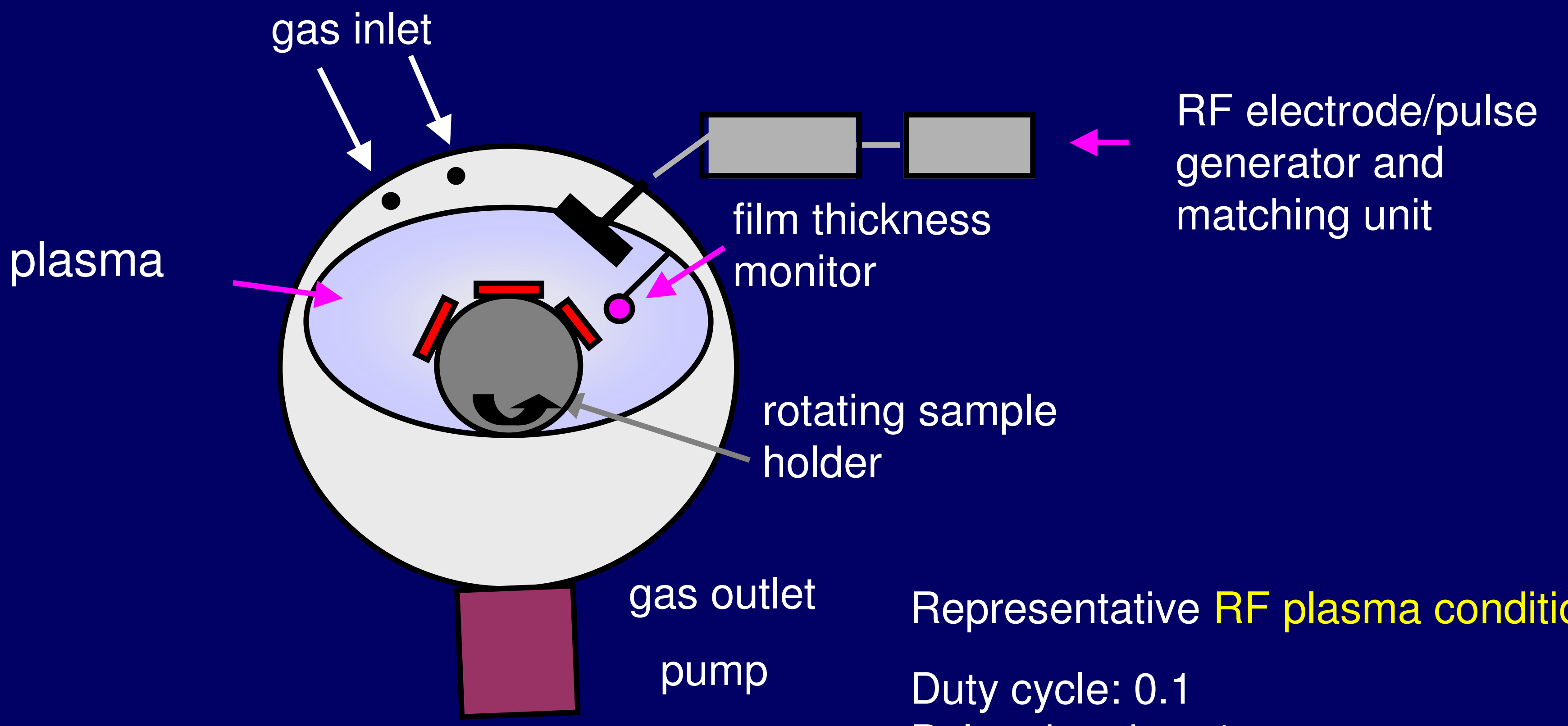
Schema for the production of metal-polymer composites:



Y : functional groups: OH, NH_2, COOH, ….

Manufacturing of metal-polymer composites

Reactor used for pulsed plasma polymerization

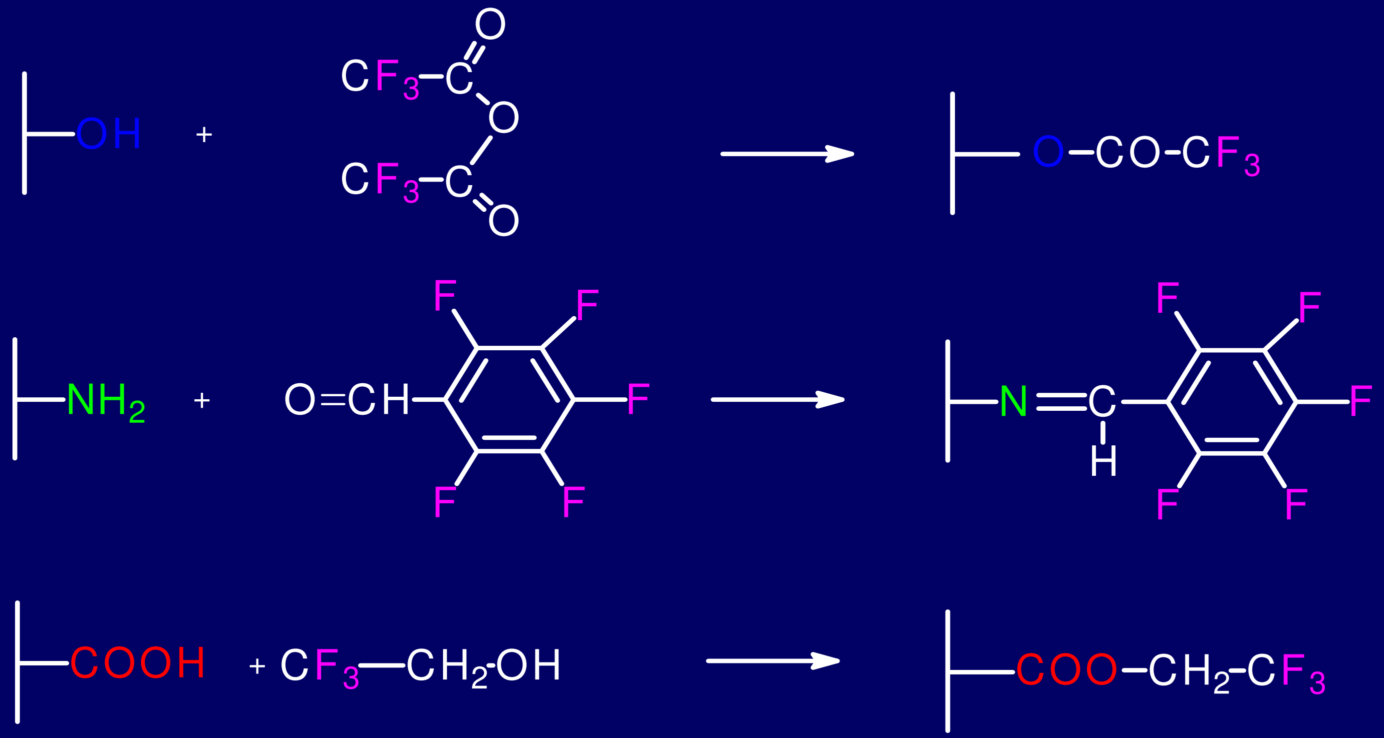


Representative RF plasma conditions:

Duty cycle: 0.1
Pulse duration: 1 ms
Wattage: 100 W / 300W (10 / 30 W_{eff})
Pressure: 10-26 Pa

Analytical characterization of plasma polymerized homopolymers and copolymers by XPS

Principle: Derivatization of functional groups (OH, NH_2 and COOH) with substances which contain external elements (e.g. F, Br, Cl,. ...]



Result: Conclusion from the concentration of introduced elements and/or deconvolution of the C1s-Peak of the derivatized surface
→ number of functional groups/100C

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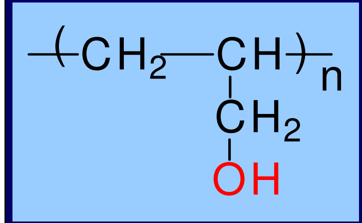
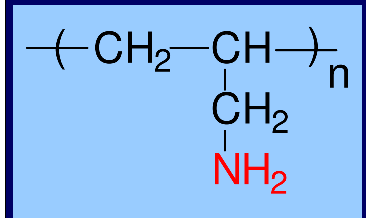
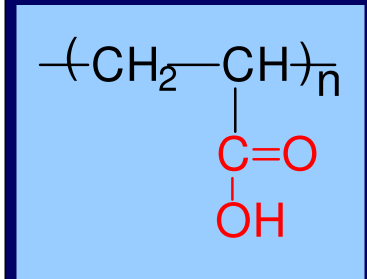
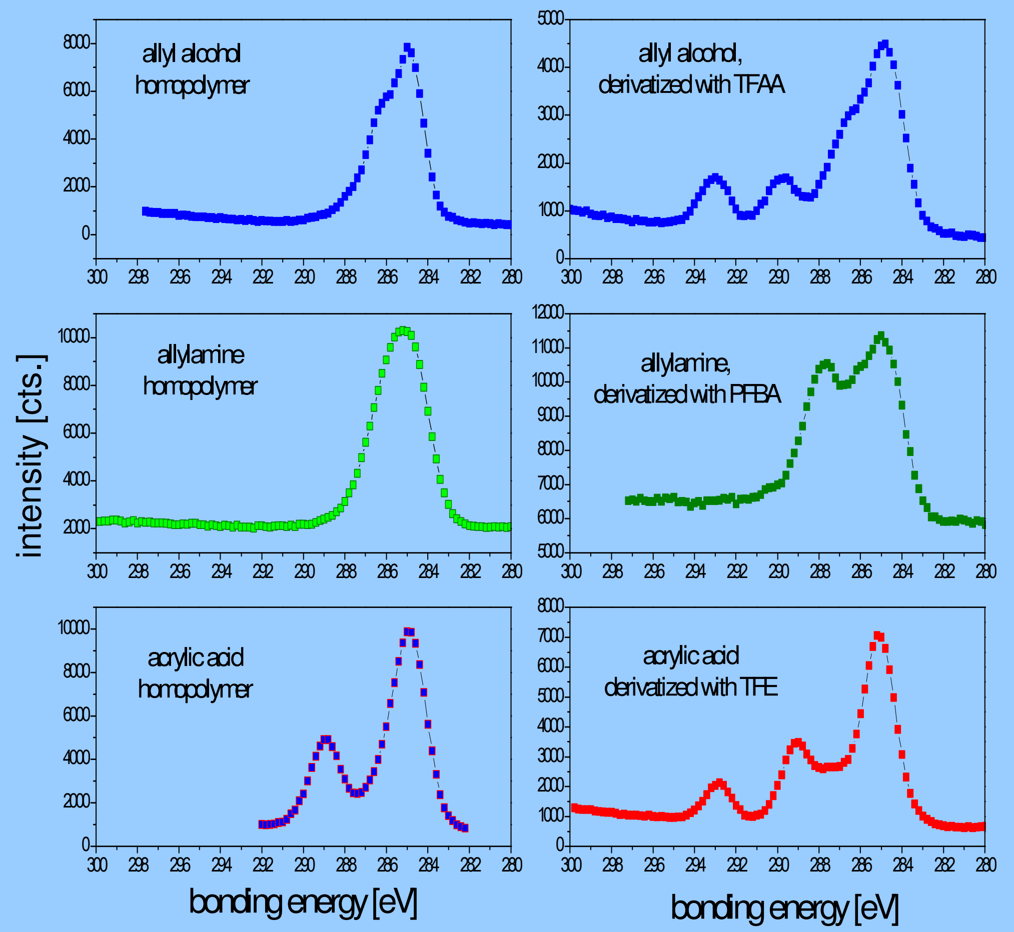
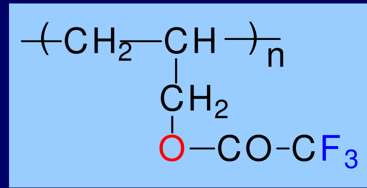
XPS: C1s-spectra of functionalized homopolymeres before and after derivatization

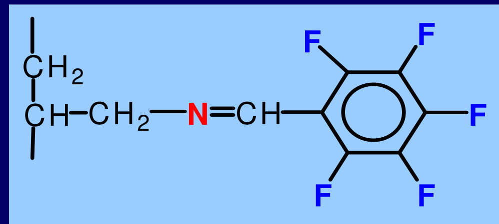


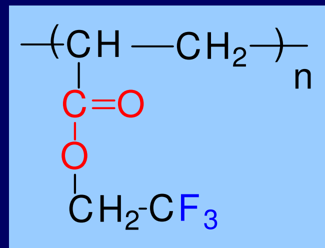






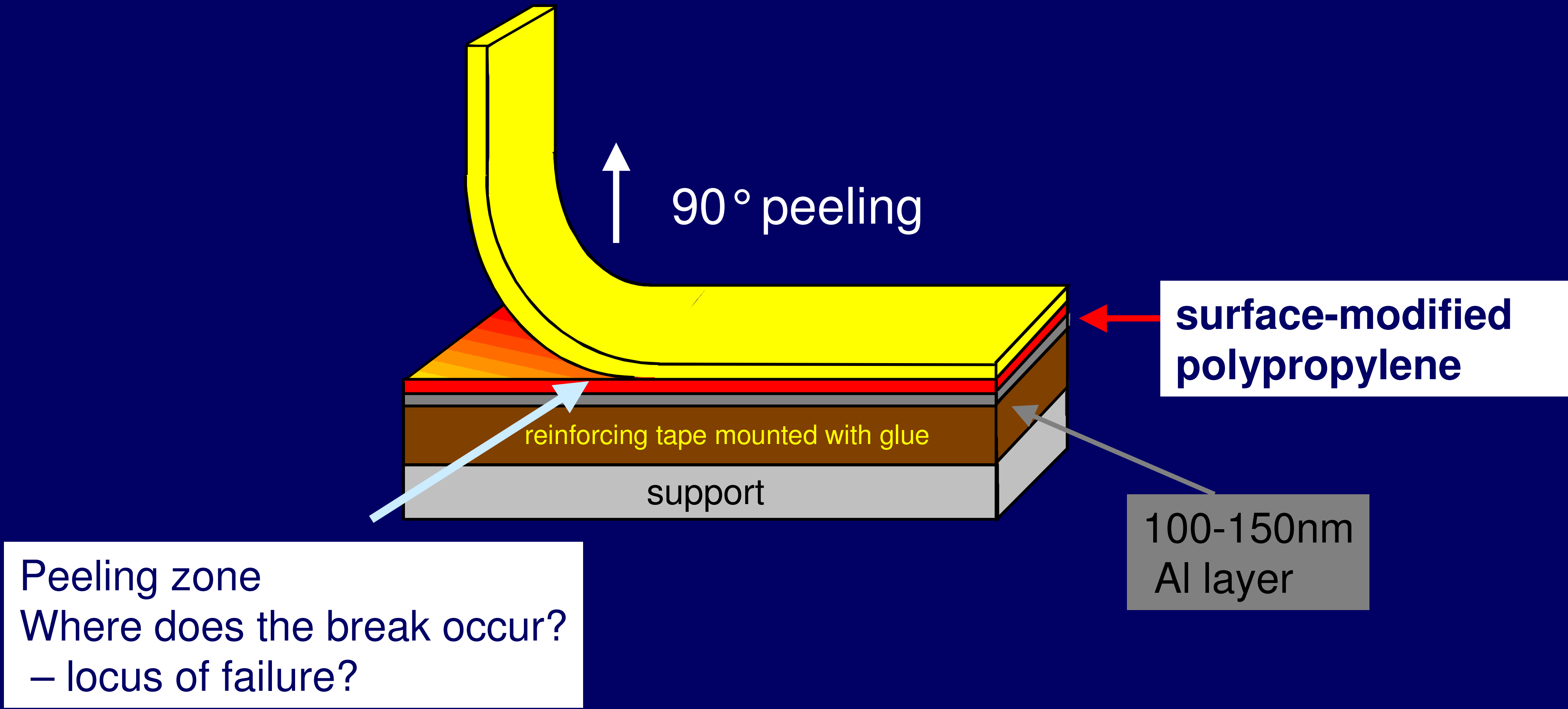






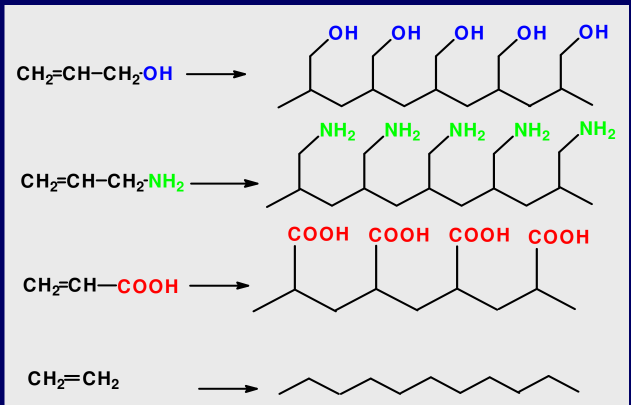
Measuring of metal peel strength deposited onto functionalized polymer surfaces

Specimen for measuring the adhesion between Al and PP



Adhesion-promoting pulsed plasma polymers

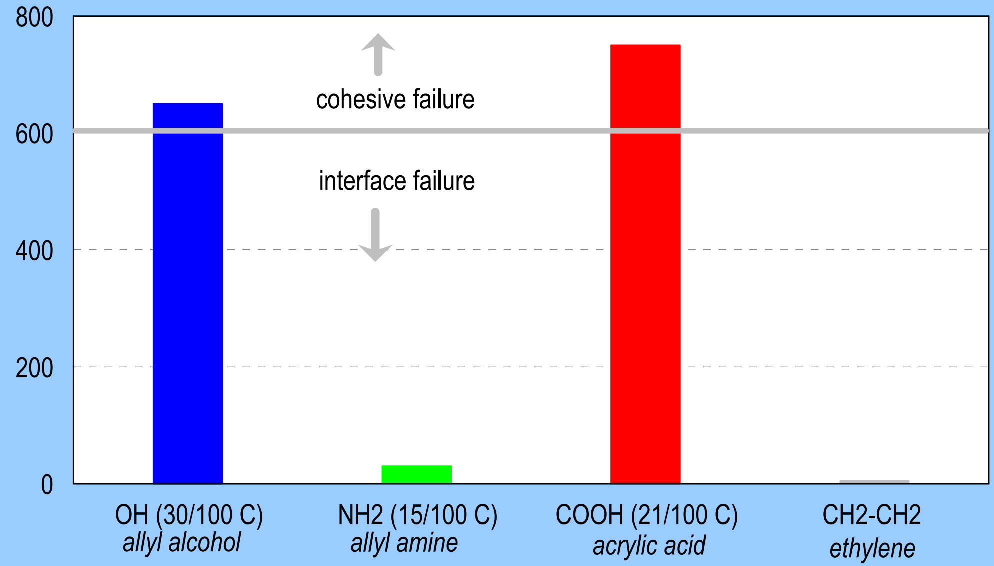
Homopolymers



Pulsed plasma-initiated (radical) homo-polymerization of functional groups-carrying monomers

Al-polymer composite

Al peel strength [N/m]



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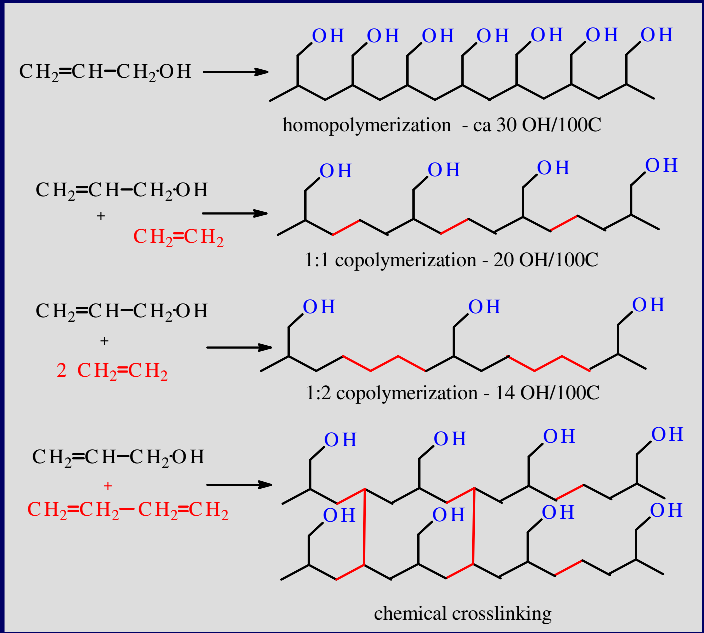
Adhesion-promoting pulsed plasma polymers

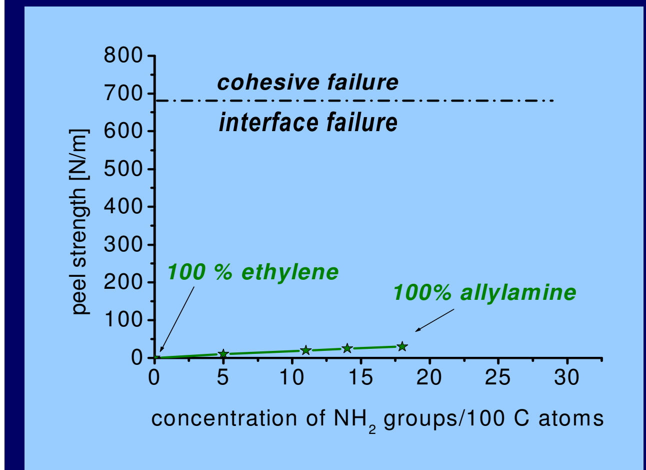
Copolymers



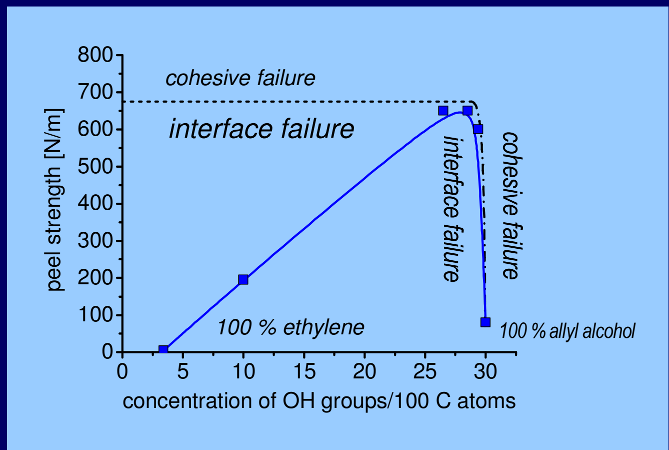
Deposition 1000Hz, DuCy 0,1, 100W

Al-polymer composite

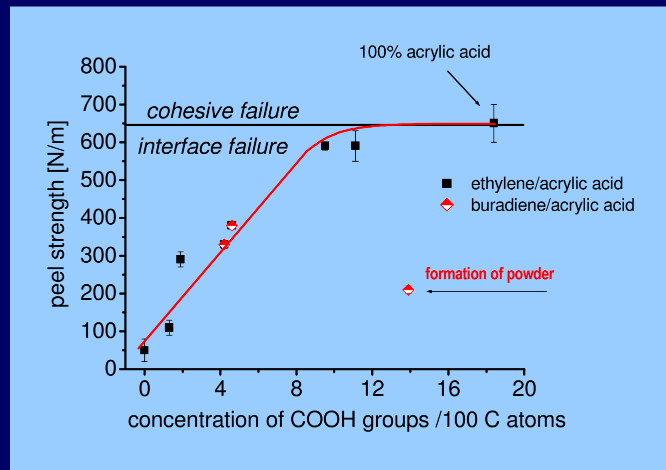
ethylene / allylamine



ethylene / allyl alcohol



ethylene (butadiene) / acrylic acid



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Analysis of peeled Al and polymer surfaces

OH groups

COOH groups

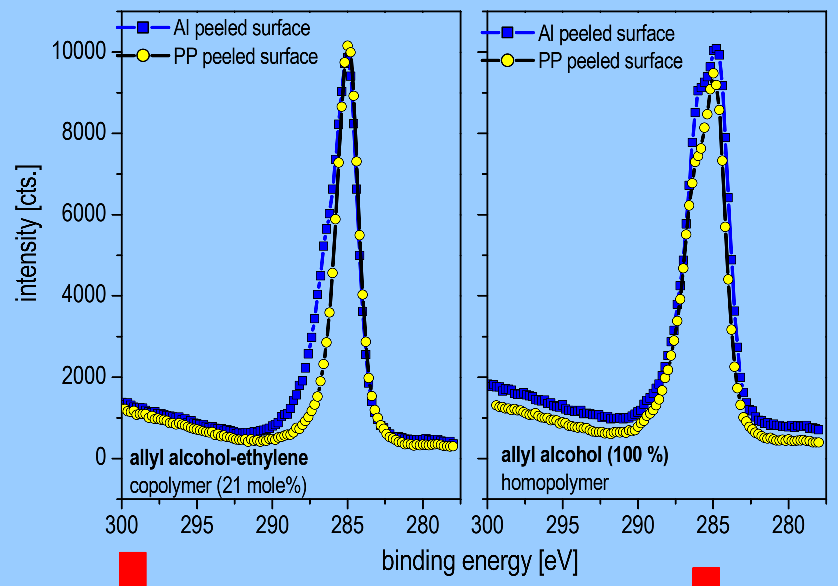
XPS-C1s signals of peeled surfaces

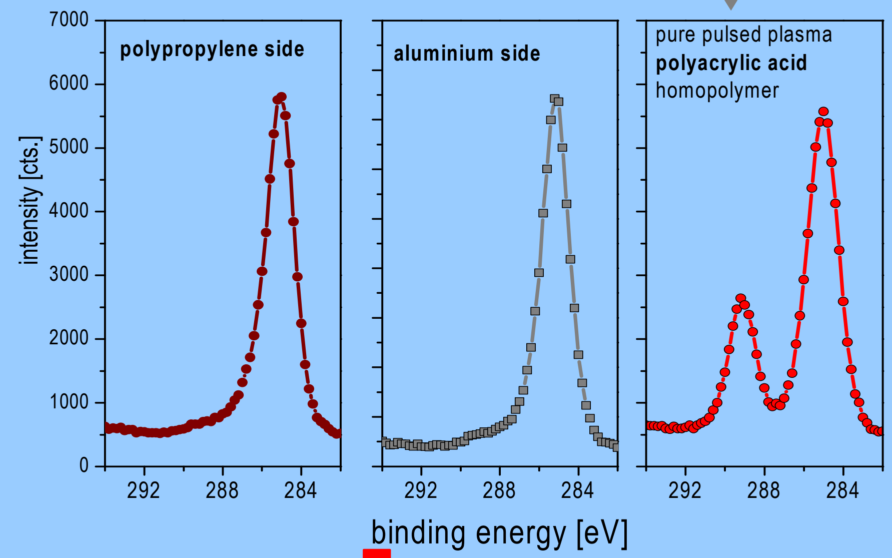
For comparison:
C1s acrylic acid
homopolymer

Al-copolymer-PP composite

Al-allyl alcohol-PP composite

Al-acrylic acid homopolymer- PP





Conclusion: peeling at PP-OH interface

Conclusion: peeling within plasma polymer

Conclusion: peeling within the PP substrate

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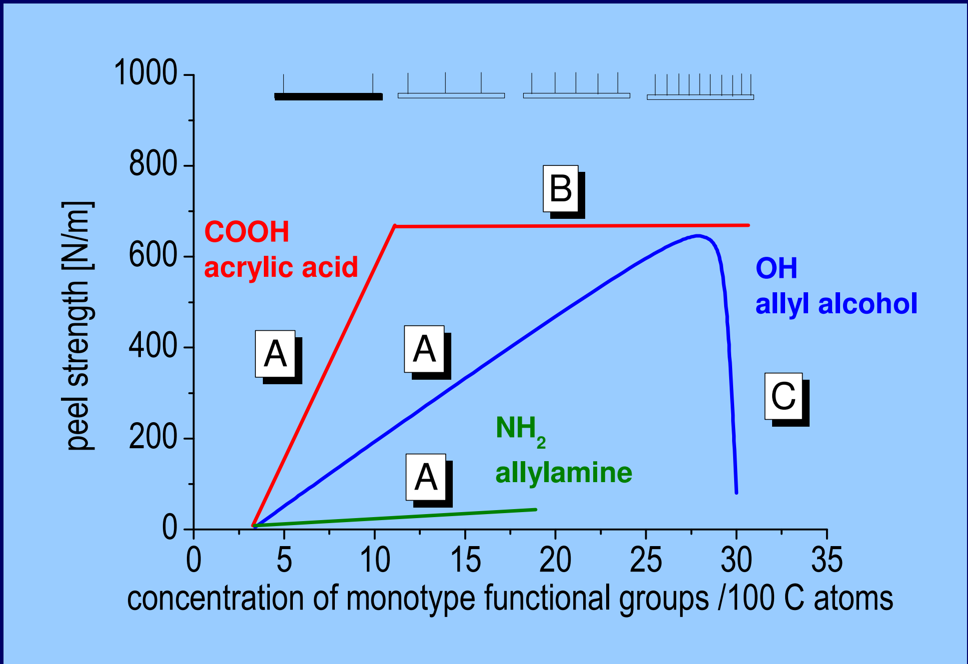
Metal peel strength of Al-PP composites

monotype functionalization, directly to surface bonded functional groups



Different slopes
~ bond strengths

Region A - Peel strength ~ conc. functional groups
Region B Plateau
Region C Decrease cohesive failure

Adhesion-promoting effect of monotype functional groups towards Al deposits

CH_2-CH_2 < NH_2 ≪ OH < COOH

Interactions: no | very weak | alcoholates | salts

Ways for introduction of spacers

1. Way: Reacting of amino-functionalized surface with an dialdehyde followed by attachment bi-(or multi-functional) substances with at least one amino group

$$|\!-NH_2 \quad + \quad O{=}HC-(CH_2)_3-CH{=}O \longrightarrow |\!-N{=}CH-(CH_2)_3-CH{=}O$$

plasma polymerized allylamine deposit

glutaraldehyde

aldehyde modified surface

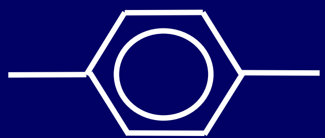
$X-R_1-NH_2$

bi(tri)functional substances

$$|\!-N{=}CH-(CH_2)_3-CH{=}N-R_1-X$$

spacer-bonded functional groups

R_1 : $-(CH_2)_5-$, $-(CH_2)_{11}-$

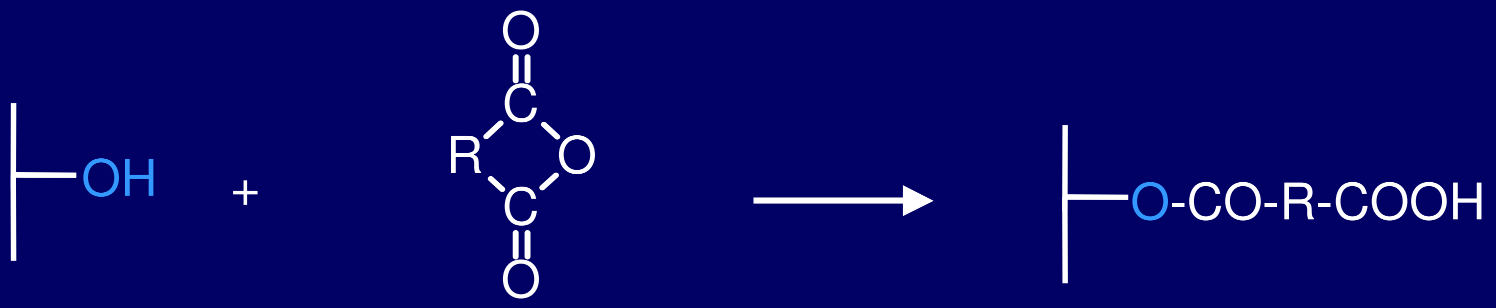


Advantage of this reaction:
all types of functional groups are producible by input of suited reaction partner

X : OH, NH_2, COOH

Ways for introduction of spacers

2. Way: Reaction of hydroxy-functionalized surfaces with anhydrides



Plasma functionalized surface

acid anhydride

Spacer attached carboxyl groups

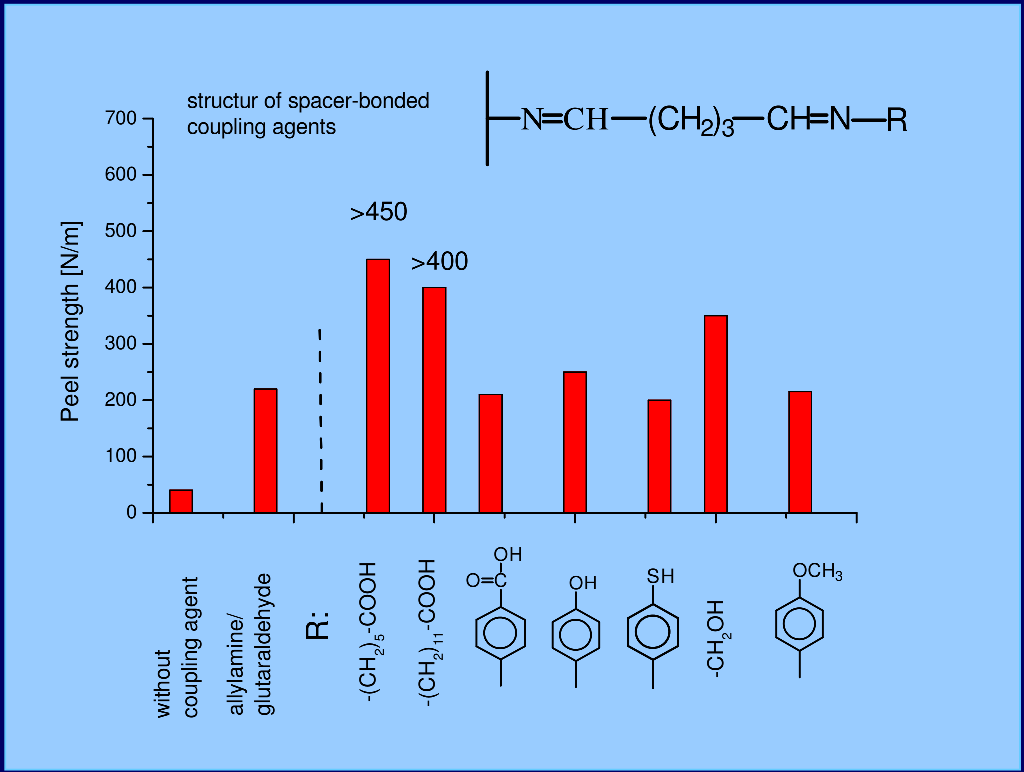
Peel strength of Al-PP composites

monotype functionalization, spacer-bonded functional groups

Peel strength = function of the following variables:

1. type of functional group
2. concentration of functional group,
3. spacer length,
4. stiffness of the spacer ???

1. Influence of the **type** of the functional group:



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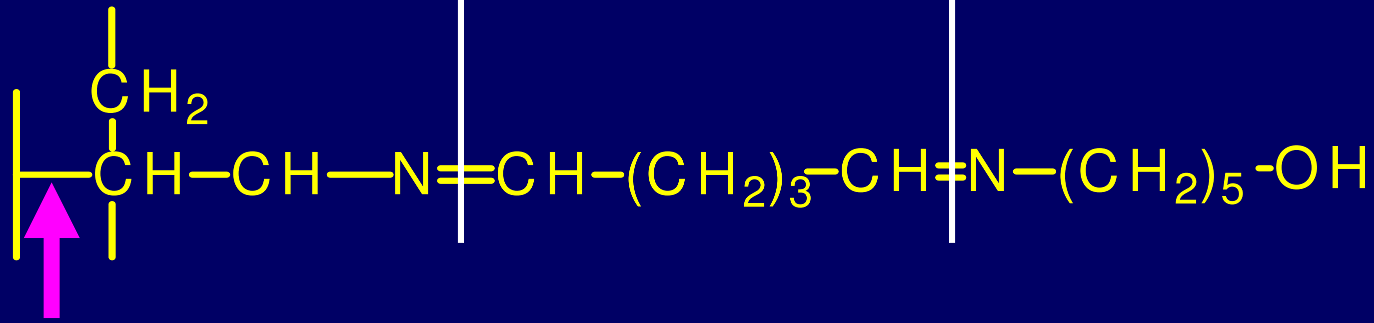
Example of peeltest curves of a spacer-linked coupling agent

Starting components:

plasma polymerized allylamine layer	glutaraldehyde spacer	1-amino-pentanol

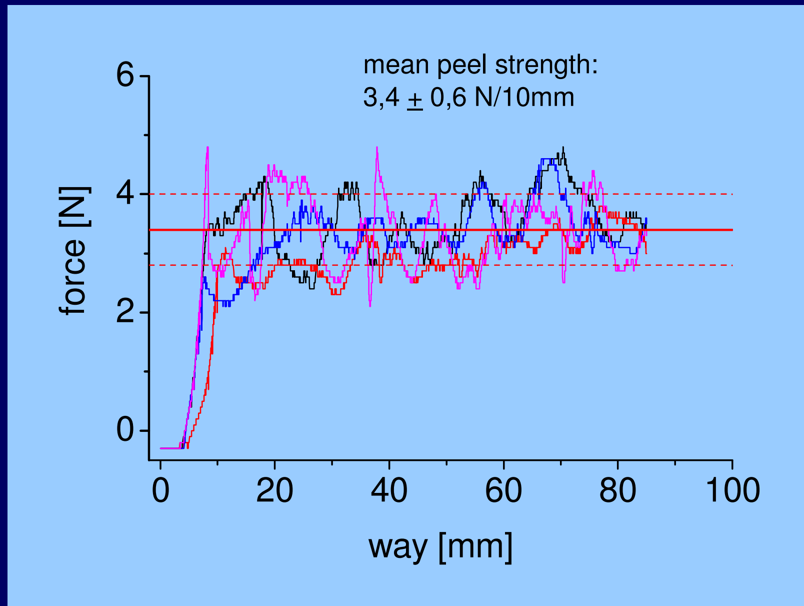
Structure:



Locus of failure: between PP and spacer-linked coupling agent

XPS of the peeled surfaces:

PP-side: 98% C, 2% O, no Al
Al-side: 87% C, 8% O, 5% N
no Al!



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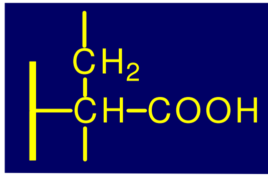
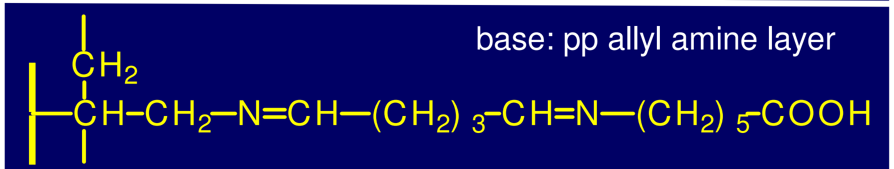
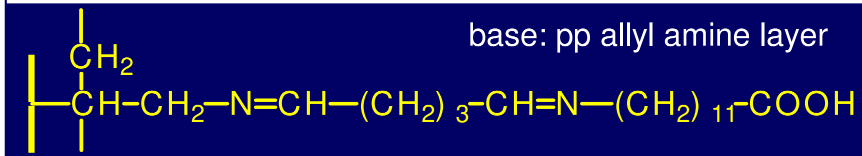
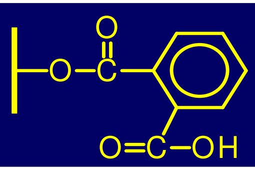
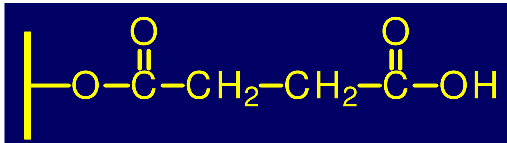
2. Variable: Concentration of functional groups - OH groups

Structure	theoretical number of OH /100C	found number of OH /100C	Peel strength [N/m]
CH_2 / $CH-CH_2-OH$ — pp allyl alcohol deposited at 1 kHz, 100 W, duty cycle 0,1	33.0	27-30	60-80*
CH_2 / $CH-CH-N{=}CH-(CH_2)_3-CH{=}N-(CH_2)_2-OH$ — base: pp allyl amine layer	10.0	4.1	440 ± 70
CH_2 / $CH-CH-N{=}CH-(CH_2)_3-CH{=}N-(CH_2)_5\text{-}OH$ — base: pp allyl amine layer	7.7	0.8	340 ± 60
CH_2 / $CH-CH-N{=}CH-(CH_2)_3-CH{=}N-$  $-OH$ — base: pp allyl amine layer	7.1	0.3	>360 ± 60
CH_2 / $CH\text{-}CH_2-N{=}CH-(CH_2)_3-CH{=}N\cdot CH(CH_2-OH)_2$ — base: pp allyl amine layer	18.2	2.7	>210 ± 60

* Locus of failure: allyl alcohol layer itsself!

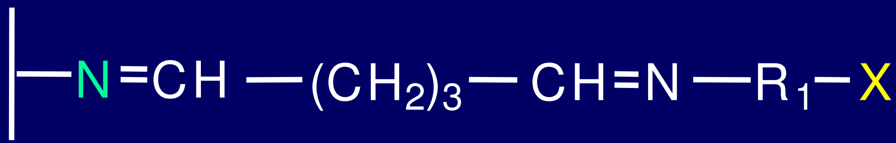
2. Variable: Concentration of functional groups - COOH groups

Structure		theoretical number of COOH /100C	found number of COOH /100C	Peel strength [N/m]
	pp acrylic acid (1kHz, 100 W, dc: 0,1	33.3	21-24	600-700 at ≥ 6 COOH/100C
	base: pp allyl amine layer	6.6	0.9	> 450*
	base: pp allyl amine layer	5.0	1.2	> 400* partially 600-700
	base: polypropylene, OH-functionalized	12.5	0.6	155 ± 10
	base: polypropylene, OH-functionalized	25.0	0.8	52 ± 16

*Break between Al and glue layer

3. Variable: Influence of the spacer length

structure:



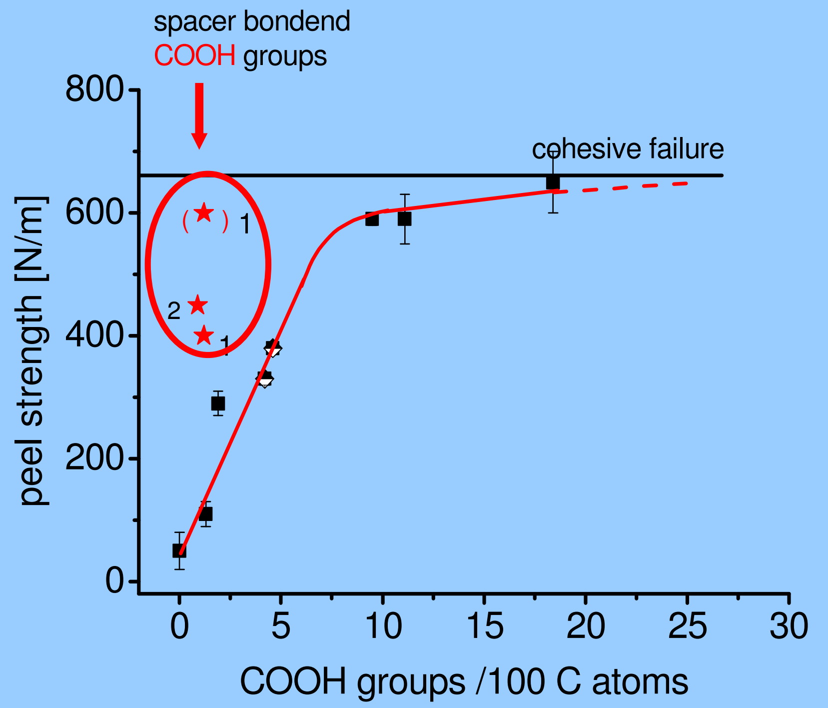
3: R1 = $-(CH_2)_2-$
4: R1 = $-(CH_2)_5-$

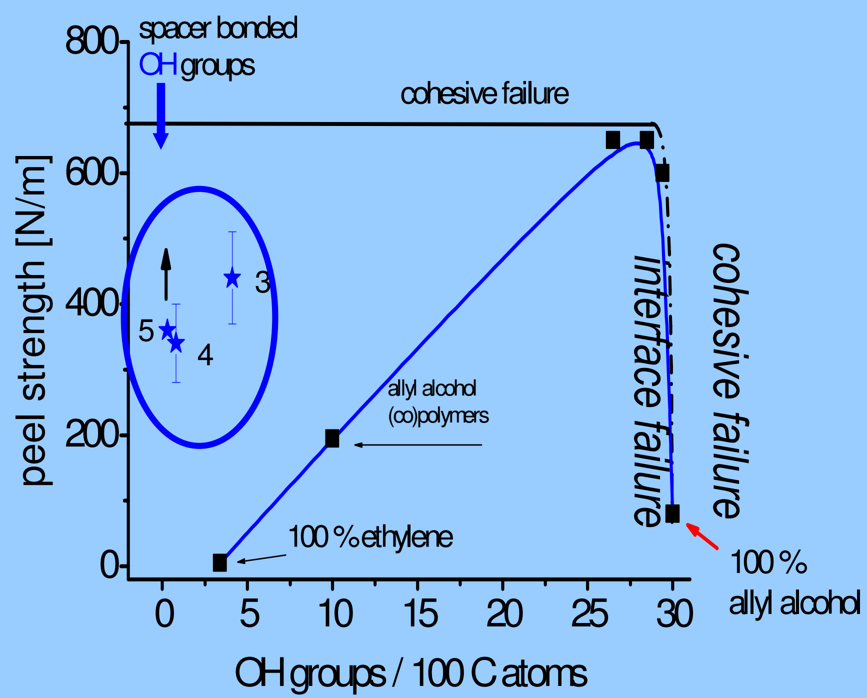
X = COOH

1: R1 = $(CH_2)_5$
2: R1 = $(CH_2)_{11}$

X = OH

5: R1 =





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Summary

- Pulsed plasma polymerization/copolymerization of functional group carrying monomers was used to produce monotype functionalized adhesion-promoting interlayers with defined concentration of functional groups.
- The maximum concentration of functional groups was adjusted for pulsed plasma polymerized allyl alcohol, allylamine and acrylic acid as:
  30 OH, 18 NH_2 and 24 COOH groups /100 C atoms
- Composites of polypropylene coated with a 150 nm thick plasma polymer layer fitted with OH, NH_2 or COOH groups and then metallized with Al showed different peel strengths:
  COOH groups gave the highest peel strength, followed by OH groups. NH_2 and CH_2-CH_2 groups were without any adhesion- promoting effect.
- To insert spacer molecules between functional group and surface 3 ways were presented: the most effective way was the deposition of an allylamine layer which was reacted with glutaraldehyde followed by reaction with bifunctional NH_2 -containing substances.
- The resulting composites showed higher peel strength compared with composites where the functional groups were directly bonded to the surface (at the same concentration).

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