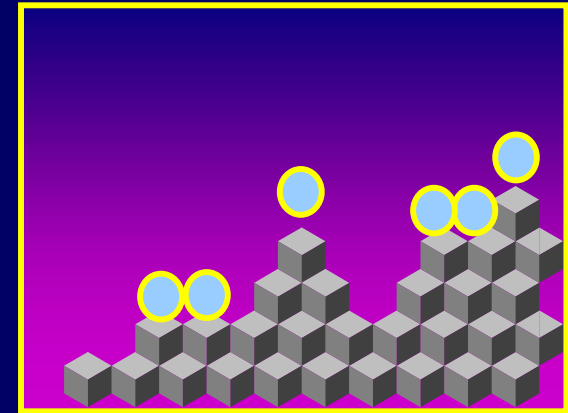


Bundesanstalt für Materialforschung und –prüfung,
Federal Institute of Materials Research and Testing

Fachgruppe VI.3: „Analyse und Struktur von Polymeren“
Department VI.3: „Analysis and Structure of Polymers“



Plasmachemical synthesis of polymeric model surfaces

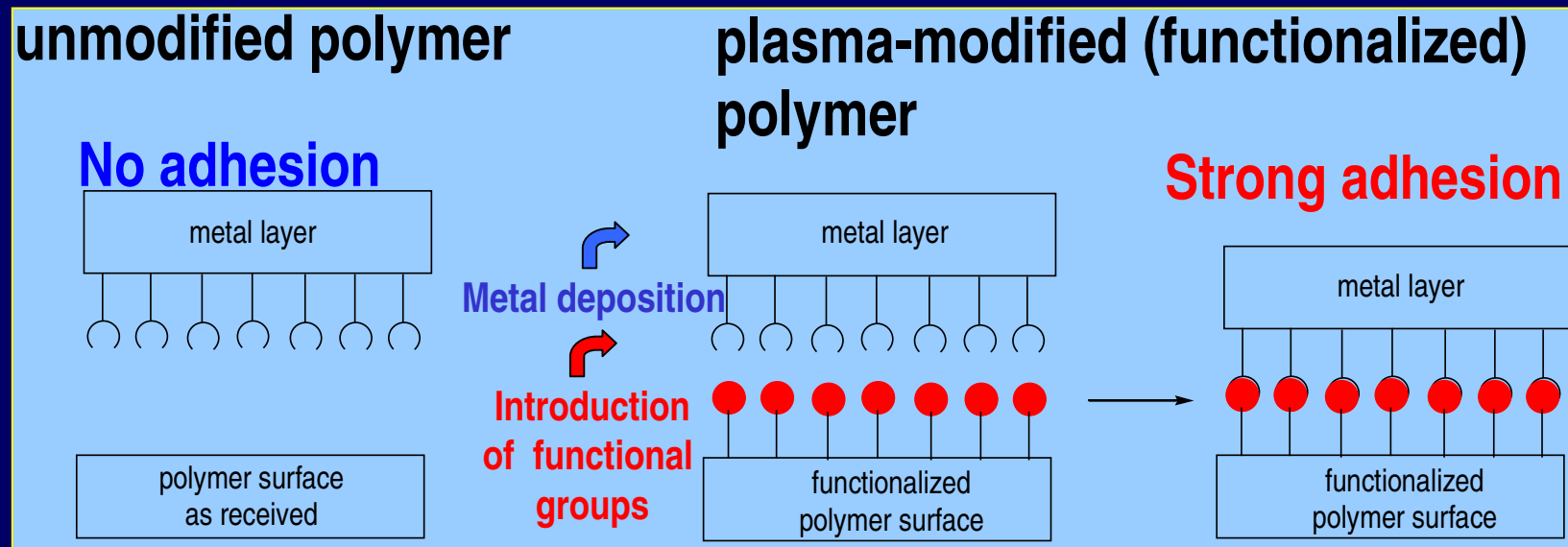
R. Mix, G. Kühn, J. Friedrich

Introduction

Basic problem of metal-polymer composites:

Poor adhesion of metals to polymers

Reason: absence of functional groups at polymer surfaces



**Solution of the problem
in two ways:**

Improvement of
adhesion in Al-PP
composites



Plasmafunctionalization
of polymer surfaces



Deposition of adhesion-promoting
function-carrying plasma polymer
layers

Differences in polymer functionalization and its effect on the adhesion

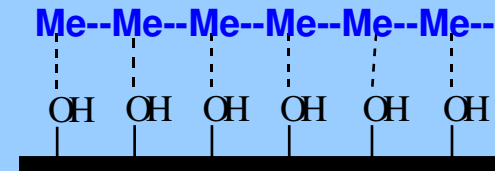
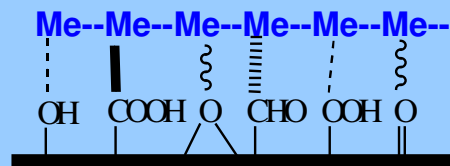
Types of surface functionalization for improving the adhesion to metals



unspecific functionalization



monotype functionalization
specific functionalization



the sum of **all products of concentration (c) x respective type of bond strength (ω)** is related to adhesion W

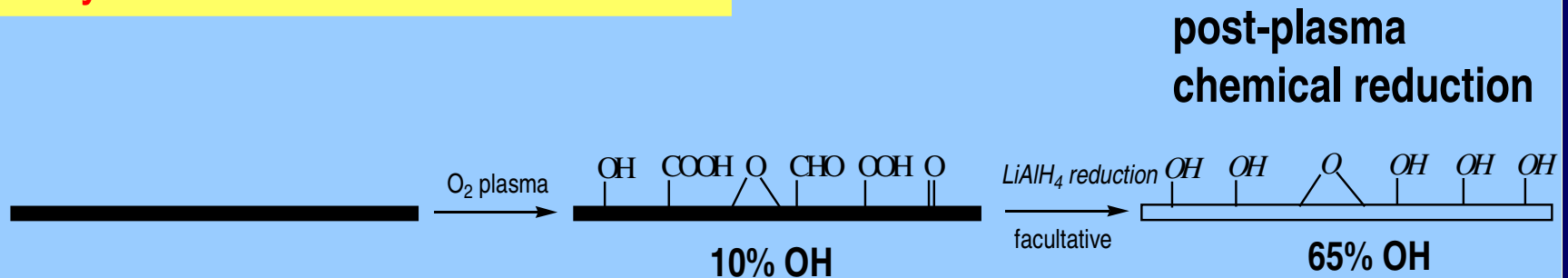
$$W = A \cdot L \cdot \sum_{i=1}^m c_i \cdot \omega_i$$

the sum of **one type** of interactions is related to adhesion

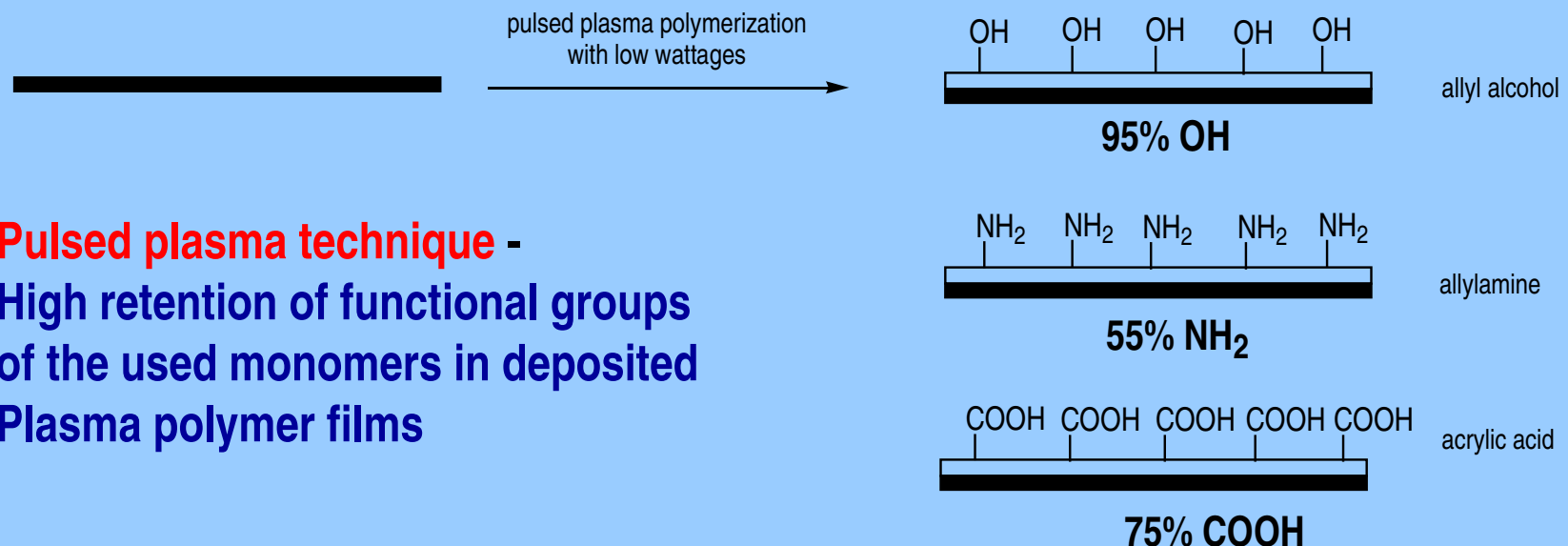
$$W = A \cdot L \cdot \sum c_x \cdot \omega_x$$

Uniform polymer surface functionalization by different types of functional groups

Polymer surface functionalization



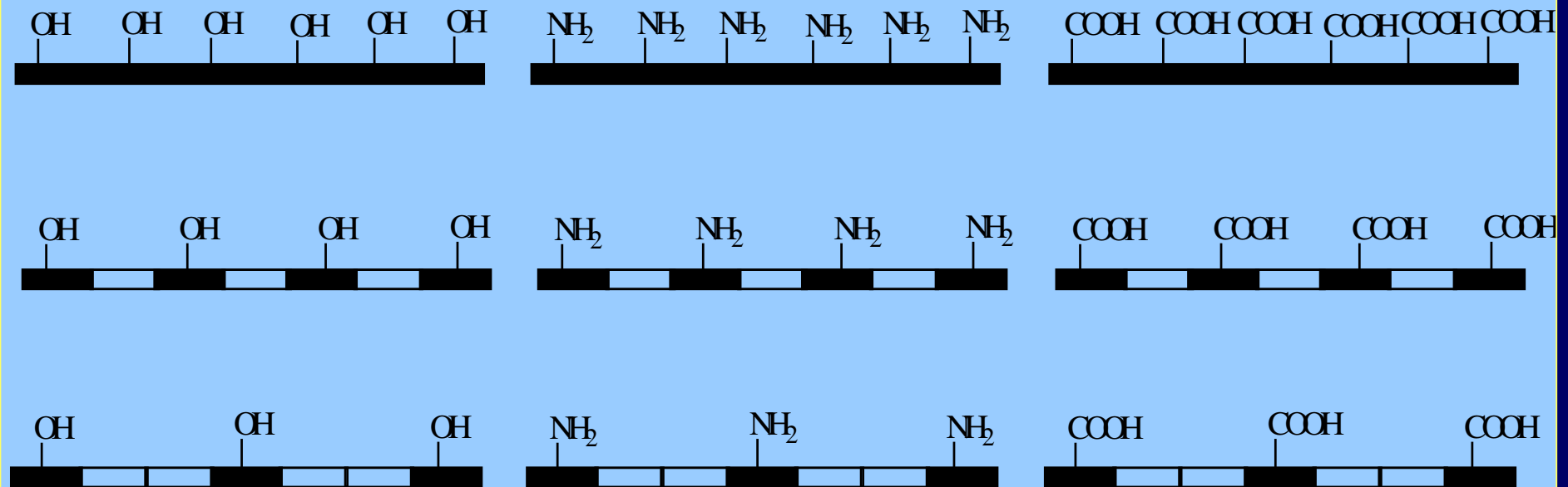
Deposition of thin functional groups-carrying plasma polymer layers



Pulsed plasma technique -
High retention of functional groups
of the used monomers in deposited
Plasma polymer films

Variation of the density of functional groups at polymer surfaces

Using the (pulsed) **plasma technique** monotype functionalized polymer surfaces with adjustable density of functional groups can be produced (**plasma initiated chemical copolymerization**)



Experimental

Plasma-assisted production of functionalized polymer surfaces

Reactor used for pulsed plasma polymerization / copolymerization and in situ metallization

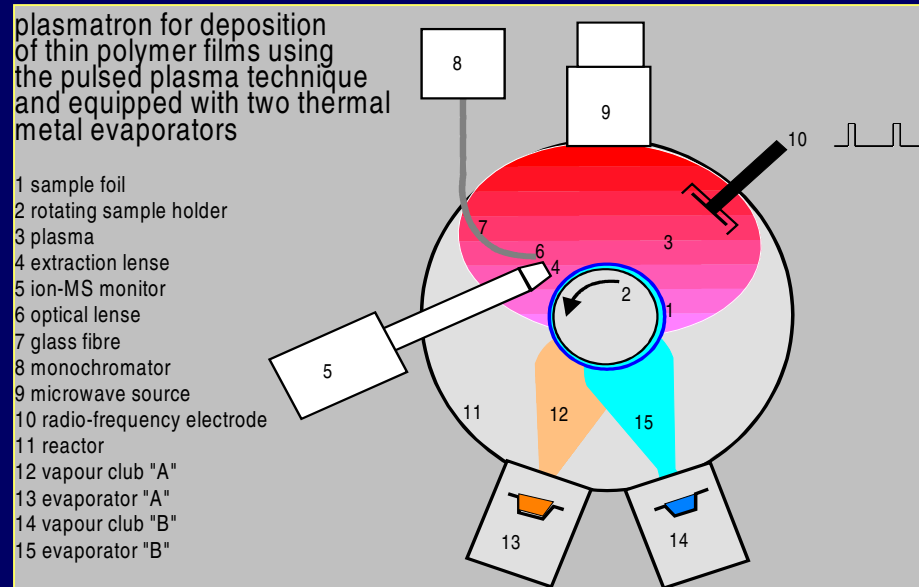
Representative RF plasma conditions:

Duty cycle: 0.1

Pulse duration: 1 ms

Wattage: 100 W / 300W (10 / 30 W_{eff})

Pressure: 10-26 Pa



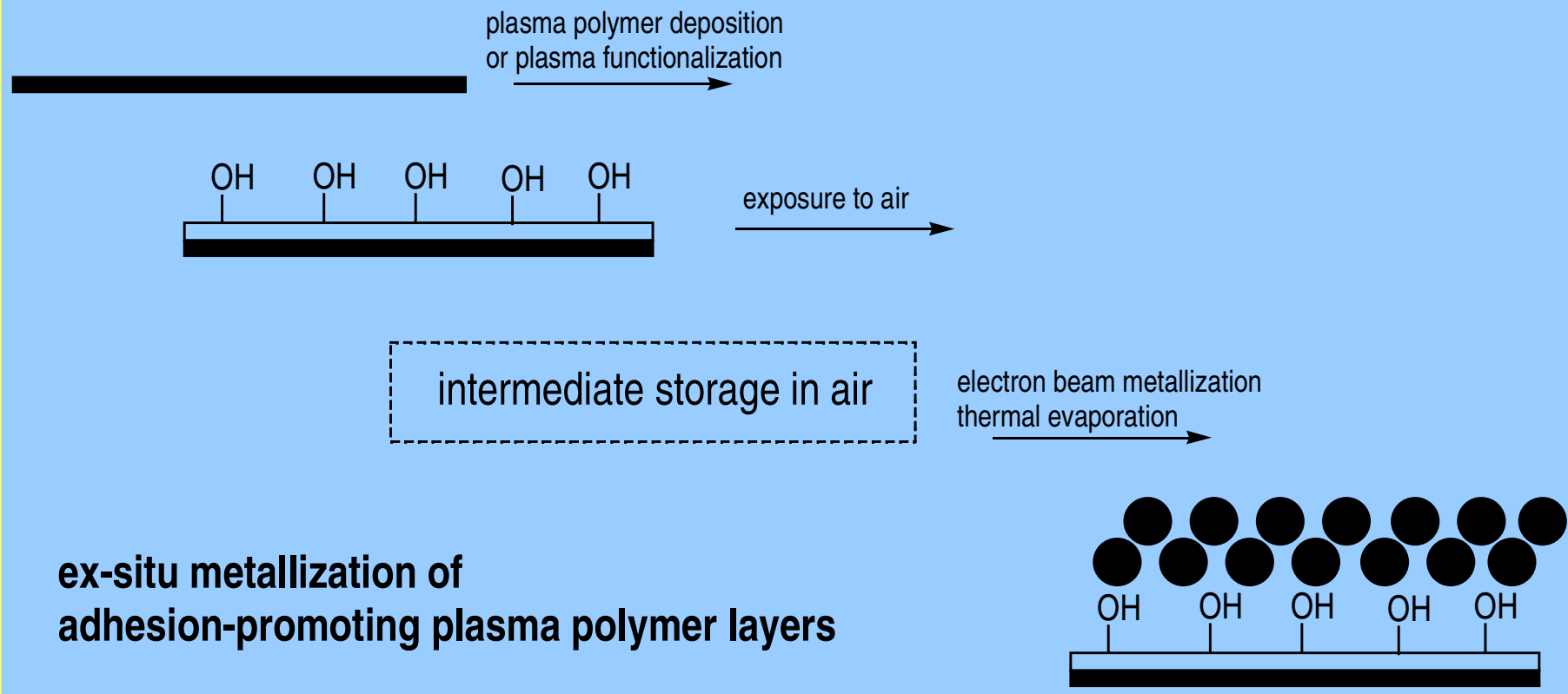
Gasplasma modification (oxygen plasma)

Representative RF plasma conditions: Pressure: 6 Pa, Wattage: 10-100 W, Time: 0.1- 30 s

Experimental

Manufacturing of metal-polymer composites

deposition of functional groups carrying plasma polymer layer

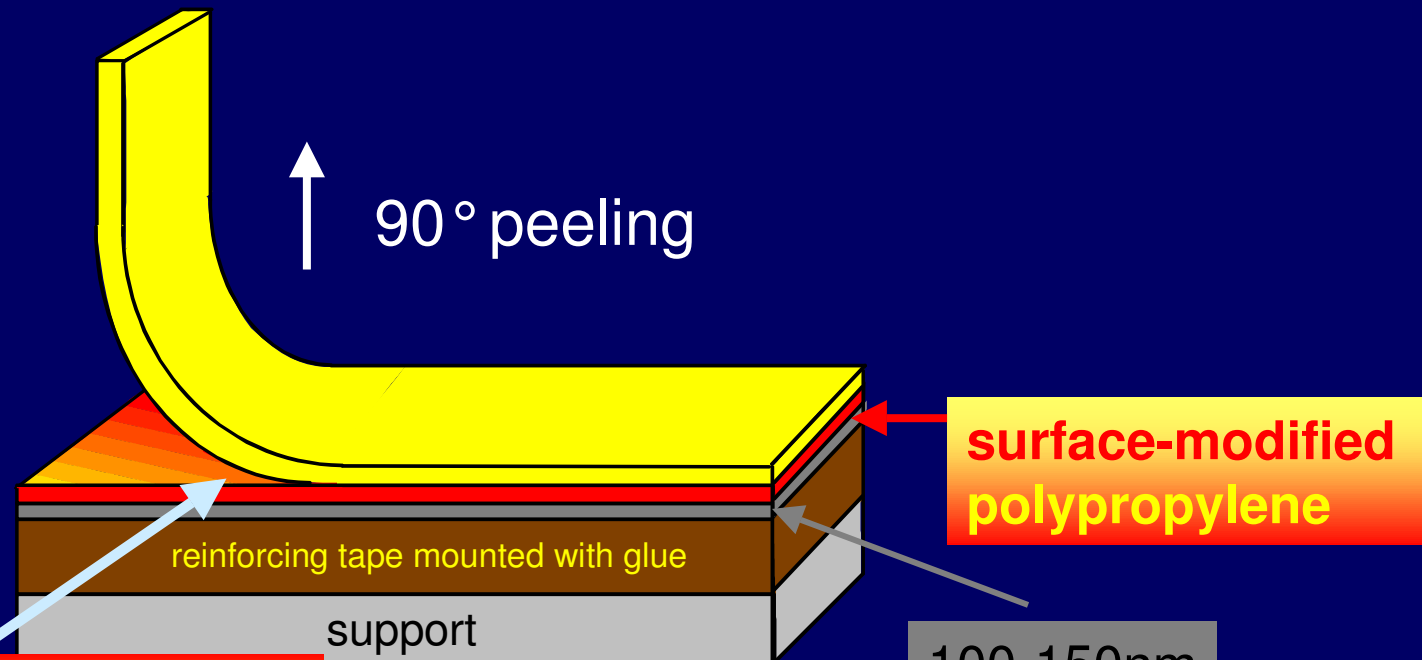


ex-situ metallization of
adhesion-promoting plasma polymer layers

Experimental

Measuring of metal peel strength deposited onto functionalized polymer surfaces

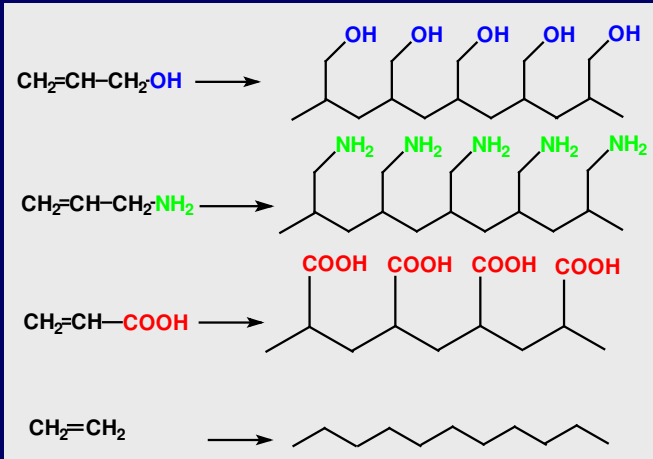
Specimen for measuring the adhesion between Al and PP



Peeling zone
Where does the break occur?
– locus of failure?

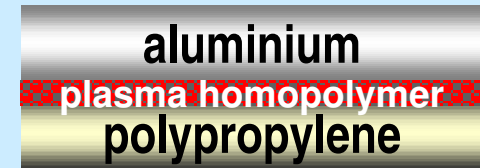
Adhesion-promoting pulsed plasma polymers

Homopolymers

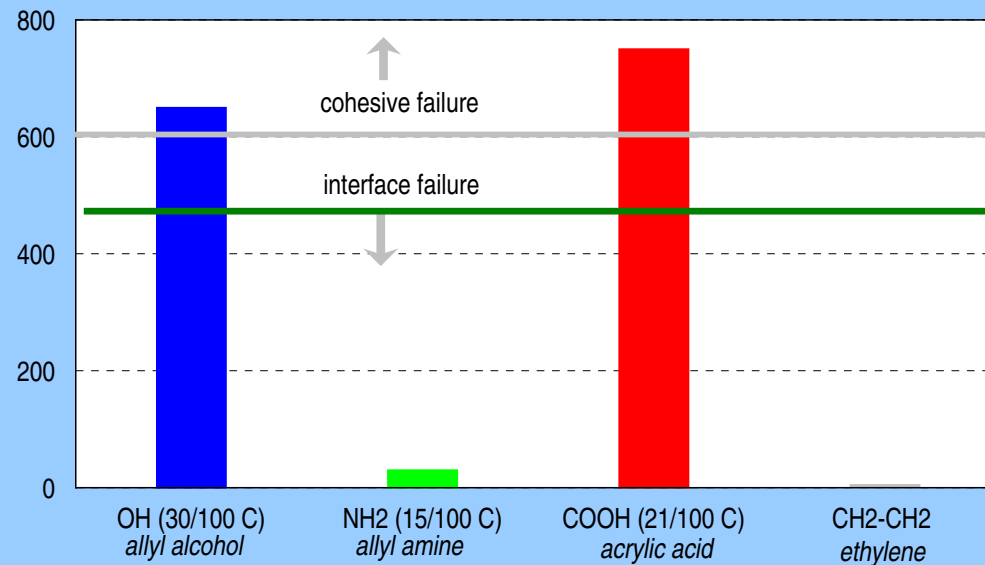


Pulsed plasma-initiated
(radical)
homo-polymerization of
functional groups-carrying
monomers

Al-polymer composite



Al peel strength [N/m]



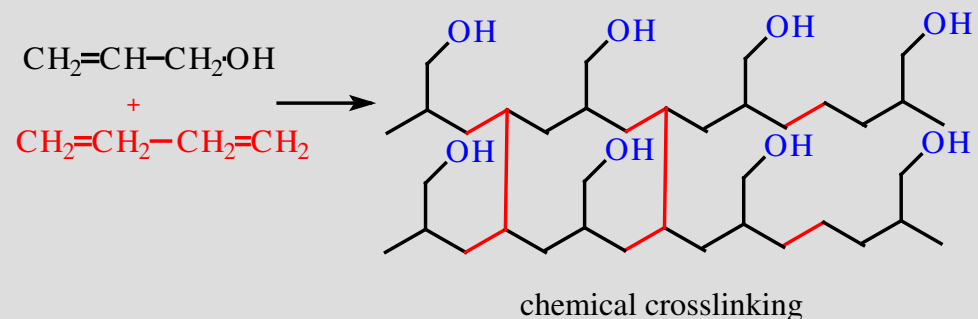
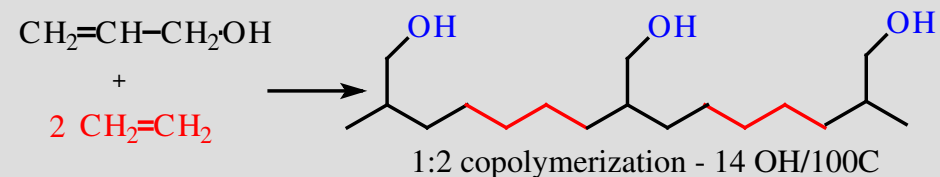
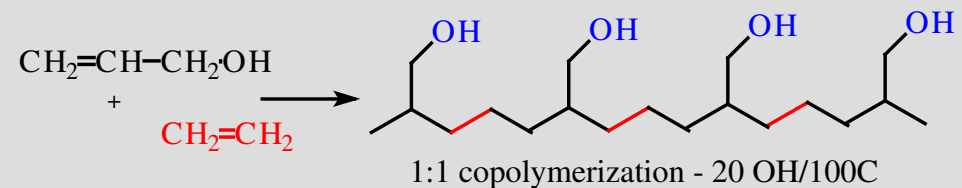
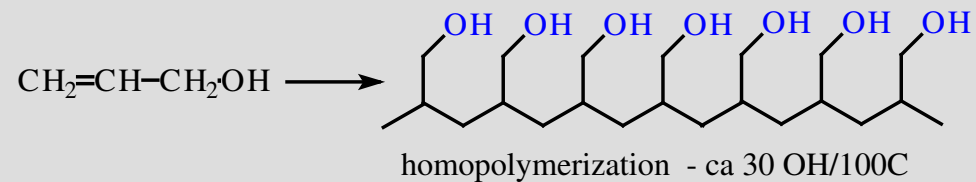
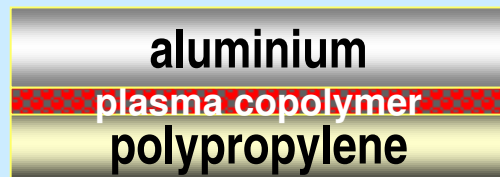
Level of
unspecific
O₂ plasma
pretreatment

Adhesion-promoting pulsed plasma polymers

Copolymers

Pulsed plasma-initiated (radical) copolymerization of functional groups-carrying and „chain-extending“ comonomers

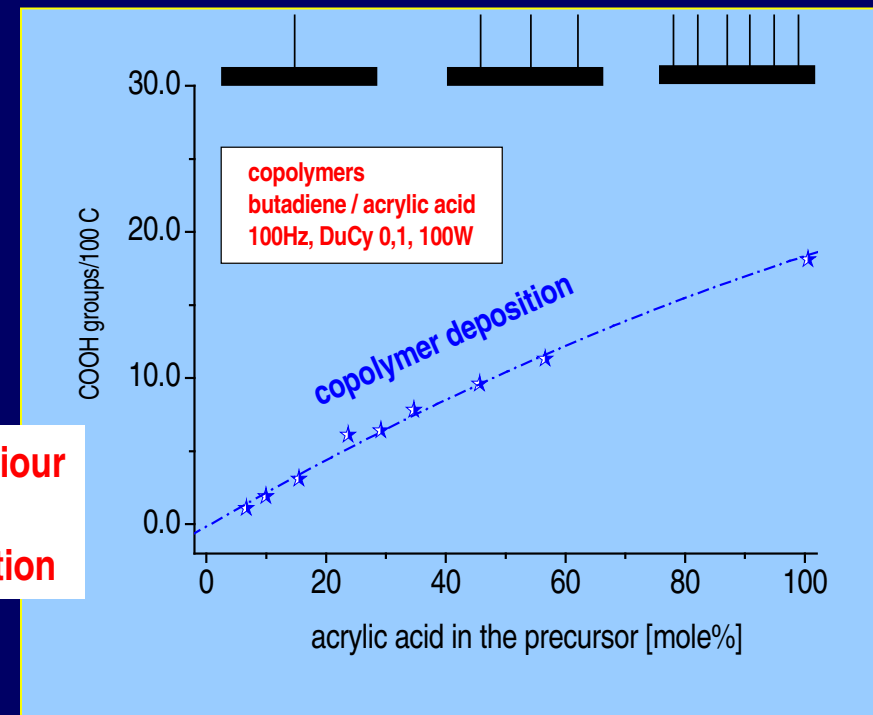
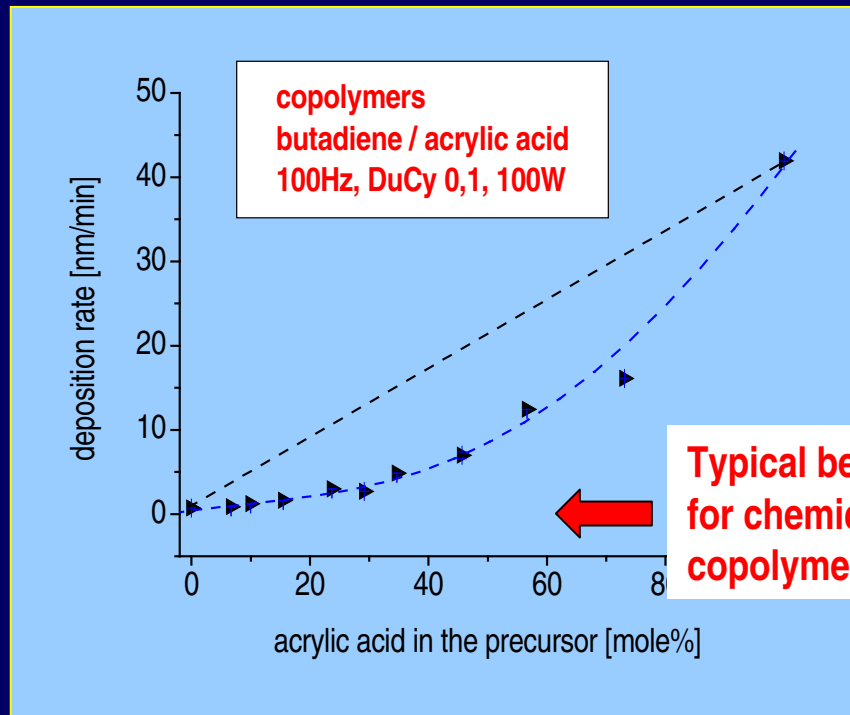
Al-polymer composite



Adhesion-promoting pulsed plasma polymers

Copolymers with COOH groups

Plasma-induced radical copolymerization of butadiene and acrylic acid



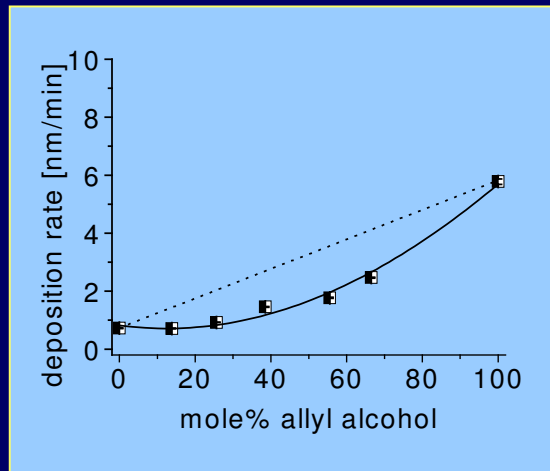
Deposition rate vs.
composition of precursor

Concentration of COOH vs.
composition of precursor

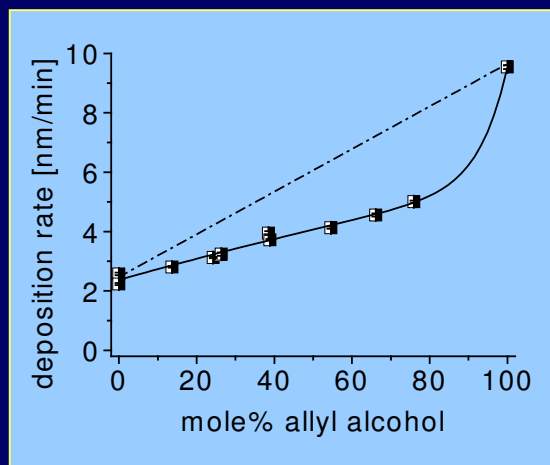
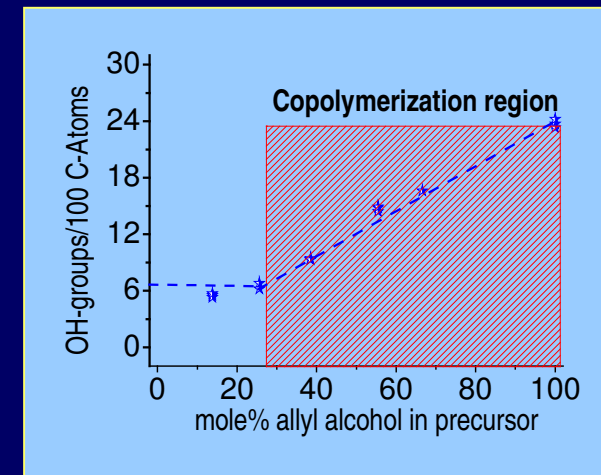
Adhesion-promoting pulsed plasma polymers

Copolymers with OH groups

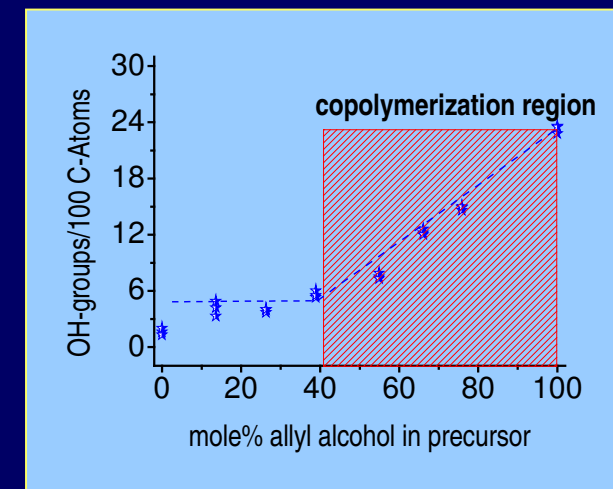
Plasma-induced radical copolymerization of allyl alcohol / butadiene



Allyl alcohol / butadiene
1000Hz, DuCy 0,1, 100W



Allyl alcohol / butadiene
1000Hz, DuCy 0,1, 300W



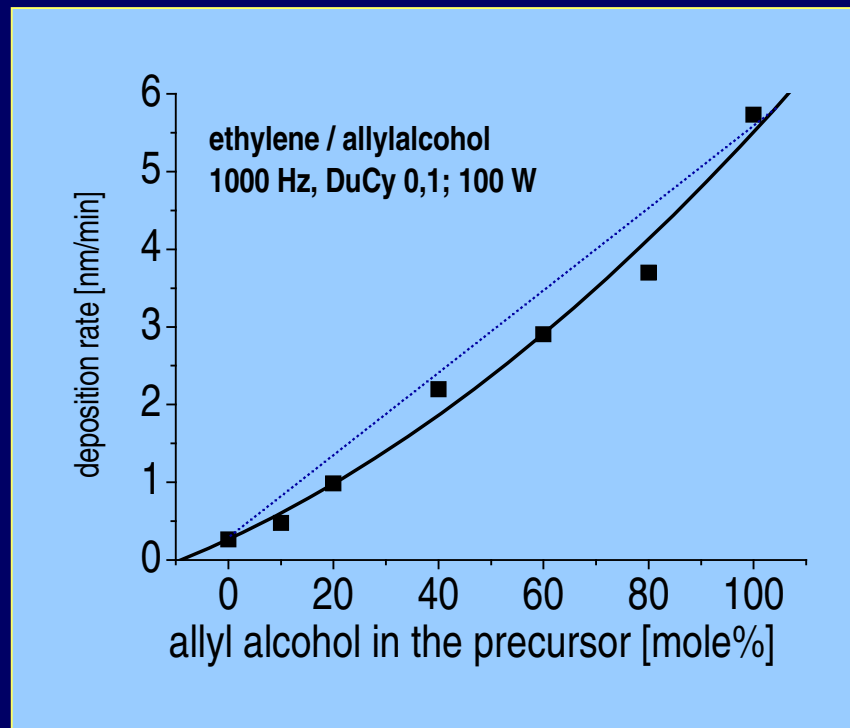
Deposition rate vs. composition
of precursor quartz microbalance

Concentration of OH vs.
composition of precursor XPS 12

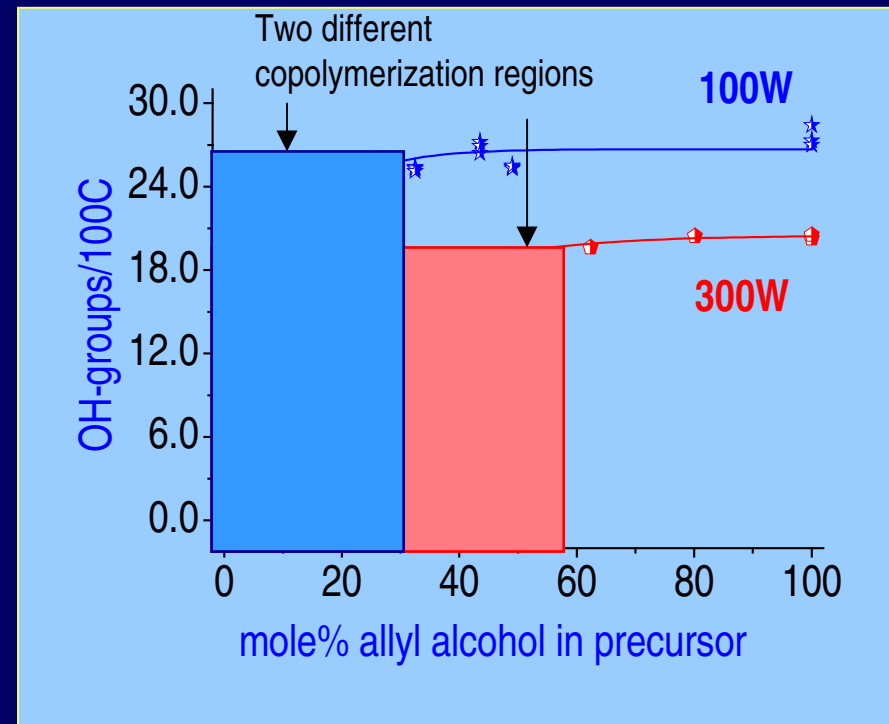
Adhesion-promoting pulsed plasma polymers

Copolymers with OH groups

Plasma-induced radical copolymerization of allyl alcohol / ethylene



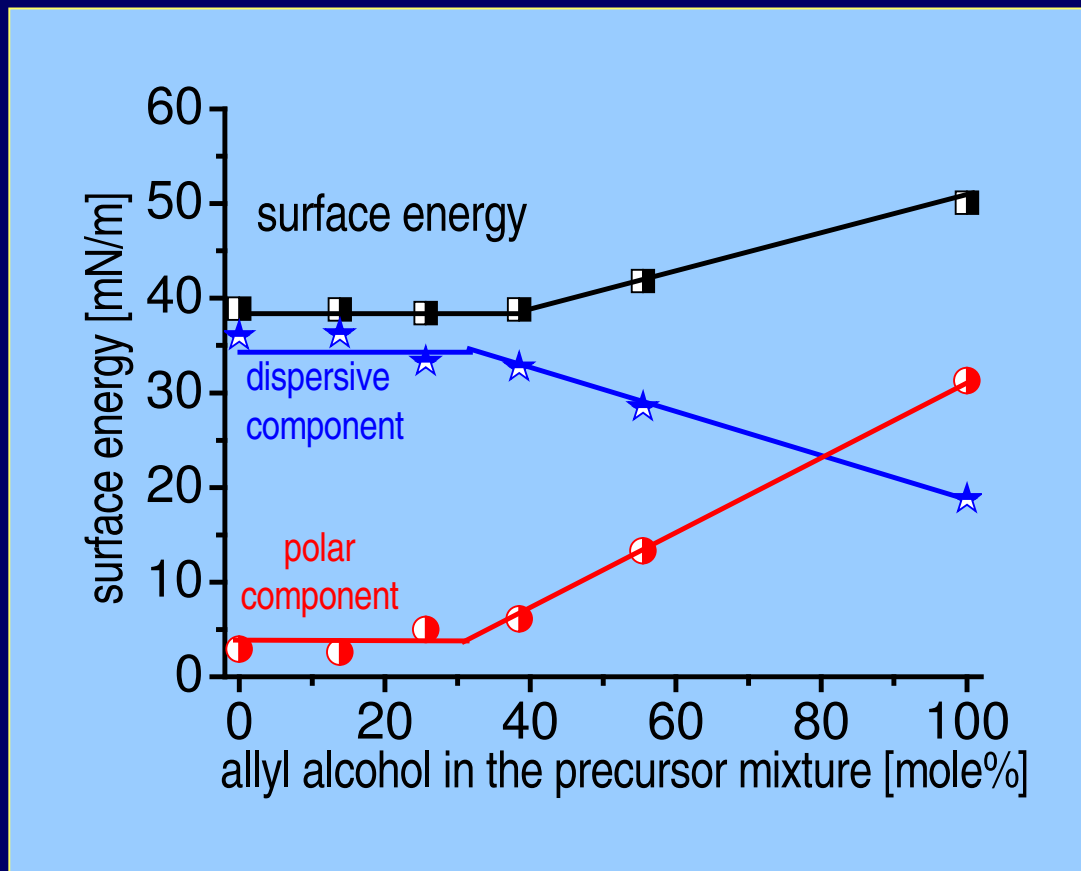
Deposition rate vs. composition of precursor quartz microbalance



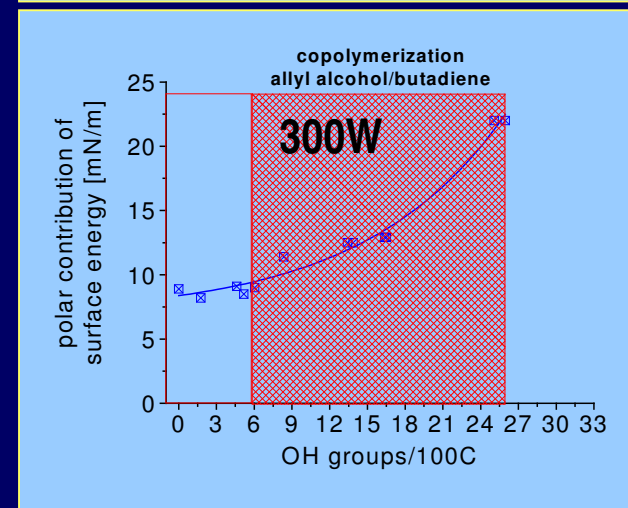
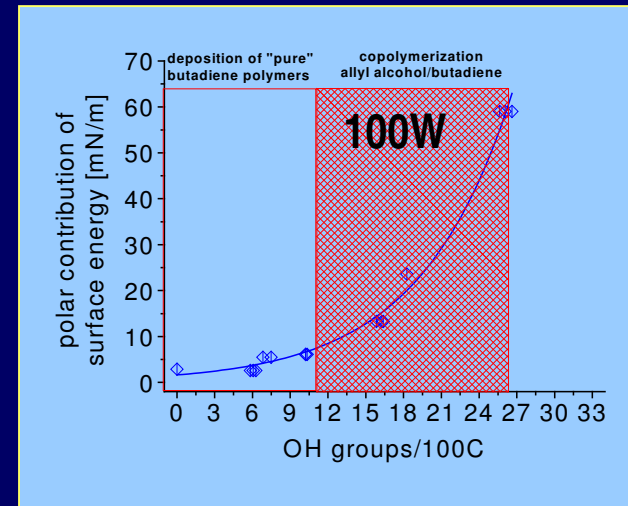
Concentration of OH vs. composition of precursor XPS

Adhesion-promoting pulsed plasma polymers

Surface energy of OH functionalized layers



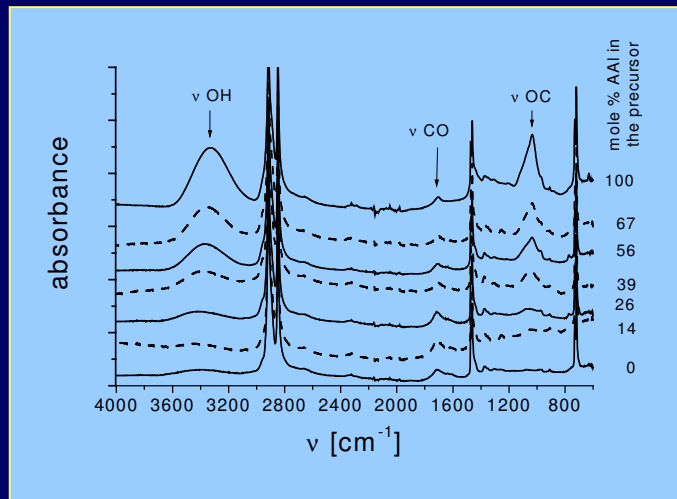
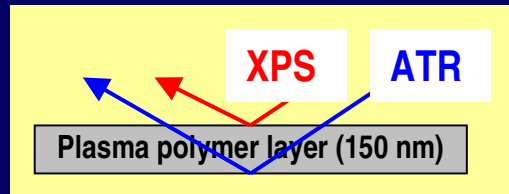
Surface energy, dispersive and polar component of allyl alcohol-butadiene copolymers (100W) vs. composition of the precursor mixture



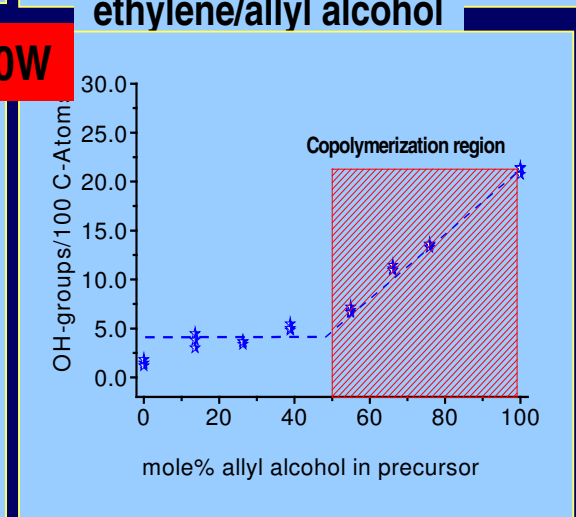
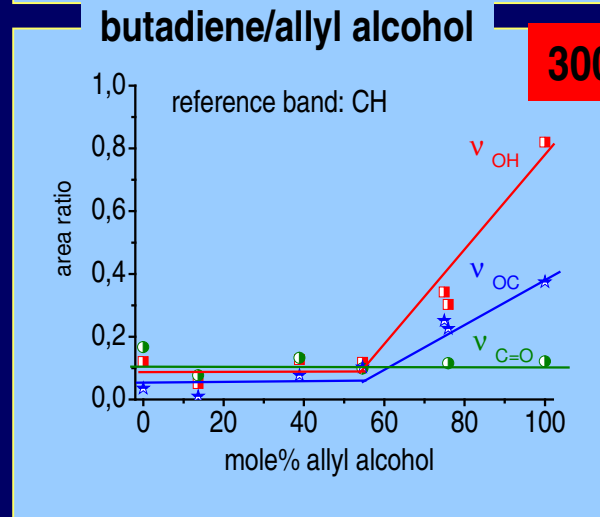
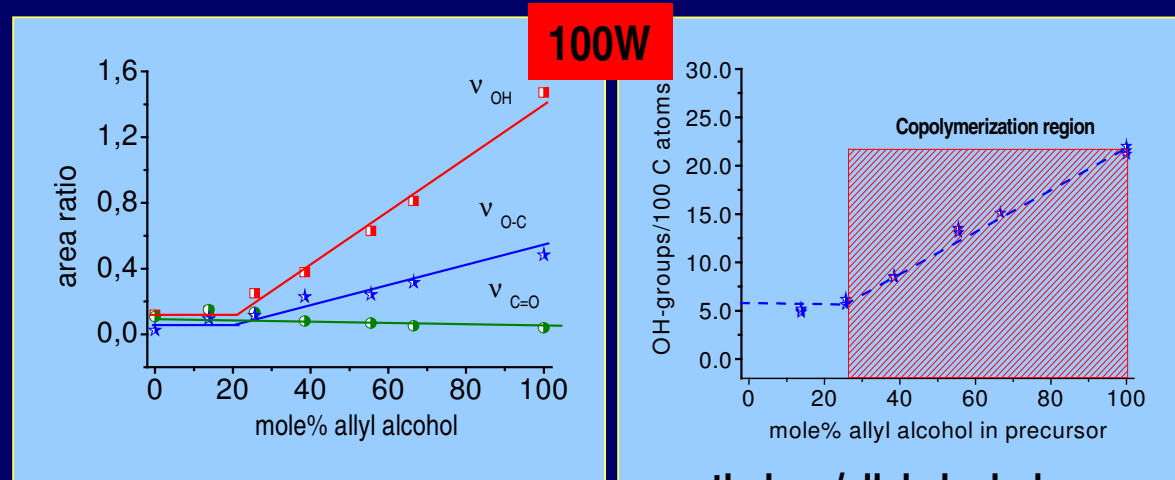
Polar component of allyl alcohol /butadiene vs. concentration of OH groups

Adhesion-promoting pulsed plasma polymers

FTIR of OH functionalized layers

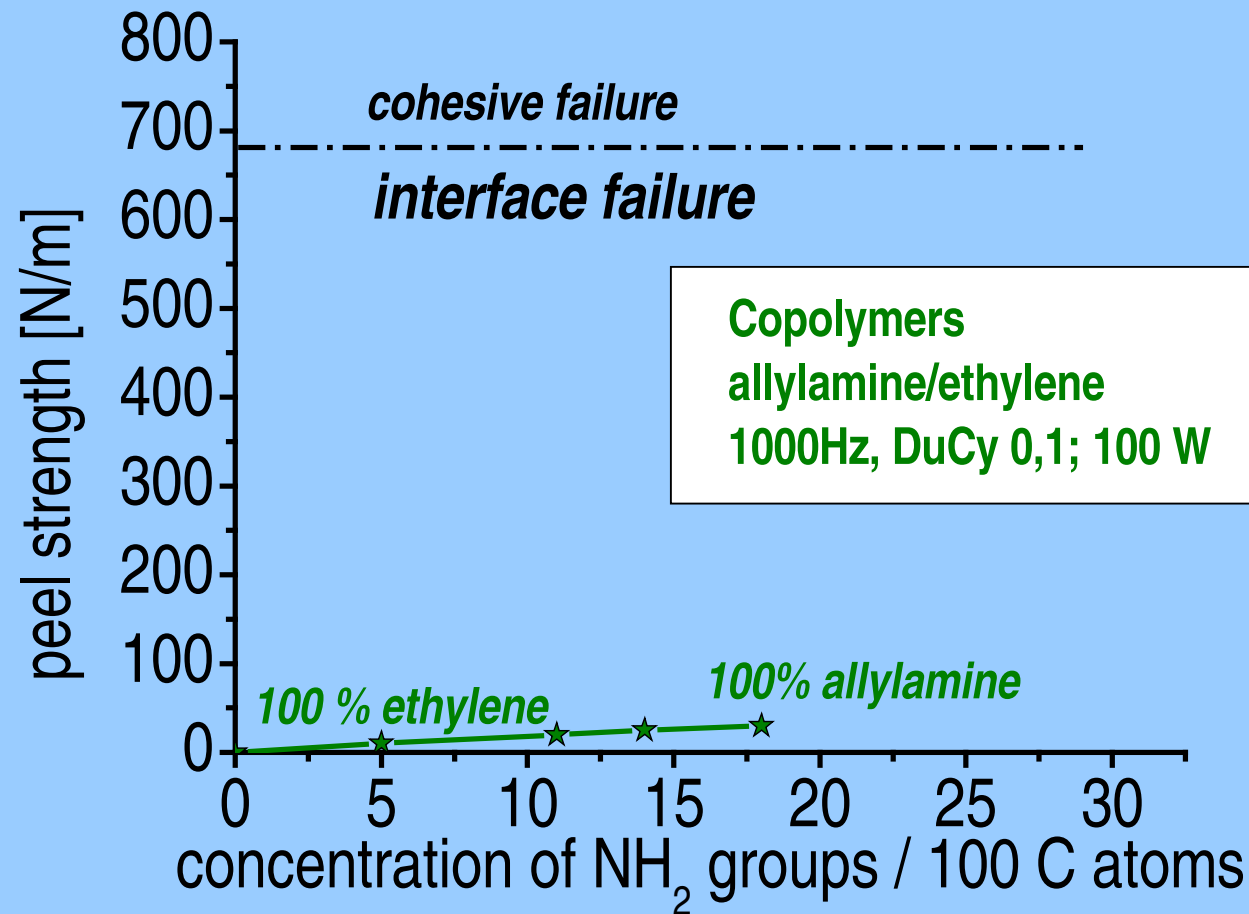


FTIR spectra of copolymers allyl alcohol / butadiene (100W) on PE in dependence on the composition of the precursor mixture



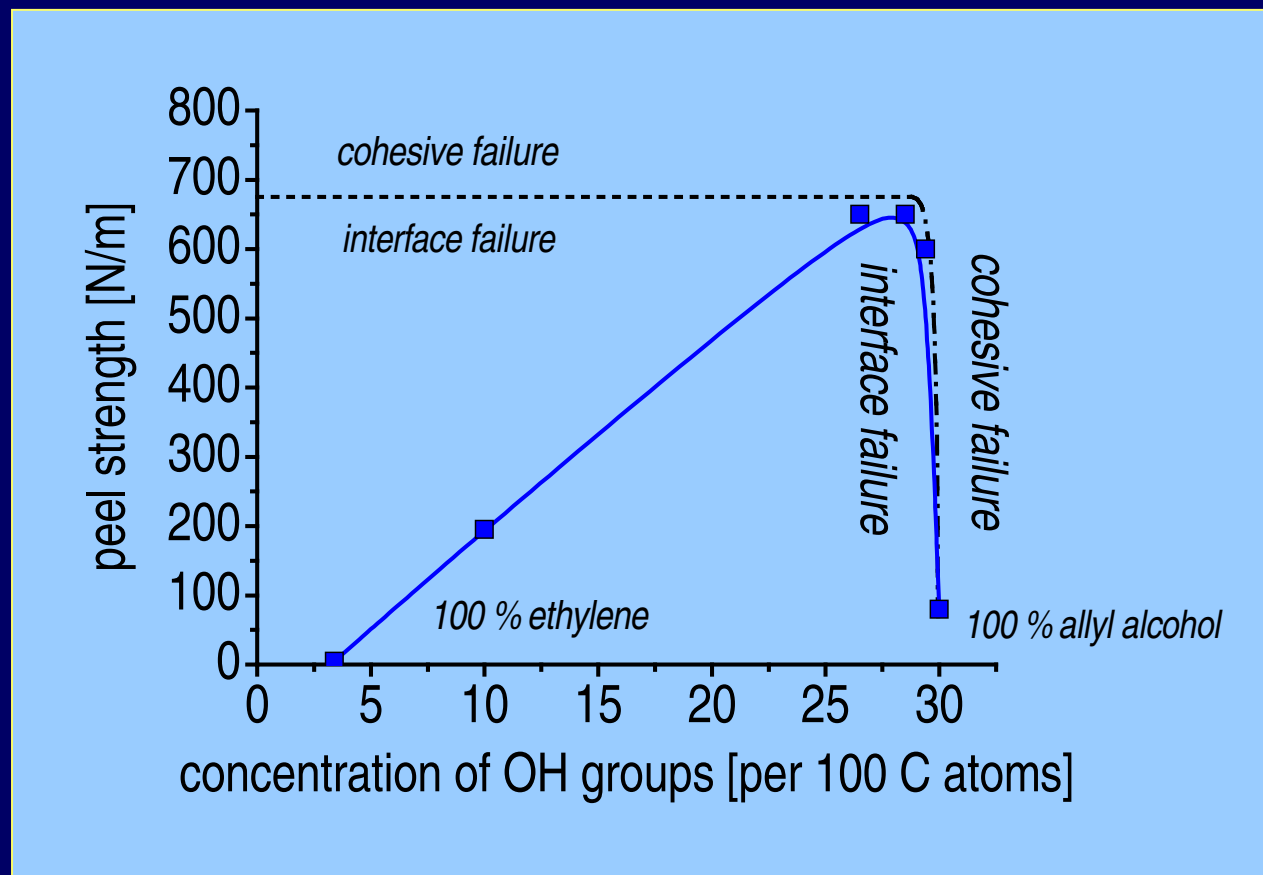
Comparison of XPS and IR results of the yield in OH groups in dependence on the composition of the precursor mixture

Metal peel strength of Al-PP composites using NH_2 groups- carrying adhesion-promoting plasma polymers



Metal peel strength of Al-PP composites using OH groups-carrying adhesion-promoting plasma polymers

Copolymers
ethylene / allyl alcohol
1000Hz, DuCy 0,1, 100W



Metal peel strength of Al-PP composites

Analysis of peeled Al and polymer surfaces

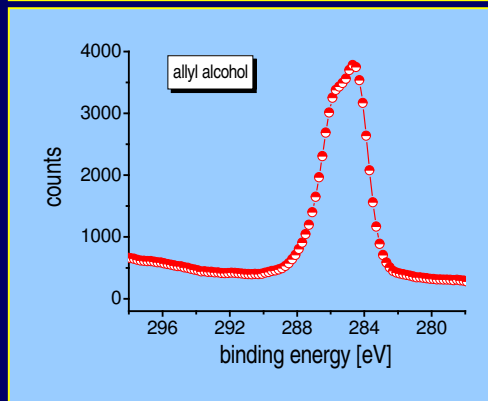
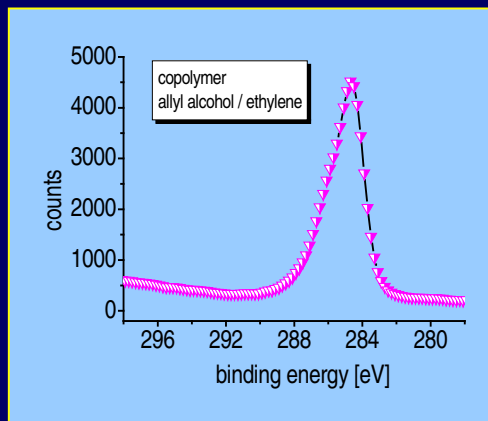
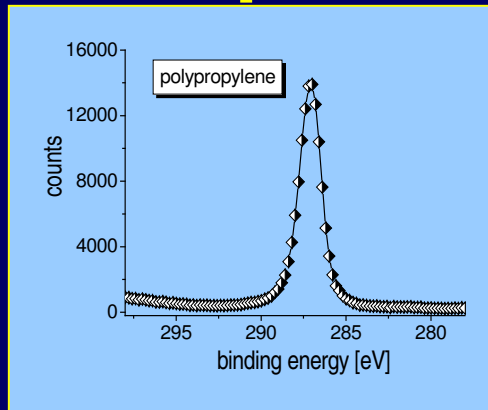
OH groups

XPS

C1s signals of propylene,

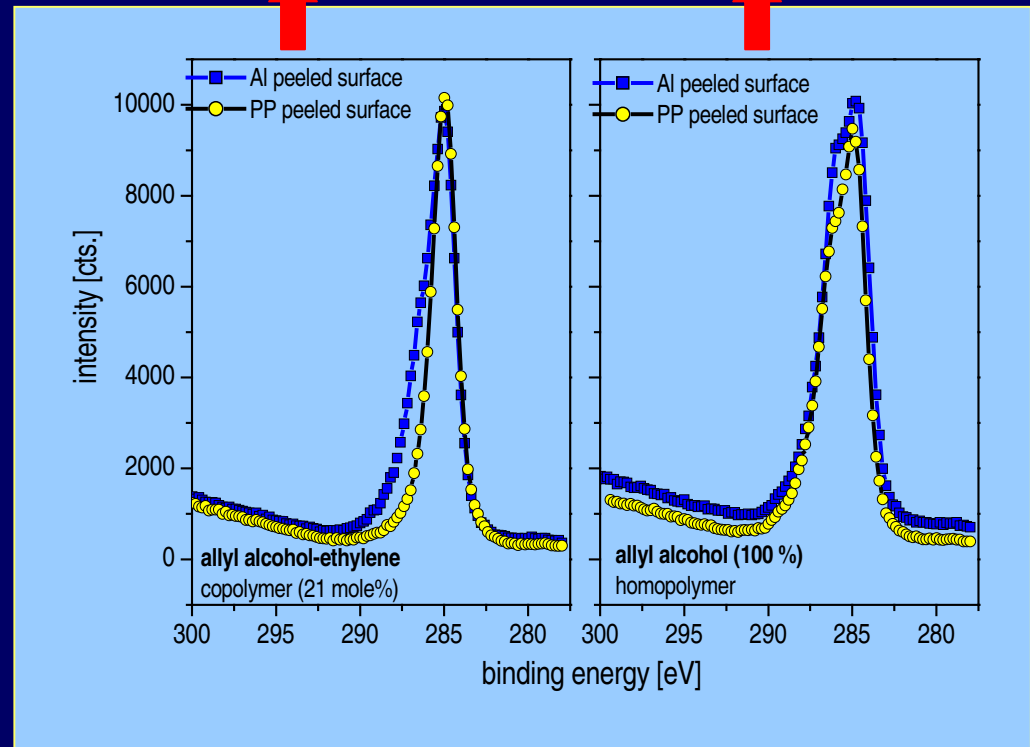
copolymer allyl alcohol/ ethylene (21 mole% allyl alcohol)

allyl alcohol homopolymer



Conclusion: peeling at PP-OH interface

Conclusion: peeling within plasma polymer

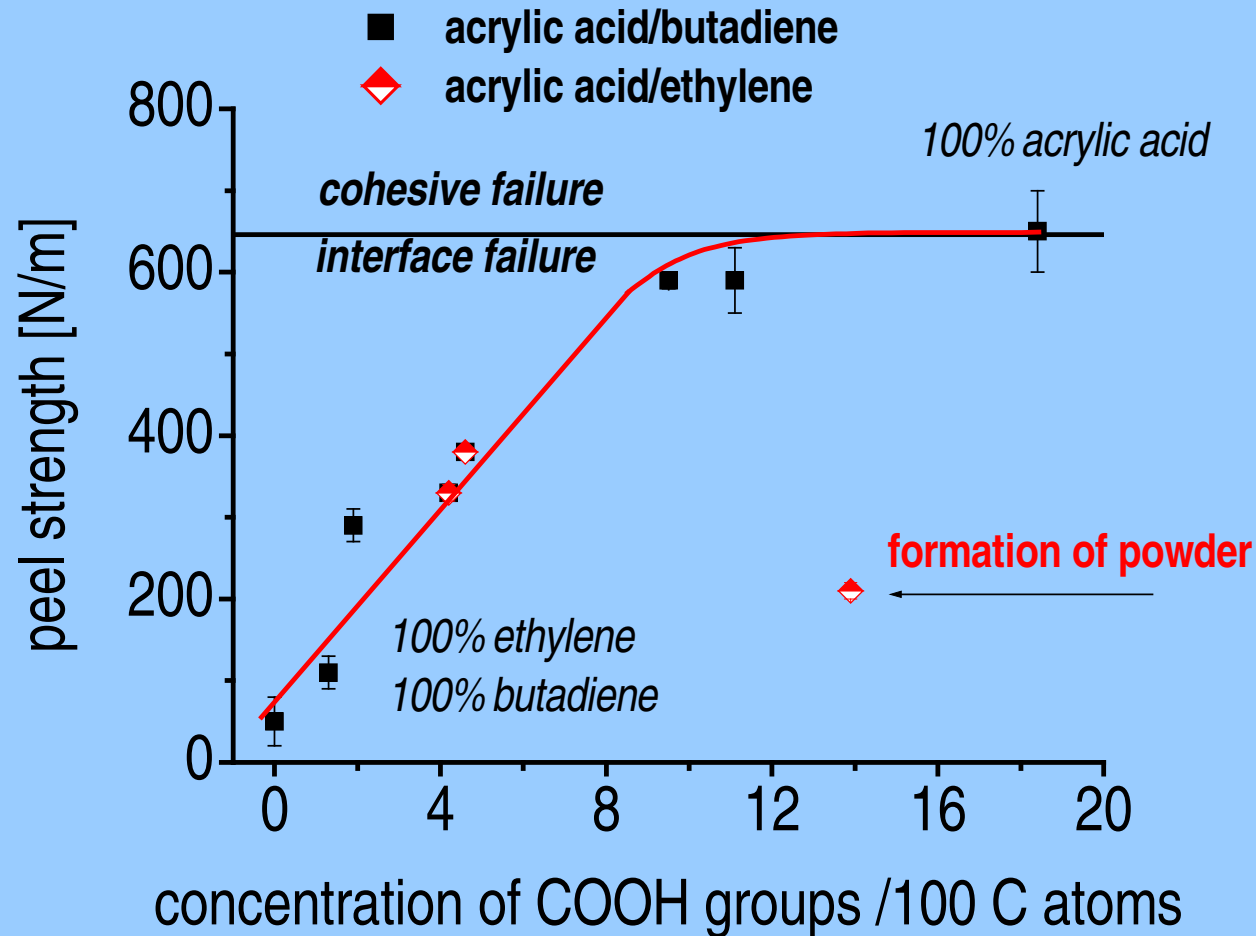


XPS-C1s signals of peeled surfaces

Al-copolymer-PP composite

Al-allyl alcohol-PP composite

Metal peel strength of Al-PP composites using COOH groups-carrying adhesion-promoting plasma polymers

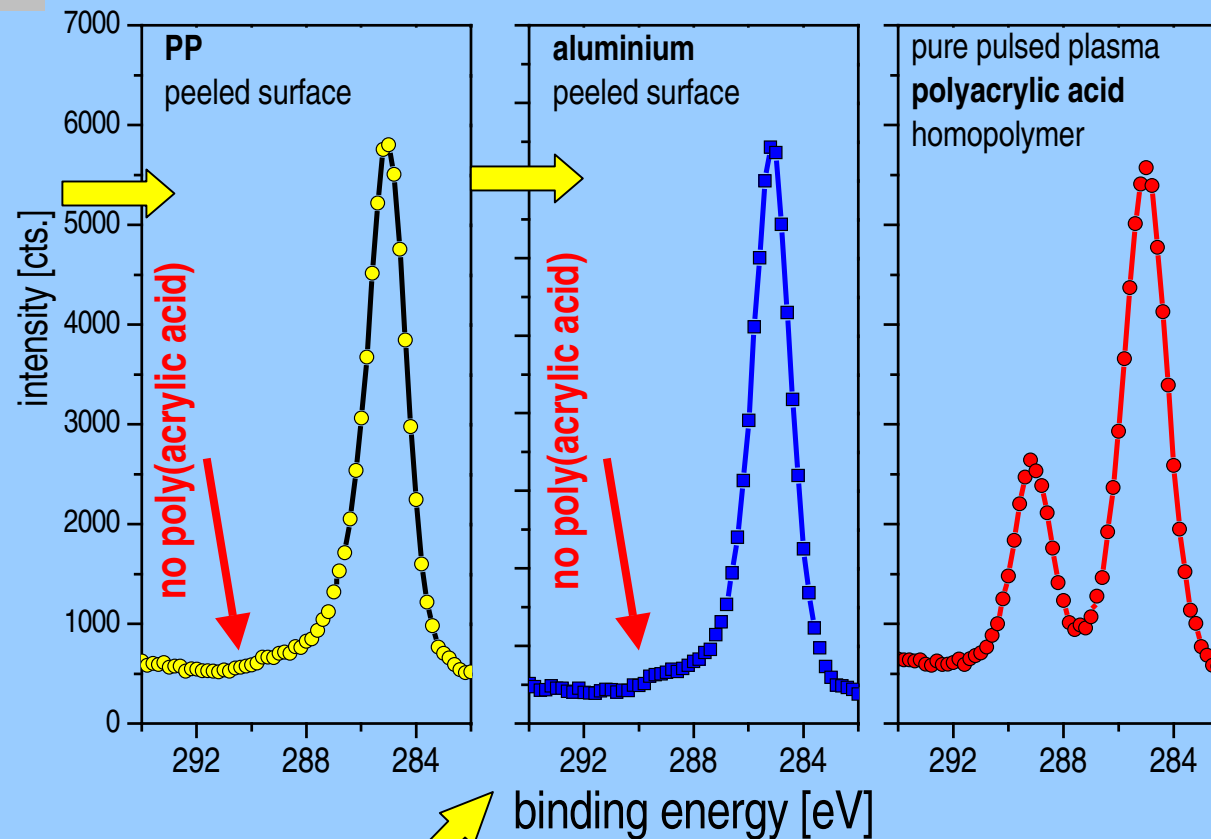


Metal peel strength of Al-PP composites

Analysis of peeled Al and polymer surfaces

COOH groups

XPS
C1s signals
of the peeled
surfaces of an
aluminium-
acrylic acid
homopolymer-
polypropylene
composite



XPS
C1s signal
of the
acrylic acid
homopolymer

Conclusion:
peeling within the PP substrate

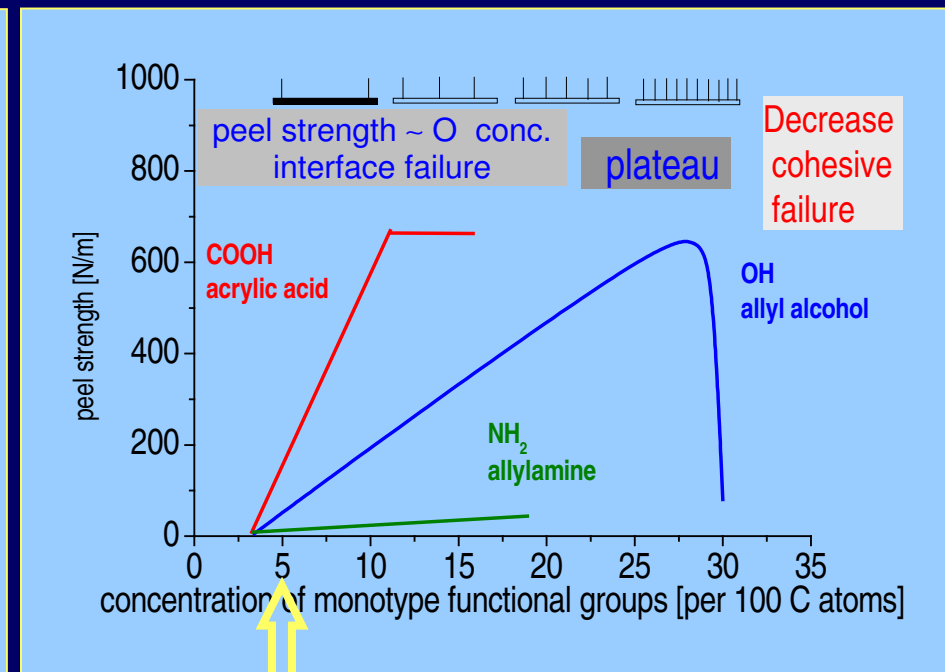
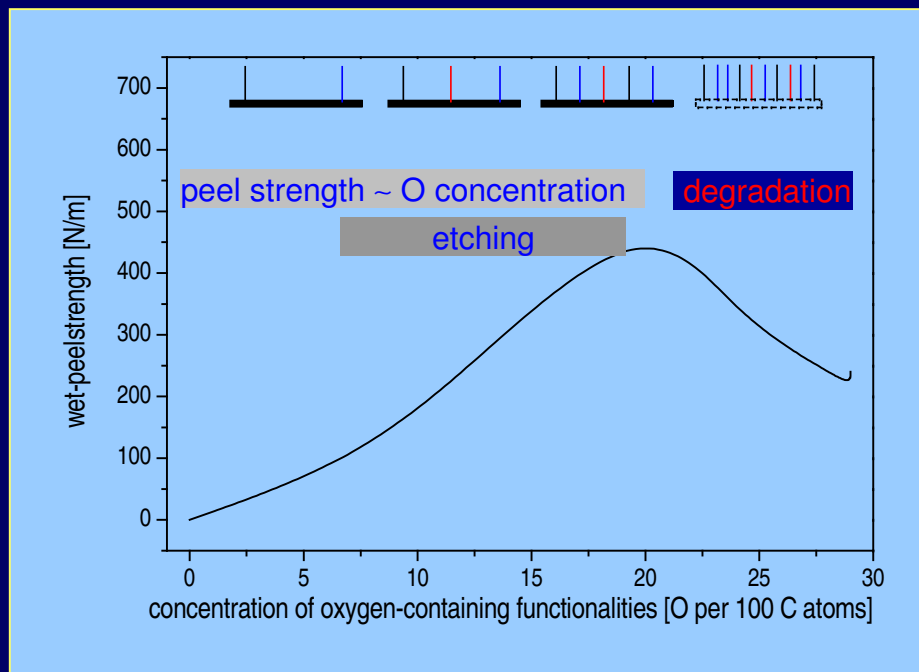
XPS-C1s signals of the peeled Al surface of
an Al-acrylic acid homopolymer-PP composite

Metal peel strength of Al-PP composites

Scheme

unspecific functionalization
of polymer surfaces

monotype functionalization by
deposition of adhesion-promoting
interlayers



Different slopes ~ bond strengths

Metal peel strength of Al-PP composites

Adhesion-promoting effect of monotype functional groups towards Al deposits



Interactions:

no

very weak

alcoholates

salts

Contribution of one
functional group per
100C atoms to peel strength

1-2 N/ NH₂

20-22N/OH

~60-65N/COOH

Summary

- The formation of **pulsed plasma** polymers of allyl and also acrylic monomers is dominated by the **plasma-initiated (plasma-on) gas-phase radical polymerization (plasma-off)**. This method offers the possibility to produce monotype functionalized adhesion-promoting interlayers.
 - Pulsed plasma polymerized allyl alcohol, allylamine and acrylic acid showed a degree of retained functional groups of **55-90% as: 30 OH, 18 NH₂ and 24 COOH per 100 C atoms**
 - In the same way a plasma-initiated radical **copolymerisation** could be realized. The density of the functional groups was differing significantly from “plasma copolymerisation” by simple mixing of monomers.
-
- Composites of polypropylene coated with a 150 nm thick plasma polymer layer fitted with OH, NH₂ or COOH groups and then evaporated with Al show different peel strengths:
COOH groups give the **highest peel strength**, followed by **OH groups**.
NH₂ and CH₂-CH₂ groups were without any adhesion- promoting effect as assumed.
 - The **limit of the peel strength increase** is reached when one component of the complete metall-polymer composite is going to change to a **weak boundary layer**.
In the case of **allyl alcohol** copolymers this seems to be the pure allyl alcohol layer, which has only a small cohesive strength, in the case of COOH groups this is the polypropylene layer itself.