1
Polymer Surface Modification with Monofunctional Groups of Different Type and Density

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Abstract

The retention of chemical structure and functional groups during pulsed-plasma polymerisation was used for producing adhesion-promoting plasma polymer layers with high concentrations of exclusively one sort of functional groups such as OH, NH_2, or COOH. The maximum content of functional groups was 31 OH using allyl alcohol, 18 NH_2 using allylamine, or 24 COOH groups per 100 C atoms using acrylic acid. To vary the density of functional groups a chemical copolymerisation with ethylene as "chain-extending" comonomer or butadiene as "chemical crosslinker" was initiated in the pulsed plasma.

The composition of these copolymers was investigated by XPS and IR spectroscopy. The concentration of functionalities was measured by XPS after attaching fluorine-containing derivatives. These labelling reactions were audited with reference substances and different markers. A set of plasma parameters was found to be a compromise between a high number of functional groups and complete dissolubility in water, ethanol or THF as needed for further chemical processing. Here, these monotype functionalised polymers are used in metal-polymer composites as an adhesion-promoting interlayer to examine the influence of type and density of functional groups on the adhesion.

1.1
Introduction

The aim of this work was to produce plasmachemically monotype functionalized polymer surfaces as models for the investigation of the influence of each type of metal-functionality interactions to the adhesion (Fig. 1). Moreover, the density of monosort functionalization with different types of functional groups (OH, NH_2 and COOH) should be varied to study the influence of the concentration of metal-functional group anchoring points (Fig. 2). Three ways to produce monotype functionalized polymer surfaces were investigated, the O_2-plasma treatment with subsequent wet-chemical reduction (vitride-Na-complex, B_2H_6, $LiAlH_4$) of the majority of O functional groups to OH groups (process 1, Fig. 3), the pulsed-plasma polymeriza-

tion of functional groups carrying monomers under retention of their functionalities (process 2, Fig. 3) and, in the same way as the pulsed-plasma polymerization, the plasma-initiated (chemical) copolymerization for varying the concentration of monotype functional groups (process 3, Fig. 3). In this work processes 2 and 3 were investigated, whereas process 1 was studied previously [1].
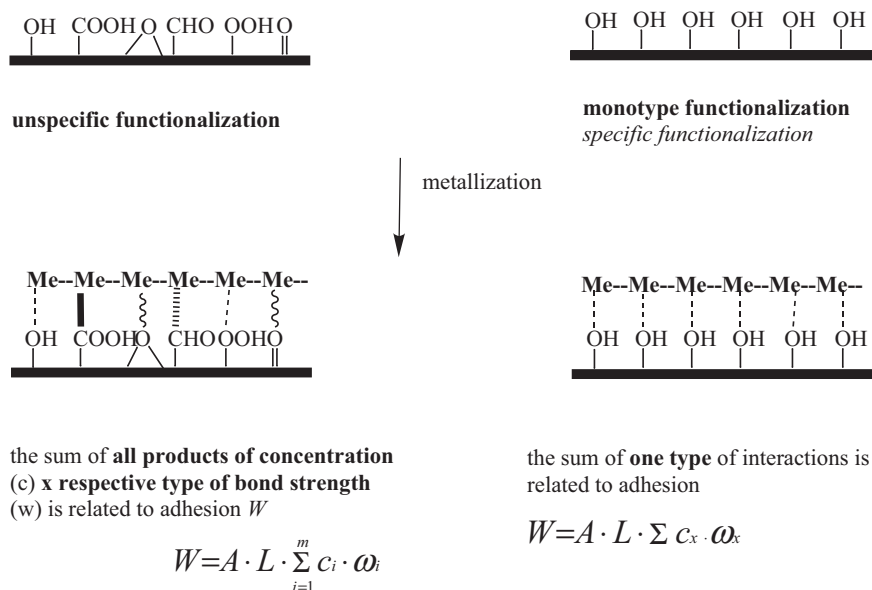

Figure 1 Scheme of unspecific and monotype surface functionalization of polymers. Attached a tentative model of summation of each type of metal-functionality interactions resulting in the global adhesion (W-adhesion, A-area, L-Loschmidt/Avogadro constant, c-concentration, ω-binding energy).

the sum of **all products of concentration** (c) **x respective type of bond strength** (w) 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

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

The general concept for the plasma polymerization was to approximate the structure of plasma polymers to that of classic polymers as much as possible. Therefore, low power input to the plasma, substrate and growing plasma polymer layer seems to be necessary because the average energy input per monomer molecule has to be <0.01 eV for a classic (pure chemical) radical polymerization. Thus, the constant energy flux in continuous wave (cw) plasma is too high. Pulsed plasma with long off-time offers an alternative and possibly a tool to initiate pure chemical chain propagations (Fig. 4).

Using chemically reactive monomers, which are qualified to undergo a classic radical chain propagation only one activation incident with ≈1.5 eV is required to start a chain polymerization with a resulting molar mass of about 100 000 and the respective polymerization degree of $X \approx 1000$. Therefore, 0.0015 eV per monomer are needed to initiate and propagate a chemical polymerization (Fig. 5). The advantage of a chemically produced polymer compared to a plasmachemically synthesized material is the defined structure, the exact stoichiometry, often the presence of a su-
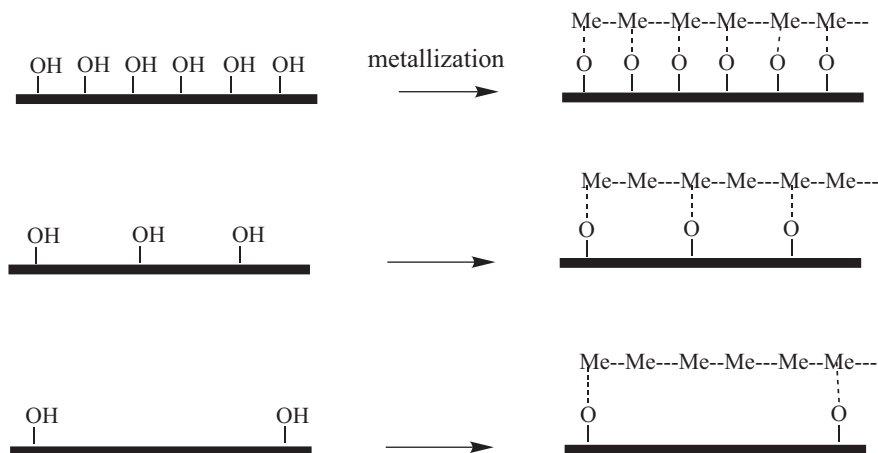
Figure 2 Schematic presentation of adhesion in dependence
on concentration of metal-functional groups anchoring points.

permolecular structure (crystallinity), the defined properties and the significantly
better ageing stability. Thus, we intend to exclusively initiate such a chemical poly-
merization through the plasma but the chain propagation should be performed on a
pure chemical way. Monomers with active double bonds as vinyl or acrylic groups or
moderately qualified allyl groups and dienes are a precondition of such a chemical
chain propagation. Using nonclassic monomers and the cw mode only a nonchemi-
cal formation of low-quality polymer layers is possible. Examples for nonqualified
monomers are alkanes (hexane), aromatic, cyclic, etc., monomers.

In practice, the low pressure and, therefore, the low sticking rate of monomers
with a radical site of a growing macromolecular chain limit the chain propagation.
Such termination reactions are radical recombination, chain transfer and dispropor-
tionation.. Therefore, the use of pulsed plasma is necessary to reinitiate the chain
propagation. Short plasma pulses (0.01 to 1 ms) activate the monomer molecules
and the surface of the growing polymer layer. During the plasma-off period reactive
monomer molecules strike the radical sites at the polymer surface, graft and thus
form the growing macromolecular chain. The chain propagation is a pure chemical
process. Using typical pulse conditions as 0.1 ms plasma-on and 1 ms plasma-off
the very reactive monomer styrene forms a polymer layer during every pulse that is
thinner than <0.1-monolayer styrene. Comparing the deposition rates of cw r.f.
plasma and pulsed r.f. plasma a difference of 1:2000 was found if the deposition
rates were referenced to the same plasma-on durations. This difference in deposi-
tion rates demonstrates the dominant role of the chemical chain propagation using
the pulsed plasma. Obviously the plasma polymerization in the cw plasma mode
can be characterized as a process of only a slight preponderance of the deposition in
comparison to the simultaneous plasma etching/sputtering of the growing polymer
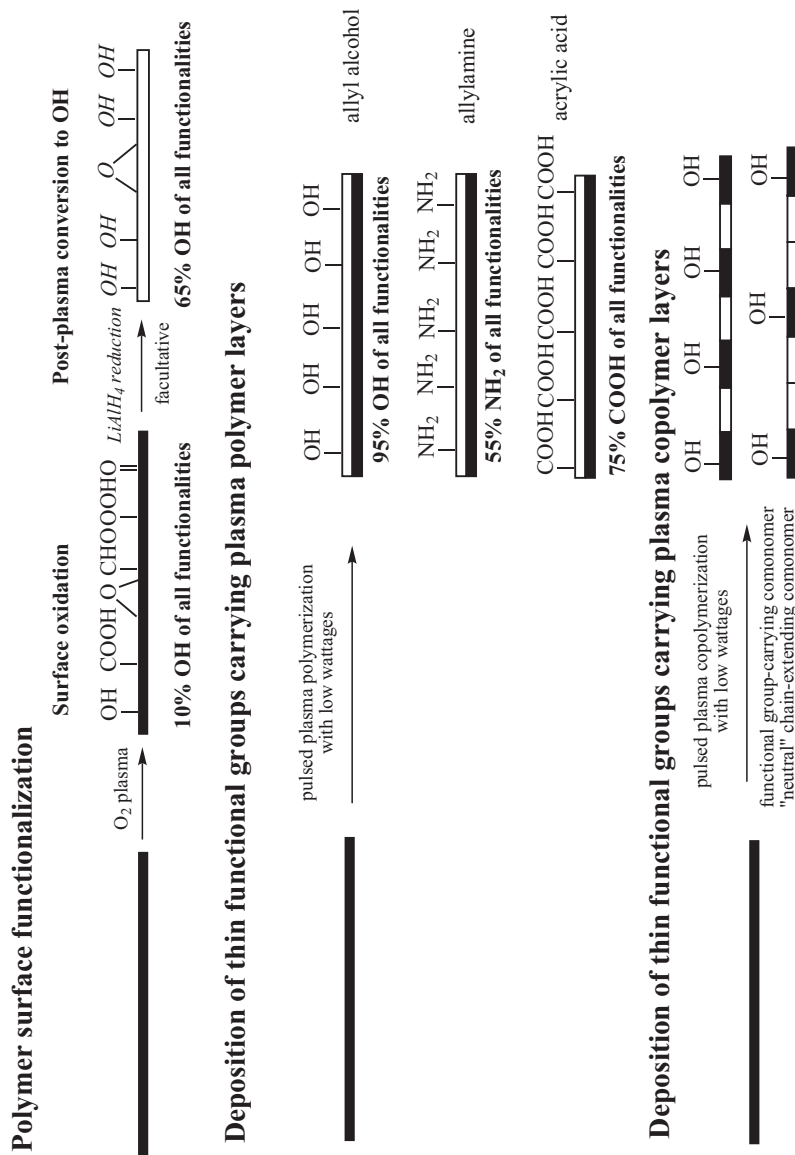layer.

Polymer surface functionalization

Surface oxidation

Post-plasma conversion to OH

O_2 plasma

OH   COOH   O   CHOOOHO   *LiAlH₄ reduction*   OH   OH   OH   O   OH   OH

facultative

10% OH of all functionalities

65% OH of all functionalities

Deposition of thin functional groups carrying plasma polymer layers

pulsed plasma polymerization
with low wattages

OH   OH   OH   OH
95% OH of all functionalities

allyl alcohol

NH₂   NH₂   NH₂   NH₂   NH₂
55% NH₂ of all functionalities

allylamine

COOH COOH COOH   COOH COOH
75% COOH of all functionalities

acrylic acid

Deposition of thin functional groups carrying plasma copolymer layers

pulsed plasma copolymerization
with low wattages

functional group-carrying comonomer
"neutral" chain-extending comonomer

OH   OH   OH   OH   OH

OH   OH   OH

OH   OH

Figure 3 General ways to produce monotype functionalised polymer surface with different types and variable concentration of functional groups using the plasma and chemical techniques. Selectivity is given in per cent of all measured functional groups.
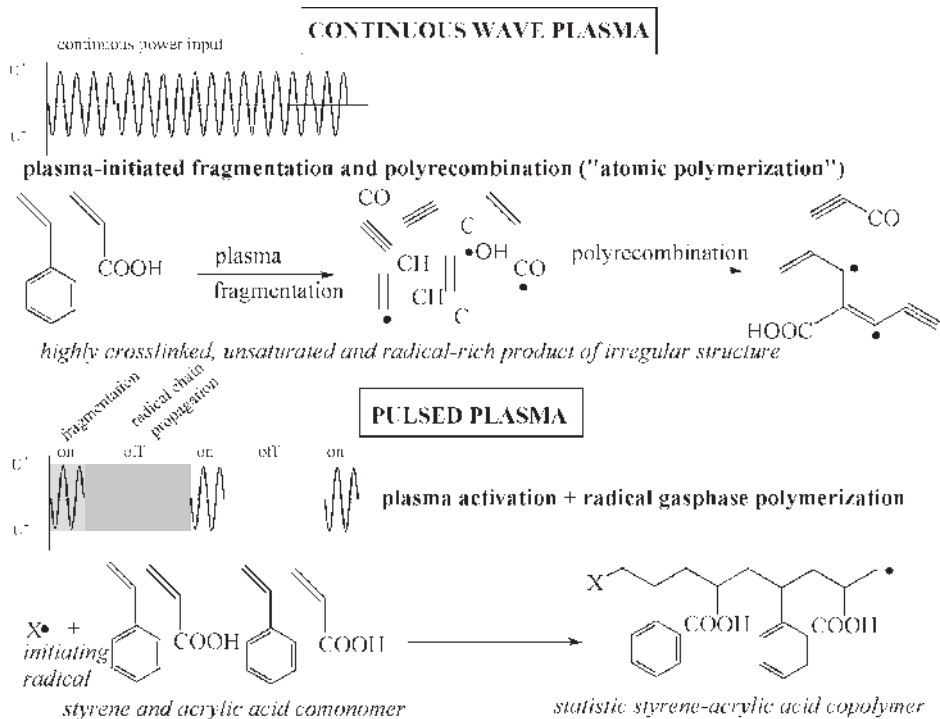
Figure 4 Principle of continuous-wave and pulsed plasmas and the expected structures of resulting plasma polymers.
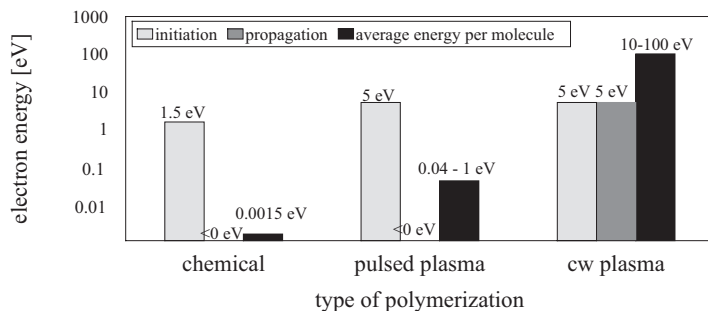

Figure 5 Comparison of energies needed for the initiation of a radical polymerization and the average kinetic energies available in different modes of low-pressure glow-discharge plasmas (pulsed plasma and cw = continuous-wave plasma; without consideration of plasma UV, self-bias, etc.).

The structure of polymer sequences formed in the plasma-off period should correspond to those of classic polymers. However, the more degrees of freedom for adsorbing molecules in the low-pressure gas phase compared to polymerizations in the liquid phase should hinder all types of supermolecular structure or tacticity. Only amorphous and atactic polymers are anticipated. Nevertheless, such structures are also chemically defined. However, these defined structures and compositions are strongly disturbed by every new plasma pulse due to the UV irradiation and particle bombardment. In addition, no hints for a significant contribution of ion–molecule reactions to the polymer formation were identified on analyzing the polymer structure. The monomers used are all qualified for a radical and not for ionic polymerizations in the gas phase.

In 1971, Westwood [2] found that the plasma polymers possess a chemically better defined structure and composition using low power input, however, unfortunately, thus-produced polymers are also characterized by inclusions of oligomers and monomers within the partially crosslinked polymer matrix. Tibbitt et al. [3] proposed an actual model of such a plasma polymer. Pulsed low-power plasma helps to avoid the excessive monomer fragmentation in the plasma phase and reduces the number of plasma-induced damages in the polymers. This opens the way for enhancing the pure chemical radical polymerization in the gas phase or adsorption layer. Pulsed-plasma polymerization was introduced first by Tiller in 1972 [4], later continued by Yasuda [5,6], Shen and Bell [7,8], and then further developed by Timmons [9,10] and our group [11–14].

The copolymerisation in pulsed plasmas was designed as a plasma-initiated (chemical) radical chain propagation reaction preferentially in the plasma-off period [13,14]. This kind of copolymerisation is strictly different from those introduced by Schüler or Yasuda [15,16]. They simply mixed two gases or monomers without any consideration of their chemical reactivities. Using the cw plasma, which fragments all monomer molecules and allows their random recombination as nondefined plasma polymers, the reactivity of comonomers does not play any role. However, the more the chemical reactions dominate the more important the chemical copolymerisation ability of comonomers becomes. In polymer chemistry this behavior is expressed in terms of copolymerisation parameters (coefficients) r_a and r_b for free-radical copolymerizations to linear, branched or crosslinked copolymers [17]. For $r_i = r_a$ and $r_i = r_b$ two of five cases are important: $r_i = 1$ both comonomers add to any active center with equal probability if $[A] = [B]$ and $r_i = ($ only homopolymerization occurs, no copolymerization. Hence, the pairs of comonomers must be accurately compiled to avoid homopolymerization. An example for a genuine classic copolymerisation is that of styrene and methylmethacrylate with $r_s = 0.52$ and $r_m = 0.46$. Vinyl, acrylic, allyl and diene comonomers are generally suited for plasma copolymerization. In Fig. 6 examples of co- and homopolymerization and also chemical crosslinking in the pulsed plasma are shown.
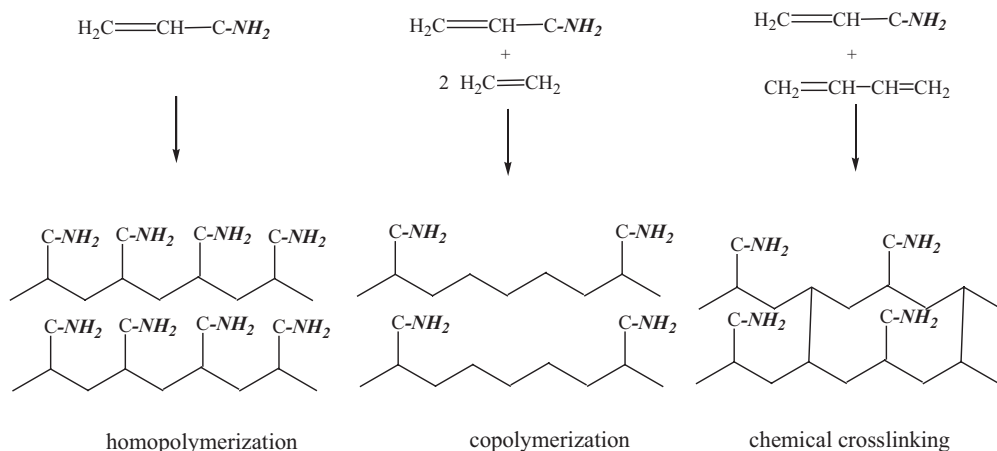
$$H_2C = CH - C\text{-}NH_2$$

$$H_2C = CH - C\text{-}NH_2$$
$$+$$
$$2 \ H_2C = CH_2$$

$$H_2C = CH - C\text{-}NH_2$$
$$+$$
$$CH_2 = CH - CH = CH_2$$

C-*NH₂*   C-*NH₂*   C-*NH₂*   C-*NH₂*

C-*NH₂*   C-*NH₂*

C-*NH₂*   C-*NH₂*

C-*NH₂*   C-*NH₂*   C-*NH₂*   C-*NH₂*

C-*NH₂*   C-*NH₂*

C-*NH₂*   C-*NH₂*

homopolymerization   copolymerization   chemical crosslinking

Figure 6 Schematics on the formation of functional group
carrying homo and copolymers as well as chemically crosslinked
copolymers.

1.2
Experimental

Plasma polymerisations were carried out in a vacuum system with a base pressure
of 10^{-3} Pa or lower. The principal design of the plasma reactor was described earlier
[12,13]. The r.f. power was varied from 50 to 300 W, the duty cycle from 0.05 to 1 and
the pressure was 25 Pa. The samples are kept under floating potential. The XPS data
acquisition was performed with a SAGE 150 Spectrometer (Specs, Berlin, Germany)
using nonmonochromatized MgK_α or AlK_α radiation with 12.5 kV and 250 W set-
tings at a pressure $\approx 10^{-7}$ Pa in the analysis chamber. This instrument is equipped
with a plasma reactor separated by a gate valve from the UHV system, where surface
treatments can be carried out at a pressure of 10^1–10^{-7} Pa. XPS spectra were
acquired in the constant analyser energy (CAE) mode at 90° take-off angle. Peak
analysis was performed using the peak fit routine from Specs. The FTIR spectra
were recorded with a NEXUS instrument (Nicolet, USA) using the ATR technique
(attenuated total reflectance) with a diamond cell ("Golden Gate", Specac, Kent,
UK). Contact-angle measurements were performed in the sessile drop mode using
water, formamide, ethylene glycol, benzyl alcohol and diiodomethane as test liquids.
The equipment consists of a G2 goniometer and the appropriate software (Kruess,
Hamburg, Germany). The derivatization of OH groups was performed using tri-
fluoroacetic anhydride (TFAA) or m-trifluoromethylphenylisocyanate (TMPI), that
of NH_2 by applying pentafluorobenzaldehyde (PFBA) or 4-trifluoromethylbenzalde-
hyde (TFMBA) and that of COOH by exposure to trifluoroethanol (TFE) [1,11]. The
number of functional groups was calculated by considering the percentage of the
introduced fluorine (F1s peak) and the theoretical stoichiometry of the derivatized
polymer. It was supposed that the XPS analysed outermost layer ($\approx$ 3 nm) was

homogeneously derivatized. The completeness of the derivatization and the absence of nonconsumed functional groups in the deposited polymer layer were checked using ATR-FTIR spectroscopy. Further methods were the C1s peak fitting (CF$_3$, COOR) or the measuring of the concentrations of introduced oxygen (OH, COOH – O1s peak) or introduced nitrogen (NH$_2$ – N1s peak). The metal evaporation onto plasma-polymer-modified PP foils was performed in situ by using a plasma reactor equipped with two sources for thermal evaporation (Ilmplasma 1200, Saskia, Ilmenau, Germany). This technique was applied for analytical purposes. For measuring the peel strength the samples are transferred to a metallizer equipped with the electron beam technique (Edwards, UK). The 90° peeling technique of metal-PP composites follows DuPont's preparation and peeling procedure. It was described in detail elsewhere [18–20].

1.3
Results

1.3.1
Kinetics of the Deposition of Copolymers

In Fig. 7 the deposition rates of different copolymerized mixtures of allyl alcohol and allylamine with ethylene, styrene and butadiene are plotted as a function of the composition of the comonomer mixture. The deposition rates of these mixtures are shown to be not quite a linear combination of those of the comonomers as expected for comonomers with different copolymerisation coefficients.

The curve regressions (nonlinearity) are characteristic of chemical copolymerizations. However, they are not yet completely understood. Moreover, the type of substrate and therefore the possibility of dissipation of charges have an influence on the deposition characteristics. Attempts were made to interpret the deposition characteristics in terms of classic copolymer kinetics. Here, the Fineman and Ross approaches were applied [21]. For example, it could be shown that the copolymer formation of the allyl alcohol-butadiene copolymerisation can be linearized by applying these methods. Two linear dependencies are found for different compositions of the comonomer mixture corresponding to preferred homopolymerization (of butadiene) and preferred copolymerisation. The structure of copolymers is alternating if $r_a = r_b = 0$, which was assumed for the investigated copolymer systems.

1.3.2
Variation of the Density of Functional Groups

Ethylene and styrene as linear "chain extenders" and 1,3-butadiene as "chemical crosslinker" were copolymerized with allyl alcohol, allylamine or acrylic acid as carrier for OH, NH$_2$ or COOH groups. Thereby the composition of comonomer mixtures was systematically varied. Then the resulting number of OH, NH$_2$ or COOH groups in the copolymers was measured by applying the derivatization methods in
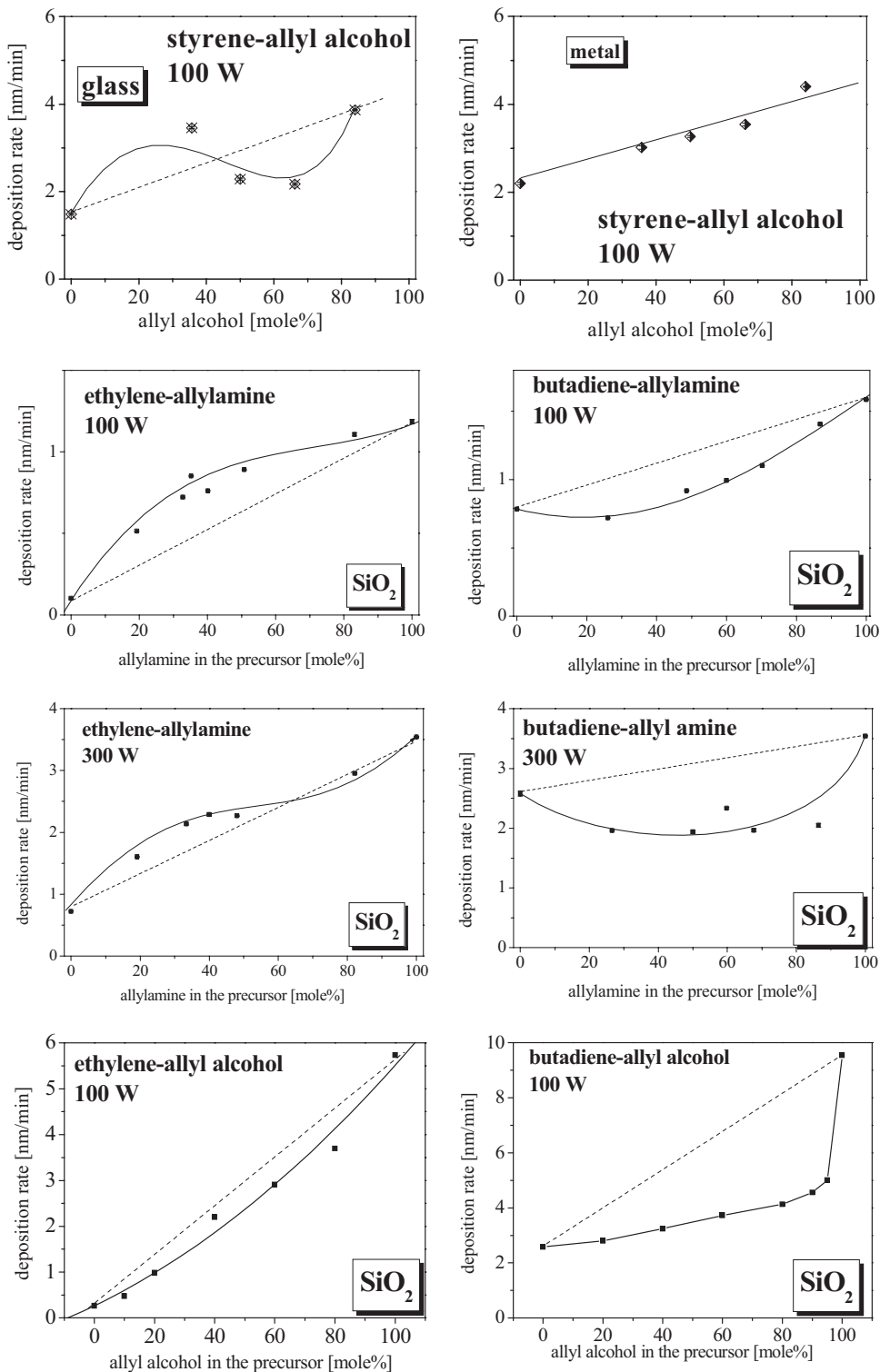
Figure 7 Different shapes of deposition rates vs. comonomer ratio on Si, glass or metal.

connection with the XPS and IR spectroscopy as described before. The structure of the copolymers is reflected in the respective C1s-XP spectra as shown for an ethylene-allyl alcohol copolymer (Fig. 8). The spectrum of the copolymer seems to be a linear superposition of the spectra of homopolymers.
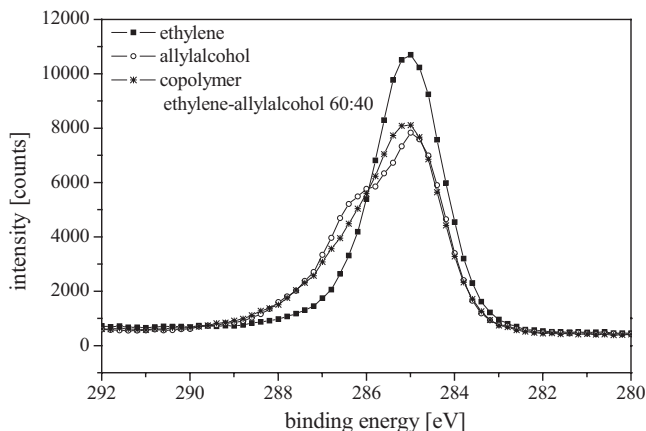

Figure 8 XPS-C1s peaks of an allyl alcohol and ethylene homopolymer and also of an allyl alcohol-ethylene copolymer.

To determine the extent of retained functional groups the copolymers were derivatized in the same manner as the homopolymers. Figure 9 shows a nearly linear correlation between the concentration of functional groups in the resulting copolymer and the composition of the comonomer mixture for the copolymerisation of acrylic acid-butadiene in the subsequent measurement of COOH groups as TFE derivatives. In Fig. 10 the number of OH groups of an ethylene-allyl alcohol copolymer, determined by derivatization with TFAA, is plotted. In the range of 60 to 100% allyl alcohol in the gas–vapor mixture of ethylene only homopolymerization of allyl alcohol can be observed. From 0 to 60% copolymerization occurs. This behavior can be observed for both the copolymerization at 100 W or 300 W. Using 300 W the maximum yield in OH groups is 23 per 100 C atoms whereas the maximum concentration is near 31 OH groups per 100 C atoms using 100 W. This can be interpreted as leaving the region of soft plasma power responsible for the preferred chemical chain propagation at polymer deposition and passing to the region of plasma parameters characteristic for the preferred fragmentation of monomers and the random recombination of fragments and atoms to irregular polymer structures. Therefore, the chemical structure of copolymers should change from a more chemically defined (100 W) to a more irregular one (300 W).

In contrast to the ethylene-allyl alcohol system the copolymerization of butadiene-allyl alcohol is dominant in the full range of allyl alcohol in the gas/vapor comonomer mixture as shown by the (nearly) linear increase in the number of OH groups with growing percentage of allyl alcohol (Fig. 10). Homopolymerization seems to be negligible. The maximum concentrations of OH groups were 29 OH groups per
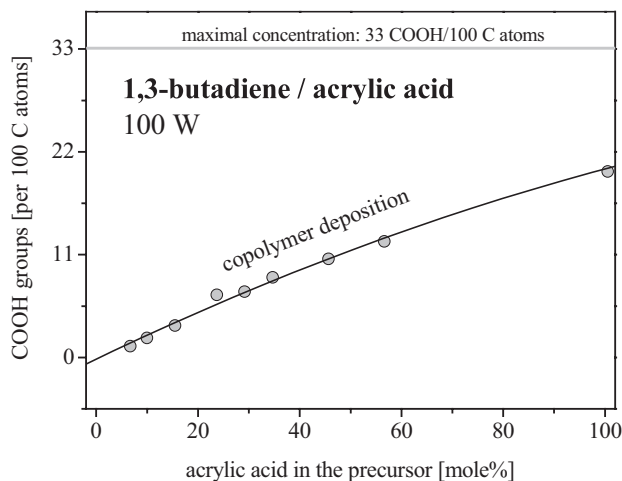
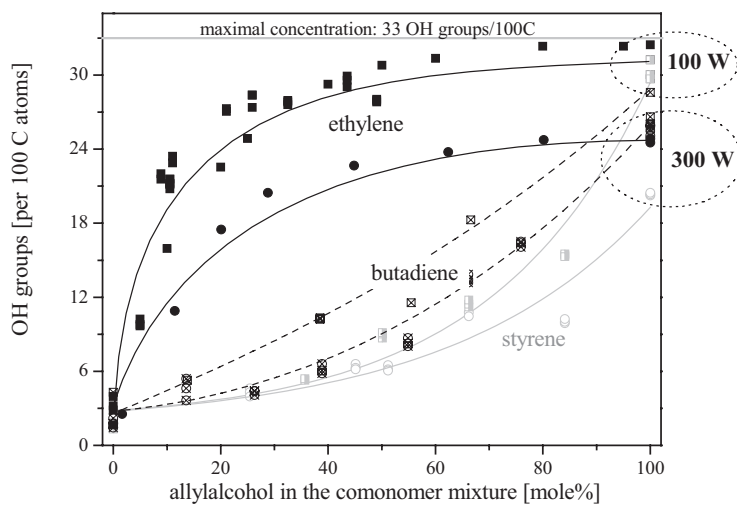**Figure 9** Yield in COOH groups at copolymerisation of acrylic acid with butadiene.

Figure 10 Yield in OH groups at copolymerisation of allyl alcohol with different comonomers.

100 C atoms using 100 W and 20 OH per 100 C atoms using 300 W. Copolymerization with styrene is dominated by its homopolymerization (0 to 50 mole% allyl alcohol, see Fig. 10).

IR spectroscopy of the ethylene-allyl alcohol copolymer confirmed roughly the results of XPS measurements using 100 W power input (Fig. 11). It should be mentioned that the recorded ATR signal collects the structural information of the complete layer (200 nm). With increasing allyl alcohol percentage the *[Blockade]*$_{OH}$ inten-

sity grows considerably in the range of 0 to 60 mole% allyl alcohol in the comonomer mixture. In the range of 60 to 100 mole% the absorbance of the [Blockade]OH signal remains constant. However, using 300 W power input, a linear dependence of the [Blockade]OH absorbance on the chemical composition of the gas/vapor mixture is observed (see Fig. 11). The absorbance of the $[Blockade]_{OH}$ signal (3350 cm^{-1}) was referenced to that of the neighbouring *[Blockade]*$_{as}$CH$_2$ vibrations at 2925 cm^{-1} used as internal standard.
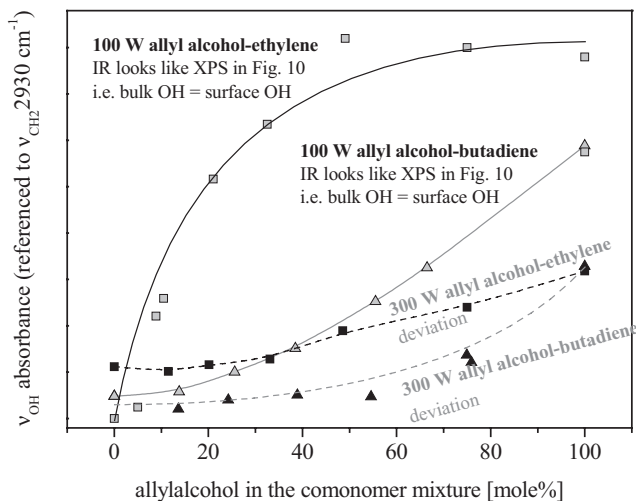
Figure 11   OH-stretching vibrations of copolymers of allyl alcohol and ethylene or butadiene.

1.3.3
Structure and Stability of Copolymers

Studies on structure and stability of pulsed plasma polymers were performed using styrene as the best-qualified (vinyl) monomer. It could be shown using FFF (field flow fractionation) that linear molecules with 20 000 Da molecular weight were synthesized. XPS and NEXAFS results corresponded completely to those of polystyrene standards [11–15]. However, deviations from classic composition and structure were found at the polymer backbone using FTIR spectroscopy. Here, branched structures were identified also using FFF (>10^8 Da). Functional groups carrying homopolymers from allyl and acrylic monomers were completely soluble, thus showing the absence of crosslinked structures. In particular, allyl alcohol was easily pulsed-plasma polymerised under retention of 95% of all OH groups introduced with the monomer allyl alcohol, e.g. 31 OH groups per 100 C atoms were detected after derivatization with trifluoroacetic anhydride. The OH layers were stable during long-time exposure (1 year) to air. COOH groups introduced by acrylic acid decomposed partially in the pulsed plasma giving a selectivity of about 75%. The resulting layers were stable during storage. Primary amino groups were difficult to retain dur-

ing the plasma-deposition process, since they further react at the nitrogen by forming secondary amines. Furthermore, they are also difficult to store since they are oxidized at the α-C atom in an auto-oxidation process resulting in an oxygen uptake up to 17 O per 100 C after 1 month exposure to air. The selectivity amounted to 55%. Copolymers show similar properties, however, they were fractionally insoluble or generally soluble. The retention of functional groups was the same as by homopolymerization. The number of functional groups could be continuously varied between 0 and the maximal number characteristic for the homopolymers.

1.3.4
Relation between Functional Groups of Copolymers and Surface Energy

The surface energy increased with higher percentage of allyl alcohol in the mixtures with ethylene or butadiene as comonomers. The pure ethylene homopolymer shows a surface energy of 36 mJ/m^2, which is slightly higher than that of conventional polyethylene (32 mJ/m^2 [22]). It is argued that some imperfections in the structure of the ethylene homopolymer (C=C double bonds, branched structures and other inhomogeneities) increase the dispersive component. However, the polar component is also near zero thus demonstrating the absence of polar groups (O functional groups). This absence of the polar component in the pure ethylene homopolymer reflects its qualification as a pure chain-extending component in the copolymer and the appropriateness of copolymers with ethylene sequences as model surfaces with variable concentrations of exclusively one type of functional group. Pulsed-plasma polymerized poly(allyl alcohol) homopolymer shows a surface energy of 50 mJ/m^2. The linear characteristic of the polar component of surface energy of allyl alcohol-butadiene copolymers between 6 and 31 OH groups per 100 C atoms reflects the copolymerisation region (see Fig. 12) whereas in the region 0 to 5 OH/100 C groups the polar component remained constant.

1.3.5
Relation between Functional Groups of Copolymers and Adhesion

Figure 1 presents the differences between unspecific and specific (monotype) functionalization of polymer surfaces for evaluating the contribution of each functional group to the adhesion (interaction) between polymers and metals.

Thus, homopolymers with OH, NH$_2$ and COOH groups are produced and the respective copolymers with ethylene or butadiene applied as adhesion-promoting interlayers in Al-PP composites. Such modified surfaces/interlayers are good models for studying the interaction between metal atoms and monotype functional groups in terms of metal–polymer peel strengths. Therefore, after evaporation of aluminum onto such model surfaces the peel strengths of the Al-plasma polymer-PP composites were measured and the loci of failure were determined. The interactions between the monotype functional groups and aluminum depend strongly on the type of functional groups (see Fig. 13): COOH > OH $\gg$ NH$_2$ > CH$_2$ [22]. This
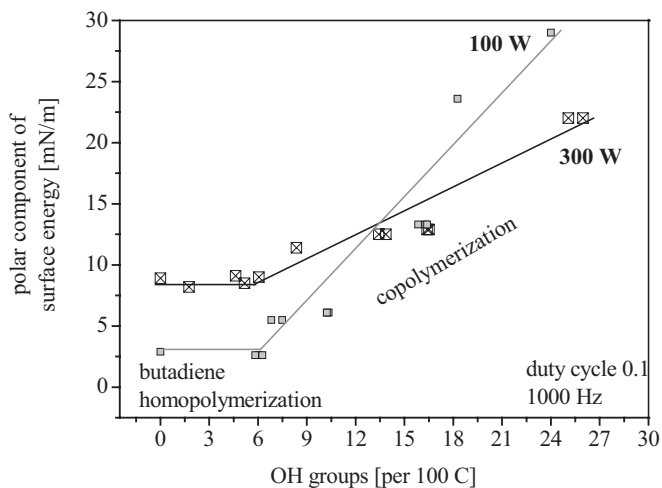
Figure 12 Correlation of polar contribution vs. concentration of OH groups (allyl alcohol-ethylene copolymer).
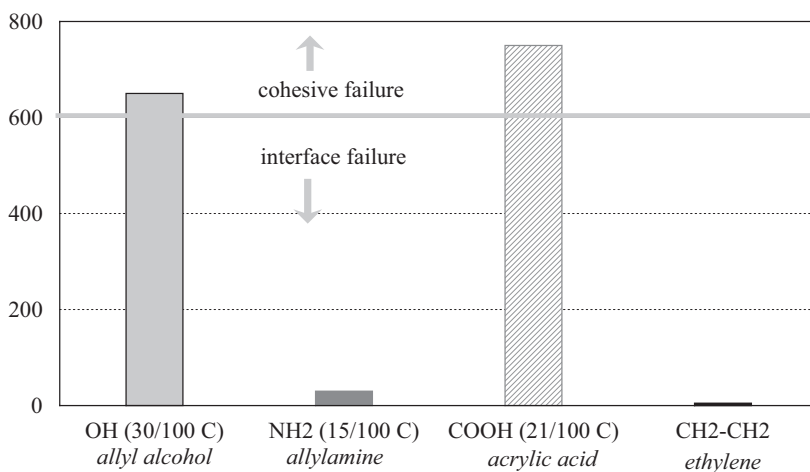

Figure 13 Comparison of Al-plasma homopolymer-PP peel strength in dependence on the type of monotype functional group.

adhesion-promoting behavior was also compared with the unspecific O_2 plasma polymer surface functionalization of PE, PP and PET, which then were evaporated with Al and form Al-polymer composites (Fig. 14). Here, maximum peel strength was measured on introduction of 20 O atoms per 100 C atoms (see Fig. 13). With PET the introduction of O functionalities in the O_2 plasma was accompanied by decarbonylation/decarboxylation of the ester groups, thus, the resulting elemental ratio remained nearly unchanged, however, the nature of O containing groups differs
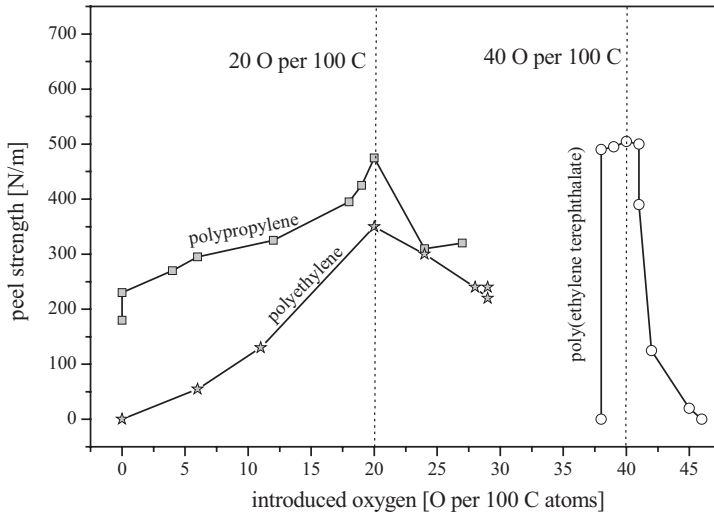
Figure 14 Peel strength of Al-O$_2$ plasma-modified PE, PP and PET composites.

from those of the original PET (Fig. 14). Using the post-plasma diborane reduction of O functional groups to produce a monotype OH group functionalised PP surface the measured Al peel strength was the same as with the unspecific O functionalization.

In the case of ethylene-allyl alcohol copolymers the maximum adhesion was measured at 27 OH per 100 C atoms. A linear dependence of peel strength on the density of OH functional groups was observed in the range of 0 to 27 OH/100C (Fig. 15). A maximum plateau of peel strength at 27 to 29 OH groups was interpreted as a suc-
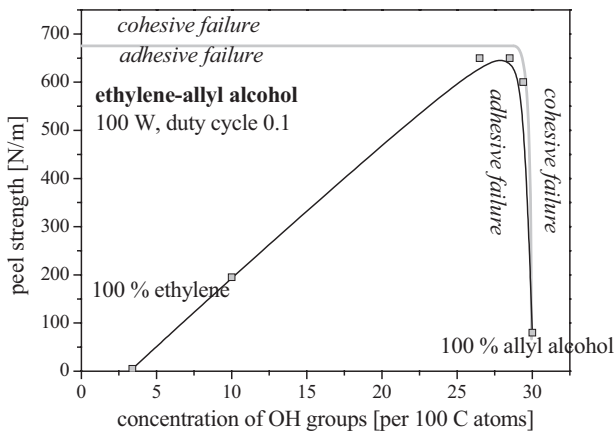

Figure 15 Peel strength of Al-copolymer composites with OH groups containing adhesion-promoting interlayers.

cessive weakening of the cohesive strength of copolymers with increasing content of allyl alcohol (> 90 mole%). Pure allyl alcohol was tacky, completely soluble and showed a low coherent strength resulting in low peel strength and a cohesive failure within the allyl alcohol homopolymer layer. As expected from the chemical point of view, NH_2 groups showed the lowest (Fig. 16) and COOH groups the highest peel strengths to Al (Fig. 17). In both cases over a wide range of concentration the Al peel strengths depend linearly on the concentration of functional groups. Only in the case of too strong interactions between Al and COOH groups was an interface failure observed within the polypropylene substrate (see Fig. 18). Using poly(allyl alcohol) the peel propagates through itself and using copolymers with allyl alcohol the peeling takes place at the plasma-polymer/PP interface (see Fig. 18).
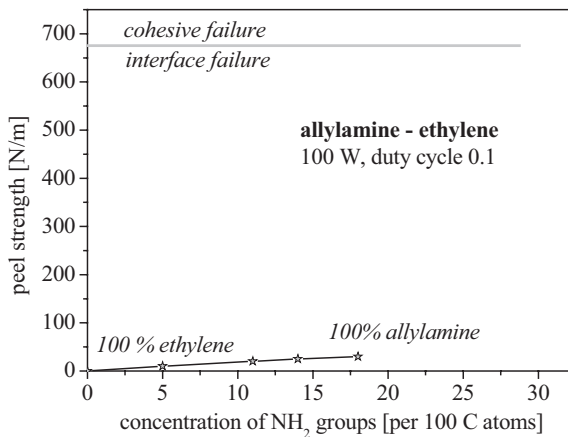

Figure 16 Peel strength of Al-copolymer composites with NH_2 groups containing adhesion-promoting interlayers.
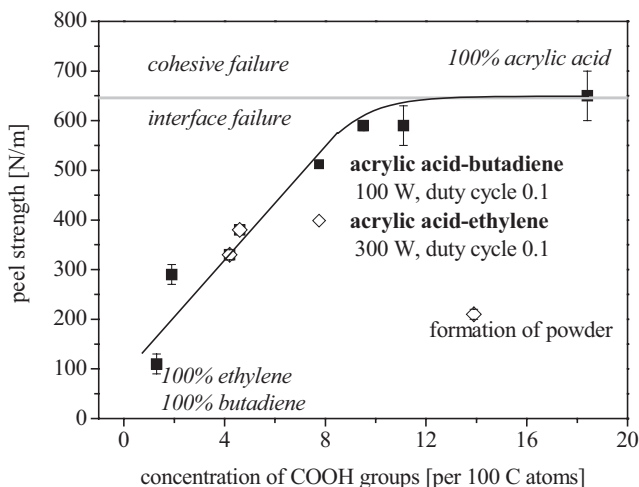

Figure 17 Peel strength of Al-copolymer composites with COOH groups containing adhesion-promoting interlayers.
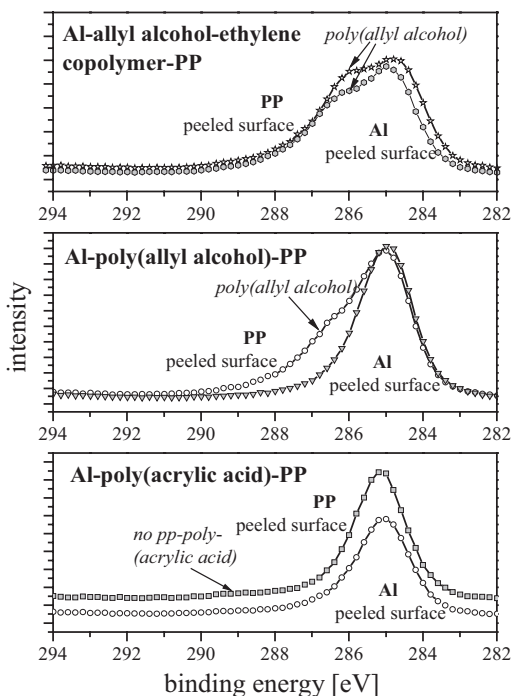
Figure 18 XPS-C1s signals of peeled Al-plasma polymer-PP composites with allyl alcohol-ethylene (60:40) comonomer, allyl alcohol homopolymer and acrylic acid homopolymer.

1.4
Discussion

The metal–polymer interactions and therefore, the peel strengths are based on the sum of discrete chemical bonds between aluminum and functional groups. CH_2–CH_2 groups do not show any interactions to aluminum and peel strength, the primary amino groups too, however, OH groups form Al-alcoholates and COOH groups form salts. The different slopes of the linear dependence with all three functionalities reflect the binding strength of these metal–polymer bonds. Thus, about 10 COOH and 27 OH sequences are needed to reach 650 N/m peel strength (maximum peel strength before appearance of cohesive failure) whereas NH_2 or CH_2–CH_2 sequences only allow weak interactions. These values correlate very well with the binding energies of Al bonds with OH and COOH groups of organic compounds in Al-alcoholates or Al-salts.

The linear increase of adhesive bond strength with growing number of functional groups at the polymer surface and the appearance of a plateau of peel strength at higher concentrations of functional groups, related to cohesive failure, correspond very well with observations on metal–polymer composites possessing functional

groups at the polymer surface [23]. Such models were chemically produced copolymers with COOH or other groups, which form aluminum- or iron-polymer composites. A correlation was found between adhesive bond strength (lap shear strength) of aluminum and the concentration of functional groups (COOH) at the polymer surface (poly (vinyl chloride)-maleic acid copolymers): $\sigma_f = \sigma_0 + k\, c^n$, whereby σ_f = measured adhesive bond strength, σ_0 = adhesive bond strength without functional groups, k, n = constants and c = concentration of functional groups [24]. Using the functional group-carrying adhesion-promoting plasma polymer layers n becomes 1 because the concentration is measured directly at the surface. The equation confirms the observed linear dependence of adhesive bond strength and concentration of functional groups at the interface. Thereby, the constant k reflects the binding energy between Al and the functional group.

1.5
Summary

Adhesion-promoting plasma polymer layers, equipped with maximal 31 OH or 18 NH_2 or 24 COOH groups per 100 C atoms, were produced by applying low wattages and using the pulsed-plasma technique. By carrying out a pulsed-plasma-initiated chemically dominated copolymerization, the density of monotype functional groups could be continuously varied between 0 and 31 OH, 0 to 15 NH_2 and 0 to 24 COOH groups. With aluminum the peel strength increased in the order: $CH_2 < NH_2 \ll OH < COOH$. Using carboxylic groups modified surfaces the adhesion at the Al/COOH interface was greater than the cohesive strength of the polypropylene substrate. The peel strength depended linearly on the density of functional groups.

Acknowledgements

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