Plasma Meets Chemistry: Combined Methods for Tailored Interface Design in Metal-Polymer Composites by Selective Chemical Reactions on Plasma Modified Surfaces

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Abstract. The applicability of polymer-metal composites is mainly determined by the durability of the adhesive strength between both components. Aluminium (Al) deposited on polypropylene (PP) exemplifies different options of interface design. By deposition of plasma polymers on PP the effect of the type of the functionality was investigated. Spacer insertion was accomplished to position the functional group away from the topmost surface. A further kind of interface design involved a partial condensation of functional groups. Hydroxyl and carboxyl groups were most effective to improve adhesion in Al-PP systems. Approximately 7-10 carboxyl or 25-27 hydroxyl groups per 100 C atoms were necessary to increase the peel strength up to ~700 N/m. In this range, the failure of the composite propagated along the interface Al-tape (no peeling of the metal). Spacer molecules between surface and functional groups provoked the effect that the number of needed functional groups for maximum adhesion was strongly reduced. Linking of the functional groups resulted in non-peelable Al-PP laminates. Two adhesion tests were applied - the peel test and the centrifuge technology. For PP foils modified with chemically bonded and additionally linked silanol groups (no peeling) an adhesive strength of (2.5 ± 0.2) N/mm² was determined by centrifuge technology. XPS inspection of both fracture surfaces indicated a sub-surface failure in the polymer.

1. Introduction

The adhesion of metal onto polyolefin surfaces is one of the most sensitive features influencing the performance and durability of such composite materials found in various consumer goods. Aluminium (Al) thermally deposited on unmodified polypropylene (PP) shows no significant adhesion. Reason is the absence of any groups at the polymer surface which are able to interact with metallic Al. The poor adhesion properties of polyolefin surfaces have to be improved which was the motivation of numerous research efforts for modification of the polymer surface. [1-4] Plasma processes proved to be a useful tool to increase the adhesion between polymers and metals. Often, a simple oxygen plasma treatment of the polymer was used to produce several interactive and reactive O-containing functional groups, which are able to generate Al-polymer interactions as precondition for well-adherent Al-polyolefin systems. Nevertheless, it was observed that the introduced O-Al interactions were of different nature and weak. Therefore, increased efforts were made to overcome simple physical interactions at the
metal-polymer interface by introduction of strong covalent bonds may be by inserted flexible spacer molecules. Following questions have to be answered:

1. Which type and which concentration of functional group are necessary for maximal adhesion?
2. Is it possible to replace numerous physical interactions by some covalent bonds with a profit in adhesion?
3. Which advantage produces the insertion of covalently bonded spacer molecules between polyolefin and metal?

Different options of interface design starting from plasma-treated and functionalized polymer surfaces were tested (Fig. 1). Pulsed plasma polymerization of functional group-carrying monomers was used to coat the PP surface with an adhesion-promoting layer, which is well-adherent to the polyolefin. Such films are pinhole-free with different functional groups such as hydroxyl, amino and carboxyl groups for anchoring the metal. The concentration of functional groups in the plasma polymer was varied applying the plasma copolymerization, thus linking comonomers with and without functional groups to layers with the desired concentrations of functional groups on its surface (type I in Fig. 1).

Subsequent chemical reactions with bi- or multifunctional substances onto these functional groups were used for introducing spacer molecules. By this way the interface between metal and polymer was flexibilized (type II in Fig. 1). A third kind of interface design involved a partial condensation of functional groups (type III in Fig. 1). If the spacer molecule contains SiOx elements the interface became hydrophobic and water molecules were repelled. Moreover, hydrolysis of SiOR groups formed adhesion-promoting SiOH groups and additionally SiOx barrier layers.

Fig. 1 Molecular design of the adhesion promotion interface (X – functional group (OH, NH₂, COOH, etc.; Y – bridge elements or groups (O, NH, …))
2. Experimental

2.1 Surface modification

Polypropylene foils (Goodfellow, UK, 100 µm thick), were ultrasonically cleaned in ether for 15 minutes. Plasma polymer layers were deposited in a cylindrical plasma reactor (Ilmvac, Germany) of 50 dm³ volume. The reactor was equipped with a radio-frequency (r.f. 13.56 MHz) generator (Advanced Energy Industries, Germany) with an automatic matching unit and a linear r.f. electrode (5 cm x 35 cm). The r.f. power was introduced to produce continuous-wave (cw) plasma or pulsed plasma with a variable duty cycle (0.1-1) and a repetition frequency of 1 kHz. Mass flow controllers were used for precise metering gases and vapours, liquid mass flow meters (Liqui-Flow®, Bronkhorst High-Tech B.V., The Netherlands) for liquid injection. A heated system of perforated metallic tubes distributed gases and vapours in the reactor. An adjustment of pressure and flow was performed by varying the speed of the turbomolecular pump. The standard pressure was adjusted to 10-25 Pa for depositing allyl alcohol, acrylic acid and allylamine as plasma polymers. These monomers were also used for copolymerization either with ethylene or butadiene in different molar ratios to vary the concentration of functional groups in the deposited plasma polymer (interface type I in Fig. 1).

A quartz microbalance was used for controlling the deposition rate.

PP films, used as substrates, were coated with 150 nm thick plasma polymer layers by applying the cw or the pulsed r.f. plasma modes (power input P = 30-300 W). The duty cycle (defined as $\text{dc} = t_{\text{pulse-on}} / (t_{\text{pulse-on}} + t_{\text{pulse-off}})$) characterizes the (plasma-on)/(plasma-off) period.

Spacer insertion was accomplished by the following chemical reactions: The samples with plasma polymerized allylamine layers deposited on PP were shaken in glutaraldehyde solution (1 % in water) for 2 hours at room temperature immediately after its removing from the reactor (to avoid auto-oxidation processes). Thus, aldehyde groups were introduced by reaction of the amino groups with glutaraldehyde, moreover, undesired oxidation at contact with ambient air was eliminated.

Subsequently, chain-extension was performed using bi- or polyfunctional substances with at least one amino group. Variation of its chain length and structure produced different spacer length, end groups and flexibility as shown in Fig 2:
The concentration of the functional groups was determined by its chemical derivatization and measuring these derivates by photoelectron spectroscopy (XPS). The reactions of hydroxyl groups with trifluoroacetic anhydride, amino groups with pentafluorobenzaldehyde and carboxylic groups with trifluoroethanol in presence of carbodiimide are described elsewhere [5]. The concentration of the hydroxyl and carboxyl groups, respectively were calculated by the following equation:

\[
C_{OH,COOH} = \frac{100 \times [F]}{3 \times [C] - 2 \times [F]}
\]

derived from the derivatization reaction with trifluoroacetic anhydride (TFAA) (1) and trifluoroethanol (TFE) (2), respectively:

(1)

(2)

[C] and [F] indicate the concentrations of carbon and fluorine measured by XPS at the TFAA and TFE, respectively, derivatized surfaces.

Generation of functional groups at the topmost surface, additionally linked, was achieved in two ways (Figs. 3 and 4). A short spacer was introduced by reaction of 3-isocyanatopropyltrimethoxysilane with the primary amino groups of the plasma deposited allylamine layer. Subsequent stepwise hydrolysis produced -Si-OH groups on the surface. Simultaneously to hydrolysis a condensation of -Si-OH groups occurs to -O-Si-O- units (Fig. 3).
Fig. 3  Scheme of synthesis of surface-bonded –SiOH groups (short spacer), additionally linked (interface type III in Fig.1).

The other method started with bromination of PP or deposition of a Br-containing plasma polymer using the bromoform plasma. The brominated surface was reacted with a long-chain spacer (1.12-diaminododecan) followed by consumption of the residual amino group with 3-isocyanatopropyltrimethoxysilane and subsequent hydrolysis/condensation (Fig. 4):

Fig. 4  Grafting of 1.12-diaminododecan and subsequent reaction with 3-isocyanatopropyltrimethoxysilane followed by hydrolysis/condensation (interface type III in Fig.1)
2.2. Test specimen assembly and composite characterization

The spacer-equipped polyolefin surfaces were Al coated using a thermal metallizer (Auto 306, Edwards, UK). The Al thickness was adjusted to 100 nm monitoring it by using a quartz microbalance. The metal-polymer adhesion was measured using the 90° peel test at a peeling speed of 25 mm/min. The peeled surfaces of the composites were inspected by XPS to obtain information on the origin of failure. These peel results were compared with those carried out by centrifuge technology [6]. The major problem of all tape-based peel tests was the limited adhesion between the adhesive tape and the aluminium layer. Often, the adhesive tape was peeled-off but the Al-polymer composite remained intact and thus metal adhesion could not be measured. Now, it is expected that the centrifuge technology will overcome this problem. The schematic diagram of this multiple sample test is shown in Fig. 5:

![Schematic diagram of the centrifuge technology](image)

The test stamps were bonded on the Al-deposited side of the metallized PP foil using cyanoacrylate adhesive (Loctite 415). The non-metallized side of the foil was fixed by a double-sided adhesive tape (TESA 4964) on the metallic reinforcement. At rotation, individual rupture events occur at increasing rotational speed. All rupture events were detected on-line outside the centrifuge using a position-coded and rpm-correlated infrared data transmission.

The centrifuge technology uses the following equation for the calculation of adhesive strength $\sigma_{A/B}$:

$$\sigma_{A/B} = \frac{F_c}{A} = \frac{m \cdot \omega^2 \cdot r}{A} = \frac{m \cdot (2 \cdot \pi \cdot \frac{n}{60})^2 \cdot r}{A}$$

with $F_c$ - centrifugal force, $A$ - fracture area, $m$ - mass of the test stamp, $n$ - critical revolutions per minute, $r$ - radius of the rotational motion and $\omega$ - angular velocity ($F_c = m^* \omega^2 r^*$).
3. Results and Discussion

3.1 Functional groups at the top-most polymer surface

Functional groups like COOH, OH and SiOH at the polymer surface provoked a significant adhesion-promotion in the PP-Al composites. Amino groups and ethylene units (without any functional groups) did not show any effect. In general, the measured peel strength of aluminium deposits on PP increased linearly in dependence on the concentration of functional groups. Near the maximum concentration of OH groups (25-27 OH per 100 C atoms) and at concentration of 8-10 COOH per 100 C atoms, a constant level of peel strength was achieved characterized by a cohesive failure in these laminates. In the case of allyl alcohol homopolymer layer a dramatic decrease of the peel strength at a maximum concentration of OH groups (~30 OH per 100 C atoms) was observed (see Fig. 6). In this case the XPS inspection of the peeled surfaces showed on both fracture areas the typical shape of the C1s peak of the allyl alcohol plasma polymer. This result is characteristic for a cohesive failure within the poly(allyl alcohol) layer (see Fig. 6).

![Graph A](image1.png)

![Graph B](image2.png)

Fig. 6 C1s peak of plasma polymerized allyl alcohol (A) and C1s peaks of both peeled sides of Al-PP composite (B) with an allyl alcohol layer interface

3.2. Functional groups bonded at flexible spacer molecules far from the original surface

The grafting of spacers with adhesion-promoting endgroups onto the deposited allylamine plasma polymer layers improved the peel strength significantly. The spacer bonded hydroxyl endgroups -N=CH-(CH\textsubscript{2})\textsubscript{3}-CH=NH-(CH\textsubscript{2})\textsubscript{3}(OH) (number 3 and 4 in Fig. 7) and -N=CH-(CH\textsubscript{2})\textsubscript{3}-CH=N-(p-C\textsubscript{6}H\textsubscript{4})-OH (number 5 in Fig. 7) showed much higher peel strength in comparison to that OH groups, which were bonded at the surface without spacer. Here, the formation of Al-O-C bonds is assumed.
Fig. 7 Peel strength of aluminium-polypropylene laminates arranged by plasma (co)polymers of allyl alcohol layers (directly bonded to the surface) and spacer-bonded hydroxyl groups

COOH groups are most efficient in adhesion promoting for the Al-PP system (cf. Fig. 8). Only 8-10 COOH groups per 100 C atoms were sufficient to produce maximal peel strength. The strong adhesion-promoting action of COOH groups was assumed to be caused by the formation of Al bidentate bondings as proposed by Alexander et al. [7]. Spacer-bonded COOH groups of the type -N=CH-(CH2)3-CH=N-(CH2)5(11)-COOH (number 1 and 2 in Fig. 8) improved the peel strength stronger in relation to COOH bonded without spacer referenced to the same concentration.

Fig. 8 Peel strength of aluminium-polypropylene laminates arranged by plasma (co)polymers of acrylic acid layers and spacer-bonded carboxyl groups

3.3. SiOH groups positioned in a short or long distance from the topmost surface, additionally linked
All peel tests of SiOR / SiOH-modified PP-Al composites did not give any result because the adhesive tape was peeled-off from the Al coating. Therefore, it was not possible to peel any aluminum from the PP surface. Thus, the real adhesion was higher than the measured peel strength. To overcome this hindrance the new developed centrifuge technology was applied. The results are represented in Figs. 9 and 10 for short- and long-chain spacer bonded SiOH groups, partially condensed, by using different hydrolysis times.

![Graph](image1.png)

**Fig. 9** Adhesion strength of Al-PP composites, PP equipped with short spacer bonded SiOH groups, additionally linked

![Graph](image2.png)

**Fig 10** Adhesion strength of Al-PP composites, PP equipped with long spacer bonded SiOH groups, additionally linked

In principle constant adhesion strength (2.2-2.5 N/mm²) was found in both cases independent on the hydrolysis time. On both fracture areas (named as metal and polymer side) their composition was estimated by XPS. In the case of short spacer-bonded SiOH groups a break in the polymer itself was detected because no nitrogen (N) on the polymer side was found. The reason for the relatively high Si content is not completely understood may be caused by a break within PP near the interface to the silane spacer. Long-chain spacer bonded SiOH groups exhibited a break in the surface layer of the PP near the interface to the silane spacer modification because it contains up to 4 % O. In one case (60 min hydrolysis times) the break occurred in deeper PP layers resulting in identical compositions of both fracture surfaces.

4. **Summary**

The nature of interactions between aluminium and different functional groups was reflected in the measured peel strengths. The succession of the adhesion-promoting effect was derived from the slope of the linear increase of the peel strengths vs. concentration of functional groups resulting in the following row:

\[ \text{CH}_2\text{-CH}_2 < \text{NH}_2 \ll \text{OH} < \text{COOH} \]
The mode of failure, either interface or cohesive, was inspected by microscopy and XPS. Most efficient groups for promoting the Al peel strength to PP were OH and any more COOH as seen in Figs. 7 and 8 probably due to formation of chemical bonds. This behaviour was confirmed when spacer bonded functional groups were applied. Spacers with stiffer chains and other end groups than OH and COOH had only slight influence on adhesion. The reason why should be the formation of covalent bidentate or ionic (salt-like) bonds between COOH groups and aluminium [8, 9] and Al-O-C (monodentate or alcoholate) bonds between OH groups and Al [10]. In comparison to high concentrations of directly to the surface bonded functional groups (8-10 COOH/100 C and 25-27 OH/100 C) a considerably lower concentration of spacer coupled functional groups (1-2 OH/100 C or 1-2 COOH/100 C) was necessary to achieve the same high level of peel strength of Al-PP composites characterized by cohesive failure in the polymer substrate.

The application of silanol groups bonded by short or long spacers to the PP surface was accomplished by reaction of 3-isocyanatopropyltrimethoxysilane with allylamine plasma polymer layers deposited on PP or by reaction of the brominated PP surface with 1.12 diaminododecane and subsequent reaction with the mentioned silane. The subsequent stepwise hydrolysis is associated with the formation of SiOH groups and their condensation to Si-O-Si units. For these modified surfaces, adhesion of Al was beyond the maximum peel strength of adhesive tapes, i.e. about 700 N/m. Using the centrifuge technology a constant adhesive strength of 2.2-2.5 N/mm² was measured. XPS inspection of both fracture surfaces indicated a sub-surface failure within the polymer may be near the interface.

5. References

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