Combination of plasma-chemical and wet-chemical processes - a simple way to optimize interfaces in metal-polymer composites for maximal adhesion

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Abstract: Different surface treatments of polypropylene (PP) were tested to improve the peel strength of aluminium-PP systems. Plasma exposure followed by chemical grafting of spacers with -SiOH endgroups and thin adhesion promoting layers deposited by aerosol-assisted DBD using aqu. solutions of classic polymers were compared. Both methods were effective, however, –SiOH terminated spacers effected no peeling also after ageing.

Keywords: adhesion polypropylene-aluminium, tailored interface structures, aerosol-assisted DBD

1. Introduction

Polyolefins are characterized by chemical inertness, good processability and light-weight properties. Problems are arising from the absence of any functional groups at the surface required for printing, metalizing and dyeing. Different ways were trod to equip polyolefin surfaces with functional groups [1]. Usually, a simple oxygen plasma treatment is sufficient to introduce different types of functional groups into the surface and to achieve sufficient wettability and adhesion. Chemical grafting is the base for production of tailored surfaces in life science, diagnostics, or other fields. It demands defined functionalization of polymer surfaces with monotype functional groups in preferably high density. One way to generate such selective functionalization is the plasma-assisted deposition of (co)polymers carrying monotype functional groups using low energy or pulsed plasmas. Preliminary works demonstrated the effect of type and concentration of functional groups on adhesion in Al-PP systems [2]. Subsequent chemical reactions of surface bonded functional groups were used to produce defined interface structure. It was found that the insertion of flexible spacer molecules has extensively improved the adhesion [3]. In continuation of these experiments the interface design was further qualified and extended to cross-linked structures by reacting with suited functionalized trialkoxysilanes. A second line to introduce monotype functional groups into polyolefin surface is the aerosol-assisted DBD modification of polymers. [4, 5] This modification offers the possibility to deposit well-adherent classic functionalized polymers onto polyolefins. This way of surface functionalization revealed positive effects in adhesion of PP-Al laminates. This paper demonstrates a comparison of both methods - the effect of a flexibilized interface design using cross-linked structures by reacting of suited substituted silanes and a simple polymer-based modification using nebulized aq. solutions of classic functionalized polymers by aerosol-assisted DBD treatment.

2. Experimental

2.1 Materials

Polypropylene foils (Goodfellow, UK, 100 µm thick), were ultrasonically cleaned in ether for 15 minutes. XPS measurements revealed an oxygen content < 0.5 atom% in the polymer surface.

2.2 Interface tailoring

A 50 nm thick plasma polymer layer was deposited on PP using allylamine. The following interface modification at the topmost surface was achieved in two ways (Fig. 1). Short spacer molecules were introduced by reaction of 3-isocyanatopropyl-trimethoxysilane with primary amino groups of the plasma deposited allylamine layer. Subsequent hydrolysis produced stepwise -SiOH groups. Simultaneously to hydrolysis a condensation of -SiOH groups occurred to -Si-O-Si- units. A second method started with bromination of PP or deposition of a Br-containing plasma polymer using bromoform plasma. The brominated surface was reacted with 3-aminopropyl-trimethoxysilane followed by hydrolysis with water. The time-controlled hydrolysis produced both, Si-OH endgroups and -Si-O-Si- groups between the spacer chains as shown in Fig. 2. Using the brominated surfaces also a long-chain spacer was grafted (1.12-diaminododecane). The resulting spacer bonded amino groups were consumed by 3-isocyanato-propyl-trimethoxysilane. Hydrolysis and the immediately parallel beginning condensation resulted in a final interface structure as represented in Fig. 3:

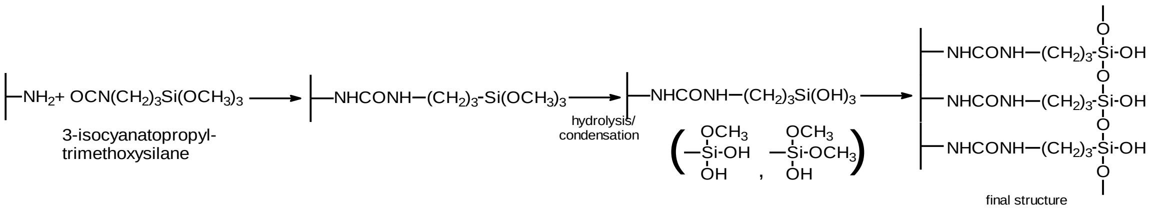

Fig. 1 Scheme of synthesis of surface-bonded –SiOH groups (short spacer, additionally linked) using allylamine deposit and 3-isocyanatopropyl-trimethoxysilane.

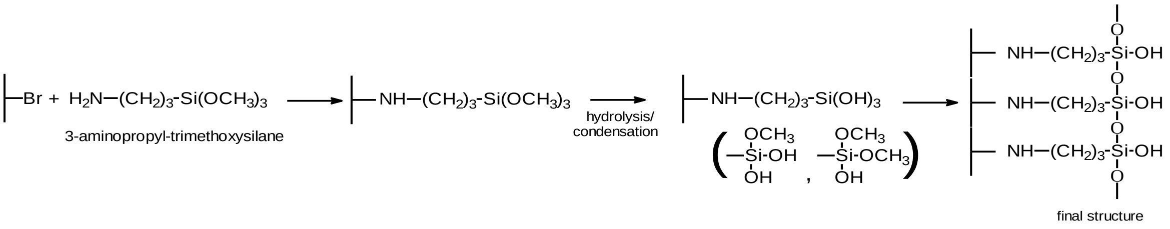

Fig. 2 Scheme of synthesis of surface-bonded –SiOH groups (short spacer, additionally linked) using brominated surface and 3-aminopropyl-trimethoxysilane.

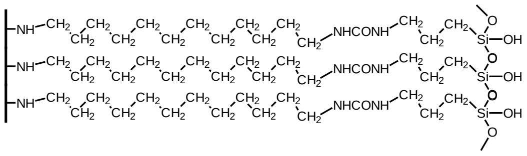

Fig. 3 Interface structure with long spacers produced by grafting of 1.12-diaminododecane on brominated PP followed by reaction with 3-isocyanatopropyl-trimethoxysilane and subsequently hydrolysis/condensation.

2.3 Model reactions for studying the effect of chain-linking of functional groups

Allylamine deposits were reacted with hexamethylene diisocyanate followed by reaction with three different 3-aminopropyl-alkoxysilanes equipped with different numbers of OCH_3 and CH_3 groups. -SiOH endgroups were formed by hydrolysis and -Si-O-Si- bonds by condensation, thus generating different interface structures (I, II and III in Fig. 4):

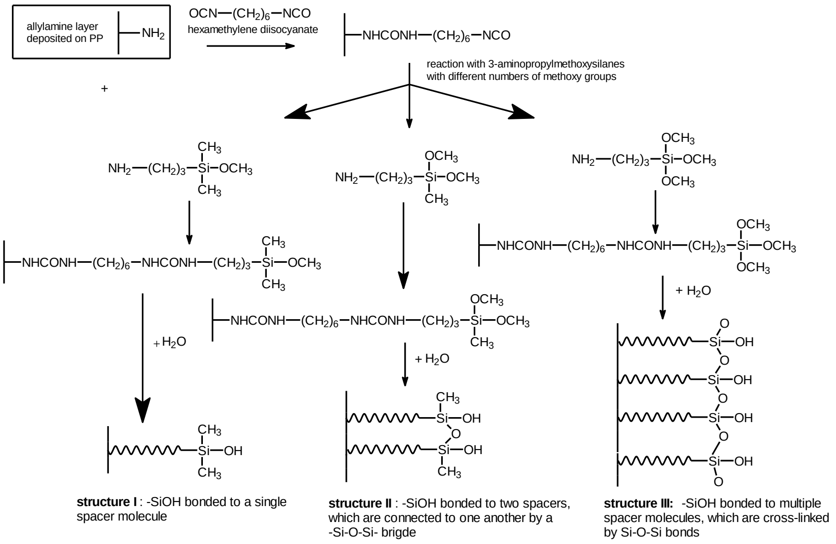

Fig. 4 Scheme for designing interface model structures fitted with -SiOH groups

2.4 Coupling of functional (conventional) polymers to the surface by aerosol-assisted DBD

Aqueous solutions (1 wt.-%) of poly(acrylic acid) (M = 1800, Merck, Germany) and poly(vinyl alcohol) (M = 31000-50000), Celvol 205S, Celanese, USA) were introduced into the DBD as aerosols. The experiments were performed using the DBD System TG 101 (Ahlbrandt GmbH, Germany) fitted with a ceramic coated drum of 48 cm length and two ceramic type electrodes of 51 cm length. The maximum energy input was 1 kW. The energy density E_d is expressed by the equation $E_d = \frac{P}{w*s} * n$ [J/cm^2] (P - power in [W], w - width of the discharge zone [cm], n = number of DBD passes, corresponding to treatment time, s – effective speed of movement [cm/s]). The samples were treated at variable energy input and at constant speed of 5 m/min (8.3 cm/s). The number of passes through the DBD plasma zone was varied between 1 and 8.

2.5 Analytical characterization

The XP data were acquired by the XP-spectrometer Sage 100 (Specs, Berlin, Germany), equipped with a 250 W non-monochromatic MgKalpha X-ray source and a hemispherical analyzer Phoibos 100 MCD-5. The angle between the axis of X-ray source and analyzer lenses is 54.9°. The analyzer is mounted at 18° to the surface normal and works in the constant analyzer energy mode (CAE). Normally the spectra were produced at 11 kV / 220 W with analyzer pass energies of 50 eV for overview and 20 eV for higher resolved spectra. The analyzed surface area was 3 x 4 mm². The measured elemental concentrations were referenced to 100 C atoms. The manufacturer´s software routine was used for quantitative XPS spectra analysis and peak deconvolution.

2.6 Peel strength measurements

Peel strength was measured with a speed of 25 mm/min using a tensile testing machine TH 2730 (Thuemler GmbH, Germany) applying the 90° peel test. The aluminium coated samples were sticked with the aluminium side on a rubber plate which was mounted on the firm support by a double-side tape (TESA 4965, Beiersdorf, Germany). Specimen dimension was 100*10 mm^2, the results were averaged over 4-5 samples.

3. Results

3.1 Peel strength of samples with special interface design

The application of alkoxysilanes producing -SiOH as terminal groups was very successful because of chemical bonding to Al and also due to an additional cross-linking realized by partial condensation of the spacer-bonded-SiOH groups. Fig. 5 shows the peel test results provoked by -SiOH endgroups bonded by short and long spacers (Fig. 5A, B and C), respectively, to the PP surface. It seems noteworthy that the bonding remained non-peelable also after storage the samples at 40°C and 90% r.h. for 940 h! The lower peel strength of the stored samples is caused by weakening of the Al-tape interface resulting in a lower level but without removing any Al.

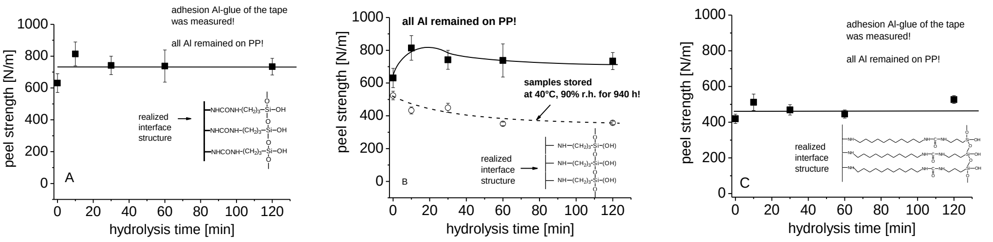

Fig. 5 Peel strength of Si-OH modified interface structures bonded by short (A, B) and long spacers (C), respectively.

3.2 Effect of cross-linking of spacer molecules

Fig. 6 documents the adhesion promoting effect of intermolecular spacer cross-linking. Different interface structures were produced by application of differently substituted 3-aminopropyl-methyl-alkoxysilanes. Single -SiOH groups (structure I in Fig. 6) bonded to a short spacer didn't promote the adhesion in any significant degree. Two adjacent chains coupled by Si-O-Si bonds equipped with -SiOH groups (structure II in Fig. 6) first became effective after hydrolysis times >20 min, (i. e. at progressed condensation degree). Cross-linked structures (III in Fig. 6) at the interface resulted in highest peel strength, restricted by limitations of the peel method itself (adhesion tape) or by cohesive strength of the polymer (cohesion failure).

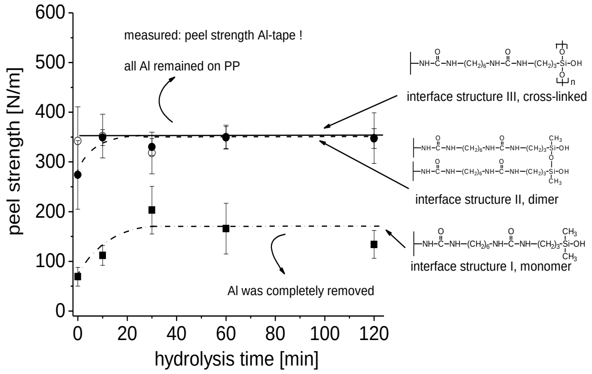

Fig. 6 Peel strength Al-PP of designed interface structures vs. hydrolysis time to prove the influence of cross-linking

3.3 Peel test of aerosol-modified samples

Nebulizing of functionalized polymers as aerosols into the DBD to modify the metal-polymer interface is a simple method to enhance the peel strength. Poly (acrylic acid) and poly (vinyl alcohol) improved the adhesion to the maximum. No aluminium could be peeled as demonstrated in Figs. 7A and 7B.

Fig. 7 Peel strength of Al evaporated PP treated by aerosol-assisted DBD using 1wt. % aqueous solutions of poly(acrylic acid) (A) and poly(vinyl alcohol) (B), respectively, in dependence on energy density.

4. Summary

Peel strength measurements of Al-PP laminates were accomplished to test tailored interface structures. Based on plasma deposited allylamine polymers short chain bonded –SiOH groups were produced by reaction of surface-bonded primary amino groups with 3-iso-cyanatopropyl-trimethoxysilane followed by its hydrolysis/condensation. A second way was the reaction of plasma brominated surfaces with 3-amino-propyl-trimethoxysilane. Long chain bonded -SiOH groups were produced by reaction of brominated surfaces with a long-chain diamine and subsequent reaction with the above-mentioned isocyanato-silane. By use of 3-aminopropyl-alkoxysilanes with 1, 2 or 3 alkoxy groups bonded by hexamethylene diisocyanate to the polymer a special interface design was realized. Thus, –SiOH groups coupled as endgroups to spacers could bond to the Al layer. Two Si-O-Si linked spacer groups or several Si-O-Si cross-linked spacer groups were also produced. It was found that the silane with the (partial) possibility of crosslinking produced the maximal peel strength. The second examined variant was the deposition of adhesion-promoting polymer layers by aerosol-assisted DBD. Using aqueous solutions (1.0 wt. %) of poly(acrylic acid) and poly(vinyl alcohol), respectively, the peel strength Al-PP was strongly enhanced. The failure was initiated in the weak boundary layer (inside) of the polymer near interface. No failure at Al-PP interface was observed.

5. References

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