Chemical structure of amino-terminated alkyl silanes influencing the strength of aluminum-polyamide joints

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Abstract. Organo-functional silane coupling agents are widely used to promote adhesion in between inorganic and organic materials. Amino-functional silanes can improve bonding with polyamide. Aiming on a mechanically performant aluminum-polyamide joints, the effect of six amino silanes of different chemical structure, namely number and type of amine groups and alkyl spacers lengths, on the joint strength is investigated by means of lap-shear testing. Higher shear strengths are found along with a more pronounced capability of the amine group to form hydrogen bonds with polyamide. The results show that an additional amine group within the organo-functional group can increase joint strength, whereas long alkyl spacers reduce the observed joint strength. It is shown that high lap-shear strengths, in maximum about 15 MPa for N-(2-aminoethyl)-3-aminopropyltrimethoxysilane are achieved and that the high reproducibility can be assured when using right processing routines.

1. Introduction

For reasons of lightweight construction, dissimilar materials are increasingly combined into load-bearing components. Well-known applications based on fiber-reinforced plastics combined with metal alloys into polymer-metal hybrids (PMH) are numerous established in aircrafts [1]. The design of the material’s interface is a key aspect and numerous methods are already applied for thermosetting resin-based PMH [2]. In order to open up broader areas of application outside of aviation, ongoing efforts are conducted to reduce production times and costs. Hereto, a promising approach is replacing thermosetting by thermoplastic resins [3]. Among others, particularly polyamide is of great interest, as it combines good processing properties with high availability and beneficial mechanical properties. Hence, appropriate interface-design techniques for polyamide-based PMH are demanded. Several studies outline the potential of e.g. laser structuring [4, 5] or grit blasting [6, 7] of the metal surface to achieve high joint strengths by mechanical interlocking with the polymer. Besides, organo-functional silane coupling agents are suitable to improve adhesion with polyamides and are already established in commercial glass fiber sizing [8]. The composition of such silane molecules is typically made up of a silicon central atom with three attached alkoxy groups and an organo-functional group. Whereas the alkoxy groups can form covalent bonds with metal or mineral substrates through hydrolysis and condensation reactions, the chemical structure of the organo-functional group determines the achievable adhesion with the polymer [9, 10]. In this context, silanes that bear amine groups which are located at the end of the organo-functional group, so-called amino-terminated alkyl silanes, are used to increase adhesion with polyamide [8, 11, 12, 13]. However, there are various amino-terminated alkyl silanes that differ from each other in the type (primary, secondary, tertiary) and number of amines, and alkyl group lengths with respect to the structure of the organo-functional group. It is reported, e.g. for basalt fiber - reinforced polyamide 6,6 and for talcum polyamide 6 composites, that adhesion with polyamide is influenced by this [12, 13]. In this context, this contribution deals with six amino-terminated...
alkyl silanes. The influence of the chemical structure of the organo-functional group on the joint strength of aluminum polyamide joints is investigated. Hereto, aluminum sheets are coated by the silanes and joined with polyamide into lap-shear specimens by heat-conductive hot pressing. Based on this, the achieved adhesion is evaluated by means of lap-shear testing.

2. Material and methods

2.1. Materials and applied silane coupling agents

Lap-shear testing of polyamide 6-aluminum specimens is carried out to study the influence of the chemical structure of the amino-functional group of silane coupling agents on the achievable bond strength. For the specimens production, polyamide 6 sheets of type Ultramid B40 from Co. BASF were shaped into the dimensions of 80 mm × 25 mm × 4 mm by water-jet cutting. Cold-rolled sheets of the aluminum alloy EN AW 6082-T6 (supplier: Co. Gemmel Metalle) in the dimensions of 100 mm × 25 mm × 3 mm were used. For the silane application on the aluminum sheets, sodium hydroxide, ethanol, and xylene (Co. Merck) were utilized. The tested silane coupling agents are listed in table 1. The given abbreviation contains the number of amino groups per silane molecule (Mono or Di). For the three silanes with one amine, the amine type (primary, secondary, or tertiary amine) is given. For the three silanes with two amines (primary and secondary amine each), the lengths of the alkyl spacers (i.e. methyl, ethyl, propyl, hexyl, undecyl) are provided. Thereby, the first abbreviated name (e.g. “Prop”) refers to the alkyl group in between the silicon atom and the secondary amine group, whereas the second abbreviated name belongs to the alkyl group in between the two amine groups.

| Silane, supplier, purity and CAS number | Abbreviation | Chemical structure |
|----------------------------------------|--------------|--------------------|
| (N,N-Dimethyl-3-aminopropyl)trimethoxysilane | Mono-tert | -O-Si-N- |
| Co. ABCR; 97 %; CAS 2530-86-1 | | |
| N-Methylaminopropyltrimethoxysilane | Mono-sec | -O-Si-N- |
| Co. ABCR; 97 %; CAS 3069-25-8 | | |
| 3-Aminopropyltrimethoxysilane | Mono-prim | -O-Si-NH₂ |
| Co. Merck; 98 %; CAS 13822-56-5 | | |
| N-(2-aminoethyl)-3-aminopropyltrimethoxysilane | Di-Prop/Eth | -O-Si-NH₂ |
| Co. Merck; 97 %; CAS 1760-24-3 | | |
| N-(6-aminohexyl)aminomethyltriethoxysilane | Di-Meth/Hex | -O-Si-NH₂ |
| Co. Gelest; 92 %; CAS 15129-36-9 | | |
| N-(2-aminoethyl)-11-aminoundecyltrimethoxysilane | Di-Unde/Eth | -O-Si-NH₂ |
| Co. Gelest; 95 %; CAS 121772-92-7 | | |
2.2. Preparation and mechanical testing of PMH specimens

For silane functionalization, the aluminum strips are pretreated by ultrasonically assisted degreasing in ethanol for five minutes, pickling in 3 % sodium-hydroxide solution at 50 °C for one minute. This is followed by thorough rinsing with deionized water and immersion in boiling deionized water for 30 min to ensure surface hydroxylation as precondition to the formation of covalent bonds with the silane. Subsequent to a 30 min air drying step at ambient temperature, five aluminum strips each are functionalized by the above-listed silane coupling agents. Hereto, the sheets are immersed in a mixture of anhydrous xylene and silane at a molar ratio of 25 to 1 at a solution temperature of 130 °C for 30 minutes. Afterwards, intense washing steps with ethanol and deionized water were performed to remove weakly bonded, residual silane molecules. The polyamide 6 sheets are pretreated by ultrasonically assisted degreasing in ethanol for five minutes and drying at 70 °C until mass equilibrium is achieved.

Based on the prepared components, lap-shear specimens (see figure 1) with an overlap length of 5 mm and overlap width of 25 mm are produced by heat-conductive hot pressing using a constant pressure of 0.2 MPa, which was applied to the joining zone. A maximum temperature of 235 °C ensures complete interfacial melting of the polyamide. A complete description of the hot-pressing process is provided in [6]. Thereafter, the specimens are conditioned using a climate chamber (VC 4018, Co. Fötsch Industrietechnik).

![Figure 1: Geometry of the produced PMH specimens.](image)

Accelerated conditioning (70 °C and 62 % relative humidity) to European standard climate is conducted according to ISO 1110 [14] until the sample mass reaches an equilibrium state. Subsequently, mechanical testing of the specimens is performed using a Z020 (Co. Zwick/Roell) testing machine equipped with a 20 kN load cell according to test standard DIN EN ISO 1465 [15]. A test speed of 1 mm/min is applied and all tests were conducted until failure.

3. Results and discussion

In order to study the influence of the chemical structure of the organo-functional group of amino silane coupling agents on the bond strength of aluminum-polyamide joints, lap-shear tests were conducted. It has to be mentioned, that the silane-coating process of the aluminum specimens was initially performed without subsequent intensive washing steps with deionized water and ethanol. Thereby, low lap-shear strengths with high scatter of the results were observed for all the tested silanes. This can be related to the ability of the amine group to form hydrogen bonds with the different functional groups of other amino-silane molecules [16] or with hydroxides attached to the aluminum surface. In consequence, the interfacial zone is partially blocked with weakly connected silane molecules instead of silane molecules that are connected to each other by strong covalent oxane bonds and with the aluminum surface. Hence, the ability of the interface to transfer high mechanical loads is lowered.

After introducing the aforementioned washing steps, significantly higher lap-shear strengths at lower scatter were determined for the tested amino silanes (see figure 2). For all specimens tested, interfacial failure is observed without apparently visible polyamide residues at the fractured aluminum surface. Mechanical tests of two reference conditions, one of them prepared by just degreasing the aluminum and
the other one by boiling water treatment of the aluminum without subsequent silanization show both negligible joints strength. Hence, it is concluded that all the tested silane coupling agents sufficiently improve adhesion towards polyamide 6.

Figure 2: Maximum shear strength ($\sigma_{\text{max}}$) according to DIN EN ISO 1465 of aluminum EN AW-6082/PA 6 joints for different amino-silane coupling agents that are used for the interfacial design.

The chemical structure of the three mono amino-silanes is similar, except for the type (tertiary, secondary, primary) of amine group that is located at the chain end of the organo-functional group. Hereby, the lowest joint strength is observed for the silane bearing the tertiary amine group (Mono-tert), higher strength is achieved with the silane with secondary amine group (Mono-sec), and the silane with primary amine (Mono-prim) provides the highest strength. This can be directly related to the capability of the individual amine types to form hydrogen bonds with the amide group of polyamide 6 that is highest for primary amine and lowest for tertiary amine. Figure 3 illustrates possible options for hydrogen bonding between the amine and amide group. Note that possible hydrogen bonding between polyamide 6 and alkoxy, silanol, siloxane and aluminum hydroxide groups are not depicted. Primary and secondary amine can form all hydrogen bonding options depicted in figure 3 (a-e), but hydrogen bonds formed by secondary group with the amide group are less strong, since the partial charge of the involved hydrogen is less pronounced compared with primary amine. The tertiary amine can only form hydrogen bonding options (b, d-e) with the amide group. Due to the basicity increasing from primary to tertiary amines, the tendency to form ammonium salts is higher, giving rise hydrogens boning options (d-e) with the amide group. However, bonds arising from ammonium salts are weak compared to hydrogen bonds between amine and amide groups (a-c), as the partial charge of the hydrogen of the ammonium group is small in relation to hydrogen of amine groups.
Figure 3: Simplified scheme of selected options for hydrogen bonding in between polyamide 6 and amine groups of specific type: Mono-prim (a, b, c: \( R_1 = H \)); Mono-sec (a, c: \( R_1 = CH_3 \); b: \( R_1 = H, R_2 = CH_3 \)) and Mono-tert (b, \( R_2 = CH_3 \)) and the corresponding ammonium salts (d, e).

For the three silanes that contain two amine groups (Di-Prop/Eth, Di-Meth/Hex, Di-Unde/Eth), namely a primary amine located at the end of the chain of the organo-functional group and a secondary amine positioned within the organo-functional group, significantly different joint strengths are recorded. This shows that not only the number and type of amine groups have an impact on the shear strength of the tested aluminum-polyamide specimens, but also the lengths of the alkyl spacers and the position of the amine groups within the organo-functional group have to be considered. Hereby, the diamino silane Di-Prop/Eth shows an increased strength that is the highest of all tested silanes, compared with the silane Mono-prim. This is in accordance with other studies that applied the same silanes Di-Prop/Eth and Mono-prim but for other material configurations [12, 13]. The increase in strength in between Mono-prim and Di-Prop/Eth can be explained by the additional amine within Di-Prop/Eth that can form an extra hydrogen bond with the amide group of polyamide 6.

Compared to that, the diamino silanes Di-Meth/Hex and Di-Unde/Eth, even though they bear two amine groups each, provide lower shear strength than mono-prim and Di-Prop/Eth. In comparison to Di-Prop/Eth, the silanes Di-Meth/Hex and Di-Unde/Eth contain longer alkyl spacers in total. Consequently, the interfacial functional density of amine groups is lower for Di-Meth/Hex and Di-Unde/Eth in relation to the overall space blocked by the silanes. This may explain the lower adhesion observed during lap-shear testing. This finding is in contrast to another study [12] that reported a higher interfacial strength for Di-Unde/Eth in comparison to Di-Prop/Eth and related this effect to more pronounced van-der-Waals interaction of the longer alkyl chains with polyamide 6,6 and chain entanglement between the polyamide 6,6 chains and the organo-functional group of Di-Unde/Eth.

In this context, no significant difference in joint strength can be observed in between Di-Meth/Hex and Di-Unde/Eth, even though Di-Unde/Eth contains significantly longer alkyl spacers. This might be related to the position of the secondary amine in Di-Unde/Eth that is next to the end of the organo-functional group and is thereby sterically better accessible for the polyamide 6 chain in order to form hydrogen bonds. In contrast, the secondary amine in Di-Meth/Hex is next to the central silicon atom and thus sterically hindered.

4. Conclusions

This contribution presented an experimental study on the influence of the chemical structure of amino silane coupling agents on the lap-shear strength of aluminum-polyamide 6 hybrids. Hereto, aluminum strips were coated by different amino silanes, joined to polyamide and tested by lap-shear tests. Appropriate coating procedures, including washing steps after the actual silane application are found to increase the achieved
joint strengths and to enable high reproducibility. The results further show that the amine type (primary, secondary, tertiary), the number of amine groups (one, two), the length of the alkyl linkers (methyl, ethyl, propyl, hexyl, undecyl) and the position of the amine groups with respect to the organo-functional group impacts the achieved joint strength. It is concluded that high adhesion in aluminum-polyamide 6 joints is achieved if the organo-functional group contains (i) a primary amine chain-end group, (ii) multiple amine groups and (iii) short alkyl spacers. Based on this, the predominant mechanism of adhesion is concluded to be hydrogen bonding in between the amine groups and the amide groups of polyamide 6. The highest lap-shear strengths are determined when using N-(6-aminohexyl)aminomethyltriethoxysilane with about 15 MPa. This is sufficiently high in comparison to competitive methods [6], which are used for the interfacial of aluminum-polyamide 6 hybrids. Furthermore, the conducted investigations show the potential of the different silanes as constituent in sol-gel solutions, which can combine high adhesion with corrosion protection for aluminum substrates in combination with fiber-reinforced polyamide 6 composites [11].

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