

Aminofunctional silane layers for improved copper–polymer interface adhesion

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Abstract The aim of this study was to characterize two different copper grades, oxygen-free copper, and phosphorous deoxidized copper, with aminofunctional silane layers on them and to study these silane layers as coupling agents in the injection-molded thermoplastic urethane–copper hybrids. The copper surfaces were as-received and modified, i.e., polished and oxidized. The copper surfaces and silane layers which were grown from solution concentrations of 0.25 and 0.5 vol% were studied with reflection absorption infrared spectroscopy (RAIRS), atomic force microscope (AFM), scanning electron microscope (SEM), and transmission electron microscope (TEM). The adhesive strengths of the copper–polymer joints were measured with peel tests and peeled surfaces were further studied with RAIRS, AFM, and FESEM. On the as-received copper surface, the silane layer was irregular and existed mainly in the surface roughness sites. This was the reason why hybrids manufactured with the as-received copper failed mostly in the silane layer. Hybrids manufactured with the oxidized copper sheets had a uniform silane layer and the hybrids failed mostly cohesively in thermoplastic urethane and had excellent peel strength values. In all silane-treated copper samples, Si–O–Si groups were formed confirming the cross-linking in the silane layer.

Introduction

Copper–polymer hybrids are used e.g., in electronic applications. Polymers have, however, poor bonding to as-received copper as the native oxide layer on the copper is mechanically weak and not easily wettable by resin. Adhesion between them can be improved for example by modifying the oxide layer [1] or by using coupling agents such as silanes [2]. Silanes are widely used to bond organic and inorganic materials and their typical structure is:



where X is a hydrolyzable group (e.g., methoxy, ethoxy, or acetoxy) and Y is an organofunctional group (e.g., amino, methacryloxy, or epoxy) [3].

Generally, a silane treatment consists of hydrolysis of silane with addition of water, silanization of the substrate, and thermal curing of the silanized substrate. During hydrolysis, the hydrolysable groups react with water forming silanol groups (SiOH) which can further react with hydroxyl groups on the metal surface (MeOH) resulting in covalent bonds (MeOSi). In addition, silanol groups can react with each other forming polysiloxanes (SiOSi) [3–5]. The interaction of silanes with metal surface oxides is complicated process and depends on the substrate metal and its oxide structure [6]. Furthermore, the organofunctional groups at the ends of the alkane chains can bond with organic materials [5].

Thickness and uniformity of the silane layers are very important factors to achieve good adhesion between metal and plastic. With too thin or thick or non-uniform layers, adhesion will suffer [3, 7, 8]. The layer thickness can be controlled mainly by silane solution concentration [7, 9, 10]. The substrate surface has an important role for silane layer structure. A rough surface may disturb the order of

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the first silane layer preventing the formation of the second layer [5] and thus may produce non-uniform layer resulting in poor adhesion in the hybrid applications [11].

The literature, e.g., [8, 12, 13], reports that producing an uniform silane layer on copper substrates is challenging. In our earlier study [11], promising results about an uniform silane layer on the stainless steel surface were achieved by producing a controlled oxide layer on the steel surface before silane treatment. So it can be assumed that also in the case of the copper surface, a controlled oxide layer would be a better substrate than a native copper oxide. The oxidation phenomenon of copper includes oxide nucleation, initial island growth and coalescence, and, finally, overlayer thickening. A copper oxide layer consists of only Cu_2O or both Cu_2O and CuO . At low temperatures, a Cu_2O layer forms first and when temperature increases, Cu_2O reacts with oxygen and CuO starts to form [14–17]. At room temperature, a native copper oxide layer is usually few nanometers thick, consisting of Cu_2O and CuO , and its surface is typically contaminated by carbon [18, 19].

The aim of this study was to study the role of the copper surface by characterizing silane layers on the as-received and modified copper and copper alloy surfaces and relate it to the adhesion in the injection-molded thermoplastic urethane–copper hybrids. Before silane treatments (with two solution concentrations), the copper surfaces were modified by electrolytical polishing and oxidation (in air at 200 °C for 25 min) treatment. The copper surfaces and silane layers on them were characterized with reflection absorption infrared spectroscopy (RAIRS) and atomic force microscope (AFM). Thickness and uniformity of the silane layers were directly studied with field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The adhesion strength of the hybrids was measured with peel tests and peeled sample surfaces were studied with RAIRS, AFM, and FESEM.

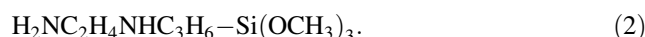
Materials and methods

Materials

Substrate materials, as metal inserts, were oxygen-free, high conductivity copper (OFE-OK), and phosphorous deoxidized copper (Cu-DHP) from Luvata (Finland). Due to very low oxide content in OFE-OK (Cu min 99.99%, O_2 max 5 ppm), it has very good electrical conductivity and because of that, its main applications are in electrical and communication industry. Cu-DHP (Cu min 99.90%, P 150–400 ppm) is used as building and construction materials because it has excellent formability and weldability [20]. The samples, $25 \times 30 \times 0.5$ mm, were cut from the sheets with normal rolled surface quality. Copper

surfaces were electrolytically polished to achieve a clean and smooth surface for surface modification. The electrolyte used was nitric acid in methanol (1:2 as volume fraction) at temperature of -50 °C.

Coupling agent between copper and polymer was amino-functional *N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane (γ -AEAPS, commercially available as Dow Corning Z-6020, Dow Corning, USA) with chemical structure:



It has hydrolysable methoxy groups to react with copper and an amino group to bond with polymer organic matter. Polymer in the injection-molded copper–silane–polymer hybrids was thermoplastic urethane (TPU, commercially available as Estane GP 85 AE nat, Lubrizol Advanced Materials Inc., USA).

Manufacturing process of copper–TPU hybrids

Manufacturing process of the copper–plastic hybrids consisted of three steps: (1) the surface modification of copper, (2) the silane treatment of copper, and (3) the injection molding of plastic onto copper. In the insert injection molding process, the silane-treated copper sheet (insert) is inserted into the mold and then, polymer is injected into the cavity, and after cooling time, the metal–polymer hybrid is removed from the mold. The aim of the modification treatments, polishing or polishing and oxidation, was to improve the bonding of silane onto the copper surface and hence the bonding between copper and polymer. Before silane treatment, a controlled oxide layer was produced on the electrolytically polished copper surfaces. According to our earlier studies with copper (OF-OK) and copper alloy (Cu-DHP) oxidation [21, 22], a dense and around 40 nm thick nanocrystalline Cu_2O layer formed on the copper surfaces in air at 200 °C within 25 min. With longer exposure time (100 min) or at higher temperature (350 °C), the formed oxide layers consisted of Cu_2O and CuO and they were very thick (100–2500 nm) and porous [22]. Our initial studies indicated that on the porous copper oxide layers, silane existed mainly in the pores and the layer was very thin and non-uniform. Therefore, in this study, oxidation treatment in air at 250 °C for 25 min was chosen. Electrolytically polished copper inserts without oxidation treatment were also used as substrates and as-received coppers, washed with acetone (3 + 3 min) and ethanol (3 + 3 min) in an ultrasonic cleaner, were used as reference substrates.

Various silane treatment parameters have been studied in our previous study [7] and the parameters in this study were based on those results. Solution concentrations were 0.25 and 0.5 vol% at natural pH 9–10 and deionized water was used as the solvent. The solution was stirred for 1 h for

hydrolysis, and the copper substrates were then dipped in solution for 5 min. Curing was performed in air at 110 °C for 10 min in the angle of 30° from the horizontal plane to allow excess of silane solution to flow off to the bottom of the copper insert.

The TPU was injection molded onto the silane-treated as-received and modified copper inserts. The size of the copper inserts used in injection molding was 100 × 11 × 0.5 mm. The TPU–steel hybrid parts were processed with an electric injection molding machine (Fanuc Roboshot α C30, Japan). Molding parameters were based on our earlier study [23]. The finished hybrid part had 0.5 mm thick copper insert and 2 mm thick TPU layer and the silane layer between them.

Characterization

FESEM

The FESEM (Zeiss ULTRApplus, Zeiss, Germany), operated at an accelerating voltage of 15 kV, was used to characterize the silane layers on the copper surfaces and the peeled sample surfaces. In our earlier studies [7, 24], very simple sample preparation method, to study the cross-sections of the silane layers, was implemented and it was also used here: the silanized copper sample was glued on an aluminum SEM stub and with a surgical blade an incision was produced through the silane layer. From the edges of the incision, the cross-sections of the layers could be characterized. Before FESEM studies, the peeled sample surfaces were carbon coated.

TEM

The cross-sections of the copper oxide and silane layers on them were studied with TEM (Jeol JEM 2010, Jeol, Japan) operated at an accelerating voltage of 200 kV. The cross-sectional samples were prepared as follows: the small pieces of the samples were cut to size $\sim 1.5 \times 1 \times 0.5$ mm, the pieces were attached to titanium grid by carbon glue and the grid was pre-thinned by hand and then with a dimple grinder (Model 656, Gatan Inc., USA) to the thickness of ~ 50 μ m. The final thinning was made with a precision ion polishing system (PIPS, Model 691, Gatan Inc., USA).

AFM

The topographies of the copper substrates, before and after the silane treatment, and the peeled surfaces (copper sides) were studied with AFM (Nanoscope E AFM/STM, Digital Instruments Inc., USA). A pyramidal probe and a 200 μ m long triangular silicon nitride cantilever were used with a

spring constant of 0.12 N/m. Both contact and constant force modes were used. Surface roughness values (R_a) were calculated from AFM images with commercial software.

RAIRS

The copper substrates and silane layers on them were characterized with RAIRS (Optics Tensor 27, Bruker, Germany, with Veemax II reflection unit from Pike Technologies, USA). The angle used was 70°, scan number 128, and resolution 4 cm^{-1} . Silane-treated sample size was 25 × 30 mm where a circular area with the diameter of 5/8" was studied. Background spectrum was collected using gold-plated mirror and 128 scans. The chemical compositions of the peeled sample surfaces (copper sides) were studied also with RAIRS. The angle used was 40° and mask size 3/8" (sample size 100 × 11 mm), otherwise the device and parameters were as above.

Peel test

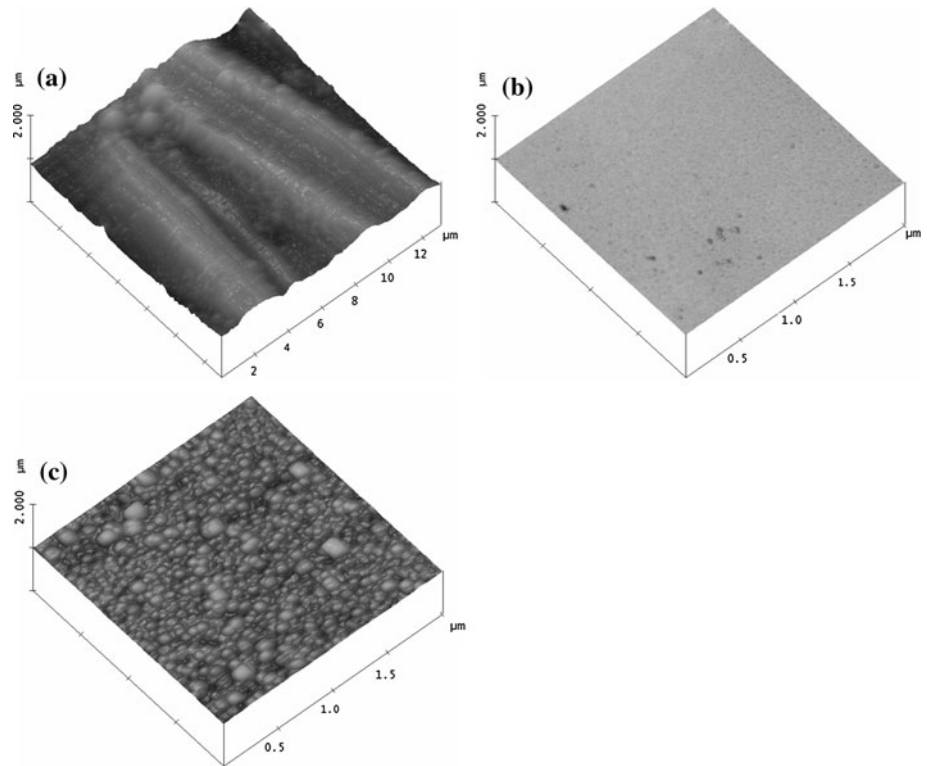
The peel strength values of the injection-molded copper–TPU hybrids were measured using 180° peel test. Samples were conditioned before testing at 23 ± 1 °C in $50 \pm 2\%$ relative humidity for 72 h. A testing machine (Messphysik, Austria) with a 1 kN load cell and 100 mm/min crosshead speed was used. The test was done for five samples. Peeled sample surfaces (copper sides) were studied with an optical stereomicroscope (model MZ 7.5, Leica, Switzerland), RAIRS, AFM, and FESEM.

Results

Characterization of copper surfaces

The copper surfaces were characterized before silane treatment because the substrate surface influences the silane layer structure and thickness. Before silane treatment, the copper surfaces were modified by electrolytical polishing and oxidation treatment in air at 200 °C for 25 min. The as-received surfaces were used as references. AFM images of the as-received, electrolytically polished, and oxidized OFE-OK surfaces are presented in Fig. 1. Their surface roughness values (R_a , calculated from 13 × 13 μ m AFM images) were 72, 7, and 8 nm, respectively. The as-received surface is much rougher compared to the modified surfaces and therefore, the presented scanned area is larger, 13 × 13 μ m, than that of the modified surfaces, 2 × 2 μ m. On the as-received copper surface, rolling lines existed (Fig. 1a). A native oxide layer formed on the polished copper surface (Fig. 1b) and a thicker oxide layer on the oxidized copper surface

Fig. 1 AFM images of **a** as-received ($R_a = 72$ nm), **b** polished ($R_a = 7$ nm), and **c** polished and oxidized ($R_a = 8$ nm) OFE-OK. Note the difference in scanned area of as-received copper



(Fig. 1c). So, the copper surfaces were significantly smoother after modifications. According to the literature, smooth surfaces are better substrates for silane layers than rough ones [5, 11]. Cu-DHP behaved similarly to OFE-OK.

The cross-section TEM image of the oxidized (in air at 200 °C for 25 min) Cu-DHP copper and the selected area electron diffraction (SAED) pattern of the oxide layer are presented in Fig. 2. The average thickness of the oxide layer is 30 nm and according to SAED pattern, its structure is nanocrystalline Cu_2O which agrees well with our earlier

study [22]. The oxide layer on the modified OFE-OK surface was similar.

The copper surfaces, without silane, were characterized also with RAIRS and the spectra of OFE-OK copper are presented in Fig. 3. As-received and electrolytically polished OFE-OK has a main peak at 650 cm^{-1} and a weak peak at 470 cm^{-1} indicating a mixed oxide structure Cu_2O and CuO [25] agreeing well with the literature [18, 19]. After the oxidation treatment at 200 °C, OFE-OK has a very strong Cu_2O peak at 650 cm^{-1} . This agrees well with

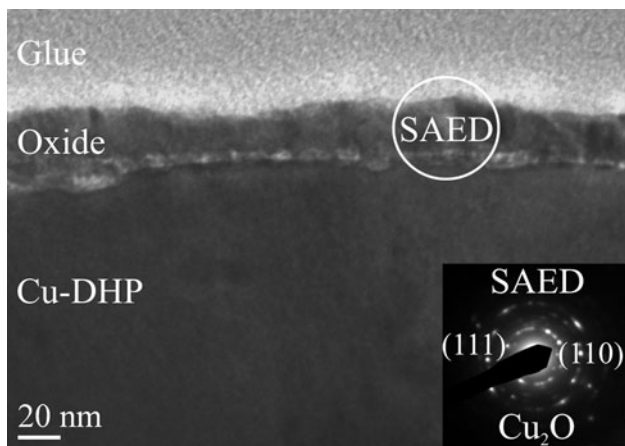


Fig. 2 TEM image of oxidized Cu-DHP and SAED pattern from oxide layer indicating Cu_2O structure

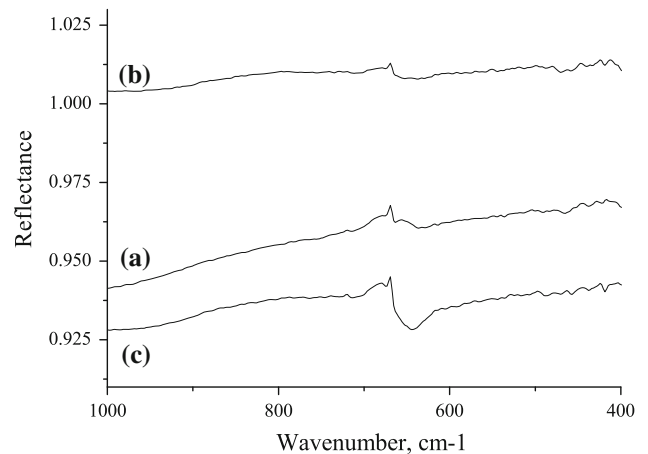


Fig. 3 RAIRS spectra of OFE-OK copper, region from 1000 to 400 cm^{-1} . (a) As-received surface, (b) electrolytically polished surface, and (c) oxidized (in air at 200 °C for 25 min) surface

TEM results. According to the intensities of the Cu_2O peaks, native copper oxide layers on the as-received and polished surface are much thinner than on the polished and oxidized copper surfaces. The spectra of Cu-DHP copper were similar to those for OFE-OK.

Characterization of silane layers on copper surfaces

AFM, FESEM, and TEM results

The topographies of the silane layers, grown from the solution concentrations of 0.25 and 0.5 vol%, on the copper surfaces were studied with AFM. On the as-received copper surfaces, silane existed mainly in the rolling lines. On the polished copper surfaces, the silane layer was uneven. The oxidized copper surface with the silane layer grown from the solution concentration of 0.25 vol% was rough ($R_a \approx 22$ nm) and the underlying oxide structure was still observed indicating a thin and uneven silane layer (Fig. 4a). In the case of the solution concentration of 0.5 vol%, the oxidized copper surface was flat ($R_a \approx 7$ nm) and the oxide was covered by silane (Fig. 4b). To get more information about silane layer thickness and uniformity, the samples were also studied by FESEM and TEM.

Fig. 4 AFM images of oxidized OFE-OK after silane treatment. Silane solution concentration **a** 0.25 vol% ($R_a \approx 22$ nm) and **b** 0.5 vol% ($R_a \approx 7$ nm)

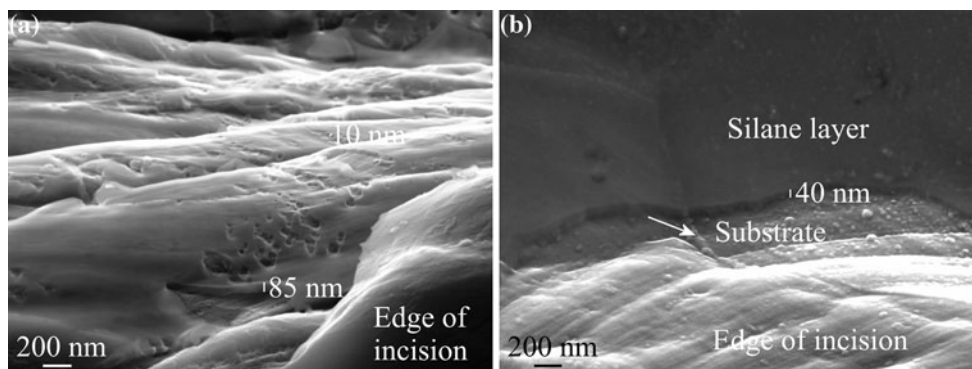
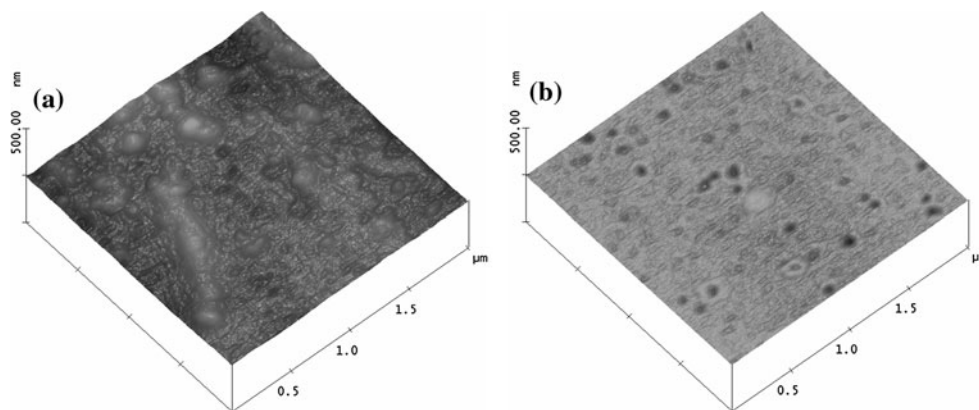


Fig. 5 FESEM images of silane layers (0.5 vol%) on **a** as-received OFE-OK with varying layer thickness and **b** oxidized OFE-OK with uniform layer thickness, grain boundary area marked with white arrow

According to FESEM studies, on the as-received copper surfaces, the silane layer thickness, grown from both solution concentrations, varied from few nanometers to around 100 nm due to surface roughness i.e., rolling lines (Fig. 5a). On the electrolytically polished copper surfaces, the silane layer was more uniform compared to the as-received surface but layer thickness varied still from 20 to 100 nm and from 20 to 200 nm grown from the solution concentrations of 0.25 and 0.5 vol%, respectively. On the oxidized copper surface, silane layer was uniform and its thickness was ~ 25 and ~ 40 nm grown from the silane solution concentrations of 0.25 and 0.5 vol% (Fig. 5b), respectively. However, on the grain boundary areas, the layer was very thin and TEM studies were needed to get detailed information about silane layer structure and underlying oxide.

The TEM images of the oxidized OFE-OK surface with the silane layer, grown from the solution concentration of 0.25 vol%, are presented in Fig. 6. In the middle area of the copper grain, the silane layer thickness is about 25 nm and it is very uniform (Fig. 6a) while, in the grain boundary area it is thin and irregular and hardly covers the oxide (Fig. 6b). Situation was similar with polished and oxidized Cu-DHP.

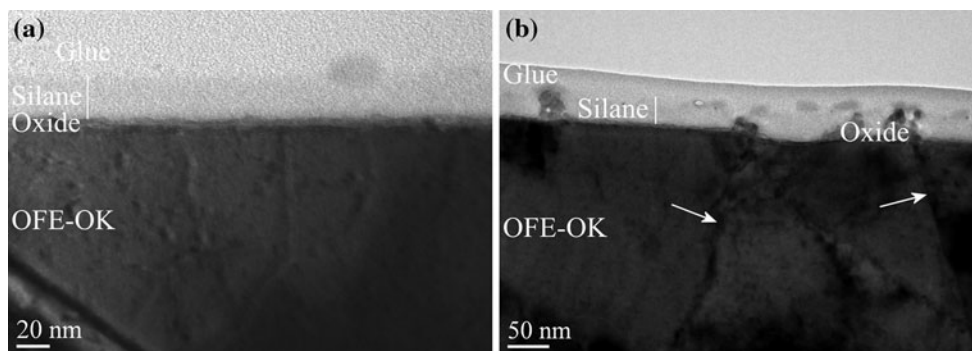


Fig. 6 TEM images of oxidized OFE-OK copper after silane treatment (0.25 vol%). **a** Middle area of copper grain and **b** grain boundary area, white arrows show grain boundaries. Note the different scale bars

The TEM images of the oxidized copper surface with silane layer, grown from the solution concentration of 0.5 vol%, are presented in Fig. 7. In the middle area of the copper grain, the silane layer thickness is ~ 40 nm and it is uniform (Fig. 7a). On the grain boundary area, the layer is thin but it looks to cover the oxide (Fig. 7b). According to TEM images of the silanized coppers (Figs. 6, 7), the underlying oxide layer is thinner than previous silane treatment (Fig. 2). This is probably due to the solubility of the copper oxide in silane solution, as reported by Boerio et al. [6]. In addition, the silane layer is thinner in the grain boundary areas than in the center of the copper grains (Figs. 6b, 7b). Probably, the silane layer formation is disturbed by impurities, e.g., Pb, Fe, S, and irregular oxide layer on the grain boundaries. Also, the possible solubility of the copper oxide in silane solution [6] seems to be less in the grain boundary areas than in the middle areas.

RAIRS results

The as-received and modified copper surfaces were studied with RAIRS after silane treatments. The spectra of the silanized Cu-DHP with the silane solution concentration of 0.5 vol% are presented in Fig. 8 and the assignments of the

RAIRS peaks are in Table 1. In all samples, the intense peaks at 1138 and 1046 cm^{-1} from the cross-linked Si–O–Si stretching vibrations are detected indicating that silane layer polymerized during the curing at $110\text{ }^{\circ}\text{C}$ for 10 min. However, in all samples of Cu-DHP and in the polished OFE-OK with the solution concentration of 0.5 vol%, a weak peak or shoulder at 930 cm^{-1} is observed, indicating a small amount of unpolymerized silanols (located at 940 cm^{-1} according to [26]). In the polished samples, silanized with the solution concentration of 0.25 vol% (not shown), the peaks at 1138 and 1046 cm^{-1} are widened and the Si–O–Si band is located at 1110 cm^{-1} indicating incomplete polymerization [9, 27]. The band at 1590 cm^{-1} (in as-received and polished Cu-DHP, both silane concentrations) or 1585 cm^{-1} (in all other samples) results from amine group deformation [6]. Boerio et al. [6] studied γ -aminosilane films deposited at pH 10.4 on copper and they assigned the peak at 1580 cm^{-1} to deformation mode vibrations of amino groups coordinated to copper ions. This peak was assigned to hydrogen bonding of amino groups of γ -AEAPS on silica surface as reported in [27] and also to hydrogen bonding and complex formation with copper [9]. The wide band at around 3300 cm^{-1} corresponding to vibrations of –OH groups was observed in all

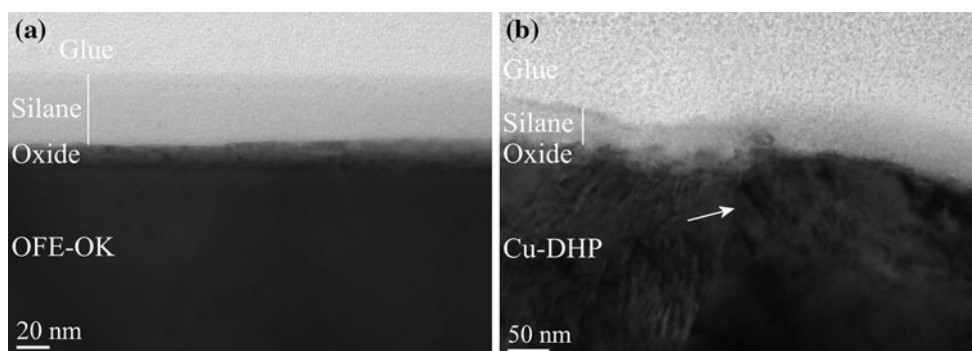


Fig. 7 TEM images of oxidized coppers after silane treatment (0.5 vol%). **a** Middle area of copper grain (OFE-OK) and **b** grain boundary area (Cu-DHP), white arrow shows grain boundary. Note the different scale bars

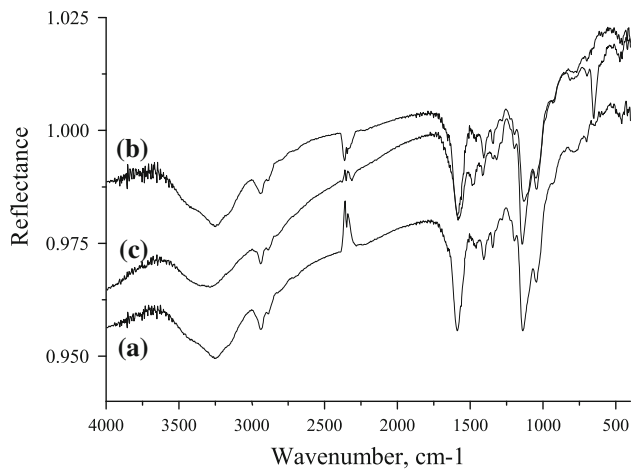


Fig. 8 RAIRS spectra of silanized (solution concentration 0.5 vol%) Cu-DHP surfaces, region from 4000 to 500 cm^{-1} . (a) As-received surface, (b) polished surface, and (c) oxidized surface

Table 1 Assignment of RAIRS peaks and their locations

Location (cm^{-1})	Assignment	Detecting
3300	H_2O	Oxidized OF and DHP
3420, 3250, 3160	$\nu \text{NH}_2, \text{NH}$	Polished OF and DHP
2940	νCH_2 as.	All samples
2885	νCH_2 s.	All samples
1590	δNH_2	All samples
1195	$\rho \text{Si-O-CH}_3$	All samples
1140	$\nu \text{Si-O-Si}$ as.	All samples
1045	$\nu \text{Si-O-Si}$ s.	All samples
930	$\nu \text{Si-OH}$	Polished OF and all DHP
650	Cu_2O	Oxidized OF and DHP

oxidized samples. The amine peaks at 3420, 3520, and 3160 cm^{-1} are clearly observed in polished coppers while those are weak for as-received and oxidized samples. It seems that the hydroxy band at 3300 cm^{-1} is not related to the intensity of Si-OH peak at 930 cm^{-1} , but rather likely belongs to absorbed water presented in the thick layers.

Characterization of copper-TPU hybrids

The TPU was injection molded on the surface of silane-treated (solution concentrations 0.25 and 0.5 vol%) as-received and modified copper inserts and peel strength values were measured by using 180° peel test where TPU is peeled from the metal insert in an angle of 180°. Without silane, no adhesion between as-received or modified copper and TPU was achieved. According to peel results (Fig. 9), the hybrids manufactured with oxidized copper insert have significantly higher peel strength values than the hybrids manufactured with as-received or polished copper inserts.

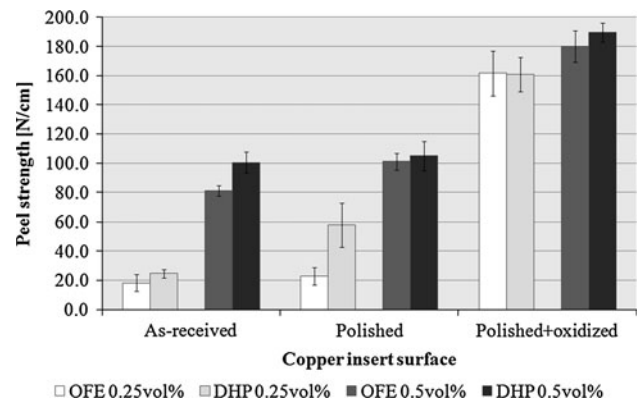


Fig. 9 Peel strengths of hybrids manufactured with various copper inserts, silane solution concentrations used 0.25 and 0.5 vol%

This is especially true for the solution concentration of 0.25 vol%. In all cases, Cu-DHP has higher bond strength values than OFE-OK.

After the peel test, the failure surfaces were studied with an optical stereomicroscope, RAIRS, AFM, and FESEM to get information about failure types. The hybrids manufactured with oxidized copper inserts had around 40 and 75% cohesive failure (determined with the aid of an optical stereomicroscope) in TPU silanized with the solution concentrations of 0.25 and 0.5 vol%, respectively. With as-received and polished inserts, no cohesive failure in TPU was detected. The FESEM images of the failed surface (copper side) of the hybrid manufactured with oxidized OFE-OK insert (silane treated with 0.5 vol%) are presented in Fig. 10. The cohesive failure in TPU (75%) is presented in Fig. 10a; copper surface is totally covered by TPU. Also the RAIRS spectrum of that sample was similar to the reference TPU spectrum. FESEM images of the same sample from remainder area (25%) are presented in Fig. 10b, c; mainly adhesive failure between silane and TPU and failure in the silane layer are detected. Even though, the oxide structure is weakly visible in Fig. 10c, silane remains on the oxide. With the silane solution concentration of 0.25 vol%, less cohesive failure in TPU (40%) was achieved and the detected failure modes were likely adhesive failure between silane and TPU, failure in the silane layer, and adhesive failure between oxide and silane. Situation was similar in the hybrid manufactured with oxidized Cu-DHP insert. Based on FESEM studies, the grain boundaries were not weak bonding areas, even if the formation of the silane layer had been disturbed (Figs. 6, 7). This was concluded by the fact that the failure did not propagate along grain boundaries as shown in Fig. 10b.

In the failure surfaces of the hybrids manufactured with as-received OFE-OK and Cu-DHP (silane solution concentrations 0.25 and 0.5 vol%), no silane was detected with

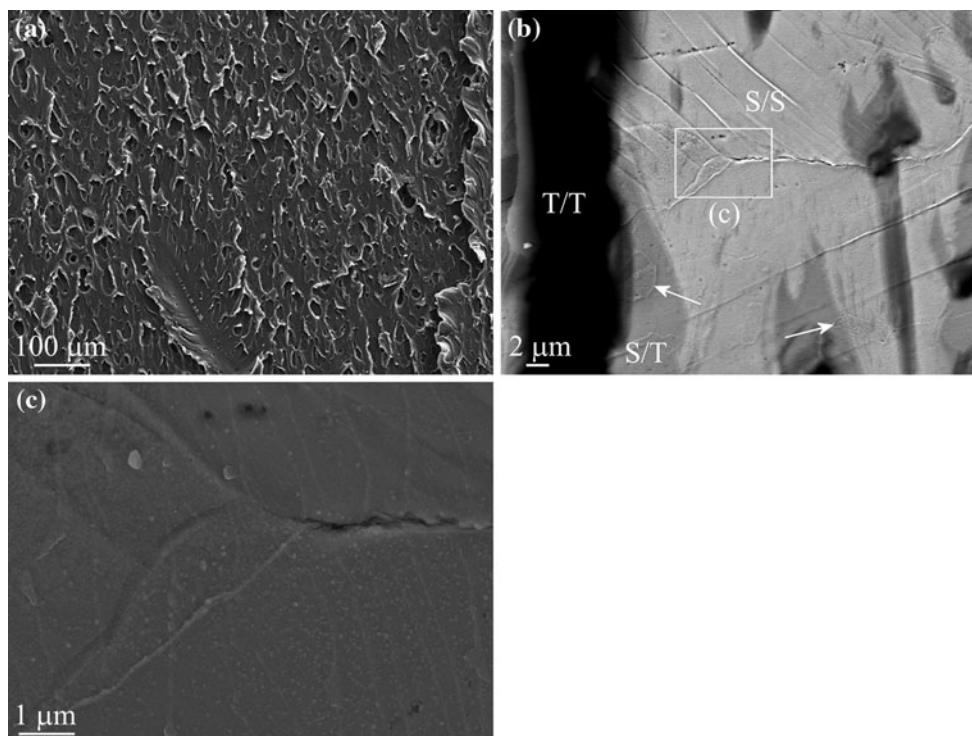


Fig. 10 FESEM images of failure surface (copper side) of copper-TPU hybrid manufactured with oxidized OFE-OK insert, silane solution concentration 0.5 vol%. **a** SE image from area of cohesive failure in TPU (75%), **b** angle-selective backscatter (AsB) image

(some grain boundaries marked with *arrows*), and **c** secondary electron (SE) image from remainder failure area (25%). Possible failure types T/T is cohesive failure in TPU, S/T is adhesive failure between silane and TPU, S/S is failure in silane layer

FESEM or AFM due to the too rough copper surface but with RAIRS, the weak peak related to silane was observed on the copper side indicating failure in the silane layer or adhesive failure between silane and TPU. According to FESEM, AFM, and RAIRS studies, the hybrids manufactured with polished (without oxidation treatment) copper inserts failed in the silane layer (silane solution concentrations 0.25 and 0.5 vol%) and also adhesive failure between silane and TPU with 0.5 vol% silane-treated inserts was observed with AFM and FESEM. Probably, the mixed (Cu_2O and CuO) native oxide layers on the as-received and polished (without oxidation treatment) copper surfaces are too thin and typically contaminated by carbon [18] to form an uniform and well-bonded silane layer compared to the oxidized copper surfaces with a controlled, ~ 30 nm thick Cu_2O layer. So, the copper surface state before the silane treatment has a significant effect on the peel strength values of the hybrids.

Conclusions

The aim of this study was to characterize silane layers on the modified copper surfaces (OFE-OK and Cu-DHP) and to study their effect on the adhesion in the copper-TPU

hybrids. As-received copper inserts were used as a reference where silane existed mainly in the rolling lines formed in the manufacturing of the copper sheet. The hybrids manufactured with the as-received copper inserts failed mostly in the silane layer due to the irregular formation of the layer. The hybrids manufactured with oxidized copper insert had a more uniform silane layer and they failed mainly cohesively in TPU, resulting in better peel strength compared to the hybrid with as-received copper insert. On the oxidized copper surfaces, the silane layer grown from the solution concentration of 0.25 vol% was around 25 nm thick but in the grain boundary areas, silane hardly covered the oxide. The silane layer formation may be disturbed by impurities and irregular oxide layer on the grain boundaries. The layer grown from the solution concentration of 0.5 vol% was around 40 nm thick and silane covered the oxide also in the grain boundary areas, even though the silane layer there was thin. In all silanized copper samples, Si–O–Si groups were formed, confirming the crosslinking in the silane layer. However, the crosslinking degree was lower on the polished copper surface as indicated by broadened and shifted Si–O–Si peaks. So, the substrate surface state has a significant effect on the silane layer structure and hence on the adhesion strength of the copper-TPU hybrid. Therefore, a controlled Cu_2O layer is needed

to achieve an uniform and cross-linked silane layer resulting well-bonded copper-TPU hybrids; a smooth surface produced by electrolytical polishing but with a native oxide layer is not enough. With both modified copper grades, OFE-OK and Cu-DHP, excellent peel strength values for hybrid structures were achieved. So, this kind of modified copper-TPU hybrids can be used in e.g., electrical (OFE-OK) and constructional (Cu-DHP) applications. However, in order to prove that this system is ready for real applications, further studies on long-term stability should be carried out.

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