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Martina Hirayama^a; Marie C. Soares^b; Walter R. Caseri^b; Ulrich W. Suter^b; Olga Goussev^c

^a Global Surface AG, Zürich, Switzerland ^b ETH-Zentrum, Departement Werkstoffe, Institut für Polymere, Zürich, Switzerland ^c EMPA, Abt. 136, Dübendorf, Switzerland

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Activated Poly(hydromethylsiloxane)s as Novel Adhesion Promoters for Metallic Surfaces*

MARTINA HIRAYAMA^{a,†}, MARIE C. SOARES^b, WALTER R. CASERI^b,
ULRICH W. SUTER^b and OLGA GOUSSEV^c

^aGlobal Surface AG, Mythenquai 20, CH-8022 Zürich, Switzerland;

^bETH-Zentrum, Departement Werkstoffe, Institut für Polymere, CH-8092 Zürich,
Switzerland;

^cEMPA, Abt. 136, Ueberlandstr. 129, CH-8600 Dübendorf, Switzerland

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A poly(hydromethylsiloxane) (PHMS) was bound to aluminum, copper and steel surfaces *via* activation with *cis*-[PtCl₂(PhCH=CH₂)₂] in solution at room temperature. The attached polymer promotes the adhesion to two-component silicone resins where the curing process is based on catalytic hydrosilylation of olefins. In lap-shear or peel tests, cohesive failure was always observed. An example shows that the adhesive joint withstood boiling water for 200 h without considerable loss of adhesive strength. It is suggested that a small fraction of the olefinic component of the resin, *e.g.*, a poly(dimethylsiloxane) containing some olefinic groups, is also connected with the attached PHMS *via* catalytic hydrosilylation, thus binding the silicone resin to the surface *via* the PHMS layer.

Keywords: Adhesion promotion; silicone rubber; polymers; ultrathin layers; metal surfaces; Si—H bonds

INTRODUCTION

A number of substances have been described so far as acting as adhesion promoters (also termed primers or coupling agents) [1–4],

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[†]Corresponding author. Tel.: +41.1.2023022, Fax: +41.1.2023051, e-mail: hirayama@globalsurface.com

amongst which the most popular are silanes. Examples of these are functionalized organotrichlorosilanes or organotrialkoxysilanes, in particular compounds of the formula $(\text{MeO})_3\text{SiR}$ and $(\text{EtO})_3\text{SiR}$, where Me = methyl and Et = ethyl; the R group typically consists of a short alkyl chain terminated with a reactive group such as amine, epoxy, or vinyl able to react with specific polymers. The organotrichlorosilanes or organotrialkoxysilanes are usually applied in the presence of water, whereupon, most likely, poly(organosiloxane)s are formed at the surface of the substrates [1, 5]. As a consequence, the efficiency of organotrichlorosilanes or organotrialkoxysilanes to promote adhesion often depends critically on the reaction conditions. The problems associated with the control of the hydrolysis required for the formation of an adhesion-promoting layer might be overcome by use of functionalized linear poly(siloxane)s, but the crosslinking required for the formation of adhering coatings gives rise to additional problems in creating thin adhesion-promoting layers [1] (the adhesion of linear poly(siloxane)s, such as poly(dimethylsiloxane) (PDMS) on inorganic surfaces, is usually poor due to their low chemical reactivity and surface energy).

Homogeneous, ultrathin silicone films on gold surfaces have been prepared with thiol-derivatized poly(siloxane)s [6] recently, and the attachment to various inorganic and organic surfaces of polymers containing Si—H groups activated with *cis*-[PtCl₂(PhCH=CH₂)₂] was described in a patent application [7]. This reaction with activated Si—H groups can be carried out with numerous commercially-available compounds at room temperature in inert solvents such as toluene and some of these reactions were also studied in greater detail on metals [8]. As a model system, we study here such a layer, derived by adsorption of activated poly(hydromethylsiloxane) (PHMS) and its ability to promote the adhesion of metal surfaces to silicone resins. Surface-bound PHMS has been shown to contain still-intact Si—H groups [7, 8] (Fig. 1), which may be used to react with two-component silicone resins that cure by hydrosilylation (Fig. 2). The thickness of such PHMS layers on aluminum, copper and iron surfaces is typically 5–8 nm [8]. In that study, metal surfaces modified by activation of PHMS were exposed to a two-component silicone resin, which shows no detectable adhesive strength on the surfaces considered, without a PHMS layer. One of the components of such resins contains molecules with Si—H

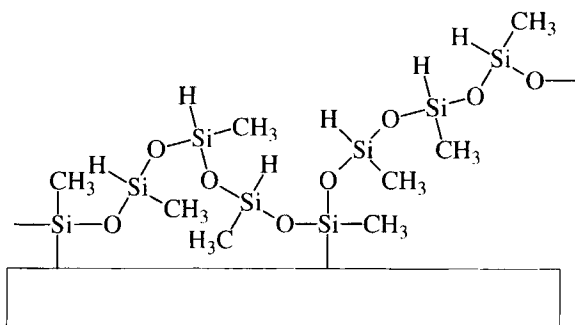


FIGURE 1 Sketch of a metallic surface modified with activated PHMS.

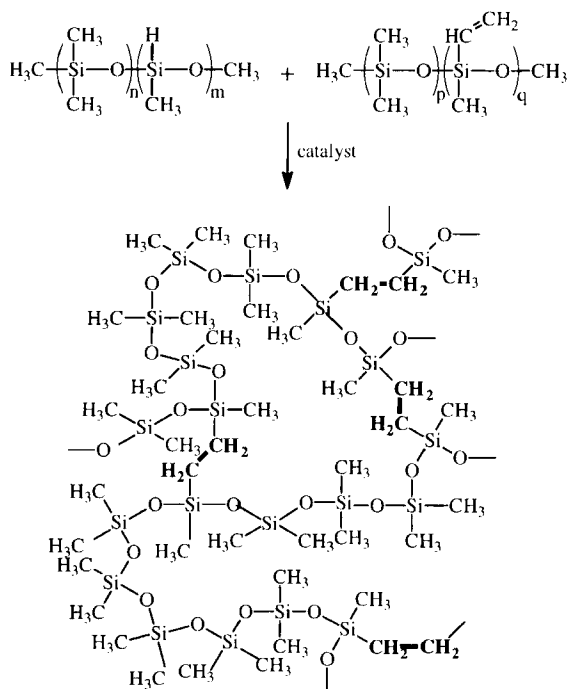


FIGURE 2 Sketch of the formation of a two-component silicone resin.

groups and the other component an olefin and a hydrosilylation catalyst, typically a platinum compound [9 - 11]. In the bulk, the two components form a linear or crosslinked poly(organo)siloxane, depending

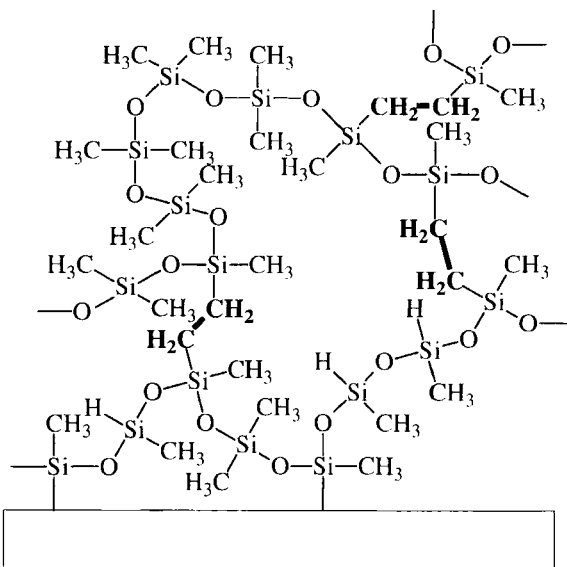


FIGURE 3 Sketch of the suggested binding of a two-component silicone resin to a metallic surface covered with PHMS.

on the chemical structure of the starting materials (Fig. 1). Here we follow the possibility that Si—H groups of the bound PHMS can also be incorporated in the crosslinked network, thus promoting the adhesion to the silicone resin (Fig. 3).

EXPERIMENTAL

The solvents were purchased in p.a. quality grade from Fluka (Buchs, Switzerland). Poly(hydromethylsiloxane) (PHMS, $M_n = 2270$), was bought from ABCR (Karlsruhe, Germany). *cis*-[PtCl₂(PhCH=CH₂)₂] was obtained from Global Surface AG, Zürich, Switzerland. Aluminum plates (AlMgSi) and V2A steel were obtained from Gerber AG (Oftringen, Switzerland) and copper (99.9%) plates from Metal-service Menziken (Menziken, Switzerland). Evaporated copper slides were prepared as reported previously [8].

In order to remove surface impurities, the metal substrates (typically 4 cm × 1.8 cm × 1 mm, if not otherwise indicated) were first cleaned

with toluene. Aluminum surfaces were pretreated with different methods: (a) Immersion in 10% w/w aqueous citric acid overnight, followed by exposure to a 10% w/w NaOH solution for 2 min, (b) immersion in 10% aqueous NaOH for 5 min, or (c) immersion in 10% aqueous citric acid in an ultrasonic bath at 50°C for 30 min. The copper substrates were immersed into pure acetic acid for 10 min and the steel substrates in *aqua regia* for 2 min. Finally, the metal plates were rinsed twice with distilled water and twice with acetone. For surface modification, the cleaned metal plates were immersed into the adsorption solutions (160 ml). The solutions contained *cis*-[PtCl₂(PhCH=CH₂)₂] (50 μM). Then PHMS was added to a final concentration of 1 mM. If not otherwise indicated, the substrates were removed from solution after 1 h and rinsed with *ca.* 30 ml of solvent.

The silicone resin, based on the commercial product Wacker RTV 601 and obtained from Schirma (Basel, Switzerland), was prepared according to the manufacturer's instructions by mixing 9 parts by weight of the component A (viscosity 5000 mPa·s), containing the olefinic component and the catalyst and 1 part by weight of the component B (viscosity 40 mPa·s), containing the hydrosilane. If not otherwise indicated, a layer of 50 μm thickness was prepared on the substrates, using a doctor blade. To avoid the formation of bubbles during the hardening process, air was removed by evacuation. Finally, the samples were heated to 100°C for 15 min, whereupon the resin cured. (Additional examples, not discussed here, are described in a patent application [7]). Experiments with LSR silicone resins from Dow Corning (Midland, USA), not reported here in detail, showed completely parallel behavior and fully support the work reported here.

To elucidate the role of substrate pretreatments, model experiments with the olefinic component of a silicone resin from Wacker (RTV 601 A) were performed with evaporated copper slides which were exposed without surface pretreatment immediately after their preparation to PHMS as described above for the copper plates. The PHMS-treated substrates were immersed in the olefinic component of RTV 601 A, immersed again in toluene for 30 min and immediately studied with IR spectroscopy at grazing incidence reflection.

Lap shear tests on single lap joints with different substrates of 1.5 mm thickness were performed at 23°C and 50% relative humidity (DIN 53 288). The shear area was 12 mm × 25 mm. The samples were

tested in a Zwick tensile testing machine at a free crosshead rate of 5 mm/min. Six samples were measured for each set to account for experimental scatter. The deviation of the extreme values from the average was typically in the region of 20%. Peel tests were performed with silicone resin layers of 5 mm thickness and 25 mm width under ambient conditions at a 90° angle with a peeling rate of 20 ± 1 mm/min. Details on contact angle measurements and IR spectra at grazing incidence reflection have been described previously [12]. Surface roughnesses of the metal plates were measured with a Tencor P10 profilometer.

RESULTS AND DISCUSSION

The metal surfaces in the previous reports on ultrathin layers obtained by activation of poly(hydromethylsiloxane) (PHMS) were prepared by thermal evaporation of the respective metals (*e.g.*, copper and aluminum) on a flat substrate (silicon) [7, 8]. However, it turned out in the course of the experiments (reported below) on adhesion promotion with PHMS, that the metal-silicon interfaces of the substrates were involved in the failure during adhesion measurements. As a consequence, the results reported below were performed with metal plates, which do not suffer from those difficulties. Besides copper and aluminum, V2A steel, which could not be deposited by thermal evaporation anyway, was also surface-modified. The metal plates were cleaned with organic solvents, water, acids or bases prior to use; the exact procedures are described in the Experimental Section. The average surface roughnesses of the cleaned aluminum, copper and steel plates, measured with a profilometer, were in the range of 1–5 μm and, therefore, considerably above the values of copper and aluminum substrates prepared by evaporation (typical roughness 1–2 nm). Without surface pretreatment, adhesion experiments analogous to those reported below were less reproducible with copper and aluminum and no significant adhesion promoting effect was observed with V2A steel.

In order to modify the metal surfaces with PHMS, the substrates were exposed first to toluene solutions containing 1 mM poly(hydromethylsiloxane) (PHMS) and 50 μM *cis*-[PtCl₂(PhCH = CH₂)₂] for

1 h at room temperature, analogous to previous reports on PHMS-modified substrates that had been prepared by thermal evaporation of copper and aluminum [7, 8]. After reaction, the advancing contact angle of water increased from 20–25° on the untreated, cleaned aluminum plates to 110–112°, from 55–60° to 105–120° on copper and from 65° to 113° on steel. These high contact angles confirm the presence of organosiloxanes [8], although the values might be too large by a few degrees because the surfaces are not ideally flat [1, 13].

Two PHMS-treated copper or aluminum plates, respectively and, for comparison, cleaned, non-modified substrates, were joined with a 50 μm layer of a two-component silicone resin (a 9:1 mixture of the components A and B of the silicone resin system RTV 601). ^1H , ^{13}C and ^{29}Si NMR spectra of the components A and B showed that component A consisted of poly(dimethylsiloxane) containing a small fraction of olefin groups. Integration of the signals in ^1H NMR spectra revealed a ratio of the olefinic and the methylsilyl hydrogen atoms of *ca.* 1:100. According to the supplier, this component also contained the platinum catalyst for the hydrosilylation reaction that enables the curing. Component B consisted of a poly(hydromethylsiloxane) with a ratio of Si—H to Si—CH₃ groups of *ca.* 1:7, as obtained by integration of the respective signals in ^1H NMR spectra. The viscosimetric molecular weight of the components A and B is roughly 50000 and 3000, respectively. Hence, component A contains on average *ca.* 13 olefin groups and component B *ca.* 6 Si—H groups per polymer chain.

After curing at 100°C for 15 min, the samples were subjected to lap shear tests, using specimens containing a silicone interlayer of 50 μm (more details on the measurement are given in the Experimental Section). Average shear strengths of mechanical joints of samples on copper, aluminum and steel are shown in Figures 4a, b and c, respectively. In all cases, the stress applied at breaking of the joint was in the range of 6–8 N/mm², corresponding to the cohesive strength of the silicone resin system. Accordingly, the failure is cohesive, *i.e.*, inside the silicon resin, as evident by eye. Without PHMS-treatment, the adhesion is not significant as the silicone resin can readily be peeled off. A few sets of samples prepared under conditions different from those mentioned above were also subjected to lap shear tests. The tests with copper specimens joined with a silicone resin film of 500 μm

thickness disclosed essentially the same results as those with the 50 μm layers (Fig. 4a). The influence of surface pretreatment was studied with aluminum substrates, where etching with citric acid and NaOH, or citric acid or NaOH alone was performed (the exact procedures are described in the Experimental Section). Also, the effect of the reaction time of activated PHMS was studied with aluminum, where reaction times of 1 h or 5 min were used. After joining the aluminum plates with

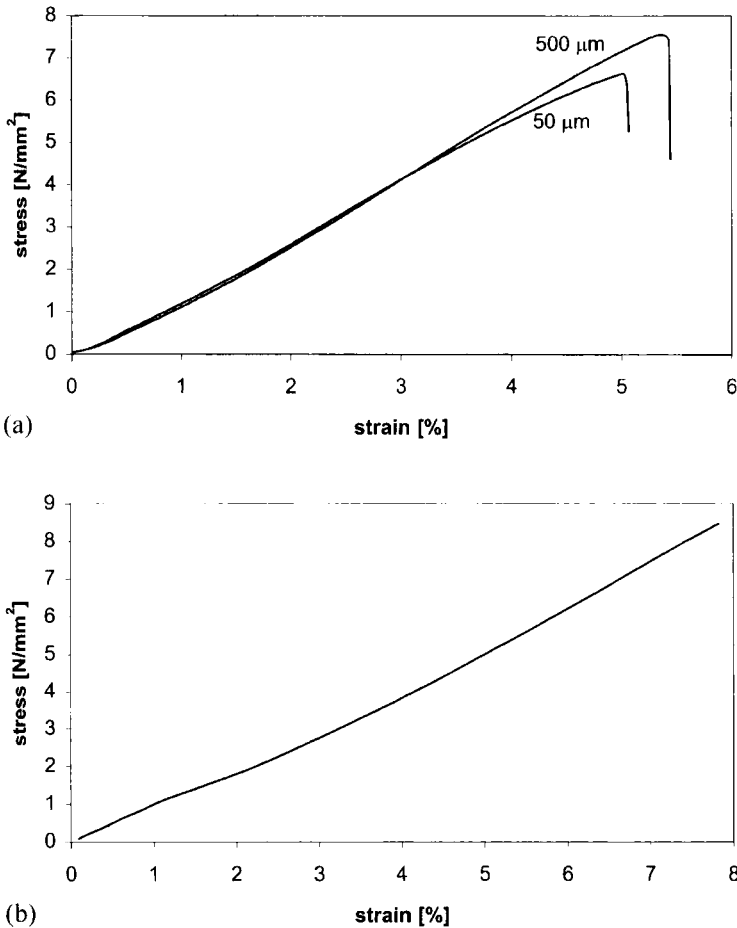


FIGURE 4 Diagrams obtained from lap shear tests of metal substrates modified with PHMS as adhesion promoter for an interlayer of a silicone resin (50 μm if not otherwise indicated): (a) copper (b) aluminum (c) steel.

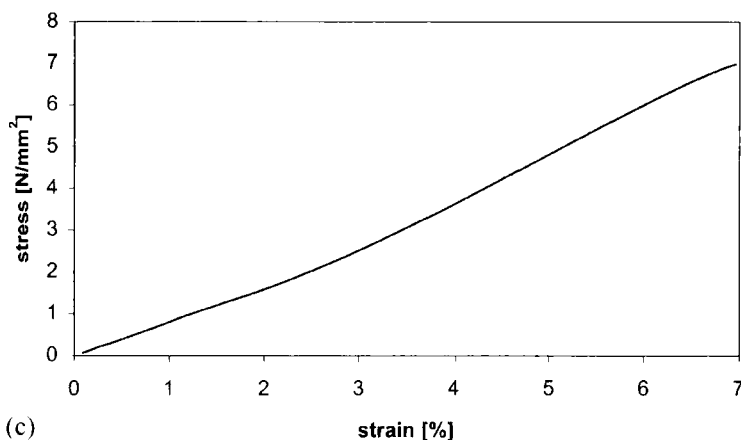


FIGURE 4 (Continued).

50 μm of RTV 601, the usual shear strengths ($6\text{--}8\text{ N/mm}^2$) were observed in all cases. All experiments clearly demonstrate that the layer formed upon PHMS treatment on the metal surfaces indeed acts as an adhesion promoter.

We assume that the adhesion-promoting effect is caused by reaction of some of the olefinic groups of component RTV A with Si—H groups of surface-bound PHMS, as described in the Introduction. Support for this hypothesis was found with model experiments on substrates prepared by evaporation of 200 nm copper on silicon wafers containing 5 nm chromium as adhesion promoter for copper to silicon. Such substrates are suited for surface investigations with infrared spectroscopy at grazing-incidence reflection. Freshly-prepared copper slides were covered with PHMS as described above for copper plates. The PHMS-covered samples were exposed to the component RTV A for 1 h at room temperature and thereafter immersed in toluene for 30 min. For comparison, blank copper substrates were also exposed to the component RTV A under the same conditions and copper substrates with bound PHMS were immersed only in toluene. All experiments were performed twice in the same day and the IR spectra were measured one after the other. No significant amounts of poly(siloxane)s could be detected in the IR spectra when the blank copper substrates were exposed to RTV A (Fig. 5a). The IR spectrum of PHMS-treated copper samples immersed in toluene showed, *e.g.*,

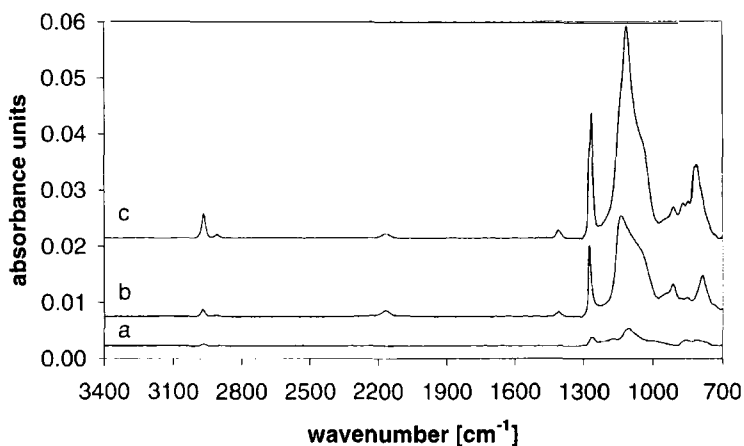


FIGURE 5 IR spectra of copper substrates after exposure of (a) RTV A (b) PHMS/*cis*-[PtCl₂(PhCH=CH₂)₂] and (c) PHMS/*cis*-[PtCl₂(PhCH=CH₂)₂] followed by treatment with RTV A.

the expected signals of $\nu_{\text{as}}(\text{CH}_3)$ at 2970, $\nu_{\text{as}}(\text{CH}_3)$ at 2912, $\nu(\text{Si}-\text{H})$ at 2167, $\delta_{\text{as}}(\text{CH}_3)$ at 1410, $\delta_{\text{as}}(\text{CH}_3)$ at 1275 and $\nu(\text{Si}-\text{O}-\text{Si})$ around 1100 cm^{-1} (Fig. 5b). Since the chemical composition of PHMS and component RTV A only differs with respect to Si—H groups and very few olefin groups, the IR spectra of PHMS and component RTV A are virtually identical, with the signals due to Si—H vibrations missing in the spectrum of component RTV A. To investigate if component RTV A reacted, the ratio of the integrated intensities of the signals at $\nu_{\text{as}}(\text{CH}_3)$ at 2970 cm^{-1} and $\nu(\text{Si}-\text{H})$ at 2167 cm^{-1} and of the ratio of the bands at $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ around 1100 cm^{-1} and $\nu(\text{Si}-\text{H})$ were considered. If component RTV A reacted with some of the Si—H groups of the surface-bound PHMS, these ratios should increase since the content of Si—H groups would decrease compared with methyl and siloxane units. Indeed, in the sets of two experiments prepared under identical conditions, the former ratio increased from 0.75 and 0.89 to 2.94 and 2.96 and the latter ratio from 51 and 63 to 110 and 111 (Spectra 5b and 5c). Except for $\nu(\text{Si}-\text{H})$, the intensity of the IR signals originally stemming from the PHMS monolayer increased after treatment with RTV A by roughly a factor of two when the samples were measured under the same conditions immediately one behind the other. According to our experience with IR spectroscopy at grazing

incidence reflection, we consider the order of this difference to be significant. We conclude, therefore, that the thickness of the bound layer of RTV A corresponds roughly to the thickness of the pristine PHMS monolayer, *i.e.*, *ca.* 8 nm [8].

The PHMS-treatment of aluminum also promotes the adhesion to other silicones, *e.g.*, LSR silicones. In preliminary experiments, no peel resistance could be measured with an LSR silicone without PHMS-treatment, while a value of 37 N/cm was found after the aluminum plates had been exposed to PHMS/*cis*-[PtCl₂(PhCH = CH₂)₂]. Again, a cohesive failure was observed. In addition, this system was immersed in boiling water for various periods of time in order to get an impression of the resistance of the adhesion promoter towards hydrolysis and temperature. Remarkably, the initial peel resistance decreased only slightly within 200 h in boiling water (Fig. 6) and the corresponding failures were of a cohesive nature. The cohesive failure suggests that the bonding of PHMS to the metal is quite strong. After 200 h exposure, the peel resistance started to decline and reached 6 N/cm after 300 h of immersion. After 300 h immersion, the failure mechanism seems to become (visually) adhesive in nature, which would imply that the bonding of the PHMS at the interface degrades.

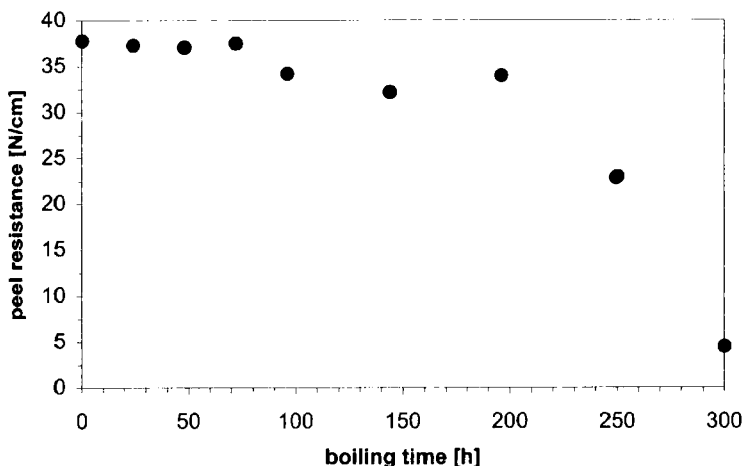
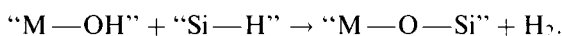


FIGURE 6 Peel resistance (90°) of an aluminum substrate modified with PHMS as adhesion promoter for an interlayer of a silicone resin after exposure to boiling water for various periods.

The above experiments clearly demonstrate that surface-bound PHMS can act as an adhesion promoter for two-component silicone resins in which one component contains olefinic groups. It has to be noted, however, that the nature of the interaction between the PHMS and the metal surfaces has not been elucidated yet [8]. Different mechanisms could explain the affinity of the activated PHMS to the metal surfaces. For example, the Si—H bonds might react in the presence of platinum complexes with metal hydroxide groups present at the surfaces of the metals exposed to ambient conditions, forming M—O—Si bonds according to the reaction



As an alternative, PHMS might react with the platinum complex *via* oxidative addition of Si—H bonds and the resulting complexes might strongly interact with the substrate, thus binding the polymer to the surface.

CONCLUSIONS

The treatment of aluminum, copper and steel plates with a solution of poly(hydromethylsiloxane) (PHMS) and the activator *cis*-[PtCl₂(PhCH = CH₂)₂] markedly increases the adhesion of two-component silicone resins that are cured *via* catalytic hydrosilylation. Such resin systems, that contain polymer chains with olefinic groups, are probably attached to the surface *via* reaction with intact Si—H groups of the surface-bound PHMS. Etching processes enhanced the reproducibility of the results at least for the materials used here; in the case of V2A steel such a procedure was even required to yield a measurable adhesion. Adhesion tests with surface-pretreated samples always yielded cohesive failures, *i.e.*, the strength of the adhesive joint was limited by the cohesive strength of the silicone resins. The adhesion-promoting effect can be retained during exposure to boiling water, for at least several days.

Due to the variety of organic and inorganic substrates that can be modified with substances containing Si—H groups in the presence of platinum compounds, it is expected that PHMS can also act as an adhesion promoter for other surfaces (including organic surfaces) and

to polymers other than poly(siloxane)s. Note in this context that the binding mechanism of the adhesion promoter may differ when different substrates are used.

Acknowledgment

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