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# Influence of High-temperature and High-humidity Aging on the Material and Adhesive Properties of Addition Curing Silicone Adhesives

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## Abstract

Silicones are commonly used as sealants when high-performance materials are required due to harsh environmental conditions. To ensure a proper sealing function, the buildup of adhesion to the adherends is a prerequisite that is often addressed by the addition of adhesion promoters. However, the investigation of the fundamental adhesion mechanisms of silicones has been widely neglected. This work focuses on adhesive bond properties with aluminum adherends without the usage of adhesion promoters. The influence of high-temperature and high-humidity aging on the adhesive bond and material properties is examined.

For this purpose, we formulated an addition curing silicone adhesive with a known composition. Aging took place for up to 56 d at different temperatures ranging from room temperature to 150 °C. In addition, we examined the influence of moisture by applying high-humidity conditions (85 °C/85 % relative humidity). Changes in bulk material properties were characterized by stress at break, strain at break, Shore A hardness and swelling degree. Moreover, Fourier-Transform Infrared (FTIR) spectroscopy provided information about the chemical processes. The adhesive properties were determined using lap-shear joints.

At high-temperature aging, the strain at break decreases while the hardness of the bulk material increases. A lower degree of swelling suggests an increasing cross-linking density. At the same time, lap-shear strengths increase and cohesive fracture patterns indicate a proper buildup of adhesion. The samples aged under high-humidity conditions show a more complicated behavior. The increase in cross-linking density proceeds slower compared to high-temperature conditions (130 °C and 150 °C) but reaches higher values after 56 d. Lap-shear strengths tend to be lower compared to high-temperature storage and are accompanied by a significant amount of adhesive failure. FTIR spectroscopy reveals reactions of the residual hydrosiloxane groups of the cross-linking agent. However, these reactions are insufficient to fully explain the observed behavior. Therefore, reactions of the siloxane backbone are suggested.

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Although no specific adhesion promoters were used, high-temperature conditions enabled a proper adhesion buildup of addition curing silicones on aluminum adherends under dry conditions. In contrast, humid conditions disturb adhesion buildup and are rather unfavorable for adhesion.

## **Keywords**

Silicone; aluminum and alloys; adhesion by chemical bonding; aging; FTIR spectroscopy; cross-linking

## **1. Introduction**

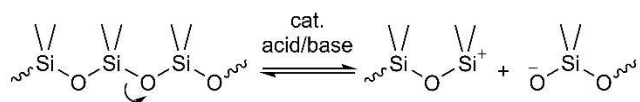
In industry, silicones find numerous applications as sealants due to their unique properties. The most common silicone is based on poly(dimethylsiloxane) (PDMS). PDMS has a very low glass transition temperature of  $-123\text{ }^{\circ}\text{C}$ [1] due to weak intermolecular interactions and a high degree of rotational freedom caused by small rotational barriers of  $<0.8\text{ kJ/mol}$  along the Si-O-Si bond.[2] Thus, the elastic behavior is retained even at very low temperatures of approximately  $-40\text{ }^{\circ}\text{C}$ , where the crystallization of many silicone sealants starts. At the same time, silicones are very resistant towards high-temperature conditions in comparison to common polymers because oxidation reactions and other radical reactions are less pronounced due to the high bond dissociation energies of the Si-O bonds (e.g.  $569\text{ kJ/mol}$  for  $\text{Me}_3\text{Si-OSiMe}_3$ ).[3] Thus, even under harsh conditions, silicones offer reliable material properties. However, degradation and the lack of buildup of adhesion to the adherend cause numerous issues in practice because they undermine the sealing and cause leakage. Therefore, knowledge about the buildup and degradation of adhesion is of high importance for sealing materials.

To understand the adhesion between silicones and polar surfaces like aluminum oxides, which are present on aluminum adherends, it is helpful to examine the chemical and physical interactions. Although the backbone of PDMS is characterized by very polar Si-O bonds, PDMS behaves rather hydrophobically due to the orientation of the nonpolar methyl groups towards the outside, which dominates the surface behavior.[4] The hydrophobic nature of PDMS is directly reflected in its water repellency. Furthermore, the work of adhesion on water surfaces is only slightly higher, but still similar compared to nonpolar hydrocarbons.[5] Regarding the physical interactions, quantum mechanical calculations revealed that hydrogen bonding is formed to a minor extent with polar surfaces like water[6] and silica [7][8][9] and that the interactions rely mainly on dispersion and dipolar attraction.[8][9] Hence, hydrogen bonds that are expected to be strong physical interactions play only a minor role in the interactions of PDMS with polar surfaces and perfectly fit the hydrophobic behavior. Therefore, it is not surprising that the adsorption of PDMS molecules on polar surfaces like glass can be easily diminished by solvents, such as water, which are able to form strong hydrogen bonds with the surface.[10][11]

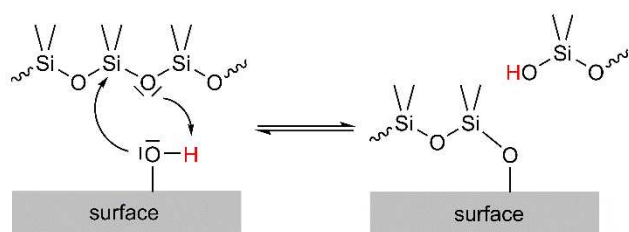
The propensity of silicones for rather weak dispersion and dipolar interactions explains the limited ability to build up adhesion with polar substrates like the aluminum oxide surfaces of aluminum adherends. In industry and research, the issue of reliable

adhesion was encountered with the development of adhesion promoters like alkoxy-silanes. The specific reactivity of adhesion promoters allows them to create a chemical link to both adherend and polymer, thereby increasing the adhesion strength through chemisorption. Over the past decades, adhesion promoters have experienced great success, and it is not surprising that there are many studies in the literature covering them.[12][13] However, with the development of adhesion promoters, the study of the fundamental adhesion mechanisms of silicones have been widely neglected. Nevertheless, silicones themselves offer an interesting chemistry that clearly differs from that of common polymers.

Due to the high polarity of the silicone backbone, Si-O bonds allow a heterolytic cleavage (**Scheme 1**). Such reactions are catalyzed by acids[14] and bases[14][15][16] and are applied, for example, for the ring-opening polymerization of cyclosiloxanes like octamethylcyclotetrasiloxane.[17] Moreover, there are numerous examples of the backbone reacting with oxidic surfaces like silica and aluminum oxide (**Scheme 2**).[18][19][20][21][22][23] This reactivity is not surprising since such surfaces generally comprise acidic/basic properties. These reactions are particularly pronounced at elevated temperatures.

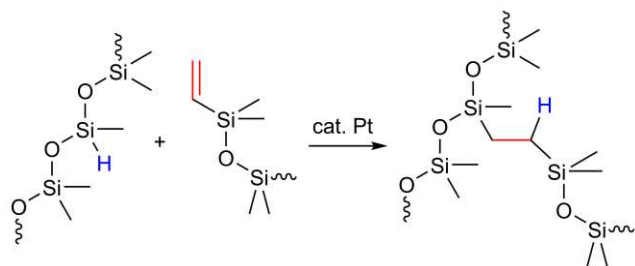


**Scheme 1.** Heterolytic cleavage of a Si-O bond of PDMS.



**Scheme 2.** Reaction of the PDMS backbone with surface hydroxyl groups.

Beyond that, functional groups that are introduced to realize the cross-linking reaction of silicone sealants are also able to interact with surfaces. Addition curing silicones contain hydrosiloxane groups (**Scheme 3**), which were shown to react with silica and aluminum oxide surfaces.[24][25][26][27][28][29] In the publication by Hirayama *et al.*, a hydromethylsiloxane component in combination with a platinum catalyst was able to act as a primer and led to strongly improved adhesion.[30][31]



**Scheme 3.** Hydrosilylation reaction that is used to cure addition curing silicones.

In light of the unique chemical reactivity of silicones, the question arises about the opportunity of adhesion buildup without specific adhesion promoters. In a previous work, we systematically changed the composition of addition curing silicones and tested their bulk material and adhesive properties.[32] We found that it is possible to build up adhesion to a certain extent without the addition of adhesion promoters. However, the lap-shear strength was quite limited to roughly 4 MPa, showing predominantly adhesive failures. In the current work, we investigate the influence of environmental conditions in triggering potential reactions of the siloxane after curing. For this purpose, an addition curing silicone sealant was formulated containing only basic ingredients, namely a vinyl-terminated PDMS as a resin, an internal polyhydromethylsiloxane as a curing agent, a platinum catalyst as well as an inhibitor to control the curing reaction, and lastly a hydrophobized fumed silica to improve the bulk material strength. No adhesion promoters were added. This material corresponds to a formulation in our previous work.[32] The influence of high-temperature and high-humidity conditions after curing are here investigated on both the bulk material and adhesive properties.

## 2. Experimental Part

### 2.1. Formulation of Silicone Adhesive

The following chemicals were used to formulate the silicone adhesive. A dimethylvinyl-terminated PDMS (1000 cSt, 28000 g/mol) from ABCR (Karlsruhe, Germany) served as a resin, containing 0.07 mmol/g vinyl groups according to the specification of the supplier. The curing agent is a (25 – 35 % methylhydrosiloxane)dimethylsiloxane copolymer (25 – 35 cSt) from ABCR (Karlsruhe, Germany) with a specified amount of 30.5 % methylhydrosiloxane groups. Hydrophobic fumed silica (Aerosil R 812 S, BET surface area: 195 – 245 m<sup>2</sup>/g) from Evonik Industries (Essen, Germany) was incorporated as a filler. As a catalyst, a platinum-divinyltetramethyldisiloxane complex dissolved in vinyl-terminated poly(dimethylsiloxane) (3 – 3.5 % Pt) from ABCR (Karlsruhe, Germany) was used, which contained 3.25 % Pt (Weight/Weight [w/w]). The inhibitor, 1-ethynyl-1-cyclohexanol, was purchased from Alfa Aesar (Ward Hill, United States).

For mixing, either a planetary mixer (ARV-310, THINKY Corporation) or a dissolver (CE03-C1, VMA-Getzmann) was used. First, the catalyst (0.8325 g) and the inhibitor (3.000 g) were diluted in resin (30.28 g and 12.005 g, respectively). Homogenization was achieved by mixing the components in a planetary mixer (1800 Rounds Per Minute (RPM), 3 min).

The planetary mixer is more suitable than the dissolver to incorporate the filler. However, due to the limited capacity of the planetary mixer used for this work, ten small portions of adhesive were mixed; these were subsequently combined and mixed with the dissolver to ensure the homogeneity of the silicone adhesive. The noted masses reflect the average of all ten portions. For each portion, a beaker was charged with resin (72.50 g) and the diluted catalyst solution (0.4393 g) was added. After homogenization with a planetary mixer (1800 RPM, 3 min), the diluted inhibitor solution was added (0.5790 g) and the mixture was homogenized again (1800 RPM, 3 min). The filler (19.3585 g) was incorporated in three steps, each accompanied by mixing (1500 RPM, 1 min). After the complete addition of the filler, the mixture was homogenized (1800 RPM, 2 min). The filler on the wall of the beaker was detached with a spatula and incorporated by mixing (1800 RPM, 3 min). Finally, the curing agent (3.0389 g) was added (1500 RPM, 1 min).

The obtained ten portions were combined and mixed with a dissolver under reduced pressure (500 RPM, 20 min, 40 mbar). After further degassing without mixing (30 min, 40 mbar), the material was transferred into beakers and again degassed with the planetary mixer (1000 RPM, 15 min, 100 mbar).

## 2.2. Preparation of Bulk Material Samples

A polytetrafluoroethylene mold comprising a cavity with the dimensions  $100 \times 100 \times 2 \text{ mm}^3$  was filled with uncured silicone material. Curing was achieved with a hot press (LaboPress P150H, VOGT Labormaschinen) for 1 h at  $130 \text{ }^\circ\text{C}$  and a compression force of 2 kN. The test specimens were punched out of the obtained silicone sheets with a cutting press (Z121, ZwickRoell). Seven S2 specimens (DIN 53504:2017-03) were used for the tensile tests, with a traverse speed of 200 mm/min (ZwickRoell). The strain was determined by an extensometer. The engineering stress at break was determined by dividing the measured force at break by the initial cross-sectional area of the S2 specimen, which was determined by measuring the real height of each specimen before testing. Both ends of three stacked S2 specimens ( $\sim 6 \text{ mm}$  thickness) were used for Shore A hardness measurements, giving 14 measurements (digi test DTAA 5241/03, Bareiss Prüfgerätebau). Additionally, discs 16 mm in diameter were punched out for the swelling measurements, whereby 10 ml toluene (99 %, Merck) was added to each specimen. The degree of swelling is defined as the mass of soaked toluene after 3 d divided by the mass of the silicone adhesive. Each swelling measurement was done with three specimens. The error bars in the diagrams depict one standard deviation.

### 2.3. FTIR Spectroscopy

A Bruker Vertex 80v equipped with a DLaTGS detector was used to record spectra in the range from 400  $\text{cm}^{-1}$  to 8000  $\text{cm}^{-1}$  and at a resolution of 4  $\text{cm}^{-1}$ . Each spectrum was averaged over 32 scans. The spectra were processed using the OPUS (Bruker) software. The samples were prepared by putting a small amount of silicone material onto a Teflon tape covering an aluminum plate. Spacers of 100  $\mu\text{m}$  were placed on the plate and a second aluminum plate covered with Teflon tape was pressed onto the first plate containing the silicone material. After curing for 1 h at 130  $^{\circ}\text{C}$ , a circular silicone sheet was obtained with an approximate radius of 1 – 2 cm and a thickness of approximately 100  $\mu\text{m}$ . FTIR spectra were recorded by measuring the transmission through these sheets.

The uncured silicone adhesive contains approximately 0.161 mmol/g Si-H groups and is defined as 100 % concentration of Si-H groups ( $I_{100}(\text{SiH})$ ), while the silicone adhesive without curing agent ( $I_0(\text{SiH})$ ) is defined as 0 % Si-H groups. Both uncured materials were placed between two KBr crystals with a distance of approximately 100  $\mu\text{m}$ , adjusted by spacers. Transmission through these two samples delivered the references for the quantification of the Si-H concentration. The Si-O overtone signal from 2027  $\text{cm}^{-1}$  to 2108  $\text{cm}^{-1}$  was used as the internal reference and the spectra were normalized to this signal. According to Lambert-Beer's law, the intensity of the signal is proportional to the concentration of the moiety causing this signal. The intensity  $I_i(\text{SiH})$  of the Si-H signal was determined by integrating the signal in the region 2108 – 2208  $\text{cm}^{-1}$ . The Si-H concentration  $c_i(\text{SiH})$  for a sample  $i$  was calculated using the following formula:

$$c_i(\text{SiH}) = \frac{I_i(\text{SiH}) - I_0(\text{SiH})}{I_{100}(\text{SiH}) - I_0(\text{SiH})}$$

By comparing the integrals of the normalized reference signal (2027 – 2108  $\text{cm}^{-1}$ ), the maximum difference lies between the uncured sample (100 % Si-H concentration) and the sample without curing agent (0 % Si-H concentration) and amounts to 12 %. According to this, a relative error of the concentration of Si-H groups is estimated as  $\pm 6$  %.

### 2.4. Acid-etch Pretreatment of Adherends

Aluminum sheet metal (100  $\times$  25  $\times$  1.5  $\text{mm}^3$ , alloy EN AW-5754 [“AlMg3”]) was used as the adherend and was obtained from Rocholl (Aglasterhausen, Germany). The acid-etch solution contained iron(III) sulfate hydrate (AnalaR NORMA-PUR, VWR International, Radnor, United States) and sulfuric acid (96%, Bernd Kraft, Oberhausen, Germany). First, the aluminum adherends were degreased in an ultrasonic bath (Sonorex Super RK1028H, Bandelin) with acetone for 5 min at room temperature. The acid-etch solution consisted of demineralized water (1725 g), concentrated sulfuric acid (471.5 mL) and iron(III) sulfate hydrate (345 g). The adherends were tempered to 50  $^{\circ}\text{C}$  in a convection oven and placed in the acid-etch solution ( $65 \pm 3$   $^{\circ}\text{C}$ , 12 min). Subsequently, the substrates were washed in two tap water baths and then in two demineralized water baths. The substrates were dried at 50  $^{\circ}\text{C}$

in a convection oven for 1 h and stored in a desiccator over silica gel at 0 % relative humidity and room temperature until the preparation of the lap-shear samples.

### *2.5. Lap-shear samples*

The lap-shear samples were prepared based on DIN EN 1465:2009-07 with an overlap of  $12.5 \pm 0.25$  mm and an adhesive thickness of 150  $\mu\text{m}$ . The thickness of the adhesive was adjusted with two distance wires that were inserted into the adhesive bond. The samples were cured for 1 h at 130 °C in a convection oven. Before further aging, the samples were left to cool down to room temperature. Seven lap-shear samples were prepared for each test, and one standard deviation is depicted in the diagram as the error bar. The fracture pattern was estimated by visual inspection.

### *2.6. Aging*

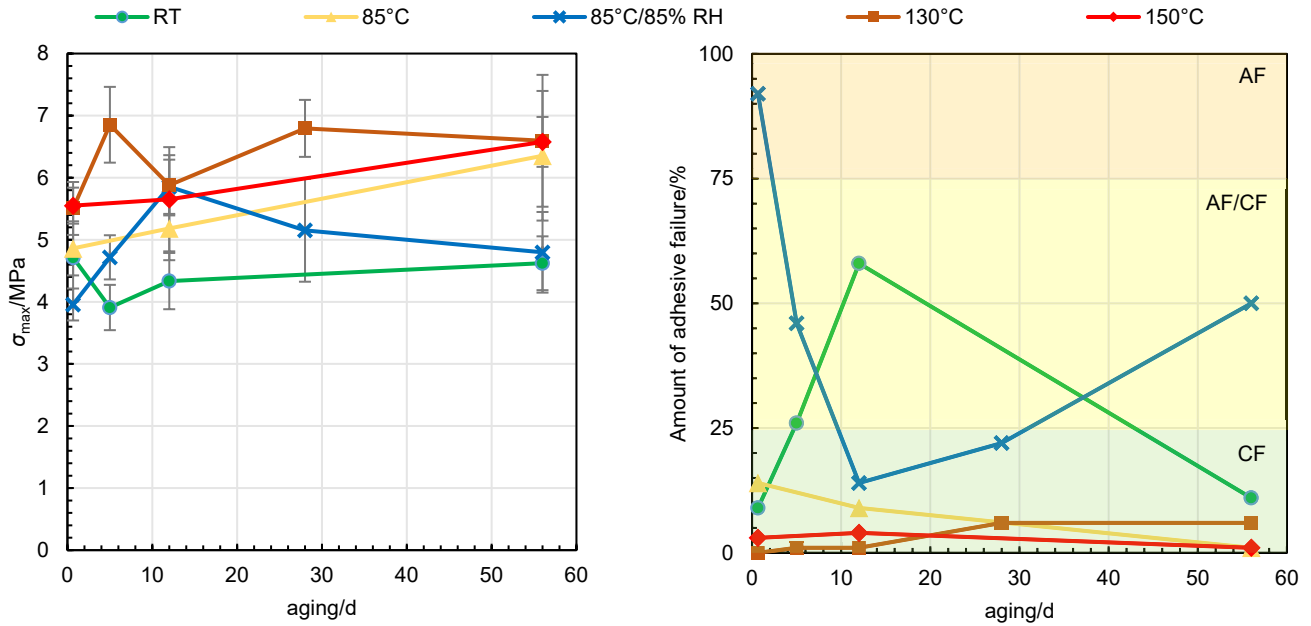
Three conditions were used to age the test specimen: Ambient conditions (RT) for the reference specimen, dry conditions in a convection oven (85 °C, 130 °C, 150 °C) and humid conditions in a climate chamber (85 °C, 85 % RH).

## **3. Results**

### *3.1. Aging of Adhesive Bond*

Adhesive bond properties were tested using single lap-shear joints after different aging conditions, namely 85 °C, 130 °C, 150 °C at low humidity and 85 °C under a humid atmosphere comprising 85 % Relative Humidity (RH) (**Fig. 1**). The samples stored at Room Temperature (RT) show an almost constant lap-shear strength over storage time (**Fig. 1**, left). At 16 h and 56 d, a cohesive failure is observed, whereas at 5 d and 12 d a mixed adhesive/cohesive failure is observed (**Fig. 1**, right). The mixed adhesive/cohesive fracture pattern shows that the adhesive and cohesive strengths are in a similar range and that the adhesion is not reliable although no harsh storage conditions were applied.





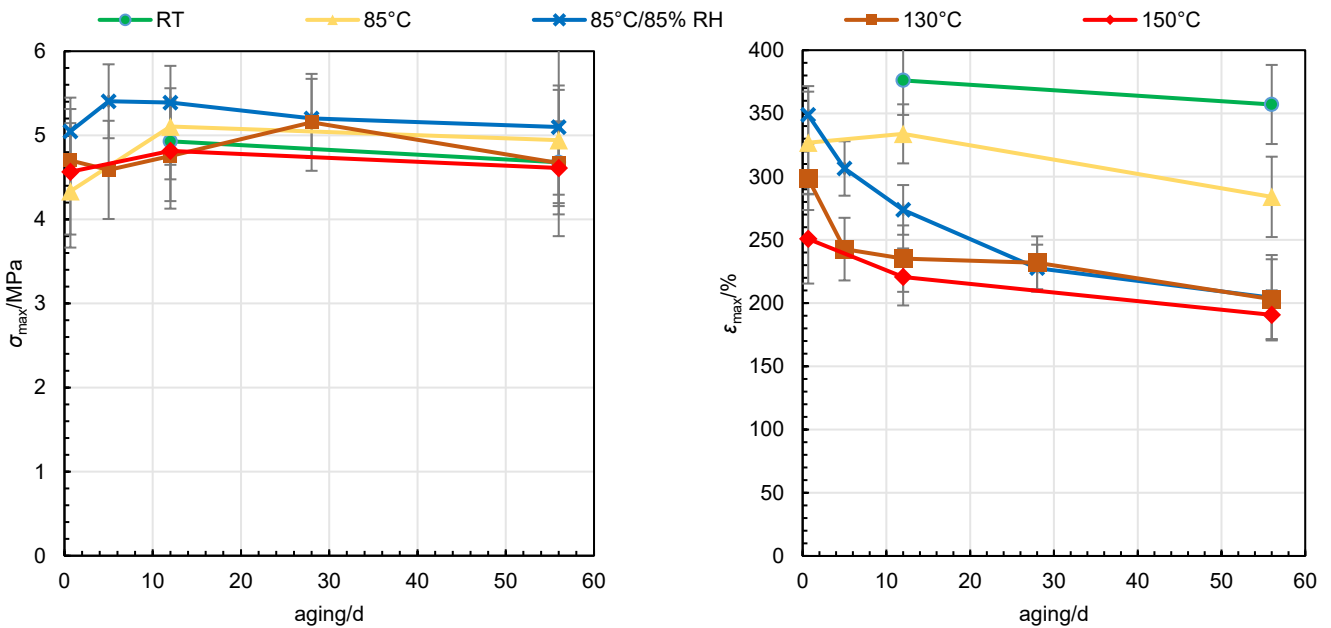
**Fig. 1.** Left, lap-shear strength vs. aging time. Right, area (in percent) showing an adhesive failure mode estimated by visual inspection vs. aging time. If the area of adhesive fracture is less than 25 %, it is classified as a Cohesive Failure (CF) and if the area of adhesive fracture is above 75 %, the fracture is classified as an Adhesive Failure (AF). In between, the fracture pattern is classified as a mixed failure mode (AF/CF).

In contrast, lap-shear strengths increase with increasing temperature and storage time (**Fig. 1**, left). The samples stored at 130 °C show exceptionally high lap-shear strengths after 5 d and 28 d storage. At 56 d, all samples stored at high-temperature and dry conditions (85 °C, 130 °C, 150 °C) reach similar strengths between 6.4 MPa and 6.6 MPa. Remarkably, some single samples even reach values of up to 7.8 MPa. This result is surprising as high-temperature storage does not age bond properties in the classical understanding of bond strength reduction. Moreover, cohesive failures prevail for all high-temperature samples in spite of the high stresses (**Fig. 1**, right), demonstrating that the adhesive strength exceeds the cohesive strength. Again, this is surprising for two reasons. First, high adhesive strengths are achievable without the use of adhesion promoters or primers. Second, the composition of a similar silicone adhesive was systematically varied in our previous study and, independent of the composition, the maximum lap-shear strength without aging amounted to approximately 4 MPa.[32] In addition, the predominant adhesive fracture patterns in our previous study showed a weak buildup of adhesion. Thus, high-temperature conditions significantly improve the bond strength. In the case of high-humidity conditions (85 °C/85 % RH), a different and more complicated picture appears. First, the lap-shear strength rises, reaches its maximum value at 12 d and subsequently declines (**Fig. 1**, left). The lap-shear strength correlates with the fracture pattern: The higher the lap-shear strength, the higher the amount of cohesive failure (**Fig. 1**, right). Compared to the samples that were stored at elevated temperature and dry conditions (85 °C, 130 °C, 150 °C), the samples stored at high humidity show lower strengths in the beginning of storage up to 5 d and at the end of storage at 56 d, but show similar strengths at a medium storage time of 12 d. Since both the adhesive and cohesive properties are important for bond strengths, the influence of elevated

temperature and humidity on the bulk material properties is evaluated and presented in the next section. In summary, the results indicate that the adhesion between silicone and aluminum adherends increases with thermal aging.

### 3.2. Aging of the Bulk Material

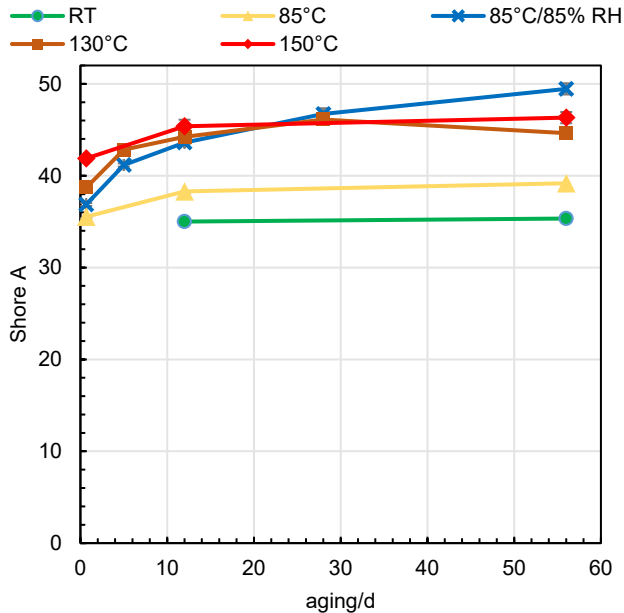
The stress at break of the bulk material shows no clear trend over time regardless of storage conditions (**Fig. 2**, left). On the contrary, the strain at break clearly decreases the higher the temperature and the longer the storage time (**Fig. 2**, right). The samples stored at RT show no significant change. A particularly fast decrease of elongation at break is observed within the first days at high temperatures (130 °C, 150 °C). The samples stored at 85 °C show only a moderate decrease that is between that of the samples stored at RT and the high-temperature samples (130 °C, 150 °C). Under high-humidity conditions (85 °C/85 % RH), the overall decrease of strain at break is more pronounced compared to dry conditions at the same temperature (85 °C). Up to 12 d, the samples stored at 85 °C/85 % RH show a smaller decrease in elongation at break compared to the high-temperature samples (130 °C and 150 °C). However, beyond 12 d storage time, the samples stored at 85 °C/85 % RH reach similar values as the high-temperature samples. After 56 d, the elongation at break is nearly halved for the samples stored at 130°C, 150 °C and at 85 °C/85 % RH.



**Fig. 2.** Tensile properties of bulk silicone samples aged under different conditions. Left, engineering stress at break vs. aging time. Right, strain at break vs. aging time.

The Shore A hardness shows a reverse trend compared to the strain at break: The higher the storage temperature, the higher the hardness (**Fig. 3**). Again, the samples stored at RT show no significant changes. The samples stored at 85 °C show only a moderate hardening over time, whereas the samples at high temperature (130 °C, 150 °C) show a pronounced and fast increase in hardness. The samples stored at 85 °C/85 % RH show at the beginning of aging a slower hardening compared to the high-temperature samples (130 °C and 150 °C), but a more pronounced hardening compared to the samples stored under dry conditions at 85 °C. However,

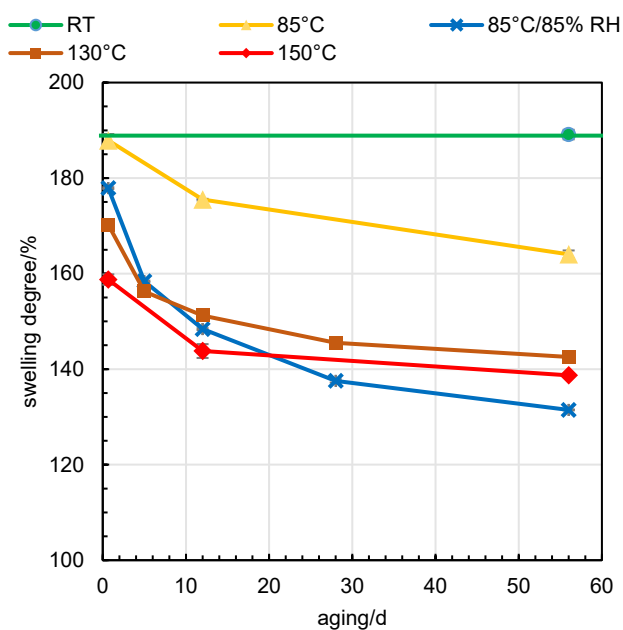
at approximately 28 d, the hardness surpasses that of all other samples and reaches the highest value after 56 d, with 49.5 Shore A. A drop of elongation at break (**Fig. 2**, right) and a rise of Shore A hardness (**Fig. 3**) indicate a higher cross-linking density of the polymer, which is confirmed by the swelling measurements in the next section.



**Fig. 3.** Shore A hardness vs. aging time of silicone samples aged at different conditions. As the error bars are very small, they are barely visible.

### 3.3. Investigation of Cross-linking Density

Cross-linking properties were evaluated by swelling measurements in toluene (**Fig. 4**). According to the Flory-Rehner equation and under the assumption that the Flory-Huggins parameter does not change during aging, a lower degree of swelling correlates with a higher cross-linking density.[33] The overall trend from above is reflected: With increasing temperature and increasing storage time, the degree of swelling decreases. The samples stored at 85 °C reveal an overall medium drop of swelling, thus reaching a medium post-cure cross-linking. On the contrary, the samples stored at 130 °C and 150 °C show a pronounced decrease in swelling characterized by a steep drop within the first few days. The high-humidity samples (85 °C, 85 % RH) show a much higher loss in swelling than the low-humidity samples (85 °C). Within the first days, the decrease in swelling is smaller at 85 °C/85 % RH compared to the high-temperature samples (130 °C, 150 °C). However, after 28 d, the swelling of the high-humidity samples (85 °C/85 % RH) falls clearly below that of the high-temperature samples (130 °C, 150 °C). Hence, in the beginning, the high-temperature samples (130 °C, 150 °C) show the most pronounced increase in cross-linking density. Nevertheless, the cross-linking density of the sample under humid conditions (85 °C, 85 % RH) exceeds that of all other samples after 28 d.



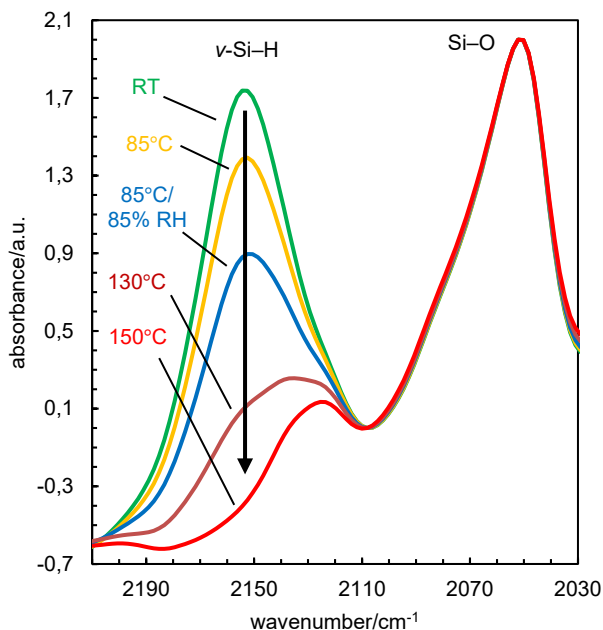
**Fig. 4.** Swelling degree vs. aging time for different aging conditions. The swelling degree is defined as the mass uptake of toluene divided by the mass of the silicone adhesive. The horizontal line shows the swelling degree of the sample stored at RT for 56 d.

### 3.4. FTIR Spectroscopy

To obtain information about the chemical reactions responsible for a higher cross-linking density, the samples were examined by FTIR spectroscopy. Attenuated Total Reflection (ATR) FTIR spectroscopy reveals almost no changes among the samples, indicating that even at 150 °C storage temperature, no tremendous changes in the chemical structure occur through oxidation or radical reactions. This confirms the stability of silicones under high temperatures. However, functional groups like the hydrosiloxane group (Si-H) or the vinylsiloxane group (C=C) cannot be observed in ATR-FTIR spectra due to their low concentration and due to the small penetration depth of the evanescent wave, which lies in the region of a few micrometers. Therefore, another strategy was followed. For this purpose, silicone sheets of approximately 100  $\mu\text{m}$  thickness were prepared and transmission spectra were recorded. Using this method, chemical groups featuring a high absorbance and high concentration, like the Si-O-Si stretching around 1050  $\text{cm}^{-1}$  or the C-H stretching around 2900  $\text{cm}^{-1}$ , cannot be evaluated because of the total light absorption at the respective wavenumbers. However, functional groups at low concentrations, like the Si-H functional group, can be clearly observed.

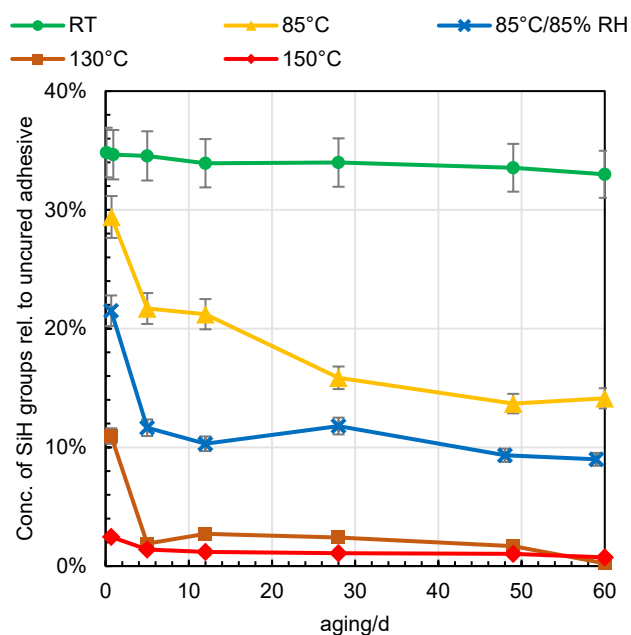
In **Fig. 5**, the region of Si-H stretching vibration and the overtone vibration from the Si-O groups is depicted after 16 h of aging. Since the overtone vibration stays constant due to an almost unchanged Si-O concentration, the spectrum was referenced to this

signal. The signal intensity of the Si-H stretching vibration decreases with increasing temperature. Additionally, the decrease of the Si-H signal intensity is more pronounced under humid conditions.



**Fig. 5.** FTIR spectra recorded by transmission through silicone sheets with approximately 100  $\mu\text{m}$  thickness. The spectra show different aging conditions of the cured silicone sheets after approximately 16 h. The Si-O overtone stretching was used as an internal reference; the minimum intensity was set to 0 a.u. and the maximum intensity was set to 2 a.u. The arrow emphasizes the decrease in intensity of the  $\nu$ -Si-H stretching signal.

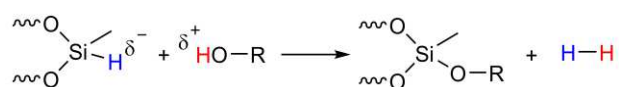
The amount of Si-H concentration was quantified for different storage times and conditions (**Fig. 6**), whereby 100 % Si-H concentration corresponds to uncured material. After curing, only 35 % of Si-H moieties remain which is less than expected. Since the Si-H to vinyl ratio was equal to 3:1 (which is a common ratio for silicone formulations), approximately 67 % Si-H moieties would have been expected after curing. This shows that curing for 1 h at 130 °C already leads to the additional consumption of Si-H groups, which continues with aging. Especially at high temperatures, almost all Si-H groups are quenched after short times. After 16 h at 130 °C, only 11 % of Si-H groups are present and after 5 d, less than 3 % of the original amount is present. At 150 °C, the decrease is even faster and after 16 h, less than 3 % of the initial Si-H groups remain. Interestingly, the concentration of Si-H groups for the samples stored at 85 °C and 85 °C/85 % RH reach a kind of threshold that was distant from total Si-H consumption. However, the sample at high humidity shows a faster and higher Si-H consumption than the sample under dry conditions (85 °C). Nevertheless, the high-temperature samples (130 °C, 150 °C) exhibit a more pronounced Si-H consumption than the high-humidity sample (85 °C/85 % RH).



**Fig. 6.** Relative concentration of Si-H groups over aging time determined by FTIR spectra. The Si-H concentration of uncured material was set to 100 % and a formulation without hydrosiloxane component was set to 0 %. The first data point at RT shows the concentration of Si-H groups shortly after curing for 1 h at 130 °C.

#### 4. Discussion

According to the data above, the increasing cross-linking density correlates with the consumption of Si-H groups. Due to the hydridic character of the Si-H hydrogen, hydrosiloxanes are able to react with protic hydrogens under formation of a silicon-heteroatom bond (e.g. oxygen or nitrogen) and under the release of hydrogen gas (**Scheme 4**). These reactions are well known in the literature as dehydrogenative coupling.[34] Protic hydrogens originate, for example, from water or other hydroxyl groups, including surface-bound hydroxyls (surface-OH). Both surface-OH and physisorbed water molecules are also present in our silicone adhesive, originating from the incorporated fumed silica. Furthermore, it is known from the literature that hydrosiloxanes are able to react with silica[25][26] and aluminum oxide[27][29] without the addition of catalysts. However, acids, bases and transition metals are able to catalyze these reactions. In our adhesive, acidic groups are available on the surface of fumed silica and a platinum-based catalyst is present to enable the curing reaction. The following discusses the reactions that are able to increase the cross-linking density of the silicone adhesive.



**Scheme 4.** Dehydrogenative coupling reaction of a methylhydrosiloxane with an OH group. The rest R can be organic, a silicone or a surface like silica or alumina.

#### 4.1. Reactions of Hydrosiloxanes under High-Temperature Conditions

The reactions (1a), (1b) and (1c) of **Scheme 5** depict the dehydrogenative coupling reactions of the Si-H groups under release of hydrogen gas. Reaction (1a) shows the conversion of Si-H with water to a silanol group within the siloxane polymer (PDMS-OH). The PDMS-OH acts as a proton donor, similar to water molecules, and is able to react with Si-H groups to yield an additional cross-link (1b). Similarly, the surface-OH from the silica act as proton donors and are able to react with Si-H groups (1c). In the case of reaction (1c), the surface of the fumed silica in the formulation serves as a kind of cross-linker. The reactions (1a) – (1c) can be accelerated by the platinum catalyst, which is intended to catalyze the hydrosilylation reaction. Since these reactions are highly exothermic, they can be seen as irreversible. In addition, the evaporation of hydrogen gas shifts the equilibrium to the right-hand side of the reactions (1a) – (1c).

Moreover, the resulting PDMS-OH from reaction (1a) is able to undergo condensation reactions with a second PDMS-OH (2a) or a surface-OH (2b).[25] Both reactions increase the cross-linking density. Dry conditions and high-temperature storage (85 °C, 130 °C, 150 °C) lead to an evaporation of water, which is reflected in the FTIR spectra by a decreasing intensity of the O-H stretching region (**SI Fig. 1**). Thus, the equilibrium of the reactions (2a) and (2b) shifts to the right-hand side with storage time. Altogether, reactions (1a) – (2b) increase the cross-linking density of the silicone adhesive.

(1a)	$\text{≡Si-H} + \text{H-OH} \longrightarrow \text{≡Si-OH} + \text{H-H}$	} Irreversible
(1b)	$\text{≡Si-H} + \text{H-OSi≡} \longrightarrow \text{≡Si-OSi≡} + \text{H-H}$	
(1c)	$\text{≡Si-H} + \text{H-O} \longrightarrow \text{≡Si-O} + \text{H-H}$	
(2a)	$\text{≡Si-OH} + \text{H-OSi≡} \rightleftharpoons \text{≡Si-OSi≡} + \text{H-OH}$	} Reaction shifts to the right side under <u>dry conditions</u>
(2b)	$\text{≡Si-OH} + \text{H-O} \rightleftharpoons \text{≡Si-O} + \text{H-OH}$	
(3)	$\text{≡Si-OSi≡} + \text{H-O} \rightleftharpoons \text{≡Si-O} + \text{H-OSi≡}$	
(4)	$\text{>O} + \text{H-OH} \rightleftharpoons \text{(OH)}_2$	} Reaction shifts to the right side under <u>humid conditions</u>

**Scheme 5.** Possible chemical side reactions of the silicone adhesive. “ $\text{≡Si-X}$ ” symbolizes a silicon to X bond ( $X = \text{H}, \text{OH}$ ), where the three other binding partners of silicon are abbreviated with “ $\text{≡}$ ”, and usually consists of methyl or oxygen from the PDMS polymer. The structure “ $\text{≡O-H}$ ” depicts the surface hydroxyl groups of either the silica surface of the filler or the aluminum oxide surface of the substrate. A single arrow depicts virtually irreversible reactions. If the equilibrium arrows have the same length, almost no exothermicity is expected. From a thermodynamics point of view, condensation reactions are slightly favored over

hydrolysis reactions. This behavior is implied with the slightly longer arrow in reactions (2a), (2b) and (4). Water molecules are emphasized in blue, additional cross-links of two polymer chains in green, and cross-links of polymer with the surface in red.

#### 4.2. Reactions of Hydrosiloxanes under High-Humidity Conditions

At high humidity (85 °C/85 % RH), the consumption of Si-H groups is much faster in comparison to dry conditions at 85 °C (**Fig. 6**). Indeed, the reaction rate of (1a) in **Scheme 5** is expected to be enhanced under high-humidity conditions due to a higher concentration of water molecules. According to the FTIR spectra, the amount of water continuously increases by storage at high humidity (**SI Fig. S1**). However, the consumption of Si-H groups at high temperatures (130 °C, 150 °C) is even faster than at 85 °C/85 % RH in spite of the dry conditions and as a consequence of a lower concentration of water molecules. A faster and more complete consumption of Si-H groups at high temperatures (130 °C, 150 °C) can be explained by higher reaction rates and that the consumption of Si-H groups increasingly takes place without Pt-catalysis, whereas a Pt-catalyst is required at lower temperatures like RT and 85 °C. In addition, the mobility of reactive groups might play an important role that can be expected to be higher at elevated temperatures.

Furthermore, it seems that the catalyst deactivates at 85 °C/85 % RH between 5 d and 12 d, as is reflected in an almost ceased consumption of Si-H groups despite the presence of water (**Fig. 6**). In contrast, the consumption of Si-H at 85 °C under dry conditions continues even after 28 d, presumably because the catalyst is still active. However, the reaction at 85 °C slows down with time because the sample is losing water and surface-OH, thus reducing the reactants of reactions (1a) and (1c).

The high-temperature samples show an almost complete consumption of Si-H moieties after 16 h (150 °C) to 5 d (130 °C), leading to pronounced changes in material properties after short aging times. However, properties like strain at break and swelling still continue to change even beyond 5 d of aging. Moreover, the sample at high humidity (85 °C/85 % RH) shows the most pronounced changes in material properties despite incomplete Si-H consumption. Therefore, the reactions of Si-H groups cannot be the single explanation for higher cross-linking densities. As already mentioned in the introduction section, the silicone backbone is also able to react with silica surfaces.[19][21][22] These reactions rely on the high polarity of the silicon-oxygen bond of PDMS and comprise mainly heterolytic bond cleavages of the backbone. The next section discusses the reactions of the silicone Si-O backbone.

#### 4.3. Reactions of Si-O-Si under High-Temperature Conditions

Reaction (3) of **Scheme 5** illustrates a reaction between the silicone backbone and a surface-OH group. As reaction products, a chemical bond to the surface and a PDMS-OH is created, which in turn is able to condense with a second PDMS-OH (2a) or a surface-OH (2b), as discussed above. Overall, an additional cross-link is created. Again, (2a) and (2b) are shifted to the right-hand side under dry conditions due to the removal of water.



These processes are driven by high temperatures. The sample stored at 150 °C clearly illustrates this behavior. According to **Fig. 6**, almost all Si-H groups were consumed after 16 h and the resulting reactions (1a) – (2b) strongly contribute to changes in the material properties. However, the material properties continue to change significantly, as can be seen by comparing the properties at 16 h with those at 12 d (**Fig. 2**, **Fig. 3**, **Fig. 4**). This can be explained by reaction (3), which continues after the total consumption of Si-H groups and leads to reactions (2a) and (2b). However, the sample dries with time and the concentration of accessible surface-OH groups diminishes, e.g. through the backward reaction of (4) in addition to reaction (3). Therefore, the change of material properties slows down and the difference between the material properties after 12 d and 56 d for the sample at 150 °C is rather small.

#### 4.4. Reactions of Si-O-Si under High-Humidity Conditions

A similar behavior as with the high-temperature samples is observed for the high-humidity samples: Although the consumption of Si-H groups levels-off after 5 d (**Fig. 6**), the cross-linking density increases continuously (**Fig. 4**). In addition, despite incomplete Si-H consumption, the highest cross-linking density of all samples is reached. Moreover, due to the higher water content at 85 °C/85 % RH, the equilibrium of reactions (2a) and (2b) are expected to be shifted to the backward direction, leading to a lower cross-linking density. Since these facts contradict the observation of the highest cross-linking density, an even more pronounced turnover of the silicone backbone can be expected. This can be explained by reaction (4), which illustrates the formation of additional surface-OH groups by hydrolysis of the silica surface. In the FTIR spectra, a rise in signal intensity is observed for adsorbed water molecules not only at approximately 3400 cm<sup>-1</sup> but also at approximately 3600 cm<sup>-1</sup>, which is an indication of the hydrogen-bonded surface-OH of the silica (**SI Fig. S1**).<sup>[35]</sup> As a consequence, the additional surface-OH shift the reactions (2b) and (3) to the right side. Based on the material properties (**Fig. 2**, **Fig. 3**, **Fig. 4**), it is clear that this process is continuously ongoing. A significant change of material properties can even be observed between 28 d and 56 d, whereas the properties of the samples stored at a high temperature (130 °C, 150 °C) reach a kind of threshold.

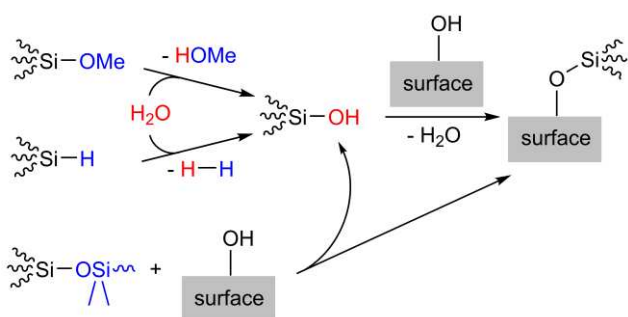
Interestingly, the samples stored at high humidity (85 °C/85 % RH) show a rise of two signals at 1710 cm<sup>-1</sup> and 1730 cm<sup>-1</sup> after 28 d of storage (**SI Fig. S1**). These signals most probably originate from carbonyl groups (C=O) and are caused by the hydrothermal oxidation of the methyl groups to aldehydes or carboxylic acids. These groups might also contribute to an increasing cross-linking density. However, the mechanism behind these processes is not yet understood. Such species were not observed in the case of the high-temperature samples (85 °C, 130 °C, 150 °C).

#### 4.5. Impact on Adhesion

In the previous sections, the discussions about possible reactions in **Scheme 5** focus on the hydroxyl groups of the silica filler. However, aluminum oxide surfaces show a similar reaction behavior with both hydrosiloxane groups [27][29] and the siloxane

backbone [20][23]. Therefore, it is reasonable to transfer the same reactions as were proposed for the silica surface-OH to the aluminum oxide surface-OH of the aluminum adherend, namely reactions (1c), (2b), (3) and (4). This means that reactions (1c), (2b) and (3) lead to a chemisorption of silicone to the aluminum oxide surface, consequently enhancing adhesion. Regarding the reactions of the hydrosiloxane, Hirayama *et al.* demonstrated that hydrosiloxanes in combination with a platinum catalyst can be used as primers to increase adhesion to aluminum adherends.[30][31] In addition, under high-temperature and dry conditions (85 °C, 130 °C, 150 °C), the equilibrium of reaction (2b) is shifted to the chemisorption side. This is also valid for reaction (3) if the emerging PDMS-OH condenses in reaction (2a) or (2b).

The chemical reactions of the Si-H groups and the siloxane backbone are comparable with those of adhesion promoters (**Scheme 6**). As an example, alkoxy-silanes are intended to yield silanols in the first step by a reaction with water to subsequently build up chemical bonds to the surface in the second step by condensation reactions with surface-OH.[12][13] In contrast, the siloxane backbone is less reactive than alkoxy-silanes and requires high temperatures for chemisorption reactions.[23] In summary, the underlying reactions are expected to contribute to chemisorption and strongly improve adhesion, which is reflected in the findings here of cohesive failure in combination with high bond strength (**Fig. 1**).



**Scheme 6.** Analogy of reactions of alkoxy-silanes (typical adhesion promoters), hydrosiloxanes and the Si-O backbone of PDMS. All reactions result in chemical bonds to the surface.

Moreover, physisorption might also contribute to adhesion buildup. As discussed in the introduction, there is a minor formation of strong hydrogen bonds between PDMS and polar surfaces like water or silica.[6][7][8][9] A similar behavior can be expected for polar aluminum oxide surfaces containing a physisorbed layer of water molecules. Dry conditions lead to the evaporation of physisorbed water from the surface. As a result of the significantly reduced water content, the physical interactions of the PDMS backbone with the surface are enhanced by dispersion and dipolar interactions. Moreover, it has been shown that silanol groups within PDMS strongly enhance adsorption, and thus interactions, on glass[11] and on silica and alumina surfaces[36]. Higher adsorption was explained by hydrogen bonds between PDMS-OH and surface-OH groups. Indeed, quantum mechanical calculations reveal that, in contrast to dimethylsiloxane groups, silanol groups are able to build up strong hydrogen bonds with

silica surfaces.[7] Thus, even if uncondensed silanol groups from reactions (1a) and (3) remain, they can be assumed to contribute to adhesion by strong hydrogen bonding interactions.

Regarding the samples stored at high humidity, the explanation of adhesion is much more complicated. The following presents a suggestion about the processes at the interphase. In contrast to dry conditions, high humidity (85 °C/85 % RH) leads to a physisorption of water to the aluminum oxide surface due to strong hydrogen bonds. However, the physisorption of water diminishes the interactions of silicone with the surface. This leads to diminished adhesion at the beginning of aging, which is reflected in significant amounts of adhesive failure at 16 h and 5 d. In contrast, the samples stored at dry conditions at 85 °C, as well as those stored at higher temperatures, suffer to a smaller extent from the diminished physisorption of silicone due to replacement by water molecules. Additionally, the hydrogen bonding of PDMS-OH from reaction (1a) competes with the hydrogen bonding of water molecules at high humidity. Therefore, despite a smaller conversion of Si-H groups under dry conditions at 85 °C (**Fig. 6**), the adhesion is higher, which is reflected in slightly higher lap-shear strengths and in cohesive failures (**Fig. 1**). However, the amount of adhesive failure at 85 °C/85 % RH at 12 d and 28 d is reduced compared to 16 h and 5 d, accompanied by an increasing lap-shear strength (**Fig. 1**). These indicate improved adhesion buildup and can be explained on the one hand by increasing chemisorption from reaction (2b) with silanols originating from reaction (1a). On the other hand, reaction (4) leads to a higher concentration of surface-OH, which in turn, leads to a higher chemisorption through reactions (3) and (2b) and thus an increase of adhesion. These reactions are the same as those responsible for the increase in cross-linking density, but in this case, they take place with the surface-OH of the aluminum oxide instead of the silica surface. However, the adhesion seems to degrade after 12 d of aging at high humidity, which is reflected in slightly decreasing lap-shear strengths and increasing amounts of adhesive failure (**Fig. 1**). This might be explained by ongoing reactions (4) and (3) leading to a high amount of cleavage reactions of the siloxane backbone near the surface and a slow decrease of adhesion. Additionally, the FTIR spectra reveal that the concentration of water in the bulk material continuously rises throughout the storage time and, presumably, decreases physisorption (**SI Fig. S1**). In the experiments by Hirayama *et al.*, the storage of test specimen in boiling water with polyhydromethylsiloxane primed aluminum substrates also led to a significant decrease in peel resistance after a delay of approximately 200 h.[31] Thus, a high concentration of moisture is disadvantageous for the adhesion between silicones and aluminum adherends.

## 5. Conclusion

The influence of the high-temperature and high-humidity aging of an addition curing silicone adhesive with known ingredients was investigated. As typical for such silicones, an excess of the Si-H compound was applied. Storage at room temperature leads to only minor changes in the bulk material properties. At high temperatures (85 °C, 130 °C, 150 °C) and high humidity (85 °C/85 % RH), the cross-linking density of the silicone material increases with aging time, accompanied by a decreasing strain at break and an increasing Shore A hardness during the period under consideration. The changes in material properties correlate with the

consumption of excess hydrosiloxane (Si-H) groups. Several reaction paths of excess Si-H groups leading to enhanced cross-linking densities were proposed. High-humidity conditions (85 °C/85 % RH) accelerate the consumption of Si-H groups compared to low-humidity conditions at the same temperature. Furthermore, the conversion of Si-H groups increases with increased temperature. Consequently, the samples stored at high temperature (130 °C, 150 °C) show the most pronounced changes in material properties at the beginning of aging due to a fast and complete conversion of Si-H groups. However, the material properties continue to change with further storage despite the total consumption of Si-H groups. In addition, the samples stored at 85 °C/85 % RH show incomplete Si-H conversion but also the most pronounced changes in material properties after long storage times. Therefore, other effects than the reactions of the Si-H groups contribute to the increasing cross-linking density. It is known that the siloxane backbone is also able to react with oxidic surfaces like the silica filler or the aluminum oxide surface of the adherends. Corresponding reactions are proposed that explain the continuously changing material properties without the further consumption of Si-H groups.

The proposed reactions of Si-H groups and the siloxane backbone can be transferred to the aluminum oxide surface of the adherend. In the case of the aluminum oxide surface, these reactions lead to chemical bonds between polymer and surface. The chemical reactions of hydrosiloxanes, as well as of the siloxane backbone, are related to those of adhesion promoters. Therefore, high bond strengths can be achieved without the addition of specific adhesion promoters. Especially dry conditions lead to high lap-shear strengths of up to 6.8 MPa. Nevertheless, the cohesive failures indicate that the adhesive strength exceeds the cohesive strength. Beside the chemisorption mechanism, the evaporation of water under dry conditions is expected to increase adhesion through physisorption. In contrast, high humidity leads to smaller lap-shear strengths, including a significant amount of adhesive fracture. This shows the overall insufficient adhesion buildup, which can be explained by the replacement of the physical interactions of PDMS by strongly physisorbing water molecules.

Overall, addition curing silicones are able to build up strong adhesion with aluminum adherends without the use of adhesion promoters or primers. The reason is the unique chemistry of siloxanes, which leads to chemisorption through reactions of excess hydrosiloxane groups and the siloxane backbone. High temperatures and dry conditions are beneficial for the buildup of adhesion through chemisorption and physisorption. In contrast, humid conditions are disadvantageous. These results are expected to be transferrable to the oxidic surfaces of metals other than aluminum as well as to glass surfaces.

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