Reactivity of Polysilazanes Allows Catalyst free Curing of Silicones

Sønderbæk-Jørgensen, René; Meier, Sebastian; Dam-Johansen, Kim; Skov, Anne L.; Daugaard, Anders E.

Published in:
Macromolecular Materials and Engineering

Link to article, DOI:
10.1002/mame.202200157

Publication date:
2022

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Reactivity of Polysilazanes Allows Catalyst-Free Curing of Silicones

René Sønderbæk-Jørgensen, Sebastian Meier, Kim Dam-Johansen, Anne L. Skov, and Anders E. Daugaard*

Silicones are typically cured at room temperature by means of metal catalyst such as tin or platinum. When networks are formed, the catalyst becomes unrecoverable, which is of economic as well as environmental concern. Very few methods for producing metal catalyst-free room-temperature-vulcanized (RTV) silicones exist and require conditions unavailable in industrial settings. Through the study of organic polysilazane (PSz) reactivity with simple alcohols by nuclear magnetic resonance, an unexpected fragmentation preference is discovered for breaking the Si–N bond rather than the Si–H; thereby, casting a new light on the fragmentation mechanism of PSzs. Utilizing the PSz fragmentation as a silyl ether coupling agent for multifunctional carbinol silicones, a method of producing catalyst-free RTV silicone networks at ambient conditions is presented. These silicone networks are proven chemically similar to a standard condensation-cured silicone and stoichiometric variations of PSz content demonstrate adjustable network properties.

1. Introduction

Silicones find application across a broad range of sectors from biomedical, pharma, and skincare to the elastomer industry due to their virtually unique mechanical properties, chemical and thermal robustness/stability, and biocompatibility.[1-3] They are functional components in a wide range of materials including coatings, sealants, and biomedical devices. Conventional preparation strategies of silicone networks proceed through condensation and hydrosilylation of polydimethylsiloxane (PDMS) polymers.[4] These techniques require metal catalysts such as tin or platinum to proceed at room temperature (room-temperature-vulcanized [RTV]) systems. However, the catalysts will also remain in the resulting elastomer networks after curing, which is of economic as well as environmental concern. As an alternative to catalytic curing, thiol-ene chemistry[5] or silirane ring-opening[6] silicones have recently been introduced, but remain challenged by limited scope of commercially available reactants. With readily available starting materials, auto-oxidative curing of hydride terminated PDMS has recently been shown to produce silicone networks without the use of catalyst at temperatures above 220 °C.[7,8] As these conditions are unsuitable for industrial settings, a means to producing metal-catalyst-free RTV silicone networks is still needed.

An often overlooked subset of silicon containing polymers is polysilazanes (PSzs). As an analogue to the –Si–O– backbone of PDMS, PSzs contain the hydrolytically unstable –Si–N– as the repeating unit in their polymer backbone.[9,10] This hydrolytic instability is a very attractive property of silazanes that is often exploited in the surface functionalization of particles and metals. For instance, hexamethyldisilazane treatments convert hydrophobic surfaces into hydrophilic surfaces without the use of catalysts.[11] Vinyl and hydride functional organic PSzs have been explored to create less dense thiol-ene and acrylic hybrid networks,[12-17] but more often than not, organic PSzs find their use as ceramics precursors through radical or hydrosilylation cross-linking with subsequent pyrolysis, as shown in Scheme 1.[18-27] Conversion of PSzs to polysiloxanes in the presence of ambient moisture leads to very thin protective coatings that are usually hard and brittle, unlike conventional soft PDMS networks.[28] It is well established that silazanes have a high affinity for alcohols. However, this affinity has so far only been employed for surface reactions, where the ability of a silazane to activate an alcohol is exploited for the preparation of a surface-bound ether.[29] Contrary to the low molecular weight silazanes, PSzs have two active silyl amine
Scheme 1. Schematic overview over possible coupling reactions of polysilazanes (PSz) to prepare silicone networks either directly through reaction with moisture, acrylics/thiols, or with peroxides (previous work)\[12,13,15,16,18,19,25,30–32\] or by reaction with multifunctional alcohols at ambient conditions without a catalyst (this work).

Scheme 2. Plausible reaction pathways of PSz with MeOH, where intermediates 1A-D, 2A-B and 3A shows the proposed pathway towards fragmentation by reaction with the alcohol species, the hydrogen and ammonia dissociation, respectively.

2. Results and Discussion

The reactivity of commercial PSzs, such as Durazane 1800 (PSz), is complex due to their multiple functional groups (hydride, vinyl, and silazane), which can react simultaneously or sequentially with alcohols. As already described in a number of publications, PSzs are generally considered to fragment through reaction with alcohols followed by dissociation of dihydrogen and free ammonia (Scheme 2)\[33\]. However, we have not been able to find studies of selectivity or preference between the two pathways, which is essential to exploiting these systems for cross-linking. The fragmentation of PSzs involves the breaking of two functional groups, Si–H and Si–N that, depending on the substituents, have relatively similar bond energies of 378 and 434 kJ mol\(^{-1}\), respectively.\[4\] This would lead to a series of possible reaction pathways, as shown in Scheme 2.
To establish the reactivity and hence most plausible mechanism, a model study using low MW models of PSz was conducted using proton nuclear magnetic resonance spectroscopy (\(^1\)H NMR) (see Figure S10, Supporting Information). As model substrates 1,3-divinyl-1,1,3,3-tetramethyldisilazane (DVTMDS) and vinylidimethylsilane (VDMS) were chosen, since they offer the same functionalities as the commercially available PSz and excludes cross-reactions on the multifunctional polymer backbone from the NMR analysis (for a reaction overview, see Scheme S1, Supporting Information). The time-resolved \(^1\)H NMR experiment of DVTMDS in the presence of one equivalent of methanol (Figure S10, Supporting Information) showed the fragmentation of the silazane model compound. The disappearance of the \(-\text{CH}_3\) chemical shift from methanol and the concurrent appearance of a new methyl silyl ether bond confirmed reaction of the alcohol with the Si–N. In addition, new vinyl signals and the disappearance of the secondary amine showed that the reaction split the silazane into two new compounds, one containing the methoxy-functionalized silane and one containing the primary amine. The development of two products (analogous to 1B in Scheme 2) confirmed a higher affinity for methanol to react with the Si–N in DVTMDS than with the formed aminosilane to release ammonia. The same experiment was conducted with a hydrosilane model compound (VDMS, Figure S10, Supporting Information), which shares the other type of functionality common to commercial PSz. While it would be possible to follow a possible fragmentation of VDMS via the \(^1\)H chemical shift of the Si–H at 4.10 ppm, it was shown that under these conditions the hydride was stable. Both the hydride and the vinyl groups remained unreacted throughout the experiment (shown by the time-integrated signals for MeOH, vinyl, and Si–H in Figure S10, Supporting Information). The same experimental setup as for the model substrates was used with the more complex commercial PSz. The polymer has a relatively low molecular weight near 800 g mol\(^{-1}\) and contains the same “primary” functionalities as the model compounds (Figure 1). The simple PSz structure shown both here and in Scheme 1 is a simplified representation of the polymer, which in \(^{15}\)N NMR can be seen to have more than six different nitrogen species (Figure S16, Supporting Information) and likely include cyclic structures. The time-resolved NMR experiment for the polymer (Figure S11, Supporting Information) was therefore more complex than the model study, although the trends shown in Figure 1 correlated to observations for the model compounds.

For the polymer conversion, the secondary amine region at 1.0–0.5 ppm proved particularly informative. Here, the broad signal from various secondary amine sites was replaced by a sharper peak at 0.49 ppm for free ammonia in CDCl\(_3\)\(^{[34]}\). In addition, the methyl group in methanol rapidly disappears during the experiment and the complexity of PSz is reflected by the appearance of three major Si–OMe signals. Hence, at least three primary siloxane products are formed in addition to a multitude of secondary products following the fragmentation. This follows that the substitutions are combinations of vinyl, Si–H, CH\(_3\), and one or more Si–Ome (Scheme 2[1B–1D]). A common denominator for the primary products is, that they are all Si–H substituted. These products are formed within few minutes, which is remarkable compared to the DVTMDS reaction, since the polymer is more sterically hindered. All the secondary Si–OMe signals follow a pattern of decreasing silicon chemical shifts, indicating multiple reactions on the PSz backbone\(^{[35]}\) opposite to what was seen for the model reactions. During reaction progress, a sharpening of the vinyl and Si–CH\(_3\) signals suggest a shortening of the PSz chain through a cleavage of Si–N bonds. This experiment therefore sheds new light on the mechanism of PSz fragmentation, revealing an unexpected preference for breaking the Si–N bond rather than the Si–H, ultimately resulting in the formation of a range of different silyl ether species.

Higher numbers of equivalents (2 and 3) and a more diverse selection of sterically hindered alcohols were evaluated as shown in Table 1. The conversion of SiH to SiOR groups is only effective with non-sterically demanding alcohols, particularly MeOH, but even with a stoichiometric excess of alcohol it is impossible to react all the SiH groups. As expected, increased steric hindrance resulted in a lower yield of silyl ethers, while benzyl alcohol did not lead to reaction of the hydrides. The reaction of the hydrides was in all cases only evident at higher reaction times, while higher reactivity of the silazane than the hydride was confirmed across the series. Hence, PSz exhibits an attractive potential to be used as an activator for condensation of alcohol species.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Remaining Si–H [%]</th>
<th>Converted R–OH [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>93</td>
<td>100</td>
</tr>
<tr>
<td>Ethanol</td>
<td>99</td>
<td>81</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>99</td>
<td>47</td>
</tr>
<tr>
<td>Tert-amyl alcohol</td>
<td>99</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 1. Results after 72 h of reaction between PSz and R-OH in CDCl\(_3\) at 25 °C.
either carbinol- or silanol-terminated prepolymers. The reactivity of carbinol silicones with PSz was studied by reaction of the linear carbinol-terminated silicone, Gelest DMS C-21 (DMS-C21), with a surplus of PSz in deuterated chloroform by $^1$H NMR as seen in Figure 2.

The reaction was followed by observing the signal for the terminal –CH$_2$–OH group of DMS-C21 at 3.75 ppm. The observed signal of DMS-C21 shifted to 3.81 ppm due to the change in shielding when carbinols were converted to silyl ethers. After 3 h, the reaction showed about 70% conversion to silyl ether and after 30 h full conversion of carbinols in DMS-C21 was observed. Results showed that the reaction of carbinol silicones and PSz at ambient temperature is feasible and spontaneous at ambient conditions, which allows the technique to be applied to wide variety of hydroxylated silicone compounds. Attempts to apply the same technique to a difunctional silanol terminated silicone, Gelest DMS-S21, was however unsuccessful, which could be attributed to the lower reactivity of the silanol compared to the carbinol.

Investigation of carbinol silicone reactivity and PSz fragmentation revealed that in order to create silicone networks, the introduction of a multifunctional carbinol, such as Siltech OH C50 (OH C50) to the reaction is necessary, as shown in Scheme 3.

Use of di- and tri-functional silicones in combination introduces chain extenders to a system that would otherwise become too rigid and brittle, and allows tailoring the system to certain mechanical properties through stoichiometric variations. A highly remarkable feature of these systems is that all investigated compositions were mixed at ambient conditions and could be cured without any precautions to exclude moisture. There was no need to mix under inert atmosphere and no foaming due to ambient moisture was observed also in the films (>100 μm thickness). FT-IR spectra were recorded of the mixture before curing and of the films after curing under ambient conditions, where the cross-sectional area was investigated (see Figure S1, Supporting Information). Results showed a disappearance of characteristic N–H (1158 and 930 cm$^{-1}$) and Si–H (2118 cm$^{-1}$) stretch bands of PSz over time in the IR spectrum. When compared to a standard reference silicone film produced by tin catalyzed condensation, the two networks appeared chemically very similar. Except for some surplus PSz that can be inferred from weak Si–N stretch bands in the final films after curing, the systems proved to yield identical spectra.

To assess gelation time and effective curing of silicone films produced by this technique, a series of compositions with 3, 5, and 7 wt% PSz and 1:1 ratio of DMS-C21 and OH C50 (2/3 hydroxyl functionality) was investigated by DMA at ambient (30 °C) and elevated temperatures (60 °C; Figure 3). From the tan (δ) curves, the shortest gelation time was observed for 5 and 7 wt% PSz, which both cured within 48 h at ambient conditions and 12 h at 60 °C. Using 3 wt% PSz led to longer gelation times of 63 and 18 h, respectively. As is common for condensation curing silicone systems, there is a long-term post curing effect, where any residual hydrides or hydroxyls will condensate and increase the density of the network.$^{[36]}$ An interesting behavior in the storage
modulus ($G'$) was observed for 5 and 7 wt% PSz, which showed a two-stage curing process irrespective of curing temperature. This behavior is not seen in conventional curing of silicone and we suggest that this could be explained by the curing mechanism itself. Initially, the PSz would be expected to fragment through cleavage of Si–N bonds forming intermediate activated species. As observed for the low molecular weight model study, the fragmentation would be favored in competition with a second nucleophilic attack on the Si. Subsequently, when the fragmentation phase is completed, the second reaction at Si would result in molecular weight build-up and network formation. This could explain the delay in tan (δ) with two opposing mechanisms, until assembly starts and the network reaches the point of gelation.

Changes in stoichiometry would be expected to affect the mechanical properties as well, but since curing in the DMA is conducted on a PET carrier, such effects cannot be separated from the influence of the matrix. Therefore cured samples without the carrier matrix were investigated by rheology (Figure S4, Supporting Information). For the three compositions with 3, 5, and 7 wt% PSz, an inverse correlation in the storage modulus was observed with a minor decrease in modulus with an increase in PSz content, corroborating the IR results that additional PSz will not lead to additional network structures, but only to entrapped silazane structures. A wide variety of combinations of carbinol species can be applied. To illustrate the versatility in the process, three additional samples with a short chain extender in ratios of 2:1 and 3:1 relative to the triol were cured with 5 wt% PSz. As expected, the short chain extender led to an increase in $G'$ (reduced distance between cross-linking points) proportional to the chain extender content by 41% and 57%, respectively, adding a significant amount to the strength of the material (Figure S4, Supporting Information).

Finally, to confirm the integrity of the networks, a Soxhlet extraction was conducted to establish the amount of soluble fractions of the network. The samples were extracted for 4 days at 72 °C in dichloromethane and subsequently dried for 3 days at 55 °C in a vacuum oven, resulting in sol fractions of 33%, 24%, and 19% for 3, 5, and 7 wt% PSz, respectively. This observation confirms that 5 wt% PSz to the carbinol silicones is the optimal composition. Subsequent exposure of the PSz-cured silicone films to water did not show any signs of hydrolysis or degradation and the films are comparable to conventional condensation.

**Scheme 3.** Cross-linking reaction of PSz and carbinol silicones forming silicone networks by activated condensation.
cured silicones. The silyl ether groups in the network structure are not prone to hydrolyze as long as they are embedded in the silicone network, which has also been observed for other types of silyl ether-based networks that are stable over time.[37] The systems are compatible to most common additives and fillers and can easily be reinforced by use of, for example, silica fillers (Figure S5, Supporting Information). In summary, all the required aspects of introducing these systems as alternatives to RTV systems have been established, though it should be mentioned that carbinol-based systems will be more expensive from a materials perspective. It is therefore a requirement that an advantage from exemption of a metal catalyst will add sufficient value or that cheaper components can be identified to bridge the price gap, before this directly can replace current RTV systems.

3. Conclusion

Our study has investigated the selectivity in reactions of low molecular weight silazanes with alcohols. We have demonstrated how this selectivity can be exploited in using polymeric silazanes as curing agents for hydroxyl functional silicones. Hence, we demonstrate a new application of PSzs in preparation of RTV silicone networks through silyl ether couplings. By using relatively small amount of PSz (5 wt%) in a mixture of carbinol-functionalized silicone, stable networks could be prepared that are essentially equivalent to classical silicone networks. Most importantly, this can be done under ambient conditions without any considerations to exclude moisture from the process. Silicone films were prepared without use of a catalyst at ambient conditions within 48 h and within 12 h at moderately elevated temperatures (60 °C). Network properties could be adjusted by changing the stoichiometric ratios of PSz and carbinols, demonstrating the versatility of the process and confirming the method for non-metal catalyzed curing of RTV silicone films.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank the Hempel Foundation for financial support to CoaST, The Hempel Foundation Coating Science and Technology Centre, and Siltech (Canada) and Merck KGaA (Germany) for donating materials. 800 MHz NMR spectra were acquired at the NMR Center DTU supported by the Villum and Carlsberg Foundation.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.
Keywords
catalyst free, curing, NMR, polysilazane, silicones

Received: April 4, 2022
Revised: May 9, 2022
Published online: June 20, 2022

[34] E. S. F. Ma, D. C. Mudalige, B. R. James, Dalton Trans. 2013, 42, 13628.