

ARTICLE

Evaluation of mechanical properties and hydrophobicity of room-temperature, moisture-curable polysilazane coatings

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Funding information

Merck KGaA

Abstract

Polysilazane coatings have a broad need in real-life applications, which require low processing or working temperature. In this work, five commercially available polysilazanes have been spin-coated on polycarbonate substrates and cured in ambient environment and temperature to obtain transparent, crack-free, and dense films. The degree of crosslinking is found to have a significant impact on the hardness and Young's modulus of the polysilazane films but has a minor influence on the film thickness and hydrophobicity. Among all five polysilazane coatings, the inorganic perhydropolysilazane-based coating exhibits the largest hardness (2.05 ± 0.01 GPa) and Young's modulus (10.76 ± 0.03 GPa) after 7 days of curing, while the polyorganosilazane-derived films exhibit higher hydrophobicity. The molecular structure of polysilazanes plays a key role in mechanical properties and hydrophobicity of the associated films, as well as the adhesion of coatings to substrates, providing an intuitive and reliable way for selecting a suitable polysilazane coating material for a specific application.

KEYWORDS

coatings, crosslinking, mechanical properties, structure-property relationships, surfaces and interfaces

1 | INTRODUCTION

Polysilazanes are polymers with a Si—N—Si backbone consisting of various substituted reactive or inert side groups at the Si and N atom sites. A wide product portfolio of polysilazanes is commercially available on the market and has been reported to be ideal precursors to ternary SiCN ceramics,¹ ceramic matrix composites,² ceramic fibers,^{3,4} and ceramic or SiO_x rich polymeric coatings.^{5,6}

Due to its liquid nature, most of the economic and simple coating methods are applicable to polysilazane systems, such as, spray coating, dip coating, and spin coating. Additionally, the well-known good adhesion of polysilazane to a variety of substrate materials, such as,

metals, glasses, ceramics, and plastics makes it a favorable material for the coating industry.⁶

Polysilazane coatings can be transformed into SiCO, SiCN, or Si₃N₄ ceramic coatings by pyrolyzing at high temperatures in air, N₂, or Ar atmosphere.^{7–9} They are promising candidates for inter-layer dielectrics,¹⁰ oxidation, or wear protection coatings^{11,12} for high-temperature applications because of their good thermal shock resistance and thermal stability. However, the high-temperature applications require processing temperatures beyond 800°C, which is impracticable for certain applications owing to the limitation of the substrate or manufacturing process.

In recent years, low temperature curing of polysilazane-based coatings has been studied for

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applications, such as, gas barrier,¹³ marine anti-fouling coating,¹⁴ anti-graffiti coating for public transportation,¹⁵ and anti-adherent coating for demolding.¹⁶ Polysilazane coatings can be cured and converted into thermoset polymeric coatings by several types of treatment, such as, thermal crosslinking,¹⁷ UV radiation,¹⁸ O₂ plasma treatment,¹⁹ and moisture curing by hydrolysis and condensation reactions.²⁰ Studies have been undertaken to explore in detail the low-temperature curing behavior and mechanism of polysilazane coatings.^{21–25} When exposing polysilazanes to moist air, it was reported by Müller et al.²² that the hydrolysis and condensation reactions are predominant even at elevated temperature during the curing process. In this context, the room temperature (RT) moisture curable polysilazane coatings prepared by simple methods draw attention to some researchers.^{14,21,26,27} Nevertheless, from the best of our knowledge, the curing behavior and the corresponding properties of polysilazane coatings under long-term ambient conditions have not been reported yet.

In this work, comprehensive characterizations of the curing behavior, film thickness, surface morphology, as well as the mechanical properties and hydrophobicity of five commercially available polysilazane-derived films cured under ambient atmosphere and temperature for 30 days were performed. The curing

rate and the degree of crosslinking of the coatings were investigated by monitoring the changes of hardness, Young's modulus, and contact angle with increasing curing time for 30 days, by means of nanoindentation and contact angle measurement. Moreover, the moisture-curing behavior of a bulk polysilazane was investigated by elemental analysis and Fourier-transform infrared spectroscopy (FTIR). In addition, the adhesion of polysilazane coatings to the polycarbonate substrates was assessed by standard cross-cut tests (DIN EN ISO 2409) in a 7-day curing period. Finally, based on the results of this study, a benchmark evaluation of the mechanical properties and hydrophobicity of different polysilazane-derived coatings is proposed.

2 | MATERIALS AND METHODS

Five commercially available polysilazanes were provided by Merck KGaA, Darmstadt, Germany, and used as received without further purification. Figure 1 depicts the simplified linear molecular structure of different polysilazanes employed in this work. To specify, Durazane 1500 rapid cure (D1500-rc), Durazane 1500 slow cure (D1500-sc), and Durazane 1800 (D1800) are denoted as polyorganosilazanes. The perhydropolysilazane (PHPS)-

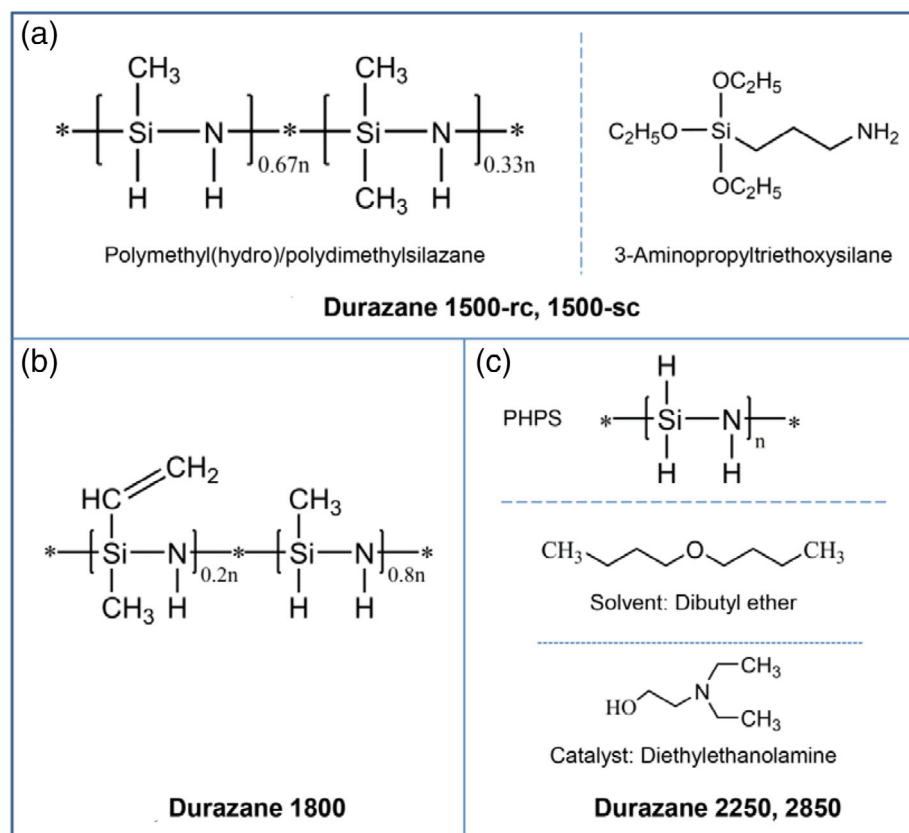


FIGURE 1 Molecular structures of Durazane polysilazanes. (a) Durazane 1500 (incl. rapid cure and slow cure). Durazane 1500 rapid cure has a higher fraction of 3-aminopropyltriethoxysilane than Durazane 1500 slow cure. (b) Durazane 1800. (c) Durazane 2250 (20 wt% solution of PHPS in dibutyl ether). Durazane 2850 is produced by further adding 0.5 wt% of diethylethanolamine as a catalyst [Color figure can be viewed at wileyonlinelibrary.com]

based polysilazanes Durazane 2250 (D2250) and Durazane 2850 (D2850) are denoted as inorganic polysilazanes.

To investigate the curing behavior of the polysilazane at RT (23°C), two flasks with 50 ml of D1500-rc liquid were bubbled with ambient air (with 40% to 55% relative humidity) and synthetic air (water content less than 2 ppmv) for 7 days, respectively. The chemical compositions of the cured samples were determined using elemental analysis (performed by Mikroanalytisches Labor Pascher, Germany) under an inert atmosphere for the nitrogen and oxygen contents. The changes of the organic groups in the cured samples were recorded by FTIR ranging from 550 to 4000 cm^{-1} on a Varian IR-670 spectrometer (Agilent) in the attenuated total reflection (ATR) mode.

All five polysilazanes were spin-coated on polycarbonate (PC) plates (Makrolon®, Bayer AG, Germany) and cured at RT in ambient atmosphere for 30 days to prepare the polysilazane films. The spin speed was tuned between 500 and 1500 rpm to achieve the industrially favorable thickness of ca. 6 μm . The thickness of the polysilazane films was measured using a stylus profilometer (DektakXT®, Bruker Corporation, Germany). The corresponding surface morphology was observed under a Philips XL30 FEG high-resolution scanning electron microscope (SEM, FEI Company).

In addition to profilometry and SEM, nanoindentation, and contact angle measurement were performed to access the variation of mechanical properties and hydrophobicity of the resultant polysilazane films during curing. The adhesion of the polysilazane coatings to the PC substrates was investigated by standard cross-cut test (DIN EN ISO 2409), using a Cross Hatch Cutter test kit (Model 295, ERICHSEN GmbH & Co. KG, Germany). The tested areas were observed and evaluated by optical microscopy (VHX-6000, KEYENCE DEUTSCHLAND GmbH, Germany). It is worth noting that the aforementioned characterization methods were only applied after the polysilazane films were dry to touch. All dried films were transparent, colorless, and adherent to the PC substrates.

The hardness and Young's modulus of the films and PC substrate were measured using a G200 nanoindenter (Keysight Technologies), equipped with a Berkovich diamond indenter tip. A continuous stiffness measurement method and a strain rate of 0.05 s^{-1} were applied in all nanoindentation experiments. On each sample, nine indentations were performed with an indentation depth up to 2000 nm (depending on the corresponding film thickness). The displayed data were chosen from an indentation depth of approximately 10% of the film thickness to avoid possible substrate effects. The hardness and Young's modulus were subsequently calculated via Oliver-Pharr method.²⁸

The hydrophobicity of the polysilazane films was characterized by static contact angle measurement using an OCA-20 goniometer (DataPhysics Instruments GmbH, Germany). At least three areas of each film and PC substrate were tested using the sessile drop method. The equilibrium shape of the water drop was described by the Young-Laplace equation and the water contact angle was estimated by fitting the contour of the drop as a function of interfacial and gravity forces.

3 | RESULTS AND DISCUSSION

3.1 | Curing behavior of bulk Durazane 1500 rapid cure

In this work, Durazane 1500-rc was applied as a reference for the investigation of the curing behavior of polysilazanes in ambient and dry air at RT. Figure 2 depicts the theoretical crosslinking reaction paths based on the following simplifying assumptions: (a) The polymethyl(hydro)/polydimethylsilazane and 3-aminopropyltriethoxysilane (AMEO) are physically mixed in D1500-rc polysilazane solution. (b) With the presence of water, all of the Si—H, Si—NH, and Si—OC₂H₅ groups are consumed and transformed to Si—O groups via hydrolysis and condensation reactions. The oxygen and nitrogen contents in D1500-rc before and after complete curing were calculated. Before curing, D1500-rc contains 16.8 wt% nitrogen and 7.2 wt% oxygen (from AMEO). After complete crosslinking, the nitrogen content decreases to 2.3 wt%, while the oxygen content increases to 29.1 wt%.

Elemental analysis of oxygen and nitrogen contents in bulk D1500-rc cross-linked for 1, 24, 72, and 168 h were carried out, respectively. As shown in Figure 3(a), without moisture, D1500-rc remains unchanged after 168 h of exposure to dry air. While in the case of curing under ambient atmosphere (with 40% to 55% relative humidity), the nitrogen content of cured D1500-rc decreases and the oxygen content increases with curing time. Within the first 24 h, the N— and O—contents were almost halved. After 72 h of curing, the oxygen content tends to be saturated, while the nitrogen content keeps declining at a relatively low rate. After 168 h, the nitrogen content decreases from 15.0 \pm 0.1 wt% to 4.7 \pm 0.1 wt%, and the oxygen content increases from 7.4 to 28.2 wt% \pm 0.3 wt% as compared with the pristine D1500-rc polysilazane. The experimentally obtained oxygen content is in good agreement with the theoretical calculation. In this context, the crosslinking degree of D1500-rc is calculated and depicted in Figure 3b. It is obvious that 90.2% \pm 0.7% of the crosslinking reactions have been completed after

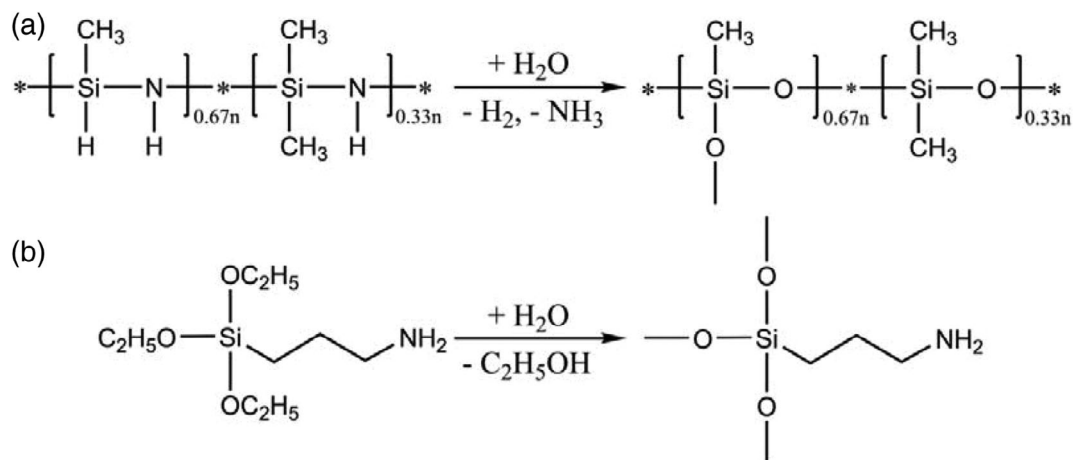


FIGURE 2 Theoretical crosslinking reaction paths of Durazane 1500-rc containing additions of 3-aminopropyltriethoxysilane

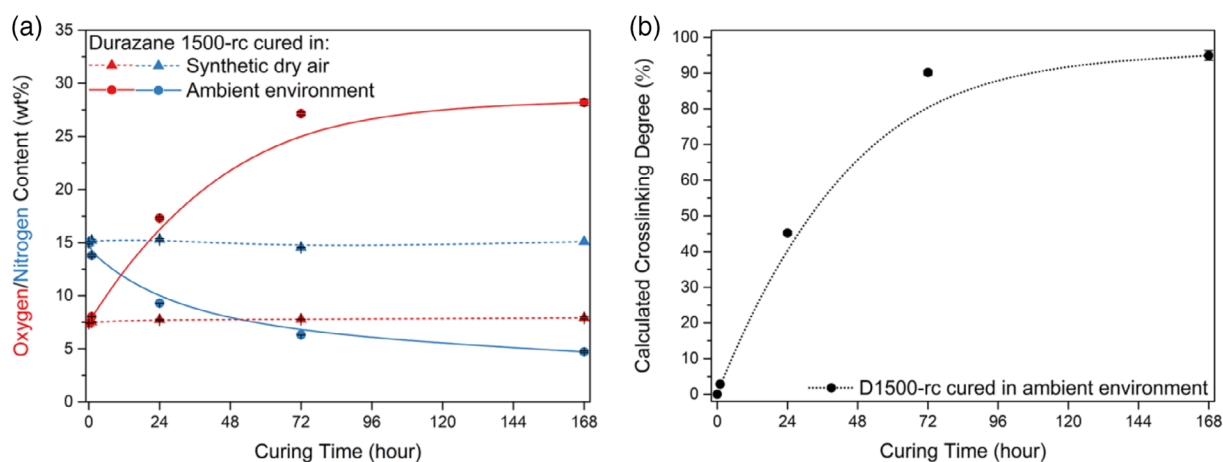


FIGURE 3 (a) Variation of elemental oxygen and nitrogen contents in the Durazane 1500-rc cured in synthetic air and ambient environment at RT for 168 h, respectively. (b) Crosslinking degree of D1500-rc as a function of curing time (based on the calculation of theoretical oxygen content) [Color figure can be viewed at wileyonlinelibrary.com]

72 h of curing in ambient environment and temperature. Further hydrolysis and condensation reactions occur slowly and 95.0% \pm 1.4% of the reactions have been completed after 168 h of curing.

The ATR-FTIR spectra shown in Figure 4 correlate well with the elemental analysis result. During curing in ambient environment at RT, hydrolysis, and condensation reactions² occur. The hydrolysis reaction leads to the loss of nitrogen by releasing NH_3 with the consumption of the N—H groups (at 1168 cm^{-1}). In the meanwhile, the Si—H groups (at ca. 2125 cm^{-1}) are consumed, and H_2 is released. The Si—O—R units (at 1077 and 1105 cm^{-1}) from the 3-aminopropyltriethoxysilane are gradually transformed into Si—O—Si (at ca. 1022 cm^{-1}) with the releasing of $\text{C}_2\text{H}_5\text{OH}$.^{21,29} In addition, Si—O—Si units are formed via condensation reaction increasing the oxygen content. In the first 24 h of curing, there are residual Si—H and N—H groups in considerable quantities. After

72 h of curing, most of the hydrolyzable groups in D1500-rc are consumed and the hydrolysis and condensation reactions slow down. After 168 h of curing, almost all of the Si—H and N—H groups in D1500-rc disappear and the curing of D1500-rc reaches a plateau state. Thus, it can be concluded that the existence of water in the atmosphere is the crucial factor for the curing process of polysilazane, while the polysilazane is stable against oxidation in air at room temperature.

3.2 | Thickness of spin-coated polysilazane films

The polysilazanes were spin-coated on PC substrates and dry to touch in ambient environment at RT. The inorganic polysilazane D2250 and D2850 coatings exhibit the shortest dry to touch time, which is around 30 s (for

D2850) to 5 min (for D2250) under the same conditions. The D1500-rc film is dry to touch in about 30 min, while the D1500-sc film requires 1 to 2 h. The D1800 film requires about 32 h to reach the dry to touch condition.

The thickness of the dry polymer films can be controlled by the spin speed (angular velocity) and the concentration of the polymer solution. The generalized correlation is empirically derived according to the following Equation^{30,31}:

$$h_f = k\omega^{-\alpha} \quad (1)$$

where h_f is the film thickness (μm), ω is the spin speed (rpm), while k and α are empirical constants. A set of

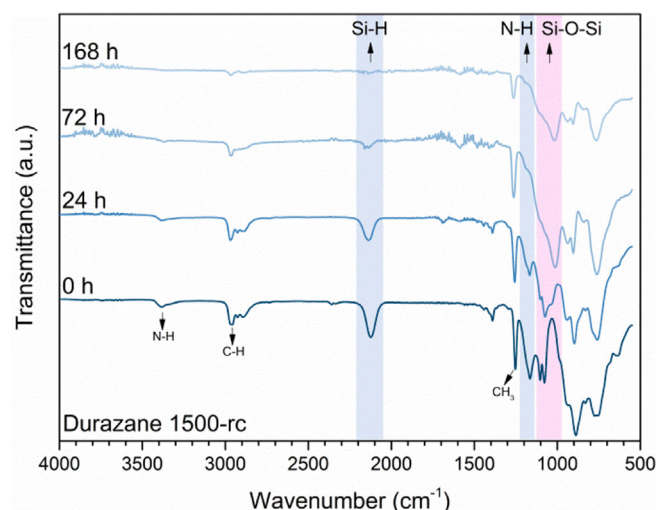


FIGURE 4 ATR-FTIR spectra of Durazane 1500-rc after 0, 24, 72, and 168 h of curing in ambient environment [Color figure can be viewed at wileyonlinelibrary.com]

factors influence the value of constants k and α , including the intrinsic properties of the polymer, type of solvent, concentration and viscosity of the polymer solution, and interaction between the solution and the substrate.

Among these five investigated polysilazanes, Durazane 1800 possesses the highest viscosity in the range of 20 to 50 mPa·s, followed by Durazane 1500-sc (20 to 30 mPa·s) and Durazane 1500-rc (12 to 20 mPa·s). Durazane 2250 and Durazane 2850 exhibit the lowest viscosity of less than 5 mPa·s at 20°C because of the presence of 80% of solvent. The influence of solution viscosity on the resulting film thickness is indicated in Figure 5(a). At the same spin speed, the higher the solution viscosity, the thicker the resulting spin-coated film.

On the other hand, the film thickness of all five polysilazane coatings decreases with the increase of the spin speed. The experimental data points are statistically fitted with Equation (1) to obtain the constants k and α . Regarding the pure polyorganosilazanes D1500-rc, D1500-sc, and D1800, the values of k are 710, 2107, 697, while α amounts 0.76, 0.88, and 0.7, respectively. As the polysilazanes D2250 and D2850 have relatively low viscosities, they have lower α values of 0.59 and 0.41, and the k value amounts 41 and 18, respectively. This phenomenon may be explained by the effect of fluid inertia.³²

In order to further characterize the polysilazane coatings without considering the effect of film thickness on the curing process, specific spin speed was selected for each polysilazane to achieve an industrially favorable film with a thickness of 5 to 7 μm . Regarding the spin parameter, that means 500 rpm for D1500-rc with a $6.12 \pm 0.21 \mu\text{m}$ film, 700 rpm for D1500-sc with a $6.11 \pm 0.07 \mu\text{m}$ film, and 1500 rpm for D1800 with a

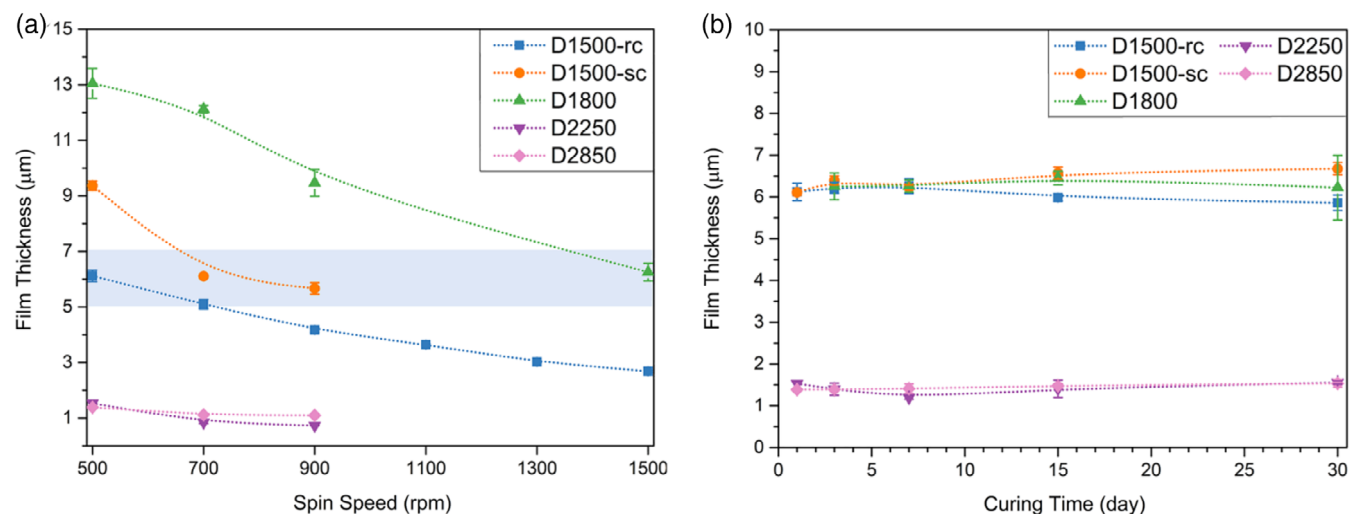


FIGURE 5 Film thickness of polysilazane coatings as a function of (a) spin speed and (b) curing time [Color figure can be viewed at wileyonlinelibrary.com]

$6.25 \pm 0.32 \mu\text{m}$ film. However, due to the low viscosity, the thickest D2250 and D2850 films that can be obtained without sacrificing the homogeneity have thicknesses of $1.53 \pm 0.01 \mu\text{m}$ and $1.39 \pm 0.01 \mu\text{m}$. The applied spin speed is limited to 500 rpm in both cases.

The as-obtained polysilazane coatings were cured in ambient environment at RT for 30 days. The development of the film thickness is recorded and shown in Figure 5(b). Although there are marginal variations during the 30 days of curing, the eventual film thickness of all five coatings is within the same range as the initial state, which indicates a minor impact of the crosslinking degree on the coating thickness. Therefore, the influence of the film thickness on subsequent characterizations can be eliminated.

3.3 | Surface morphology of polysilazane coatings

The surface morphology and cross-section of the as-obtained polysilazane coatings were further studied by scanning electron microscopy. Figure 6 shows SEM micrographs of the surface and cross-section of a Durazane 1500-rc coating after 30 days of crosslinking in ambient environment and temperature. The SEM images of D1500-sc, D1800, D2250, and D2850 coatings are shown in Figure S1 (supporting information) accordingly. The resultant films are dense, crack-free, and with a smooth surface.

3.4 | Mechanical properties of polysilazane coatings

Nanoindentation was employed to characterize the mechanical properties of the polyorganosilazane coatings with thicknesses of about $6 \mu\text{m}$ and inorganic polysilazane coatings with thicknesses of about $1.5 \mu\text{m}$. The progression of the hardness and Young's modulus of the mentioned polysilazane coatings during the 30 days of

curing in ambient environment at RT were investigated and are shown in Figure 7.

As illustrated, the inorganic polysilazane (D2250 and D2850) films exhibit higher hardness and Young's modulus values as compared to the group of polyorganosilazane films (D1500-rc, D1500-sc, and D1800). After curing for 7 days, the D2850 coating reaches the highest value of hardness ($2.05 \pm 0.01 \text{ GPa}$) and Young's modulus ($10.76 \pm 0.03 \text{ GPa}$) among all investigated films. The subsequent slight decrease in hardness and Young's modulus is discussed in terms of microcracks formed in the coating during the indentation.³³

In the case of the D2250-derived coating, the hardness and Young's modulus reach values of 0.64 and $3.59 \pm 0.01 \text{ GPa}$, respectively, after 15 days of curing. Compared with polyorganosilazanes, the inorganic polysilazanes have a considerably higher amount of hydrolyzable Si—H groups, that react with water to form Si—OH groups, which in turn condensate to form a highly cross-linked Si—O—Si network.

Among the three polyorganosilazane coatings cured for 30 days, the D1500-rc coating shows the highest hardness and Young's modulus of 0.29 and 2.9 GPa, respectively. Durazane 1500-sc coating, which contains less hydrolyzable 3-aminopropyltriethoxysilane substituted groups if compared with D1500-rc and thus exhibits lower hardness and Young's modulus of 0.11 and 1.4 GPa, respectively. Durazane 1800 coating possesses the lowest hardness and modulus of 0.05 and 0.4 GPa, respectively, since it has the least number of hydrolyzable groups, which leads to the lowest degree of crosslinking among all the investigated polysilazanes. Moreover, the additional vinyl groups in D1800 may sterically hinder the crosslinking reactions.

For all coatings, the hardness and Young's modulus increase rapidly during the first three days of curing. Then, the corresponding growth rate slows down because of the reduced number of hydrolysis and condensation reactions owing to the insufficient hydrolyzable groups after a certain period. Besides, the hardened surface of the coating prevents the diffusion of atmospheric H_2O into the polysilazane and further slows down the

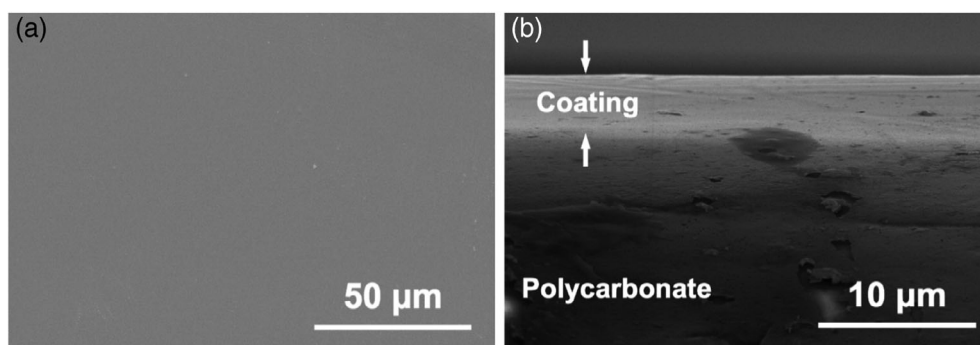


FIGURE 6 SEM images of (a) the surface and (b) cross-section of Durazane 1500-rc coating cured in ambient environment and RT for 30 days

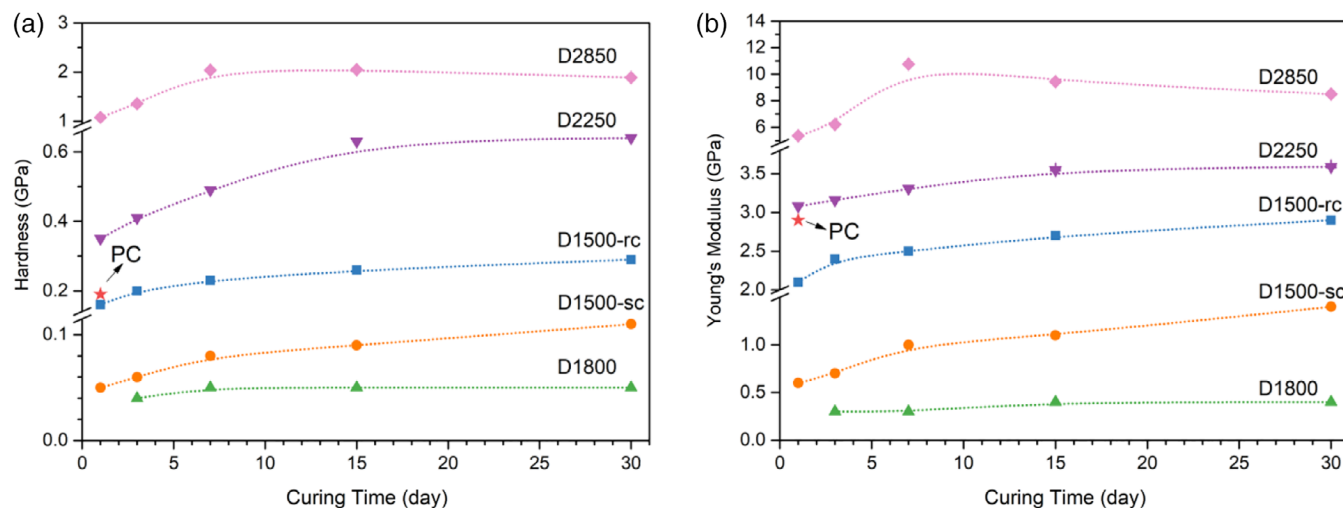


FIGURE 7 (a) Hardness and (b) Young's modulus of polysilazane coatings on PC as a function of the curing time [Color figure can be viewed at wileyonlinelibrary.com]

hardness/Young's modulus growth. After 7 or 15 days of curing, the above values of D2250, D2850, and D1800 coatings reach plateaus gradually, which to a certain extent indicates the limits of the crosslinking degree for the specific polysilazane coatings cured in ambient environment at RT. However, the hardness and Young's modulus of D1500-rc and D1500-sc coatings grow further slowly but continuously after 30 days of curing. Taking into account the results shown in Figure 3 and 4, it is interesting to see that even though the hydrolysis and condensation reactions seem to reach plateaus after 3 days of curing, the 3D-network of D1500-rc obviously further crosslinks, indicating possible physical crosslinking processes through hydrophobic interaction and chain entanglement³⁴ in addition to chemical crosslinking reactions.

The hardness and Young's modulus of the used polycarbonate substrate are measured as 0.19 and 2.9 GPa, respectively. The relatively higher values of D1500-rc, D2250, and D2850 films imply potential applications of the polysilazanes as protective coatings on PC-based materials.

3.5 | Hydrophobicity of polysilazane coatings

Hydrophobicity is considered to be a crucial factor for anti-fouling and anti-graffiti coatings. Figure 8(a) shows the water contact angle of polysilazane coatings during curing under ambient conditions at RT for 30 days. A similar tendency describing the change in contact angle with curing time for all coatings can be observed. Consider the D1500-rc coating as an example, the hydrophobic groups, such as, Si—H¹⁶ and Si—CH₃²³ result in a hydrophobic surface with a contact angle of $94.6^\circ \pm 0.5^\circ$.

During the crosslinking reactions, the formation of hydrophilic Si—OH and Si—NH₂ groups as well as the consumption of hydrophobic Si—H groups lead to the reduction of the water contact angle to $90.4^\circ \pm 0.8^\circ$.³⁵ Subsequently, a hydrophobic recovery^{36,37} appears, which could be explained by the combined effect of condensation reaction, diffusion, and reorientation of polar groups. On the one hand, the number of hydrophilic Si—OH and Si—NH₂ groups is reduced due to condensation reactions. On the other hand, the molecular mobility is hindered by the highly cross-linked Si—O—Si network and thus the reorientation of polar Si—O bonds³⁸ toward the polar water droplet becomes difficult. In the end, a contact angle of $95.4^\circ \pm 0.7^\circ$ is obtained for the D1500-rc coating after curing under ambient conditions for 30 days.

From Figure 8b, the D1800 coating exhibits the highest contact angle of $103.3^\circ \pm 0.5^\circ$ because of the existence of a large number of hydrophobic groups, such as, Si—CH₃ and Si—CH=CH₂ groups which cannot be involved in the crosslinking reactions at RT. Comparatively, D1500-rc and D1500-sc coatings are less hydrophobic with contact angles of $95.4^\circ \pm 0.7^\circ$ and $98.4^\circ \pm 2.4^\circ$, respectively. Furthermore, the PHPS-based D2250 and D2850 coatings present less hydrophobicity with contact angles of $83.9^\circ \pm 0.8^\circ$ and $85.9^\circ \pm 0.8^\circ$, respectively. Moreover, the contact angle of the uncoated PC substrate is measured as $97.3^\circ \pm 1.3^\circ$.

3.6 | Adhesion of polysilazane coatings to polycarbonate substrate

The adhesion of polysilazane to most surfaces is known to be good due to the chemical reactions of Si—H, Si—NH

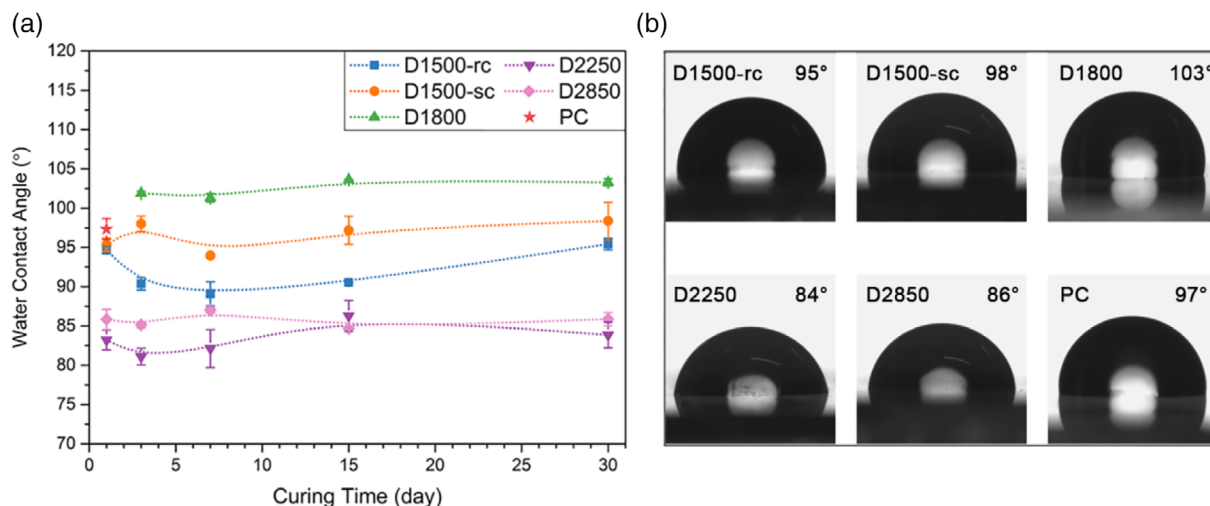


FIGURE 8 (a) Water contact angle of polysilazane coatings on PC as a function of curing time. (b) Sessile water droplets on polysilazane coatings after 30 days of curing and PC [Color figure can be viewed at wileyonlinelibrary.com]

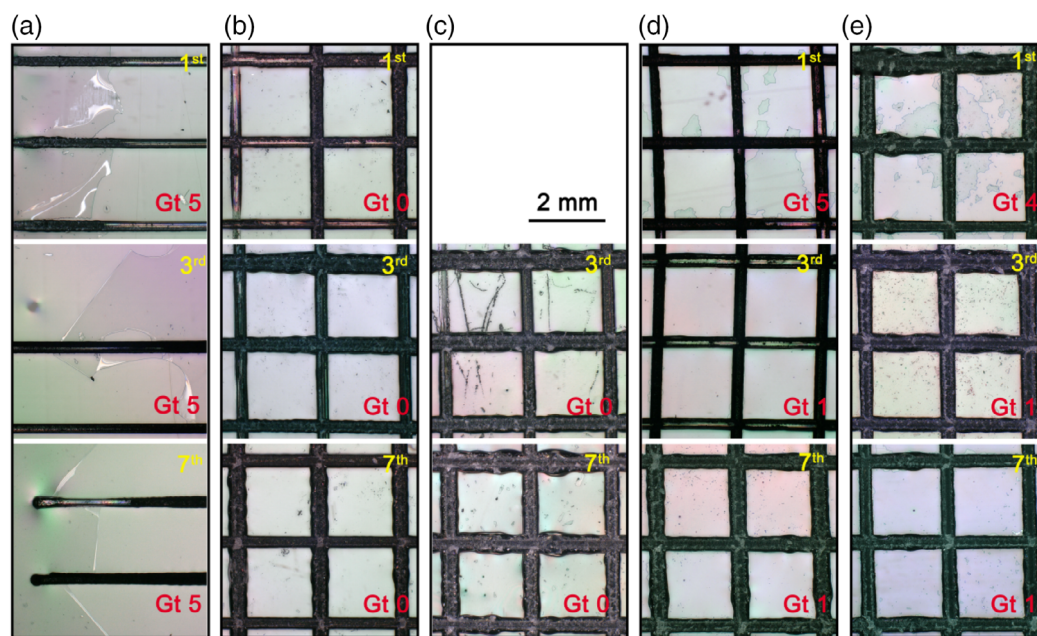


FIGURE 9 Optical microscopy images of polysilazane coatings on polycarbonate substrates after standard DIN EN ISO 2409 cross-cut tape test: (a) D1500-rc, (b) D1500-sc, (c) D1800, (d) D2250, (e) D2850 coatings after 1, 3, and 7 days of curing in ambient environment, respectively [Color figure can be viewed at wileyonlinelibrary.com]

groups with the —OH groups and the adsorbed water molecules on surface, which form subsequently oxygen bridges between the polysilazane coating and the substrate.^{16,39,40} Figure 9 shows the optical microscopy images of five polysilazane coatings cured after 1, 3, and 7 days and with the standard cross-cut tape test being performed. According to the DIN EN ISO 2409, coatings are classified from Gt 0 (best adhesion, without any detachment of the coating after the test) to Gt 5 (worst adhesion, detachment of the coating >65% of the tested area). Among all five polysilazane coatings, D1500-sc

(Figure 9(b)) and D1800 (Figure 9(c)) coatings exhibit excellent adhesion to polycarbonate substrates, showing no coating spalling once they are dry to touch. Due to the higher fraction of 3-aminopropyltriethoxysilane in D1500-rc, the adhesion of the coating to the PC substrate is not enough to withstand the pull-off strength of the tape and the entire coating has been peeled off (Figure 9(a)).

Unlike the aforementioned polyorganosilazane coatings, the adhesion of the inorganic polysilazane coatings to the PC substrates improved along with the curing time.

After one day of crosslinking, D2250 (Figure 9(d)) and D2850 (Figure 9(e)) coatings display poor adhesion to the substrates, which is attributed to the lower amount of oxygen bridge between the diluted polysilazane (contains dibutyl ether as solvent) and substrate surface. As curing time increased, due to the much thinner thickness (ca. 1.5 μm), water molecules from the atmosphere reach the interface of the coating and substrate to further form oxygen bridges. Hence, the adhesion of D2250 and D2850 coatings to the PC substrates is improved from Gt 5 and Gt 4 to Gt 1, respectively.

4 | CONCLUSIONS

This work reports on a comprehensive investigation of the mechanical properties and hydrophobicity of five commercially available Durazane polysilazane films that are moisture-curable at room temperature and provides a guideline on the coating material selection. It can be confirmed that water is indispensable for the crosslinking of the polysilazane. In wet air, hydrolysis and condensation reactions result in the crosslinking of the polysilazanes and formation of a 3-dimensional polymeric network, while, the polysilazanes are stable against oxidation in dry air at RT.

Spin coating was proved to be an effective technique for the preparation of dense and crack-free polysilazane coatings. The relation between the film thickness and spin speed was empirically derived and can be applied for future research to adjust the coating thickness by selecting appropriate spin parameters. Moreover, it is found that the coating thickness is independent of the curing time.

The hardness and Young's modulus of the polysilazane coatings were determined by nanoindentation. PHPS-based polysilazane coatings have higher values than that of the polyorganosilazane coatings and the used PC substrate. This feature makes PHPS a candidate material as protective coatings for PC-based materials. Unlike the other polysilazane coatings with hardness and Young's modulus reaching plateaus after 7 or 15 days of curing, D1500-rc and D1500-sc coatings continue to harden even after 30 days of curing, indicating that in addition to chemical crosslinking reactions, physical crosslinking occurs as well during the curing process.

The water contact angle measurements show that the polyorganosilazane coatings are more hydrophobic than that of the PHPS-derived coatings. Different from the continuous increase of hardness and Young's modulus, the water contact angles of the polysilazane films firstly decrease at the early stage of curing, then, go through a recovery process and finally reach similar values as measured at the early stage.

Finally, the analyzed properties of the different polysilazane coatings cured in ambient atmosphere at room temperature can be roughly ranked as follows:

1. Curing rate: D2850 > D2250 > D1500-rc > D1500-sc > D1800
2. Hardness and Young's modulus: D2850 > D2250 > D1500-rc > D1500-sc > D1800
3. Hydrophobicity: D1800 > D1500-sc > D1500-rc > D2250 > D2850.
4. Adhesion to polycarbonate: D1500-sc = D1800 > D2250 = D2850 > D1500-rc

ACKNOWLEDGMENTS

The authors would like to acknowledge Merck KGaA for the financial support of this research project. The authors would also like to thank the Physical Metallurgy Division of TU Darmstadt, Germany (Prof. K. Durst, funding by DFG, DU 424) for the provision of the nanoindentation experimental facilities. Open Access funding enabled and organized by ProjektDEAL. WOA Institution: TECHNISCHE UNIVERSITÄT DARMSTADT.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTION

Ying Zhan, Conceptualization, Methodology, Validation, Investigation, Data Curation, Writing-Original Draft, Visualization. Ralf Grottenmüller, Conceptualization, Methodology, Resources, Writing-Review & Editing, Supervision, Funding acquisition. Wei Li, Validation, Investigation, Writing-Review & Editing. Farhan Javaid, Validation, Investigation, Writing-Review & Editing. Ralf Riedel, Conceptualization, Resources, Writing-Review & Editing, Supervision, Project administration, Funding acquisition.

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SUPPORTING INFORMATION

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How to cite this article: Zhan Y, Grottenmüller R, Li W, Javaid F, Riedel R. Evaluation of mechanical properties and hydrophobicity of room-temperature, moisture-curable polysilazane coatings. *J Appl Polym Sci.* 2021;e50469. <https://doi.org/10.1002/app.50469>