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Research Article

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Structuring of hydroxy-terminated polydimethylsiloxane filled by fumed silica

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Abstract: The term "structuring" used in silicone rubber describes a phenomenon of the increase in the viscosity of polydimethylsiloxane filled with silica during storage, which limits the applications of the room temperature vulcanized (RTV) silicone rubber in the field of aerospace and military. In this pursuit, the present study was envisaged to solve the problem of structuring of the RTV. A solvent-free method was used to hydrophobize the hydrophilic silica with hexamethyldisilazane. An RTV composition prepared using eight parts of hydrophobic silica with 2.91% C content exhibited a viscosity of less than 100 Pa s, with no significant change in 21 days. In contrast, eight parts of the hydrophilic fumed silica showed an initial viscosity of RTV to be greater than 2,000 Pa s. Silica samples with different adsorbed water content were used to prepare the RTV compositions. It was found that the viscosity of the RTV prepared using the sufficiently dried silica was 5.6 times lower than that of the wet silica. The "dissolution" model of the silica–silica hydrogen bonds in water was proposed. Furthermore, the change in the viscosity of the RTV compositions at different temperatures in the range of −15°C to 30°C was studied. The viscosity of RTV stored at −15°C for 34 days did not change significantly, whereas that stored at room temperature increased from 100 to 1,710 Pa s within 21 days.

Keywords: PDMS, RTV, crepe hardening, structuring, fumed silica

1 Introduction

Silicone rubber is a synthetic polymer that combines the advantages of both inorganic and organic materials. It possesses excellent heat, chemical, and ultraviolet radiation resistance and exhibits a second-lowest surface tension after the fluorine-containing materials. Moreover, silicone rubber can withstand a wide range of temperatures from −50°C to 200°C. All these special properties lead to its diverse application in fields such as aviation, aerospace, medical, construction, and electronics.

The main polymer component of silicone rubber is polydiorganosiloxane, whose backbone consists of repeated R_2SiO units. Various types of silicone rubber that possess different chemical and physical properties, thereby being applied in contrasting fields, could be obtained by varying the side group −R in R_2SiO unit and the terminal groups of polydiorganosiloxane chains. α,ω-dihydroxy polydimethylsiloxane (HPDMS), a typical derivative of polydiorganosiloxane, has two Si–OH groups on its end, and legion $(CH_3)_2SiO$ repeated units constituting its backbone. HPDMS is generally used to produce the room temperature vulcanized (RTV) silicone rubber. The instance of RTV products includes mold making RTV, adhesives, coatings, sealants, electronic thermal conductive adhesives, etc.

RTV adhesives for aviation, aerospace, and military purpose strictly require high mechanical strength, which often makes designers to add too many parts of fillers (mainly fumed silica) to HPDMS. On one hand, RTV system is rendered too thick to handle, owing to the high proportion of fumed silica in HPDMS. On the other hand, an increase in the silica content increases the rate of the viscosity of RTV system during storage. The anomaly of the increase of the viscosity during the storage of rubber-filler system is called "structuring" or "crepe

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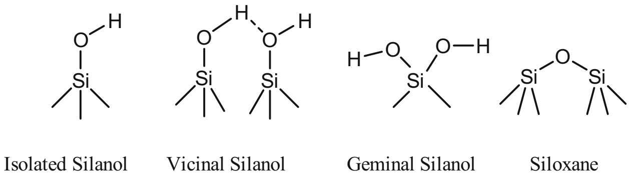

Figure 1: Types of silanol and siloxane on the surface of silica.

hardening" (1,2). In the field of fluid RTV, the term "structuring" is often used.

Four types of silanol and siloxane on the surface of silica determine the surface chemistry of the fumed silica-isolated silanol, vicinal silanol, geminal silanols, and siloxane (3) as shown in Figure 1.

The hydrophilic types including the isolated silanol and geminal silanol are more active than others; therefore, they are the prime groups to adsorb the polymers and react with the silanes (4). In vicinal silanol, the adjacent two silanol groups are bridged by a hydrogen bond. As a result, it exhibits a weak reactivity than the isolated and geminal silanol, but adsorbs water to a greater extent (5). Aerosil 200 (commercially available fumed silica by Degussa AG) has a surface Si–OH density over 2.8 OH/nm^2 (6), which means that there are at least 5.6×10^{20} silanol groups on its surface for 1 g of sample. Massive silanols on the surface of silica enable the contact and then adsorb HPDMS physically after a mere physical mixing of silica and HPDMS.

Vondráček and Schätz found that the activation energy of the bound rubber formation (structuring) to be 16.8 kJ/mol (2). The activation energy indicated that the structuring involved physical adsorption such as hydrogen bond than chemical interactions.

Cochrane and Lin (7) proposed that the alternating oxygen atoms on the polysiloxane chain formed a large number of hydrogen bonds with the massive hydroxyl groups on the surface of the fumed silica without chemical hydrophobic treatment. There were often long segments of polysiloxane adsorbed on the silica surface in this way, and the rest of polysiloxane segments were dissolved in the polymer mass in a random conformation or were adsorbed on the other silica particles. These findings agreed with the earlier researchers (8) and provided an explanation of the mechanism of the thickening effect and structuring effect of fumed silica in methyl vinyl silicone rubber. It also partially explained the case of HPDMS. In addition to the hydrogen bonding between the silanol groups on the silica and the oxygen atoms in the polysiloxane chains, in the case of condensation cured HPDMS-fumed silica system, the hydrogen bonds between the silanol groups of silica and the silanol groups on the end of HPDMS also play a critical role. These exclusive hydrogen bonds, which are absent in the vulcanized liquid silicone rubber and high temperature vulcanized silicone rubber, lead to far more serious thickening and structuring issues (4).

For the use of RTV silicone rubber in the aviation, aerospace, and military application scenarios, more parts of silica (more than 25 parts by mass) need to be added to obtain the requisite mechanical properties. This renders a rapidly increasing viscosity during the storage of the adhesives, and the expired waste is inevitable. In this context, the surface chemistry of silica and its effects on the thickening properties and storage structuring need research attention. The answers to these questions are crucial in guiding the research on the high-end RTV adhesives.

In the present study, we focused on the structuring behavior of HPDMS-fumed silica system and studied the influencing factors with the corresponding underlying mechanisms. The factors taken into consideration were the silanol content of the silica surface, the degree of moisture absorption of the silica, the level of silazane treatment, the storage temperature, and the presence or absence of low molecular weight dimethicone.

2 Experimental

2.1 Materials

HPDMS (10 and 5 Pa s) and dimethicone (10 Pa s, DMS, trimethylsilyl-terminated polydimethylsiloxane) were provided by Jinan Yingyu Chemical Co., Ltd. (Jinan, China). Aerosil 200 and Aerosil R8200 (Evonik Industries, China) was purchased from the Chengdu Haipu Chemical Products Co., Ltd., China. The specific surface area of Aerosil 200 and Aerosil R8200 was 203 and 148 m^2/g, respectively. C content of Aerosil R8200 was 3.8 wt%. Carbon in Aerosil R8200 was introduced by treating with hexamethyldisilazane (HMDS), which was intended to render the silica to be hydrophobic. HMDS (≥98%) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd., China.

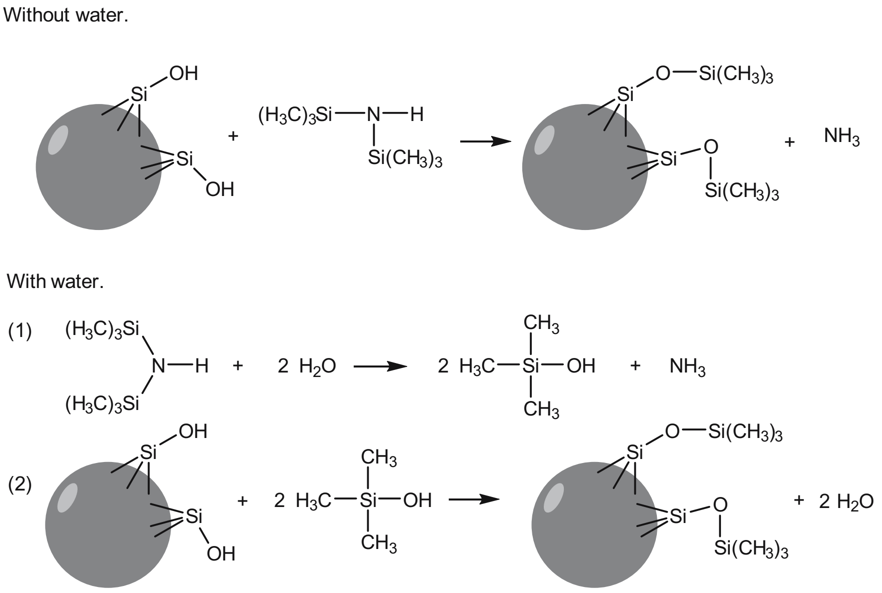

Figure 2: Reaction between silanol on surface of silica and HMDS.

2.2 Method

2.2.1 Varying the C content of silica

Silazane compounds, such as HMDS, have been widely used in the hydrophobic treatment of synthetic amorphous silica (9–12). A solvent-free treatment method was developed in our study, in contrast to most of the numerous published methods that used a lot of solvents (11,13,14). The reactions occurring during the treatment are shown in Figure 2 (11). The reactions occurred whether water was present or not and altered the hydrophilic hydroxyl groups to hydrophobic trimethylsilyl groups.

2.2.2 Experimental

Aerosil 200 silica was subjected into a three-necked flask equipped with a reflux condenser, stirring transposition, and a constant pressure funnel containing the required quantity of HMDS. The valve of the constant pressure funnel was turned on and HMDS was added into three-necked flask drop by drop with continued stirring at room temperature for 1 h. Subsequently, the flask was heated up to 100°C and the reaction was continued for 2 h. Finally, the silica was dried at 120°C at a vacuum of 0.1 mPa to remove the residual volatiles such as HMDS, NH_3, and H_2O. To obtain the silica samples with different C content, the mass ratio between the silica and HMDS was varied (Table 1). Infrared spectroscopy analysis, specific surface area analysis, and elemental analysis were used to test the resulting fumed silica to determine its specific surface area, C content, and residual ammonia. Finally, the treated samples of silica were mixed with HPDMS. The parameter level was calculated by Eq. 1:

$$\text{Level} = \frac{2 \cdot MN_\text{A}}{161.4 \times 10^{18} \cdot mA}, \tag{1}$$

where M is the mass of used HMDS, N_A is the Avogadro's number, 161.4 is the relative molecular mass of HMDS, 10^{18} is the coefficient to convert m^2 to nm^2, m is the mass of used silica, and A is the specific surface area of used silica and multiplied by 2, as one HMDS molecule generates two trimethyl silanol. The parameter level implies the amount of trimethyl silanol groups that react with 1 nm^2 silica surface in ideal state.

Table 1: Different levels of treatment of Aerosol 200 and HMDS

Codes	Aerosil 200 silica (g)	HMDS (g)	Level (groups/nm^2)
Level-A	38.0	2.9	2.80
Level-B	43.7	4.6	3.87
Level-C	31.0	4.6	5.48
Level-D	38.0	8.0	7.73

Table 2: Characterization of untreated and treated hydrophobic silica surface

Treatment level code	Aerosil 200	Level-A	Level-B	Level-C	Level-D
Treatment level, $-Si(CH_3)_3$ density ideally (groups/nm^2)	—	2.80	3.87	5.48	7.73
C content (wt%)	0	1.87	2.27	2.36	2.91
Specific surface area (m^2/g)	203	147	147	147	148
$-Si(CH_3)_3$ density[a] (groups/nm^2)	0	2.13	2.58	2.68	3.29

[a] Calculated based on specific surface area and C content.

2.2.3 Varying the adsorbed water content of silica

Silica samples were exposed to a 100% relative humidity atmosphere for different time intervals. Aerosil R8200 silica samples have adsorbed water content in the range of 0.66–1.59 wt%. In our previous work, we found that the water absorption content of the fumed silica exhibited a significant role in the rate of structuring, which was detrimental to the material. In the present study, the fumed silica with different contents of adsorbed water was mixed with HPDMS to study its effect on the structuring phenomena.

2.2.4 Effect of storage temperature

Surprisingly, we found that the viscosity of the adhesive made by mixing the HPDMS and fumed silica increased slowly, particularly in the cold environment. Various quantities of silica were used to fill HPDMS, and the viscosity of the composition was continuously monitored. The temperature of the compositions was adjusted to 25°C before the viscosity measurement. Code AR30-R refers to the composition mixed by 100 parts by mass of HPDMS and 30 parts by mass of Aerosil R8200 fumed silica and stored at a temperature of 22–30°C. Code AR30-L refers to the same composition but stored at −2°C, whereas Code AR30-VL refers to the same composition but stored at −15°C.

2.2.5 Presence or absence of low molecular weight dimethicone

To study the influence of the presence of non-reactive DMS (DMS, trimethylsilyl-terminated polydimethylsiloxane), three samples of DMS with different viscosities were added into the mixture of silica and HPDMS.

2.3 Characterizations and measurements

The surface chemistry of silica was characterized by the Nicolet-6700 Fourier transform infrared (FT-IR) spectra (Thermo Electron Scientific Instruments Corporation, USA). The C content of the silica was measured by the Vario EL cube elemental analyzer (Elementar Analysen Systeme GmbH, Germany). The specific surface area of silica was measured using the ASAP 2020 M automatic specific surface area and porosity analyzer (Micromeritics Instruments Corporation, USA). The viscosity of all the mixtures and polydimethylsiloxane (PDMS) was measured by the NDJ-8S viscometer (Shanghai Lichen Bangxi Instrument Technology Co., Ltd., China).

3 Results and discussion

3.1 Elemental analysis of hydrophobic silica

The results of the elemental analysis of hydrophobic silica samples are shown in Table 2. It was observed that the dose ratio of HMDS to fumed silica depended on the C content of the resulting silica.

Figure 3 shows the FT-IR spectra of Aerosil 200 and four kinds of HMDS-treated fumed silica samples. It can be seen that the infrared spectra of HMDS-treated fumed silicas were analogous to that of Aerosil 200. Only a few weak peaks were exclusive in the fumed silica after the hydrophobic treatment. Among all the curves, the broad absorption peak at 3,438 cm^{-1} was ascribed to the asymmetric stretching vibration of O–H in bridged Si–OH groups. The peak at 1,635 cm^{-1} corresponded to the bending vibration absorption of O–H in physically adsorbed water. The broad strong peak at 1,105 cm^{-1} corresponded to the asymmetric stretching vibration absorption of Si–O–Si. The peaks at 811 and 475 cm^{-1} were

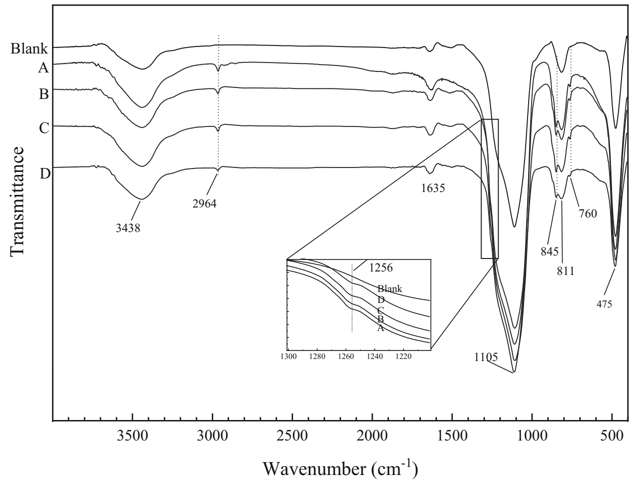

Figure 3: Fourier transform infrared spectra of Aerosil 200 and three kinds of treated fumed silica.

assigned to the symmetric stretching vibration absorption of Si–O. Compared with blank curve, few new exclusive absorption peaks were found on curves A, B, C, and D. The peak at 2,964 cm^{-1} was ascribed to the stretching vibration of C–H in Si–Me. The peaks at 1,256, 845, and 760 cm^{-1} corresponded to the characteristic peaks of the –OSiMe$_3$. As mentioned before, the C content of the treated silica was less than 3.5%. Therefore, the peaks about –Me were quite weak than those from SiO$_2$. The peak at 1,256 cm^{-1} was hardly observed because of the shielding effect of the strong Si–O–Si absorption peak. These characteristics indicated that the –OSiMe$_3$ groups replaced the –OH groups partly, and HMDS-treated hydrophobic-fumed silica was prepared successfully using the solvent-free method.

3.2 C content of treated hydrophobic silica

From Figure 4, it can be seen that the group Level-D (7.73) exhibited the lowest initial viscosity and the most stable viscosity during the storage. The initial viscosity of the group Level-A (2.80) was 4.5 times that of the group Level-D, and the viscosity was 2.2 times the initial viscosity after storing for 3 weeks. The group Level-B (3.87) showed a heavy thickening effect and a higher degree of structuring, but lower than that of the group Level-A. The initial viscosity of the group Level-C (5.48) was almost the same as that of Level-D, but the viscosity increased to 2.6 times the initial viscosity after 18 days of storage. As a control, eight parts of Aerosil 200 could make the RTV composition viscosity greater than 2,000 mPa s and was useless.

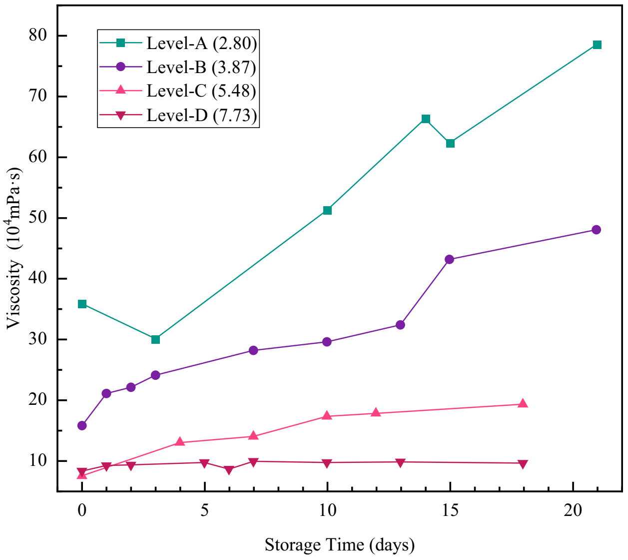

Figure 4: Viscosity change of RTV compositions prepared with different grades of hydrophobic silica samples.

The model proposed by Cochrane and Lin (7) showed a similar result. They suggested that a large number of trimethylsilyl groups on the surface of the fumed silica prevented the long PDMS molecular chains from adsorbing on its surface. The trimethylsilyl groups themselves repelled the PDMS molecular chain, whereas the steric hindrance effect of the trimethylsilyl groups hindered the adsorption of the PDMS by the silanol groups close to the trimethylsilyl groups. In other words, the introduction of trimethylsilyl groups achieved the rejection of PDMS through the above two mechanisms. This indicates that after being fully hydrophobized, the thickening and structuring effect of fumed silica was greatly weakened.

3.3 Adsorbed water content

Figure 5 shows the RTV compositions prepared using the four types of Aerosil R8200 silica, viz. Dry-0, Dry-1, Dry-2, and Dry-3 that contained 1.86%, 1.59%, 0.93%, and ~0% adsorbed water content, respectively. The compositions were prepared by mixing 100 parts by mass of HPDMS and 30 parts Aerosil R8200 silica. The significant influence of the silica adsorbed water content on the thickening effect was significantly indicated by comparing the initial viscosity of the compositions. The initial viscosities of compositions in descending order of the water content were found to be 91, 94, 81, and 53 Pa s, respectively. The initial viscosity of Dry-3 was almost half of that of Dry-0. With an increase in the water adsorbed by the silica, there

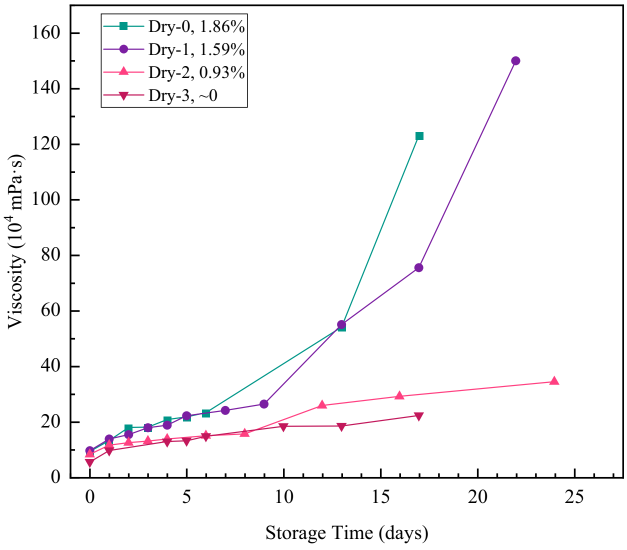

Figure 5: Effect of storage on the viscosity of HPDMS-fumed silica compositions with Aerosil R8200 silica containing different physically adsorbed water content.

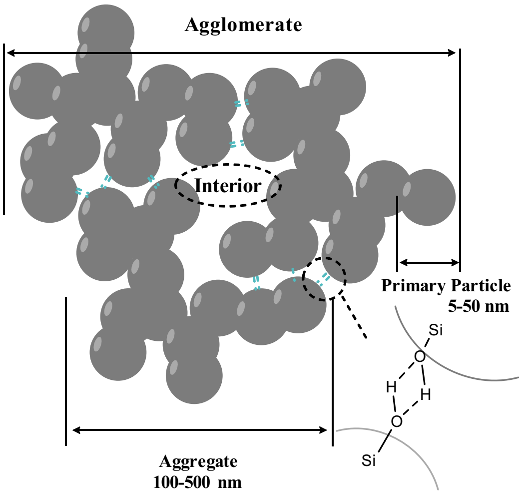

Figure 6: Fumed silica in a static solid state.

was a corresponding increase in the thickening of the silica – HPDMS mixture.

The structuring behavior of the RTV composition was a time-dependent process and was found to be more affected by the physically adsorbed water content than the thickening effect. After storage for 7 days, their viscosities were 271, 239, 151, and 155 Pa s in descending order of the water content of the fumed silica. At this time, the viscosity of Dry-0 was 1.7 times that of Dry-3. After 17 days of storage, their viscosities were 1230, 754, 297, and 221 Pa s, respectively. At this time, the viscosity of Dry-0 was 5.6 times that of Dry-3. In most cases, the RTV compositions with a viscosity greater than 1,000 Pa s were regarded worthless. The results indicated that it was necessary to properly remove physically adsorbed water by drying it at 110°C before the fumed silica was used to formulate the RTV compositions, which effectively extended the shelf life of the composition.

To ascertain the mechanism of this effect, it is important to understand the difference in the structure and surface chemistry between the fumed silica alone and in the fumed silica-polysiloxane composition. As shown in Figure 6, the fumed silica exists in a static solid state before use in the form of a large number of isolated primary particles but exists in the form of aggregates and agglomerates in the case of hydrogen bonds or van der Waals bonds. The aggregates are formed by the sintered primary particles and do not disintegrate in the physical process. In case of the fumed silica used in RTV compositions, in the beginning, a large amount of silica surface does not get exposed to the PDMS pool and forms a vacuum interior because of the large number of physical bonds that combine the aggregates into weakly bound agglomerates (see Figure 7). Consequently, the hydroxyl groups on this part of the silica surface cannot adsorb the PDMS molecules and cannot increase the viscosity. Because of the existence of free water and the freedom of silica endowed by the liquid, the hydrogen bonds that play a leading role in the combination of aggregates into agglomerates get "dissolved" in the water and the agglomerates get separated into aggregates, with an increase in the storage time. Subsequently, the vacuum

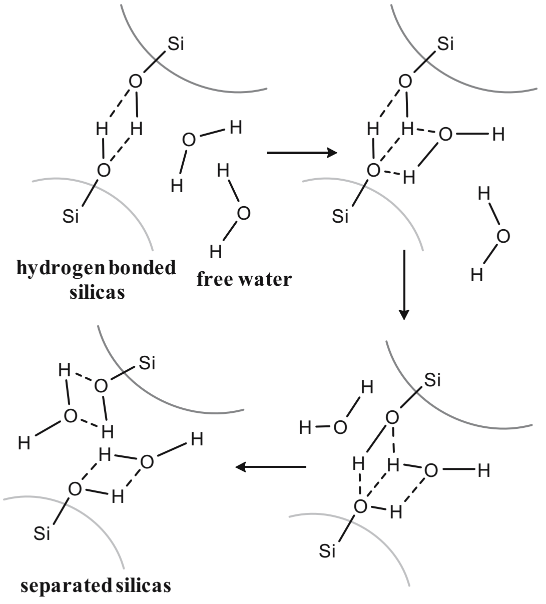

Figure 7: "Dissolution" of aggregates by free water after mixing with PDMS.

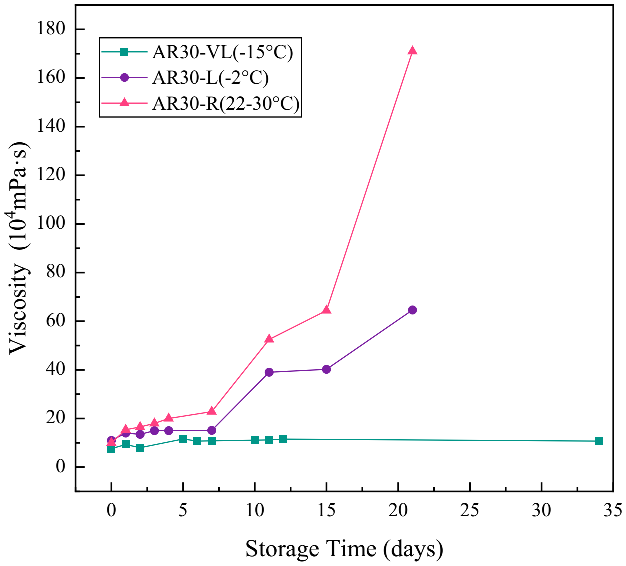

Figure 8: Effect of storage temperature on the viscosity of the RTV and fumed silica mixture.

interior of agglomerates ceases to exist. As a result, more fresh silica surface is exposed to PDMS and adsorbs the PDMS molecules, and the viscosity of the RTV composition increases accordingly. The "dissolution" process occurs after adding the curing agent (or exposure to moisture, when the composition is a one-component RTV). Because of the existence of too much of adsorbed water, the "dissolution" process progresses in the storage period.

3.4 Storage temperature

As shown in Figure 8, it can be observed that the storage temperature undoubtedly influenced the changes in the viscosity. When the RTV composition mixed with 30 parts by mass of hydrophobic-fumed silica was stored at a room temperature (22–30°C), the viscosity doubled from the initial 100 to 200 Pa s within 4 days and reached to 1,710 Pa s on the 21st day. When it was stored in an environment of −2°C, the period for the viscosity to double the initial viscosity was about 8 days, and the viscosity was 650 Pa s on the 21st day of storage. When stored at −15°C, the viscosity of the RTV composition did not change significantly and was found to be 110 Pa s on the 34th day of storage. This shows that a reasonably low storage temperature can significantly increase the shelf life of the RTV composition.

The Si–O–Si chain in the PDMS has an excellent flexibility, which makes the silicone rubber crystallize at about −60°C. If the side groups are not introduced with phenyl groups, the silicone rubber crystallizes at much lower than other organic rubbers at about −90°C (15). PDMS has a very low glass-transition temperature of about −120°C (15), and it is a non-entangled polymer. Naturally rendered silicone rubber exists in a liquid state at room temperature. The siloxane segment undergoes a thermal movement relatively freely in the polymer-silica particle pool, until this segment is captured by the hydroxyl group on the silica surface by forming a hydrogen bond, thereby losing the freedom of thermal movement and entering a stable form with lower energy. In this theoretical model, the higher the temperature, the shorter is the polysiloxane segment, the greater is the freedom of movement, and the more opportunities exist for siloxane and terminal hydroxyl groups to be captured by the silanol on the surface of the silica. This explains the temperature-dependent structuring of the silicone rubber, especially of the RTV compositions.

When stored at −15°C, the temperature is closer to the softening point of PDMS. As a result, the PDMS chain is rigid and less active than that stored at room temperature. Therefore, the oxygen in the Si–O–Si and in the Si–OH at the end of the HPDMS chain has a restricted movement, and it is difficult to form physical and chemical bonds that lead to structuring. In contrast, when stored at room temperature or higher, the polysiloxane moves relatively freely, the interactions mentioned above occur more frequently, the structuring is rapid, and the viscosity of the RTV composition increases quickly. When stored at −2°C, the rate of structuring is regularly between the room temperature and −15°C. So far, we can conclude that a reasonably low storage temperature is very effective in extending the shelf life of the RTV composition.

3.5 Effects of non-reactive dimethicone

Table 3 shows the compositions using the different base polymer formation to find out the effects of dimethicone

Table 3: RTV compositions using different base polymer formation

Groups	HPDMS (10 Pa s)	Dimethicone (10 Pa s)	HPDMS (5 Pa s)	Aerosil R8200
a	90 + 10	—	—	30
b	90	—	10	30
c	90	10	—	30
d	—	100	—	30

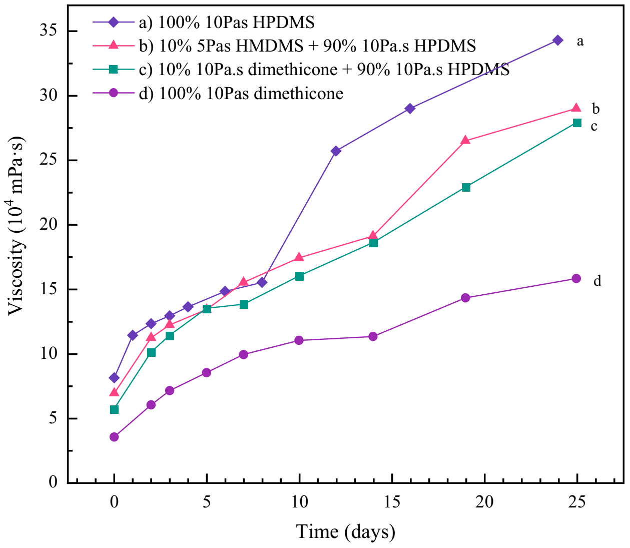

Figure 9: Changes in viscosity during the storage of RTVs using different polymer formation.

on RTV and to understand the influence of silanol groups in HPDMS on the structuring. The obtained viscosity data are shown in Figure 9.

On comparing group a with group b, it was observed that after the replacement of 10 wt% of the base polymer HPDMS with a lower viscosity HPDMS, the viscosity of the RTV composition lowered. However, there was no observable decrease in the speed of its structuring. Comparing group a with group c, we found that a replacement of 10 wt% of the base polymer HPDMS with dimethicone with the same viscosity, but without hydroxyl end groups, slightly reduced the viscosity and slightly slowed down the structuring process of the RTV composition. Comparing group a with group d, it can be seen that although the viscosity of the base polymer was the same, the thickening effect and the structuring that occurred with the addition of 30 parts of fumed silica were quite different. The initial viscosity of group a was 81 Pa s and group d was 35 Pa s. After storage for 24 days, the viscosity of group a was 343 Pa s and group d was 158 Pa s. By calculation, after changing the terminal trimethylsilyl group of dimethicone to Si–OH, the initial viscosity was 131% higher, and the viscosity after storage of 24 days was 117% higher. This shows that the terminal silanol groups of HPDMS have a greater contribution to the thickening and structuring effects of the HPDMS-fumed silica system.

We propose an effective explanation for this result. On one hand, the silanol groups at the end of the HPDMS chain have a strong polarity, and it is much easier to form hydrogen bonds with the silanol groups on the surface of the fumed silica, as compared to the Si–O–Si on the main chain. On the other hand, a silanol group at the end of the HPDMS chain can form two hydrogen bonds with a silanol on the silica surface, whereas a Si–O–Si in the HPDMS chain can only form one hydrogen bond and is hindered by steric hindrance.

4 Conclusion

The present study was undertaken to investigate the effect of varying conditions like silica hydrophobicity level, adsorbed water content of silica, storage temperature, and polymer matrix constitution of RTV on the thickening and structuring phenomena. Following conclusions were drawn out from the present study:

(1) The use of hydrophilic-fumed silica significantly thickened the RTV composition. Hydrophobic treatment of the fumed silica with HMDS solved this problem to some extent.
(2) The viscosity of the RTV composition prepared using dried silica was 5.6 times lower than the wet one after storing for 17 days. Adequately dry fumed silica at 110°C can be very helpful for the structuring process.
(3) Storage at −15°C prevented the structuring of the RTV composition. When 30 parts of hydrophobic-fumed silica by mass were mixed with HPDMS and stored at −15°C, no significant change in the viscosity was observed after 34 days.
(4) In case of the HPDMS-fumed silica compositions, the thickening and the structuring effect were contributed by the hydroxyl groups from the hydroxyl-terminated polysiloxane.

Furthermore, a “dissolution” model of the silica-silica hydrogen bonds in water was developed to explain the effect of the water adsorbed by silica on the structuring process. It was found that the adsorbed water by the silica was converted to water in its free form after mixing. Subsequently, the water in its free form dissolved the hydrogen bonds between the silica agglomerates and released a renewed silica surface, thereby increasing the viscosity of the HPDMS-fumed silica composition.

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Conflict of interest: The authors state no conflict of interest.

Data availability statement: The data used to support the findings of this study are available from the first author upon request.

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