

Effects of Polymeric Curing Agent Modified with Silazanes on the Mechanical Properties of Silicone Rubber

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ABSTRACT: Polymeric curing agent modified with hexamethyldisilazane (PCA-D), or with hexamethylcyclotrisilazane (PCA-T), was used to improve the mechanical properties of hydroxyl-terminated polydimethylsiloxane (PDMS) rubber. The structure and the gel time of PCA were characterized by ²⁹Si NMR and shear viscosity measurement, respectively. The PCA modified with silazanes was more stable in storage than that without treatment (PCA-0). Chemical bonds were formed during the reaction of silazanes and PCA according to ²⁹Si NMR results. The crosslink density (γ_c) and the mechanical properties of

PCA/PDMS rubber were determined by swelling equilibrium and stress-strain tests. It was found that PCA treated with both silazanes could better enhance the mechanical properties of PCA/PDMS rubber compared with PCA-0. PCA-T/PDMS rubber, with additional crosslinks, was the best among the three types of PCA/PDMS rubber on the mechanical properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1057–1062, 2009

Key words: mechanical properties; rubber; fillers; silazane; swelling

INTRODUCTION

Silicone rubber, with many excellent properties such as good resistance against heat and cold, outstanding hydrophobicity, and excellent electroinsulating properties, has been widely used in many devices to withstand very crucial conditions or environment.^{1,2} The mechanical properties of rubber have been commonly enhanced by silica as a filler to improve its mechanical properties to fulfill the practical needs.^{3,4} Fumed silica used in most cases would generate crepe hardening and make up high-viscosity system, which means poor processing property. The viscosity of rubber mixes could be reduced if blended silica is surface-modified,⁴ but a relatively much lower viscosity is preferable.

Silica generated *in situ* is an alternative to reduce the viscosity of rubber mixes.^{5,6} Mark et al.^{7,8} has presented a method to use excess tetraethylorthosilicate (TEOS) to permit the simultaneous curing and filling of the elastomer *in situ*. This approach could increase the mechanical properties of silicone rubber and avoid the high viscosity of silica/PDMS compound. But excess TEOS would cause large volume shrinkage and cracking of the vulcanizates because

of the release of excess ethanol. The problem of volume shrinkage must be solved before this technique can be used industrially.

A new kind of polymeric curing agent (PCA) was developed in our lab.⁹ It was prepared by cohydrolysis condensation of dimethyldiethoxysilane (DDS) and polyethoxysiloxane (partial hydrolyzate of TEOS). This PCA was used to cure hydroxyl-terminated PDMS, and function as filler *in situ*. The PCA, with its residual hydroxyl groups, was not very stable in storage and tended to condense to form a gel.^{10,11} Silazanes were well known for their ability to react with hydroxyl groups and give rise to Si—O—Si linkage,^{12–14} thus in this previous work, PCA was treated with hexamethylcyclotrisilazane (HMCTS) to prolong its storage stability. It was found that silazane-modified PCA differed from the untreated PCA sharply on the gel time and the mechanical properties of the corresponding vulcanizates, therefore it was our concern to further investigate the modification of PCA with silazanes. In this article, two kinds of silazanes: hexamethyldisilazane (HMDS) and HMCTS were used as modification agents. The type of silazanes and their content used in the PCA might strongly affect the storage stability of PCA. Moreover, the mechanical properties of the corresponding vulcanizates depended on the structure of the PCA. Chemical bonds formed during the reaction of silazanes and

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PCA were determined by ^{29}Si NMR measurements. The gel time of PCA, the mechanical properties and the crosslink density of the corresponding PDMS rubber were studied systematically.

EXPERIMENTAL

Materials

Polyethoxysiloxane (E-40, partial hydrolyzate of tetraethoxysilane, containing 40% SiO_2) was obtained from Tiangang Chemical, China and used without purification. DDS, chemical pure (CP), HMCTS, analytical reagent (AR), dibutyltin dilaurate (AR), and toluene (AR) were supplied by Beijing Chemical Reagent Company, China. DDS was purified by distilling, and the distillate at 113–114°C was collected. HMDS was provided by Bluestar New Chemical Material, Jiangxi Xinghuo Organicsilicone Plant. HMDS (bp 125°C) was fractional distilled at ambient pressure, and the distillate around 124–126°C was collected. The α,ω -dihydroxypolydimethylsiloxane (PDMS) ($\bar{M}_n = 7.4 \times 10^4$ g/mol, $\bar{M}_w = 1.0 \times 10^5$ g/mol, polydispersity = 1.35) was obtained from Beijing Second Chemical Factory, China.

Synthesis and treatment of polymeric curing agent

PCA was synthesized according to our previous article.⁹ An example was given as follows. In a 1000 mL three neck flask, 74.0 g DDS, 124.0 g E-40 and 13.6 g deionized water were mixed in 600 g toluene. The mixture was stirred magnetically at 60°C until a clear homogeneous liquid was obtained. Ethanol formed in the reaction was instantly removed by distillation through a packed column. Then solvent was removed under vacuum, and PCA-0 was obtained. In the case of PCA modified with HMDS (PCA-D), HMDS was added to the crude product of PCA-0 before solvent was removed, and the mixture was refluxed at 100–110°C for 4 h. At last, the solvent and excess HMDS were extracted under vacuum (20 Pa, 100°C, 2 h). PCA modified with HMCTS (PCA-T) was synthesized in similar ways. The final products were stored in a sealed plastic bottle at room temperature.

Manufacture of PCA/PDMS rubber

The hydroxyl-terminated PDMS was mixed with various contents of PCA-0, PCA-D, or PCA-T, then 0.35–0.5 phr dibutyltin dilaurate catalyst was added and the mixture was stirred for 5 min at ambient conditions. The mixtures were poured into 2-mm thick molds. After removing air bubbles under vacuum the compounds were vulcanized at room tem-

perature for 24 h, and then postcured at 60°C for 2 weeks in an air oven.

Measurements

During intervals of 180 days, the shear viscosities of PCA were determined with a Wells-Brookfield cone and plate micro viscometer (programmable DV-II + viscometer, Brookfield Engineering Laboratories, Stoughton, MA) till gel formed at 25.0°C \pm 0.1°C. The tests were taken every 12 h during the first several days until the increase of viscosities slowed to a certain level, after then the viscosities was measured every 5 days.

^{29}Si NMR spectra were acquired on a Bruker DMX 300 spectrometer (Bruker instruments, Switzerland) with a 5 mm broad-band $^1\text{H}/\text{X}$ double resonance liquid-state probe. Chloroform (CDCl_3) was the solvent. Tetramethylsilane was used an external standard and chromium acetylacetonate ($\text{Cr}(\text{acac})_3$) was the nonpolar paramagnetic relaxation agent.

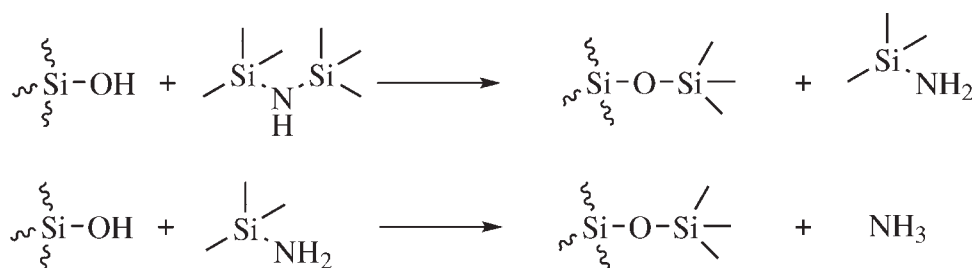
Dumbbell-shaped specimens for mechanical tests were prepared in accordance with ASTM D 412-98a specification. Stress-strain behavior of the cured samples was determined with a universal test machine (Instron 5565, Instron, Canton, MA) at room temperature. The initial length of the sample trips between the two clamps was 10 mm and the crosshead speed was 200 mm/min.

Crosslink density was determined by swelling measurement. PCA/PDMS rubber films (about 0.2 g) were weighed and put into excess anhydrous toluene at 25.0°C \pm 0.1°C.¹⁵ At intervals of 12 h, samples were taken out of toluene and weighed, then immersed into fresh toluene again. Swelling equilibrium was achieved when the swollen samples reached a constant weight. Then samples were

TABLE I
Gel Time of PCA Modified with Various Contents of Silazanes

Sample ^a	R (%)	Gel time(days)
PCA-0	0	6
D1	2.5	90
D2	5	>180
D3	10	>180
D4	15	>180
D5	20	>180
D6	25	>180
T1	2.5	30
T2	5	90
T3	10	>180
T4	15	>180
T5	20	>180
T6	25	>180

^a D indicates HMDS-modified PCA; T represents HMCTS-modified PCA.



Scheme 1 Reaction of PCA with HMDS.

placed in vacuum desiccators and dried until they reached constant weight. According to Flory's equation,^{16,17} the crosslink density (γ_e) of the rubber samples could be calculated by the following equation,

$$\gamma_e = \frac{\rho}{M_c} = -\frac{\ln(1 - v_2) + v_2 + \mu v_2^2}{V_1 \times (v_2^{1/3} \times v_0^{2/3} - v_2/2)} \quad (1)$$

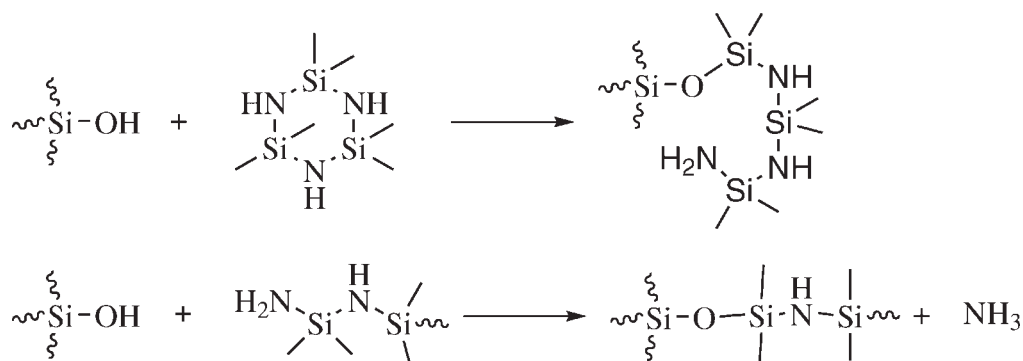
where M_c was the molecular weight between crosslinks; ρ was the density of the polymer (0.978 g/mol); V_1 was the molar volume of the solvent (106.27×10^{-3} L/mol, toluene); v_2 was the volume fraction of polymer in the swollen condensation-cured PDMS rubber and could be looked upon as the reciprocal of the equilibrium swelling volume; Dilution was taken into account to a volume fraction (v_0) of polymer at formation of PDMS rubber; μ was the polymer solvent interaction parameter.

RESULTS AND DISCUSSION

Gel time and characterization of PCA

The addition of silazanes has effectively eliminated the silanol groups in the original PCA. The gel time of different kinds of PCA was shown in Table I. For convenience, the ratio R was defined as follows,

$$R = \frac{[\text{NH}]}{[\text{Si}]} \times 100\% \quad (2)$$



Scheme 2 Reaction of PCA with HMCTS.

where $[\text{NH}]$ represented the number of Si-NH groups in silazane; $[\text{Si}]$ referred to the number of Si atoms in the untreated PCA.

As can be seen, the gel time of PCA-T or PCA-D was much longer than that of PCA-0. The content of silanol groups in PCA-T or PCA-D decreased as the content of silazanes increased. The gel time, strongly depending on the concentration of silanol groups, was prolonged as R increased. When R was more than 5%, the gel time of PCA-D was more than 180 days. Moreover, when R was more than 10%, the gel time of PCA-T was also more than 180 days. Silanol groups could react with silazanes, thus the silanol groups of PCA were blocked, which was shown in Schemes 1 and 2. It could be clearly seen in the ^{29}Si NMR graph (Figs. 1 and 2) as the content of HMDS addition increased, the signals of Si-OH and Si-OEt groups at -11.1 to -12.5 ppm decreased sharply, while the peaks of trimethylsiloxane groups around 11 – 12.8 ppm increased. Similar results can be found in the ^{29}Si NMR of HMCTS-modified PCA, while the signals were more complex. As can be seen in Figure 2, the signals around -2.9 ppm (O-Si-N), -6.3 to -6.5 ppm (O-Si-N, N-Si-N), -8.8 ppm (O-Si-O) suggested a mixture of six member cyclotrisilazadioxane or cyclotrisildiazoxane structure according to literature.^{18,19} It was well demonstrated in the literature that the addition of HMCTS might introduce an organic layer containing nitrogen to the silica surface,^{20,21} but the detailed formation process of hexa-cyclic structure was ambiguous.

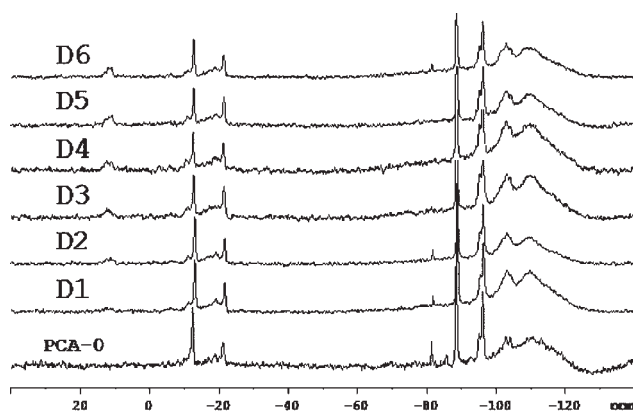


Figure 1 ^{29}Si NMR of PCA modified with different content of HMDS.

Additionally, when R was not more than 10%, the gel time of PCA-D was longer than PCA-T. This could be explained according to the structure of the silazanes. HMDS eliminated the silanol groups, whereas HMCTS acted as a bridging agent between two silanol groups. That was to say, when HMCTS reacted with one silanol group, it did not terminate the reaction site, but only reduced the risk of condensation between silanol groups. However, as the value of R increased, most of the silanol groups were blocked, and the gel time of the two kinds tended to be infinite.²²

Effect of silazane content on the mechanical properties of PCA/PDMS rubber

PCA modified with silazanes could not only increase storage stability, but also improve the mechanical properties of PCA/PDMS rubber. The mechanical properties of PCA/PDMS rubbers were shown in Table II. As can be seen, the tensile strength and elongation at break of the vulcanizates filled with PCA-D or PCA-T were better than that with PCA-0. The crosslink density of PCA-D/PDMS rubber was

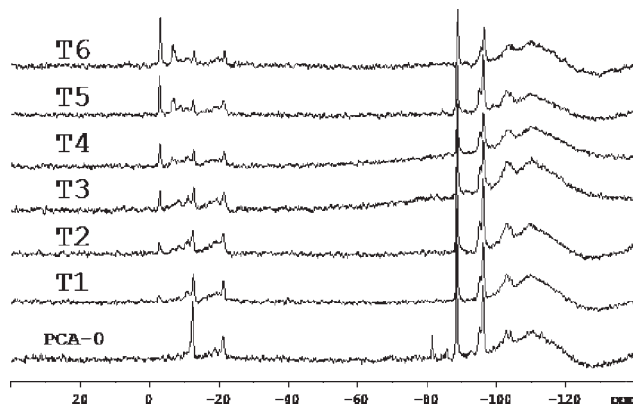


Figure 2 ^{29}Si NMR of PCA modified with different content of HMCTS.

TABLE II
The Characteristics of PCA /PDMS Rubber

Characteristics of the vulcanizates	PCA used in the PCA/PDMS rubber ^a												
	PCA-0	D1	D2	D3	D4	D5	D6	T1	T2	T3	T4	T5	T6
Tensile strength (MPa)	1.46 ± 0.14	1.81 ± 0.18	2.05 ± 0.11	2.24 ± 0.19	2.47 ± 0.06	2.37 ± 0.17	2.25 ± 0.13	1.62 ± 0.08	1.93 ± 0.26	3.03 ± 0.10	2.75 ± 0.28	2.43 ± 0.08	2.15 ± 0.09
Elongation at break (%)	184 ± 10	281 ± 26	296 ± 18	325 ± 30	304 ± 11	310 ± 25	320 ± 26	201 ± 9	238 ± 20	263 ± 10	297 ± 34	228 ± 9	222 ± 8
γ_c (10^{-4} g/cm ⁻³)	3.88 ± 0.13	3.71 ± 0.18	3.51 ± 0.14	3.37 ± 0.11	3.27 ± 0.16	3.12 ± 0.14	3.04 ± 0.15	4.00 ± 0.15	4.16 ± 0.12	4.53 ± 0.17	4.10 ± 0.13	3.95 ± 0.09	3.91 ± 0.12

^a PCA/PDMS (wt) = 60%.

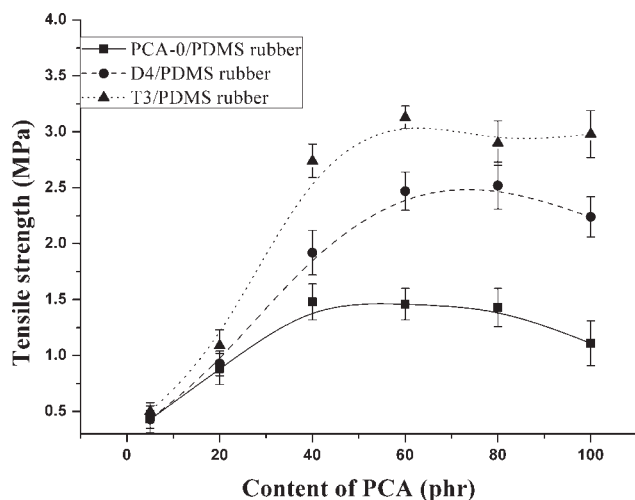


Figure 3 Effect of PCA content on the tensile strength of PCA/PDMS rubber.

lower than that of PCA-0/PDMS rubber, yet the mechanical properties of the former were better. This phenomenon was not surprising because the treatment of PCA by HMDS can reduce its silanol groups, and the degree of chain immobilization in PCA/PDMS rubber was mitigated.^{23,24} As the silazane treatment level increased, the mechanical properties of the PCA/PDMS rubber gave a similar maximum for both silazanes, which coincided with the literature²⁵ that dealt with the modification of traditional silica.

The crosslink density of PCA-T/PDMS rubber was relatively the largest among the three, this probably was because that HMCTS not only acted as a bridging agent, but also could form cyclic structures as mentioned above and provide additional crosslinks. The additional crosslinks in PCA-T/PDMS rubber were responsible for the rubber's relatively

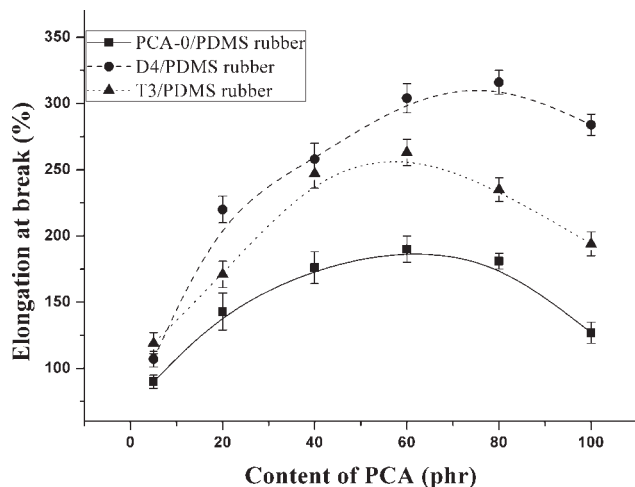


Figure 4 Effect of PCA content on the elongation at break of PCA/PDMS rubber.

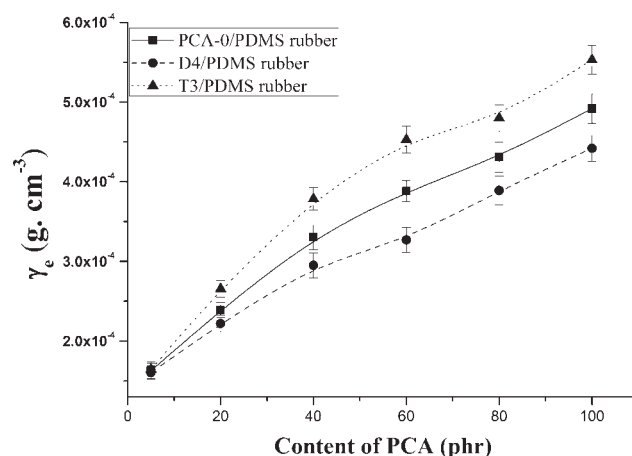


Figure 5 Effect of PCA content on the crosslink density (γ_c) of PCA/PDMS rubber.

less elongation at break and better tensile strength when compared with that of PCA-D/PDMS.

Effect of PCA content on the mechanical properties of PCA/PDMS rubber

The content of PCA used in the PCA/PDMS rubber strongly affected the mechanical properties of the vulcanizates. As shown in Figure 3, regardless of the types of PCA, the general tendency was similar: along with the increase of the PCA content, the tensile strength went up to a vertex, then slightly decreased. Similar rule could be found in the case of elongation break toward the content of PCA (Fig. 4). In both systems, 60 phr of PCA seemed to be the best content. However, the crosslink density would go straight upward with the increase of PCA (Fig. 5). These facts suggested the importance of proper ratio of curing agent in the practical process.²⁵ From Figures 3–5, we also concluded that, the vulcanizates cured with PCA-D or PCA-T behaved better in all of those mechanical properties mentioned above. Among the three types of PCA, PCA-T was the best one.

CONCLUSIONS

Polymeric curing agent (PCA) was modified with two types of silazanes: HMDS and HMCTS. Both silazanes could prolong the storage time of the PCA. And the modified PCA could endow the PCA/PDMS rubber with much better mechanical properties compared with PCA-0. PCA modified with HMCTS was the best on reinforcement of PDMS rubber, for it could not only reduce the reaction between silanol groups of particles, but also give rise to bridging between particles and PDMS molecules. The formation of cyclic structures in PCA-T might provide additional crosslinks as well, whereas

in PCA-D, HMDS functioned only as a silanol eliminator. As the content of PCA used increased, the mechanical properties of the rubber increased to a vertex, the best point of the PCA content was found to be 60 phr. In a word, the silazane treatment gave an effective way to improve the storage stability of PCA and the mechanical properties of silicone rubber.

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