

Polymeric Curing Agent Reinforced Silicone Rubber Composites with Low Viscosity and Low Volume Shrinkage

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ABSTRACT: A new type of polymeric curing agent (PCA) was synthesized to improve processing property, increase mechanical properties, and decrease volume shrinkage of silicone rubber. The PCA was prepared by co-hydrolysis condensation of dimethyldiethoxysilane (DDS) and polyethoxysiloxane, then modified by hexamethylcyclotrisilazane (D_3^N). Commercial silica and tetraethoxysilane (TEOS) were used as controls simultaneously. The properties of polydimethylsiloxane (PDMS) composites were characterized by shear viscosity measurements, room temperature mass loss, linear volume shrinkage, stress-strain tests, swelling behaviors and thermogravimetric analysis (TGA). PDMS compo-

sites using PCA show lower shear viscosity than those using commercial silica. Compared with the traditional PDMS/TEOS curing systems, PDMS/PCA curing systems behave relatively lower volume shrinkage, better reinforcement and thermal properties. In short, PCA acts as a good compromise in providing the best balance of processing property, volume shrinkage, mechanical properties and thermal stability in silicone rubber composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1624–1631, 2008

Key words: elastomers; polysiloxanes; reinforcement; swelling; thermal properties

INTRODUCTION

Elastomer of polydimethylsiloxane (PDMS) is one of the most widely explored silicone rubbers because of its extremely low glass transition temperature and high thermal stability over a wide range of temperature. However, because PDMS elastomers in unfilled state cannot form strain-induced crystallization, their mechanical properties are extremely poor. To avoid this disadvantage, reinforcing fillers are required in most applications. Great enhancement of mechanical properties could be achieved by blending filler particles, especially highly structured silica, into the polymers before vulcanization.^{1–3} However, to control the degree of particle dispersion is difficult due to silica particles tendency to agglomerate. The utilization of highly structured silica in elastomers would generate crepe hardening and make up high-viscosity system, which means poor processing property.⁴ It is necessary to increase mechanical properties and improve processing property of silicone rubber by developing new fillers.

Sol-gel techniques, which facilitate the precipitating of *in situ* reinforcing particles within polymer matrix, have been developed fast in the past several decades.^{5–10} The *in situ* technique for generating reinforcing silica filler, consists of hydrolyzation and condensation of an alkoxy silane such as tetraethoxysilane (TEOS). The technique of simultaneous curing and filling of an elastomer material is one of the most used methods.^{11–14} It takes place by blending enough TEOS to end-link hydroxyl-terminated PDMS chains and generate silica *in situ* during the vulcanization process. This method provides a useful approach to improve processing property, increase mechanical properties of silicone rubbers, while excess TEOS may cause large volume shrinkage and the cracking of the condensation-cured PDMS because of the release of excess ethanol. Silicone rubbers with good mechanical properties, low viscosity, and low volume shrinkage are intensively required to fulfill the applications in various areas. In the present article, new polymeric curing agent (PCA) was designed to solve the problem. PCA was prepared by cohydrolysis condensation of dimethyldiethoxysilane (DDS) and polyethoxysiloxane, then modified by hexamethylcyclotrisilazane (D_3^N). The PCA was used to crosslink hydroxyl-terminated PDMS chains and reinforce the elastomer *in situ*.

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Commercial silica and TEOS were used as controls simultaneously. Shear viscosity property, volume shrinkage property, stress-strain behavior, swelling, and thermal properties of PDMS composites were studied.

EXPERIMENTAL

Materials

Polyethoxysiloxane (E-40, partial hydrolyzate of TEOS, containing 40% SiO₂) was obtained from Tiangang Chemical, China and used without further purification. Dimethyldiethoxysilane (DDS, CP), hexamethylcyclotrisilazane (D₃^N, AR), and dibutyltin dilaurate (AR), toluene (AR) were supplied by Beijing Chemical Reagent Company, China. DDS was purified by distilling at 114°C. Commercial precipitated silica (hexamethyldisilazane-treated, specific surface area, ~ 200 m²/g) was purchased from Nanchang Kehong Chemical, China. The α,ω -dihydroxyl (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 characterization of PCA

The PCA was synthesized by cohydrolysis condensation of DDS and E-40, then modified with D₃^N. In a 1000-mL-three-neck flask, 74.0 g DDS, 124.0 g E-40 and 13.6 g deionized water were dissolved in 600 g toluene. The mixture was continuously stirred magnetically at 60°C until a clear homogeneous liquid was obtained. Ethanol formed in the reaction was simultaneously removed by distillation through a packed column. Then 23.0 g D₃^N was added and the system was maintained refluxing for 4 h. Finally, PCA was obtained by removing the solvent under reduced pressure.

Condensation-curing of PDMS/PCA and PDMS/TEOS compounds

The hydroxyl-terminated PDMS was mixed with different content of PCA or TEOS, then 3.5 ~ 5 wt % dibutyltin dilaurate catalyst was added and the solution 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 temperature for 24 h and then were postcured at 60°C for a week in an air oven. The composition of silicone rubber compounds was summarized in Table I.

Preparation of PDMS/silica compounds

The hydroxyl-terminated PDMS was mixed with different contents of commercial silica. These com-

TABLE I
Information of PDMS/PCA and PDMS/TEOS
Compounds

Sample designation	Type of curing agent	Content of curing agent (phr)	Content of dibutyltin dilaurate (phr)
PCA-5	PCA	5	0.35
PCA-20	PCA	20	0.35
PCA-40	PCA	40	0.37
PCA-60	PCA	60	0.38
PCA-80	PCA	80	0.37
PCA-100	PCA	100	0.37
T-5	TEOS	5	0.5
T-20	TEOS	20	0.47
T-40	TEOS	40	0.45
T-60	TEOS	60	0.43
T-80	TEOS	80	0.43
T-100	TEOS	100	0.4

pounds were mixed in a three-roll mill twice at 25°C. The viscosities of the compounds were determined for comparison.

Measurements

Gel permeation chromatograph tests

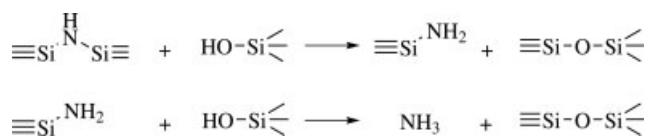
The molecular weight and distribution of the PCA was measured by Gel permeation chromatograph (GPC) [Waters 2410, RI detector (Waters instruments, Rochester, MN), toluene eluent, 1.0 mL/min, column (porosity: 10 μ m, Waters Strage HT 4)] at room temperature. Narrow molar mass polystyrene standards (Waters associate) were used for the universal calibration.

NMR spectra measurements

¹H-NMR and ²⁹Si-NMR spectra were acquired on a Bruker DMX 300 spectrometer (Bruker instruments, Switzerland) with a 5-mm broad-band ¹H/X double resonance liquid-state probe. Chloroform (CDCl₃) was the solvent. Tetramethylsilane (Beijing chemical reagent company) was used an internal standard in ¹H-NMR test. In ²⁹Si-NMR measurement, tetramethylsilane was used an external standard and chromium acetylacetonate (Cr(acac)₃) was the nonpolar paramagnetic relaxation agent.

Shear viscosities measurements

The shear viscosities were recorded at 20–80°C with a Wells-Brookfields cone and plate micro viscometer (programmable DV-II+ viscometer, Brookfield Engineering Laboratories, Stoughton, MA). Shear rate was adjusted by utilizing the spindle (CPE-51 : 1-768 s1) in the viscometer depending on the required torque.



Scheme 1 The reaction of Si-NH groups with Si-OH groups.

Stress-strain measurements

Dumbbell-shaped specimens for mechanical tests were prepared in accordance with ASTM D 412-98a specification. Tensile properties of the samples were determined with a universal test machine (Instron 5565, Instron Corp, 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.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of condensation-cured PDMS rubbers were carried out on a thermogravimetric analyser (TGA, Perkin-Elmer, Pyris 1 TGA, Boston, MA) at a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 40 mL/min. The weight of each sample was 3–5 mg, and the sample was heated from 30 to 800°C.

Room temperature mass loss measurements

The room temperature mass loss was recorded at room temperature to observe the volume shrinkage and the long-term stability. The condensation-cured PDMS composites were placed in the air at room temperature until no significant weight change. The room temperature mass loss was determined by the equation below,

$$m = (M_0 - M_1)/M_0 \times 100\% \quad (1)$$

where, M_0 was the mass of the composites before vulcanization and M_1 was the mass of cured films posted in the air at room temperature.

Linear volume shrinkage tests

The linear volume shrinkage (S) was calculated by the length changes of condensation-cured PDMS films according to the equation,

$$S = (l_0 - l)/l_0 \times 100\% \quad (2)$$

where, l_0 was the length of the mold used in preparation of condensation-cured PDMS films, and l was the length of the cured sample.

Swelling measurements

Polymer-filler interaction was determined by swelling measurement. Condensation-cured PDMS films (about 0.2 g) were weighed and put into excess anhydrous toluene at $25 \pm 0.1^\circ\text{C}$.¹⁵ At intervals of 12 h, each was removed and weighted. Swelling equilibrium was achieved when the swollen samples reached a constant weight. It took about 72 h. After that samples were placed in vacuum desiccators and dried until they reached constant weight.

RESULTS AND DISCUSSION

Analysis of the role of hexamethylcyclotrisilazane in synthesis of PCA

The storage stability of the PCA strongly depends on the content of the terminal-hydroxyl groups. As Xie et al.^{16–18} have illustrated, Si-NH groups can effectively eliminate the Si-OH groups (Scheme 1). Hexamethylcyclotrisilazane was used in the system to eliminate the silanol groups and link the siloxane chains. Due to the elimination of excess Si-OH groups, PCA can be stored in a stable liquid state for months.

Analysis of the structure of PCA

PCA contained D^n $[(\text{CH}_3)_2\text{Si}(\text{OEt})_{2-n}(\text{O}_{0.5})_n]$ and Q^m $[\text{Si}(\text{OEt})_{4-m}(\text{O}_{0.5})_m]$ structures named linear and net-like siloxanes, respectively. D^n was generated from DDS and D_3^N , while Q^m was generated from E-40. PCA was characterized by GPC, $^1\text{H-NMR}$ and $^{29}\text{Si-NMR}$ (Fig. 1–Fig. 3). GPC: \bar{M}_n , 1555 g/mol; PDI, 4.20. $^1\text{H-NMR}$ (CDCl_3), δ (ppm): 3.87 (m, $-\text{Si}-\text{OCH}_2\text{CH}_3$), 1.23 (t, $-\text{Si}-\text{OCH}_2\text{CH}_3$), 0.12–0.17 (s, $-\text{SiCH}_3$). $^{29}\text{Si-NMR}$, δ (ppm): -11.5 to 13 ppm (D^1), -17 ppm (D^2 -Q), -19 ppm (D_C^2 -D) to -22 ppm (D^2 -D), -89 ppm (Q^1), -95 and -96 ppm (Q^2),

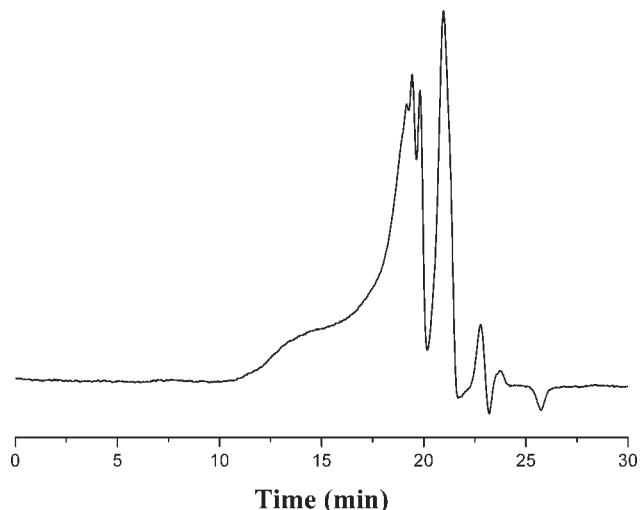


Figure 1 GPC curve for PCA.

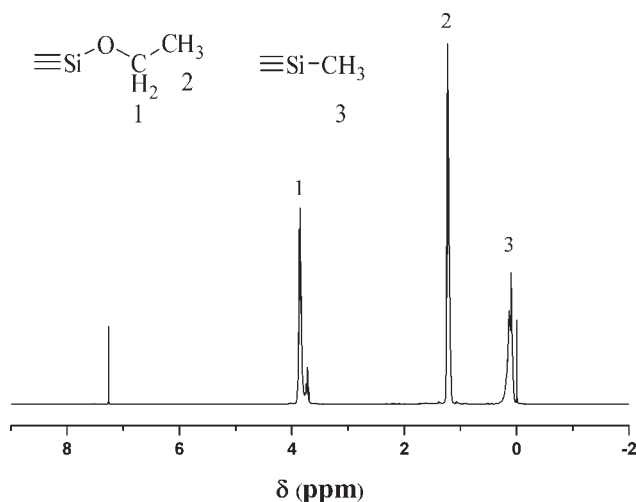


Figure 2 $^1\text{H-NMR}$ spectrum for PCA.

-103 to -104 ppm (Q^3). These signals of D^n and Q^m in $^{29}\text{Si-NMR}$ were in accordance with the literature.^{19,20}

In most cases, it is convenient to determine the average number molecular weight of linear polymers on the basis of $^1\text{H-NMR}$ spectrum. \overline{M}_n can always be calculated according to the structural formula below. That is $[(\text{EtO})_3\text{SiO}]_3\text{SiOSi}(\text{OEt})_2\text{O}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_2\text{OEt}$, $[\text{OEt}]/[\text{CH}_3] = 12/2n$, where $[\text{OEt}]$ and $[\text{CH}_3]$ are the intensities of $\text{Si-CH}_2\text{-CH}_3$ and Si-CH_3 in $^1\text{H-NMR}$, respectively. Compared with that measured by GPC, the average number molecular weight value for PCA on the basis of $^1\text{H-NMR}$ spectrum was 1205 g/mol.

Shear viscosities of PDMS/silica and PDMS/PCA compounds

It was well documented that the viscosity of rubber mixes could be reduced if blended silica was sur-

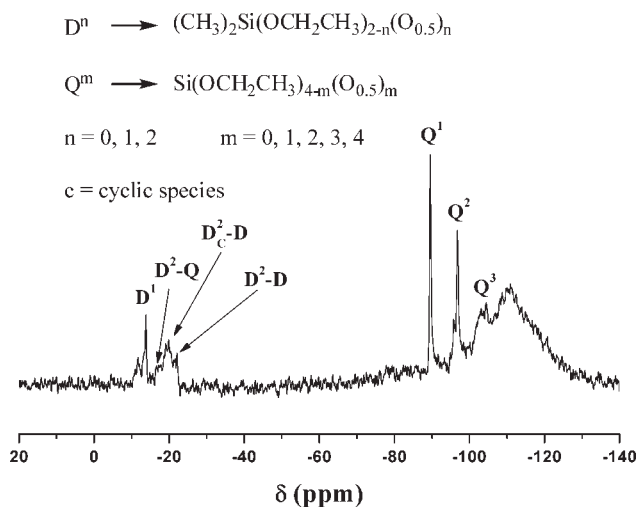


Figure 3 $^{29}\text{Si-NMR}$ spectrum for PCA.

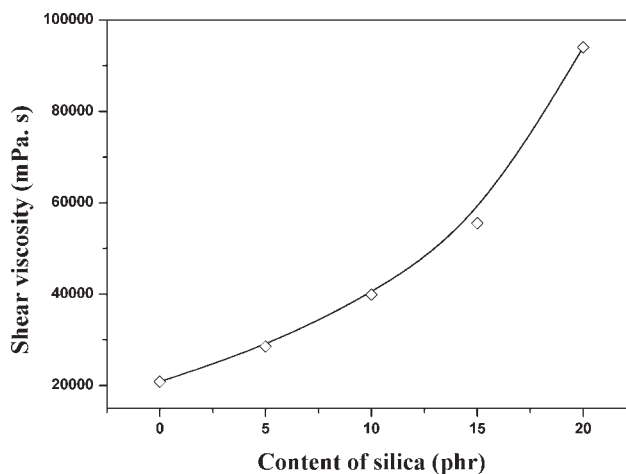


Figure 4 Effect of silica content on the shear viscosity of PDMS/silica compounds.

face-modified.³ But a relatively much lower viscosity was preferable for practical needs. Moreover, it was still difficult to control the dispersion of silica in PDMS matrix. As shown in Figure 4, the shear viscosity of PDMS composites filled with silica increased rapidly as the content of silica increased. However, the processing problem was indeed solved by using PCA. The shear viscosities of PDMS/PCA compounds were studied in a wide range of temperature (Fig. 5). Shear viscosity of PDMS/PCA compounds decreased as the content of PCA increased. For example, the shear viscosity of PDMS/PCA compounds with 80 phr PCA was merely 1/3 of that of PDMS matrix at 20°C, and correspondingly it was nearly 1/4 of that of PDMS matrix at 80°C. The curves also showed the effect of the content of PCA changed the shear viscosity more effectively at low temperature than high temperature. In addition, the temperature affected the shear viscosity more remarkably at low content of PCA than high content.

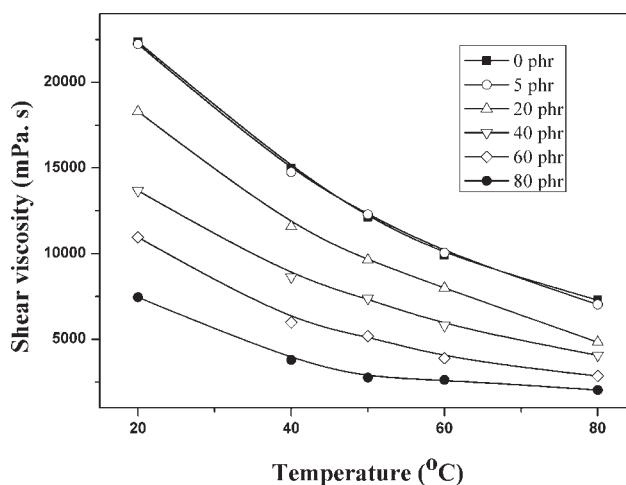


Figure 5 Shear viscosity-temperature behavior of PDMS/PCA compounds.

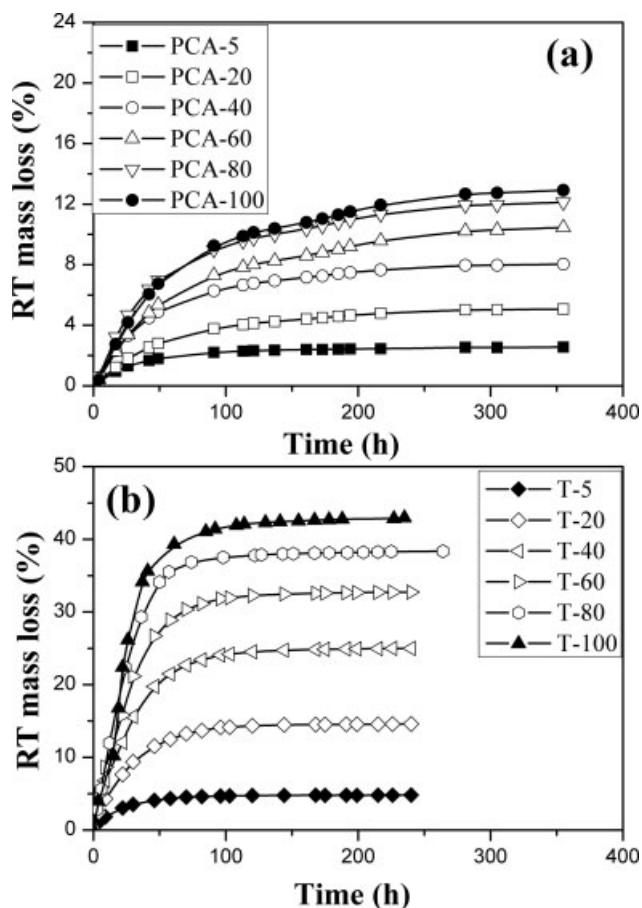


Figure 6 Effect of the curing agent contents on the room temperature mass loss of PDMS/PCA (a) and PDMS/TEOS (b) curing system.

The low viscosities of PDMS/PCA compounds could be attributed to the structure of PCA. Both PCA and PDMS had linear siloxane chains, thus the chains of PCA and PDMS were likely to move and be entangled. When PCA was blended with PDMS, a homogenous system could be obtained due to the good compatibility between PCA and PDMS. In addition, the volume fraction of PCA in the PDMS composites increased as the content of PCA increased. As a result, PDMS/PCA compounds behaved low shear viscosity. The remarkable decrease in shear viscosity had great benefit on the processing property.

Analysis of the volume shrinkage at room temperature

The volume shrinkage of condensation-cured PDMS was due to excess ethanol release. It could be investigated by room temperature mass loss and linear shrinkage tests. Figure 6 showed the room temperature mass loss of PDMS/PCA and PDMS/TEOS curing systems, respectively. PDMS/TEOS curing

system quickly reached constant weight in less than 150 h, while for the system cured with PCA, it was 350 h. The room temperature mass loss increased with the increase of the content of curing agents. PDMS/PCA and PDMS/TEOS curing systems show very different maximum room temperature mass loss values. The maximum room temperature mass loss of condensation-cured PDMS filled with 100 phr PCA was 12.9%, whereas it reached 43.0% when condensation-cured PDMS was filled with 100 phr TEOS. As shown in Figure 7, the linear shrinkage of PDMS/PCA rubber was almost a quarter of that of PDMS/TEOS rubber. For example, the linear volume shrinkage of condensation-cured PDMS filled with 100 phr PCA was nearly 4.7% and far lower than the 17.7% of the sample filled with 100 phr TEOS.

These differences could be attributed to the molecular differences and activity of curing agents. TEOS was a small-molecule compound, while PCA was a polymer with a complex structure. TEOS had a larger density of ethoxy groups than PCA. The hydroxyl groups which hydrolyzed from ethoxy groups of TEOS were more likely to contact and condense with each other in comparison with that in PCA. Ethanol was released more quickly in PDMS/TEOS curing system. Therefore, the crosslinking networks filled with TEOS dimensionally more quickly stabilized compared with PDMS/PCA curing system. The slower ethanol was released, the less defect of PDMS/PCA curing system may have, which would bring about better reinforcement. Moreover, the amount of ethanol from TEOS was more than that from PCA when the same amount of curing agents was used. Compared with PDMS/PCA rubber, PDMS/TEOS rubber showed larger maximum room temperature mass loss and linear shrinkage.

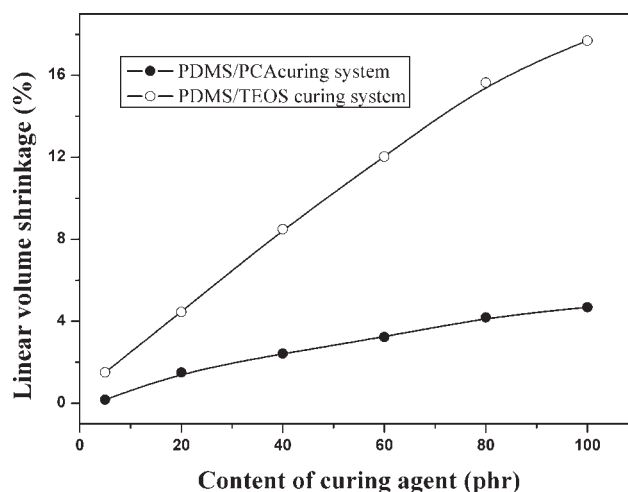


Figure 7 Effect of the curing agent contents on the linear volume shrinkage of PDMS/PCA and PDMS/TEOS curing system.

Therefore, when condensation-cured PDMS was filled with a large amount of TEOS, it shrank too seriously to utilize in industry. PCA had less detrimental effect on the volume shrinkage of condensation-cured PDMS compared with TEOS.

Stress-strain behaviors

The dynamic stress-strain curves for PDMS/PCA and PDMS/TEOS curing systems were shown in Figure 8. It was clearly seen that the nominal stress of the condensation-cured PDMS rubber increased as the content of PCA and TOES increased. Condensation-cured PDMS filled with less than 60 phr PCA had better mechanical properties than that filled with the same amount of TEOS [Fig. 8(b)]. For example, when the content of curing agents was 40 phr, the ultimate strength of PDMS/PCA rubber was 3.03 MPa, while the ultimate strength of condensation-cured PDMS with 40 phr TEOS was 1.39 MPa.

To our cognition, it may originate from that PCA that had stronger interaction with PDMS chains than TEOS. As shown in Figure 9, PDMS chains were crosslinked with PCA by condensation between end

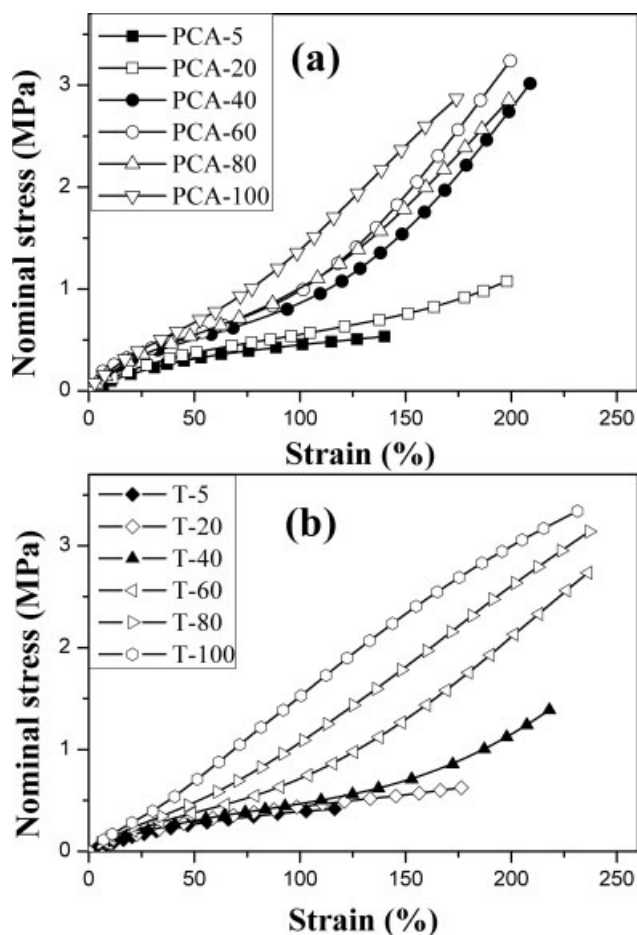


Figure 8 Stress-strain curves for condensation-cured PDMS using PCA (a) and TEOS (b).

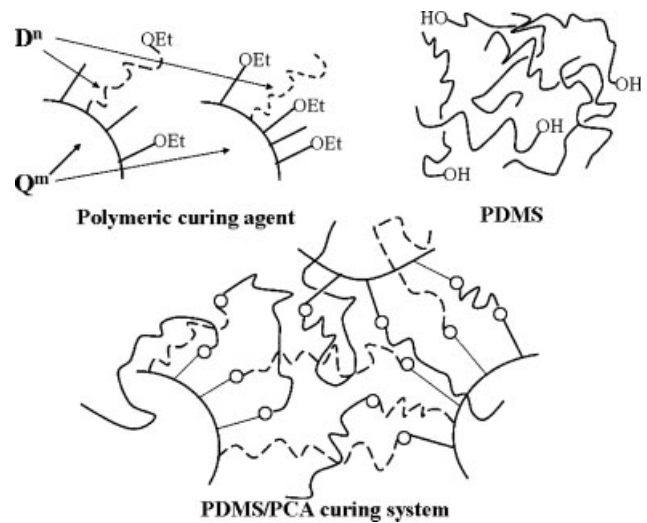


Figure 9 Schematic diagram of crosslinking network for PDMS/PCA curing system.

hydroxyl groups of PDMS chains and hydroxyl groups hydrolyzed from ethoxy groups in Dⁿ or Q^m structure. Meanwhile, the cohydrolysis condensation also resulted in the special particles which reinforced the condensation-cured PDMS. Stable netlike elastomers formed through the interpenetration and intertwist of PDMS chains with the Dⁿ and Q^m structure of PCA. However, such an interpenetration would not occur when filled with small molecule of TEOS. Therefore, PDMS/PCA rubber had more crosslinks than PDMS/TEOS rubber, which resulted in better reinforcement. But when the amount of PCA was higher than 60 phr, the ultimate mechanical properties decreased as phase separation occurred. Compared with TEOS, large amount of PCA may result in phase separation earlier.

The stress-strain behavior could also be represented by the plot of reduced stress ($[\sigma^*]$) against the reciprocal elongation according to the Mooney-Rivlin equation,

$$[\sigma^*] = \sigma / (\alpha - \alpha^{-2}) = 2C_1 + 2C_2\alpha^{-1} \quad (3)$$

where, σ was the nominal stress, $\alpha = L/L_0$ was the elongation of relative length of the sample, and $2C_1$ and $2C_2$ were constants independent of α .

Figure 10 showed the results of stress-strain test by dependence of reduced stress on reciprocal elongation. Both PDMS/PCA and PDMS/TEOS curing systems showed an initial drop in reduced stress followed by an upturn with the increase of elongation.^{11,12} In the case of large amount of curing agents, the upturns in reduced stress at high deformation were significant. Larger amount of curing agents gave bigger upturns. However, in the case of low amount of curing agents almost no upturn appeared. The upturns in reduced stress

demonstrated intensive interaction between particles and PDMS. It was a remarkable fact that the reduced stress of condensation-cured PDMS with less than 60 PCA phr was higher than that with the same amount of TEOS. It indicated that PCA brought about more intensive reinforcing effect in condensation-cured PDMS than TEOS.

Swelling behaviors

The interaction between polymer and filler was very critical for reinforcement of silicone rubber composites. Equilibrium swelling behavior of silicone rubber composites indicated polymer-filler interaction.^{21,22} According to Flory's equation,²³ crosslink density (γ_e) could be calculated by the following equation,

$$\gamma_e = \frac{\rho}{M_c} = \frac{\ln(1 - v_2) + v_2 + \mu v_2^2}{V_1 \times (v_2^{\frac{1}{3}} \times v_0^{\frac{2}{3}} - v_2/2)} \quad (4)$$

where, M_c was the molecular weight between crosslinks; ρ was the density of the polymer (0.978 g/

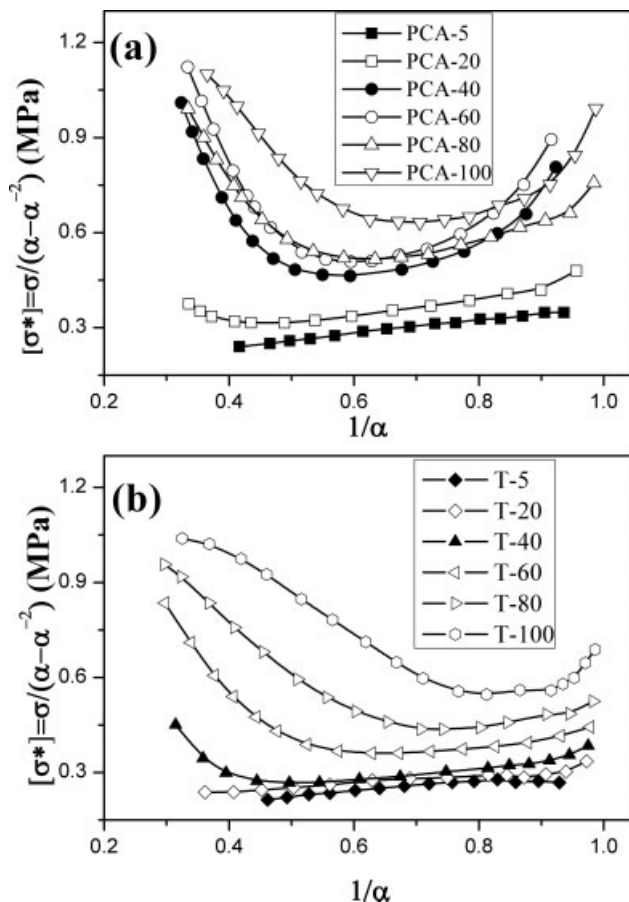


Figure 10 Reduced stress as a function of reciprocal elongation of condensation-cured PDMS using PCA (a) and TEOS (b).

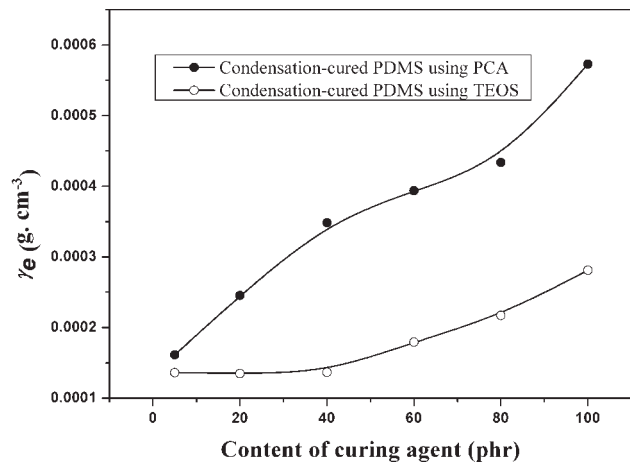


Figure 11 Effects of PCA and TEOS contents on the crosslinking density (γ_e) of condensation-cured PDMS.

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.

Some illustrative results calculated from the eq. (4) were shown in Figure 11. The crosslink density (γ_e) increased as the content of curing agents increased, which indicated good interaction between PDMS and particles generated from curing agents. The crosslink density justified chemical crosslinks between polymer and filler. Condensation-cured PDMS filled with less than 60 phr TEOS showed only a slight increase in γ_e as the content of TEOS increased, but γ_e of PDMS/PCA curing system increased more remarkably. It was supposed that the interpenetration and intertwist of PDMS/PCA curing system brought about more chemical crosslinks. Therefore, the interaction between PDMS and particles generated from PCA was better than that from TEOS. Better reinforcement was achieved when the content of curing agent was less than 60 phr. Too much PCA would bring about excess chemical crosslinks. When the content of curing agent was more than 60 phr, γ_e of PDMS/PCA rubber was so large that the mechanical properties of PDMS/PCA rubber decreased, while γ_e of PDMS/TEOS rubber was in a reasonable scope, thus the mechanical properties of PDMS/TEOS increased.

Thermogravimetric analysis

Curing agent played an important role in the thermal stability of silicone rubber.²⁴ It was intensively demanding to study the thermal stability of silicone rubber filled with PCA since PCA provided the best

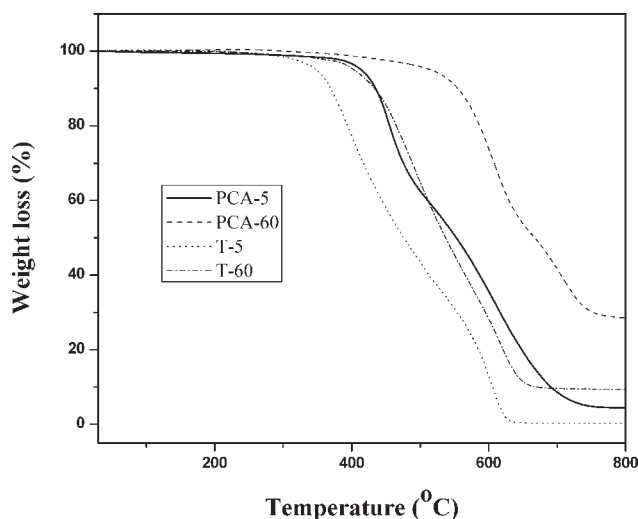


Figure 12 TGA curves of condensation-cured PDMS with PCA and TEOS.

balance in shear viscosity, volume shrinkage and mechanical properties among PCA, silica, and TEOS. Figure 12 showed some typical TG curves of PDMS/PCA and PDMS/TEOS curing systems. The thermal decomposition temperatures of condensation-cured PDMS filled with 60 phr curing agent were higher than those with 5 phr curing agent. The condensation-cured PDMS filled with PCA showed much higher thermal decomposition temperatures than that with the same amount of TEOS. Generally, the thermal stability of condensation-cured PDMS was improved as the content of curing agent increased because the terminal hydroxyl groups of polymer chains were deactivated.²⁵ In contrast with PDMS/TEOS system, PDMS/PCA rubber was more thermal stable because main-chain degradation of PDMS was inhibited through the interpenetration and intertwist of PDMS chains with PCA.

CONCLUSIONS

In summary, a new type of polymeric curing agent (PCA) was synthesized to assure the crosslinking and provide the reinforcing for the polymeric matrix. The agent improved the processing property of

the PDMS/PCA system due to its relatively lower viscosity. PDMS/PCA curing system showed lower volume shrinkage and longer curing time. Moreover, because of good interaction between PDMS chains and particles generated *in situ*, the reinforcement was excellent. Finally, the new curing system brought about better thermal stabilities compared with PDMS/TEOS system. All these advantages made this system a promising candidate in particular coating and grouting materials.

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