Novel Polymethoxylsiloxane-Based Crosslinking Reagent and its *In-Situ* Improvement for Thermal and Mechanical Properties of Siloxane Elastomer

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ABSTRACT: Polymethoxylsiloxane (PMOS) with dense pendant silicone-methoxy groups was synthesized from cyclosiloxane monomers by ring-opening polymerization and dehydrocoupling reaction. Synthesis reactions were followed by IR spectroscopy and ^{29}Si NMR analyses. PMOS was used as crosslinking reagent for room temperature vulcanized polydimethylsiloxane (PDMS), and the apparent activation energy for crosslink reaction was 3.92 kJ/mol. TEM study shows that many dispersed high crosslink density PMOS phases were formed in siloxane elastomer as well as the PDMS networks, and the crosslink density increased from PDMS networks to PMOS phases gradually, without a clear interface. It was detected that these PMOS phases improved the thermal and mechanical properties of siloxane elastomer significantly because of their *in-situ* microscale improvement effect. TG analysis demonstrated that thermal decomposition process of PMOS crosslinked siloxane elastomer was divided into three stages, the second one corresponding to a possible loss of some new structures, and the residual mass at 500°C was 66 wt %. The crosslink density went up as the loading of PMOS increased. Tensile stress and elastic module increased twice and three times, respectively, when the PMOS content increased from 15.1 to 41.6 wt %. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3788–3795, 2008

Key words: crosslinking reagent; polymethoxylsiloxane; room temperature vulcanized siloxane elastomer; *in-situ* reinforcement

INTRODUCTION

Siloxane elastomers are semi-inorganic polymers with high thermal stability, good weather resistance, low surface tension, and unusually high permeability.[1–3] Their unique physical and chemical performances have found applications in industries ranging from aerospace to biomedicine. Despite their benefits, however, siloxane elastomers have also some disadvantages in practical uses, and the major one lie in their low tensile strength in the absence of fillers because of weak intermolecular forces between polymer chains.[4,5] Therefore they generally require reinforcing fillers in most of their applications to take full advantage of the attractive properties.

The usual improvement processing of siloxane elastomers involves the blending of reinforcing fillers, such as silica (SiO₂).[6] Other commonly used fillers include titania (TiO₂),[7,8] zirconia (ZrO₂), and calcium carbonate (CaCO₃).[9] While the processing problems with blending technique exist and have encouraged the incorporating of fillers through sol–gel *in-situ* reinforcement, and this sol–gel approach also permits good control of particle sizes and size distributions.[10–14] All these fillers above, however, can not supply a firm combination between the fillers and siloxane elastomer, and the fracture of materials usually begins from these interfaces.[15,16] Some investigations showed that the use of concentrative crosslinking might be one of the effective methods to improve the strength of siloxane elastomer, and they could distribute stress well by crosslinkages in vulcanizates without the problem of weak interface. These crosslinking systems include 1,3-bis (methylphenylethynylvinyl) disiloxane, phenylethynylvinyldiethoxysilane, 1,1,3,3-tetramethyl-1,3-diphenylethynyldisiloxane, tetraphenylethynylsilane.[17–19] But most of these crosslinking reagents are small molecules without plenty reactive groups to form dense enhancing phases and have a disadvantage of needing expensive transition-metal catalysts such as platinum.[20]

Compared with these crosslinking systems mentioned above, a macromolecule crosslinking reagent with plenty of silicone-methoxy groups will be a good choice for the enhancement of siloxane elastomer, which may result in a dense crosslinked net-

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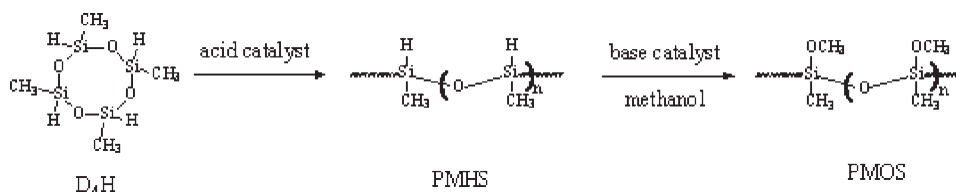
Scheme 1 Synthesis of polymethoxylsiloxane (PMOS).

work avoiding weak interfaces and be easy for use in room temperature without transition-metal catalysts. At the same time, the thermal degradation of siloxane elastomer may also have some changes as a consequence of the formation of dense network.

In the recent past, a variety of studies in our laboratory have been focused on investigating polysiloxane-based crosslinking reagents with many pendant alkoxy groups.[21] Some synthetic methods could introduce a variety of functional groups to a siloxane molecular in facile condition. For example, dehydrocoupling between Si—H and alcoholic O—H bonds has commonly progressed under catalytically mild conditions by the elimination of hydrogen molecules.[22] In addition, the byproduct, hydrogen, can be easily removed from the reaction mixture. The alkoxy groups could react with atmospheric moisture.[23] This may help to produce polysiloxane with rich pendant reactive groups as room temperature crosslinking sites.

In this investigation, polymethoxylsiloxane (PMOS) with dense pendant methoxy groups was synthesized from cyclosiloxane monomers by ring-opening polymerization and dehydrocoupling reaction, then the crosslinking reaction took place with moisture via hydrolyzation and condensation to form *in-situ* reinforcing phases (Schemes 1 and 2), which were confirmed by IR spectroscopy and ^{29}Si NMR analyses. And the apparent activation energy of crosslink reaction was calculated. We also report subsequent investigation of their mechanical, thermal, and morphological properties as a function of PMOS content, so as to evaluate the *in-situ* improvement effect of this novel crosslinking reagent. These results were compared with tetraethoxysilane (TEOS) crosslinked siloxane, as TEOS is used as a current crosslinking reagent for siloxane elastomer. The PMOS phase dispersion was characterized using TEM and their crosslink densities were calculated. The results demonstrated that PMOS could be approached as a new kind of crosslinking reagent and *in-situ* reinforcing filler for siloxane elastomer in room temperature without transition-metal catalysts.

EXPERIMENTAL

Materials

All reagents were commercially obtained and dried over activated 4 Å sieves. 2,4,6,8-tetramethylcyclote-

trasiloxane (D$_4$H), hydroxyl-terminated polydimethylsiloxane (PDMS, M_n = 36 × 10^3 g/mol) were supplied by Dow Corning Corporation. D$_4$H was dried over calcium hydride (CaH$_2$) and purified by distillation. Methanol was also purified by distillation. Catalysts for the synthesis of PMOS were prepared in our laboratory.

Synthesis of PMHS and PMOS

The polymethylhydrosiloxane (PMHS) was synthesized by the reaction of D$_4$H with an amount of acid catalyst under nitrogen atmosphere at presence of the polar additive THF. Then the PMOS was obtained by the dehydrocoupling reaction of PMHS and methanol with an amount of base catalyst (Scheme 1). The technique of synthesis was described in detail in a previous patent.[21] All volatiles were subsequently removed under vacuum.

Crosslinking of PDMS by PMOS

PMOS and its blends with hydroxyl-terminated PDMS were cured in the curing equipment at room temperature with 0.3 wt % dibutyltin dilaurate (dibutyltin di- duodecanate, IUPAC name) catalyst (from J&K Chemical, Beijing, China) for 24 h. The scheme of curing equipment is shown in Figure 1, in which the specimen was poured in a fluororesin mould. The crosslinking was achieved by the hydrolyzation of Si—OCH$_3$ groups and the condensation of Si—OH groups (Scheme 2). The cure equipment was filled with air and kept at 100% relative humidity by using about 10-mm depth of water in sealed state. Because methanol was released which would dissolve in water, lower its activity and hence the relative humidity, the liquids were periodically changed.
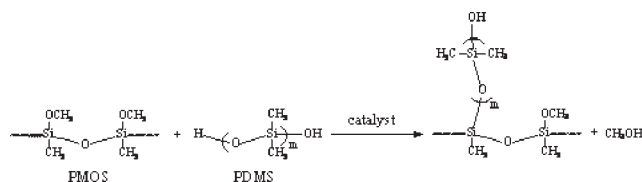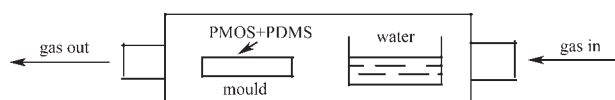

Scheme 2 Crosslinking reaction of PDMS and PMOS.

Characterizations and measurements

Fourier transform infrared and solid-state (^{29}Si) nuclear magnetic resonance

Fourier transform infrared (FTIR) spectra measurements were performed using a Nicolet Nexus 670 (FTIR) instrument (USA). The spectra obtained at resolution 4 cm^{-1} in the range 3200–500 cm^{-1}. Solid samples were prepared as pellets using spectroscopic grade KBr. Solid-state (^{29}Si) nuclear magnetic resonance (NMR) spectra measurements were recorded on a Bruker AV300 MHz spectrometer using 4-mm specimen tube.

Measurement of gel times

The technique of studying the kinetics crosslinking reaction is described in detail in a previous article.[24] A mobile, constituted by a bar terminated by a calibrated ball ($\theta = 16$ mm), is immersed into the uncrosslinked resin and vibrated by a pendular movement. The viscosity increases as a consequence of the increase in molecular weight and the amplitude of the pendulum decreases. Forces on the ball are proportional to the viscosity of the medium. This technique shows the sharp increase of the viscosity, which may correspond to gelation when vitrification of the medium occurs after gelation. This parameter is strongly influenced by the sample volume and surface area. The system was optimized for 130 g, and the optimal surface area was 60 cm^2. All experiments were conducted in an air atmosphere. Data from this technique are shown in Figure 3.

The apparent activation energy

The apparent activation energy of crosslinking reaction was determined from the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

Equation (1) can be written:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A \tag{2}$$

where, k_0 was preexponential factor, k was the rate of constant, E_a was the apparent activation energy, T was reaction temperature, and R is 8.31 J/(mol·k).

For the gel time t_{gel}, $k \cdot t_{gel} = C$. As a result, eq. (2) has the following form:

$$\ln\frac{1}{t_{gel}} = -\frac{E_a}{R}\frac{1}{T} + \ln A \tag{3}$$

According to eq. (3), a plot of $\ln(1/t_{gel})$ vs. $1/T$ would give a slope from which the apparent activation energy can be calculated.

Thermogravimetric and dynamic mechanical thermal analysis

Thermogravimetric analysis (TG) was performed on a Perkin–Elmer TGS-2 under nitrogen ambience with a heating rate of 10°C/min in the 25–800°C temperature range. Dynamic mechanical thermal analysis (DMTA) was performed in the temperature range from −120 to −10°C using a polymer laboratories mechanical thermal analyzer (DMTAV, Rheometyic Scientific, USA). The specimens used in the experiment had a width of 6 mm and a thickness of 1 mm. The DMTA was used in tensile mode at a frequency of 10 Hz. The heating rate was 3°C/min.

Transmission electron microscopy

The morphology structure of the PMOS crosslinked siloxane elastomer was observed by transmission electron microscopy (TEM). The ultrathin sections were cut from the sample in liquid nitrogen, and were stained with osmium tetraoxide (OsO$_4$) to obtain sufficient contrast. A Hitachi (Japan) H-800 TEM, with an acceleration voltage of 100 kV, was used to observe the ultrathin sections.

Mechanical testing

Specimens with a dumb-bell shape according to ISO/DIS 37-1990 type. Three specifications (1 mm thickness and 2 mm width) were prepared. Tensile tests were performed in a universal tensile testing machine (CMT4104) operated at a cross-head speed of 10 mm/min. The specimen's elongation was derived from the extensometer separation of 18 mm. The E-modulus was determined from the initial slope of the stress–strain curve (1–5% strain range of stress–strain curve). Samples were tested at 21°C and the average value of each quantity was reported. The parameters determined were: elastic module (MPa), stress (MPa), and elongation at break (%).

Average crosslink density

Data obtained in mechanical analysis could be used to study the average crosslink density.[25,26] In the me-
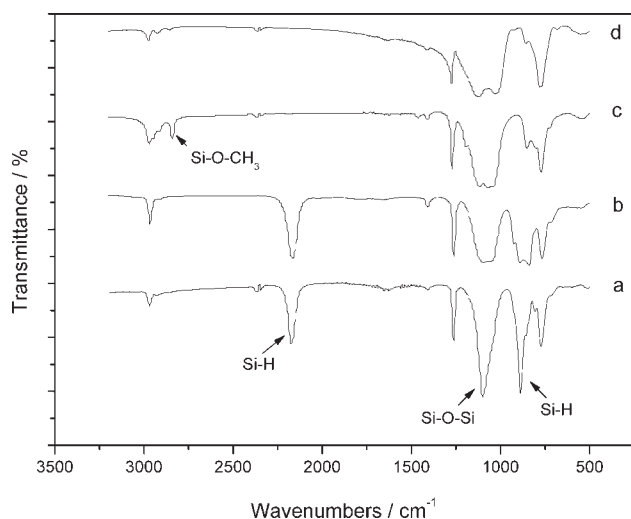
Figure 2 FTIR spectra: (a) D_4H; (b) PMHS; (c) PMOS; (d) PMOS crosslinked siloxane elastomer.

chanical measurements, the Helmholtz free energy of the network has the following form[27]:

$$\Delta F_{el} = \frac{1}{2}\gamma_e RT(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \qquad (4)$$

where γ_e is the crosslink density, which can be described by the number of mols of subchain units (chains between crosslinkages) per gram of sample, $\lambda_i (i = x, y,$ and $z)$ represents the elongation in three dimensions, T is room temperature, and R is 8.31 J/(mol·k).

For uniaxial extension, the mechanical stress, σ (in Pa), can be written:

$$\sigma = \frac{1}{A}\left(\frac{\partial \Delta F_{el}}{\partial l}\right)_{T,V} = \rho_p \gamma_e RT(\alpha - \alpha^{-2}) \qquad (5)$$

where A is the area of the sample under the force action, α is the elongation.

Equation (5) can be used to evaluate the mechanical measurements, leaving γ_e as adjustable parameter, and the average crosslink density can be calculated.

RESULTS AND DISCUSSION

Characterization of the synthesis of PMOS

The FTIR spectra of D_4H, PMHS, PMOS, and crosslinked siloxanes are shown in Figure 2. From spectrum (a) to spectrum (b), the signal of Si—O—Si broadens, which indicates the ring-opening polymerization of D_4H. From (b) to (c), the signal of Si—H disappears while that of Si—O—CH_3 emerges, which reflects the dehydrocoupling reaction of PMHS and methanol. From (c) to (d), the signal of Si—O—CH_3 disappears and that of Si—O—Si

broadens, which suggests the hydrolyzation and condensation of PMOS and PDMS. FTIR spectra confirm the design of synthesis in Schemes 1 and 2.

The solid-state ^{29}Si NMR analyses show the detailed information about Si units presenting in the polymer chain of PMHS and PMOS. The signal at -34.94 ppm is assigned to the silicon in the [SiO(CH_3)H] units, the signal at -48.34 ppm to the silicon in the [SiO(CH_3)(OCH_3)] units and another at 9.78 ppm to the silicon in the [SiO(CH_3)$_3$] units. Results from ^{29}Si NMR analyses demonstrate the dehydrocoupling reaction of PMHS, and the shift of signal from -34.94 to -48.34 ppm reflects that Si—H groups change into methoxy groups.

The molecular weight (M_n) of PMOS is 3.6×10^3 g/mol with a polydispersity around 2 and a yield up to 90%. Its refractive index is 1.4037.

Gel time and the apparent activation energy of crosslinking reaction

Gel time curves of crosslinking reactions with different PMOS content are shown in Figure 3. Gel time decreases with an increase in crosslinking temperature, but the dependence becomes weak when the content of PMOS increases from 15 to 47 wt %. It can also be noticed that gel time increases with the increase in PMOS loading. It seems that more the PMOS, more time is needed to accomplish the crosslinking reaction. From the definition of gelling time, which is the time of the molecular or the gel degree up to a certain degree, if PMOS content loaded more, the number of reactivity groups is more, so that more water in the air is needed to penetrate in. Moreover, since PMOS is a macromolecular crosslinking reagent, the diffusivity of molecular chain will have an important role on the reaction speed. Therefore, more the PMOS, more time is needed to
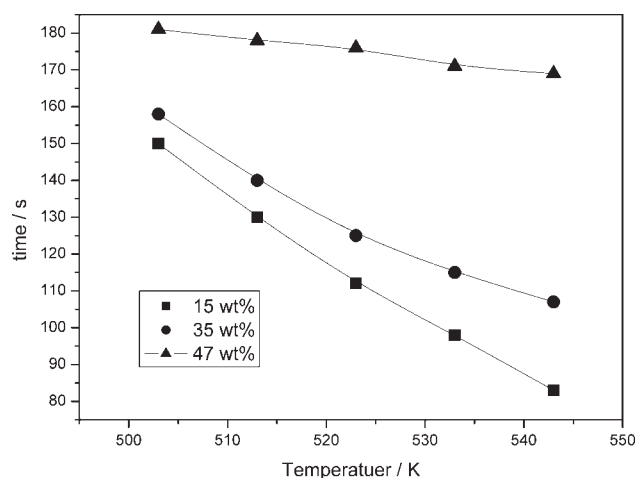

Figure 3 Gel time versus temperature for different loading of PMOS.

Compositions and Mechanical Performances of PMOS Crosslinked Siloxanes and TEOS Crosslinked Siloxane

No	PMOS loading (wt %)	Stress (MPa)	Density (g/cm^3)	Module (MPa)	Elongation at break (%)	Crosslink density (10^{-3} mol/kg)
a	TEOS[a]	0.221	0.63	0.430	51.4	2.80
b	15.1	0.678	0.80	0.734	92.4	3.77
c	26.3	1.278	0.95	1.296	98.6	5.60
d	34.9	1.731	0.97	1.947	88.9	8.24
e	41.6	2.035	1.02	3.084	66.0	12.41

[a] The mol % of reactive sites of TEOS (ethoxy groups) in the sample No. (a) was equal to the mol % of reactive sites of PMOS (methoxy groups) in the sample No. (b) (siloxane elastomer with 15 wt % PMOS).

accomplish the crosslinking reaction as well as the diffusion of molecules.

For crosslinking reactions with 15, 35, and 47 wt % PMOS, the apparent activation energy obtained by eq. (3) have values of 32.90, 21.96, and 3.92 kJ/mol, respectively. The apparent activation energy decreases with the incorporation of PMOS.

Heat resistance properties of PMOS crosslinked siloxane elastomer

Hydroxyl-terminated PDMS can be crosslinked by PMOS with moisture at room temperature. To evaluate the *in-situ* improvement effect of this novel crosslinking reagent, the thermal properties of siloxane elastomers as a function of PMOS content were studied. The compositions of siloxane elastomer samples are presented in Table I. To make a comparison, we also made samples crosslinked by TEOS.

The thermogravimetic curves of crosslinked siloxanes are shown in Figure 4. For TEOS crosslinked siloxane, the residual mass at 500°C is 31 wt %. While for siloxane crosslinked with 15, 35, and 47 wt % PMOS, the residual masses at 500°C are 44, 53, and 66 wt %, respectively. The TG curves exhibit that the residual mass at 500°C increases with the loading of PMOS, and all of PMOS crosslinked siloxanes have more residual mass than TEOS crosslinked siloxane. It is known that siloxane undergoes stepwise degradation of the backbone and oxidation of the methyl groups above 200°C. Although the Si—C bond is thermodynamically less stable than the Si—O bond, thermal degradation of siloxane occurs by depolymerization through the Si—O bonds' rearrangement below 400°C via kinetically favored paths, leading to the production of cyclic oligomers.[28-30] While PMOS is a branched molecule with rich pendant methoxyl groups, which has the ability to destroy the helical coiling structure of siloxane and form *T* structure units in the chain networks. Both the branched structure of PMOS and its capacity to form *T* unit prevent the rearrangement of Si—O bonds in siloxane. PMOS blocks the formation of the cyclic oligomers, and the rate of thermal degradation decreases. As a

result, PMOS crosslinked siloxanes have better thermal resistance than TEOS crosslinked siloxane, and the thermal resistance increases with the PMOS weight percent.

To perform a further investigation on the thermal resistance of PMOS itself, the sample of pure crosslinked PMOS itself was prepared and its thermal stability was tested under the same conditions as samples mentioned above. The TG curve of crosslinked PMOS under nitrogen atmosphere is shown in Figure 4. The TG curve exhibits that the residual mass of crosslinked PMOS at 500°C is 95 wt %, which is much higher than those of siloxane elastomers. Pure crosslinked PMOS shows an excellent thermal stability and its 10% mass loss temperature is about 760°C.

It seems like that there are three mass loss steps on the TG curves of PMOS crosslinked siloxanes: the step around 350°C, the step between 400 and 600°C, and the step above 750°C. The second step is more obvious as the increase of PMOS, and the third one can not be seen when PMOS loading is low. It is also shown in Figure 4 that TEOS crosslinked siloxane elastomer and pure crosslinked PMOS begin to decompose around 350 and 750°C, respectively. These three mass loss steps can possibly explain the
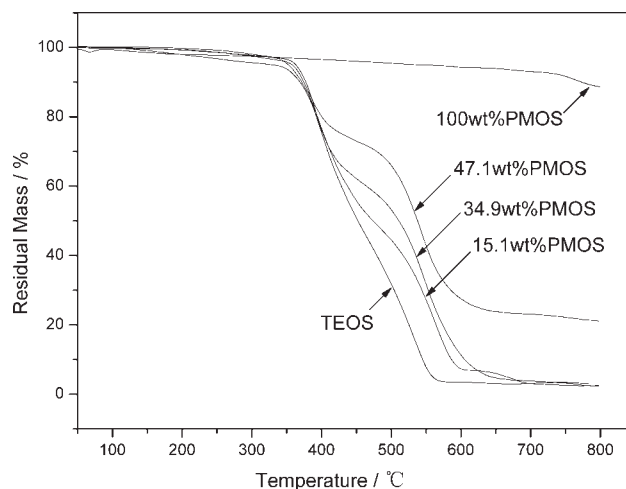

Figure 4 Thermogravimetric curves of crosslinked siloxanes with TEOS and different weight percents of PMOS.
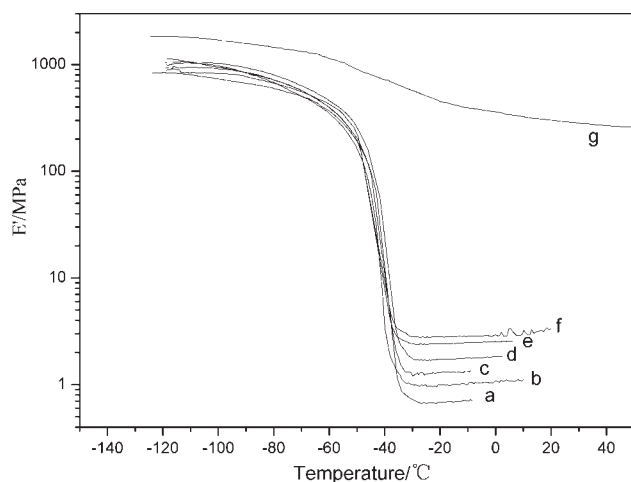
Figure 5 Storage modulus E' curves of crosslinked siloxanes: (a) TEOS; (b) 15.1 wt % PMOS; (c) 26.3 wt % PMOS; (d) 34.9 wt % PMOS; (e) 41.6 wt % PMOS; (f) 47.1 wt % PMOS; (g) 100.0 wt % PMOS (crosslinked PMOS).

unique phase dispersion structure of PMOS crosslinked siloxanes. In the course of crosslinking reaction, excessive PMOS chains will form PMOS phases by the hydrolyzation and condensation of their rich pendant methoxy groups, and cause the third mass loss step above 750°C. The first mass loss step around 350°C seems to correspond to the decomposition of structures like PDMS networks. While the second mass loss step between 400 and 600°C may be due to the existence of some new structures between PMOS phases and PDMS networks. The mechanism of these new structures is still under investigation. Since the second step is more obvious as the increase of PMOS loading, these new structures will improve the thermal resistance of siloxane elastomer along with the PMOS phases.

Mechanical properties of PMOS crosslinked siloxane elastomer

To evaluate the *in-situ* improvement effect of this novel crosslinking reagent, the mechanical properties of siloxane elastomers as a function of PMOS content were studied. The compositions of siloxane elastomer samples are presented in Table I. To make a comparison, we also made samples crosslinked by TEOS.

The DMTA curves of dynamic storage modulus (E') versus temperature are shown in Figure 5. For TEOS crosslinked siloxane, the network is formed by long chains of PDMS. While for PMOS crosslinked siloxane, the network has many dense PMOS phases which will restrict the movement of chain segments. The value of E' increases as the loading of PMOS goes up, demonstrating that more dense PMOS phases are formed in the network. Being different

with other reinforce fillers such as SiO_2, a gradient region between the PMOS phase and PDMS network will be formed instead of a clear interface. The increase of crosslink density, however, is mainly due to the increase of PMOS dense phases rather than the gradient regions. The gradient region does not have a size big enough to cause an obvious change in the storage modulus E' curves. To make a further characterization, we added the dynamic loss tan δ curves of siloxane elastomers as a function of PMOS content in Figure 6. The peak of tan δ curves of PMOS crosslinked siloxane are slightly wider than that of TEOS crosslinked siloxane, as well as a little shift to higher temperature, which can be contributed to the effect of these small gradient morphology.

Pure crosslinked PMOS is also detected by DMTA, and result of E' is shown in Figure 5. For pure crosslinked PMOS, the network is dense because of the rich methoxyl groups. This dense network will limit the movement of siloxane chains. In Figure 5, E' of siloxane elastomer falls down quickly around −50°C, but that of crosslinked PMOS decreases much less, which shows the restriction of molecular movement.

The results of mechanical testing are shown in Table I and Figure 7. The mechanical testing indicates that as the increase of PMOS loading, there will be more PMOS phases to disperse the stress in crosslinked siloxane, so as to increase the mechanical properties of siloxane elastomer. Tensile stress and elastic module of the siloxane elastomer increase significantly, and elongation at break decreases. When the PMOS loading increases from 15.1 to 41.6 wt %, tensile stress increases twice, elastic module increases three times and elongation at break falls a third.
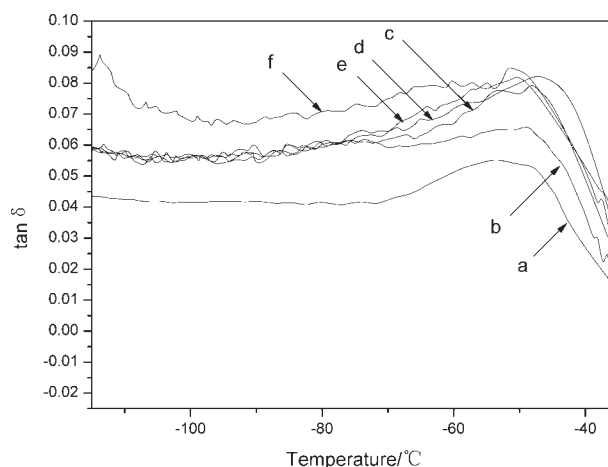

Figure 6 Dynamic loss tan δ curves of crosslinked siloxanes: (a) TEOS; (b) 15.1 wt % PMOS; (c) 26.3 wt % PMOS; (d) 34.9 wt % PMOS; (e) 41.6 wt % PMOS; (f) 47.1 wt % PMOS.
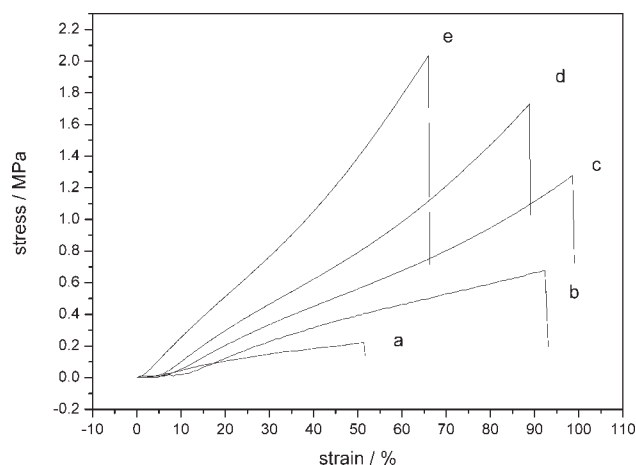
Figure 7 Stress–strain curves of the PMOS crosslinked siloxane and TEOS crosslinked siloxane: (a) TEOS; (b) 15.1 wt % PMOS; (c) 26.3 wt % PMOS; (d) 34.9 wt % PMOS; (e) 41.6 wt % PMOS.

Figure 9 Phases dispersion structure of the PMOS crosslinked siloxane elastomer: (a) PDMS; (b) PMOS; (c) gradient regions.

Phase dispersion structure of PMOS crosslinked siloxane elastomer

The phase dispersion structure of PMOS crosslinked siloxane elastomer was characterized using TEM. TEM micrographs are shown in Figure 8, in which the bright regions represent PDMS networks while the dark regions represent the PMOS phases. Many microscale (1 μm) dispersed high crosslink density PMOS phases are *in-situ* formed in siloxane elastomer. Being different from fillers such as SiO_2, there seems to be a gradient region between the PMOS phase and PDMS network instead of a clear interface, and the crosslink density increases from PDMS network to PMOS phase gradually.

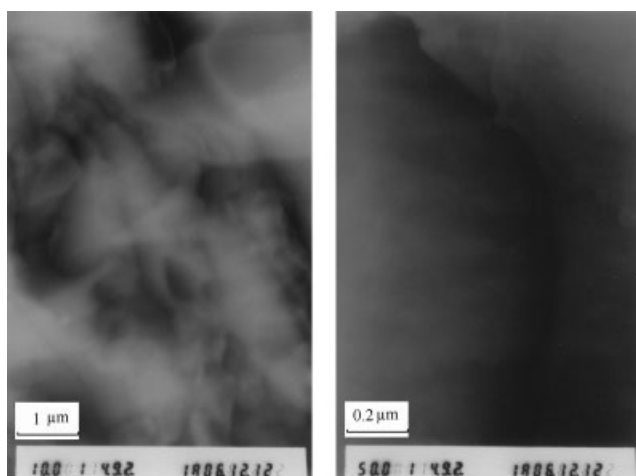According to TEM micrographs and TG curves of PMOS crosslinked siloxanes, there seems to be three kinds of regions in the PMOS crosslinked siloxane: PDMS networks, PMOS phases and the new gradient regions. In the course of crosslinking reaction, excessive PMOS chains will form high crosslink density phases by the hydrolyzation and condensation of their rich pendant methoxy groups. The hydroxyl-terminated PDMS chains turn to networks because of the hydrolyzation and condensation between their hydroxyl end groups and the methoxy groups of PMOS. As the molecular weight of PDMS (10^4 g/mol) is much higher than that of PMOS (10^3 g/mol) and both of them are linear molecules, chains of PDMS will form a loose network and those of PMOS turn to dense phases. The imaginable phases dispersion structure is shown in Figure 9. There seems to be some gradient regions between PMOS phases and PDMS networks, where the crosslink density increased from PDMS networks to PMOS phases gradually, without a

Figure 8 TEM micrographs of siloxane elastomer with 47 wt % PMOS. The ruler bars correspond to 1.0 and 0.2 μm, respectively.

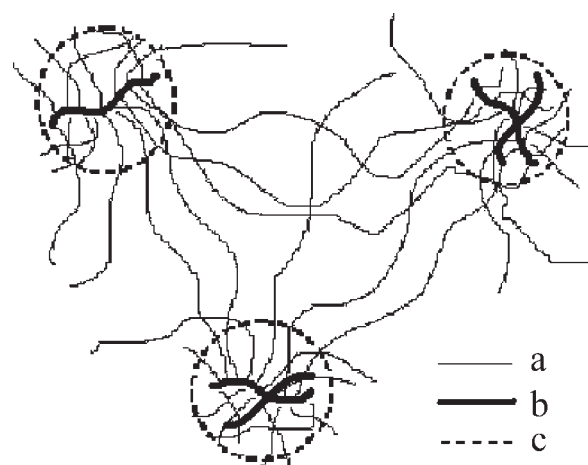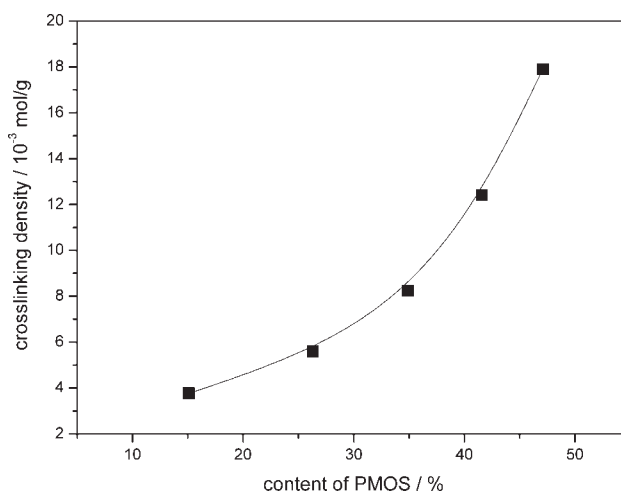**Figure 10** Average crosslink density of PMOS crosslinked siloxane.

clear interface. The detailed structure of these new regions is still under investigation.

Average crosslink density of PMOS crosslinked siloxane

Data obtained in mechanical analysis of PMOS crosslinked siloxane could be used to study the average crosslink density of siloxane phase dispersion structure. According to eq. (5), the average crosslink densities of PMOS crosslinked siloxanes are calculated and shown in Figure 10. The average crosslink density increases as the loading of PMOS goes up, demonstrating that more dense PMOS phases are formed in the network. For our samples, during crosslinking reaction excessive PMOS chains will form micro dense PMOS phases, and he hydroxyl-terminated PDMS chains gather around PMOS phases. Gradual linkage will be formed with PMOS phase as its center. Although the crosslink density has a gradual variation inside linkage phases, these micro linkage phases themselves are assumed a statistical distribution in the whole polysiloxane network. The calculation result here actually is the average crosslink density of the sample studied. The average crosslink density increases as the loading of PMOS goes up, which could be used to reflect the point that more PMOS dense phases have been formed.

Compared with TEOS, PMOS is a macromolecular crosslinking reagent with rich reactive sites. In the course of crosslink reaction, many PDMS chains will gather around one PMOS chain. The crosslink density will not only depend on the amount of reactive crosslink sites but also depend on the gathering effect of many PDMS chains around one PMOS chain. Therefore, the crosslink density of No. b (PMOS 15.1 wt %) is higher than that of No. a (TEOS) in spite of the same mol % of reactive sites.

CONCLUSIONS

By ring-opening polymerization and dehydrocoupling reaction of D_4H, PMOS with dense pendant methoxy groups was synthesized. Synthesis reactions were affirmed by IR spectroscopy and ^{29}Si NMR tests. PMOS can be used as crosslinking reagent for room temperature vulcanized siloxane elastomer, and the apparent activation energy for crosslinking reaction is 3.92 kJ/mol. TEM shows that many dispersed high crosslink density PMOS phases are formed as well as the PDMS networks, and the crosslink density increased from PDMS network to PMOS phase gradually, without a clear interface.

Compared with other crosslinking reagents such as TEOS, PMOS is a good crosslinking reagent for room temperature vulcanized siloxane elastomer because of its *in-situ* reinforcement of the dispersion

PMOS phases. Both mechanical testing and thermal performance of PMOS crosslinked siloxane elastomer indicate that these PMOS phases are capable of absorbing the stress and block the formation of cyclic oligomers, so as to improve the mechanical properties and thermal resistance of siloxane elastomer. TG analysis shows that thermal decomposition process of PMOS crosslinked siloxane elastomer takes place in three steps, the second one corresponding to a possible loss of some new structures. The residual mass of the PMOS crosslinked siloxane elastomer at 500°C is 66 wt %. The crosslink density goes up as the PMOS loading increases. Tensile stress and elastic module increase twice and three times, respectively, when the PMOS loading increases from 15.1 to 41.6 wt %.

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