Polymethylsilsesquioxane and Hydroxyl-Terminated Polydimethylsiloxane Composite: Vapor Incubation before Thermal Curing

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ABSTRACT: A composite film of polymethylsilsesquioxane (PMSQ) and hydroxyl-terminated polydimethylsiloxane (PDMS) was prepared by incubating PMSQ prepolymer and PDMS solution in a vapor environment before thermal curing. Vapor incubation has a significant influence on the morphology and properties of the cured composite, and the vapor incubation was conducted under three different conditions, i.e., acidic, neutral, and basic. In the acidic vapor of a pH rather lower than the isoelectric point (IEP) of the silanol, the reaction between PMSQ and PDMS through silanol condensation was promoted by the protonation of silanol. PDMS rubber particles with a domain size of about 100 nm were formed in PMSQ matrix, and the flexible modulus of the film was improved. While, the morphology of the resultant film was smooth and uniform after incubation in a neutral water vapor. The basic vapor facilitated the gelation of composite due to high pH inducing more rapid silanol condensation in PMSQ than phase separation. Moreover, excellent optical transparency, insulation, and thermal stability of the composite were also retained after the PDMS incorporation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1454–1461, 2009

Key words: hydroxyl-terminated polydimethylsiloxane; polymethylsilsesquioxane; silanol condensation

INTRODUCTION

As a typical class of organic-inorganic hybrid, polysilsesquioxanes (PSQ) has aroused considerable attention because of its unique architecture which contains an inorganic silicone-oxygen framework covered by organic substituents.[1] PSQ is usually prepared from tri-functional silanes by hydrolytic[2] or a nonhydrolytic[3] sol–gel process with a random, ladder, cage, or partial cage structure. The first commercialization of silicones began with silsesquioxane, which was used for electrical insulation at high temperature.[4] Silsesquioxane-based materials also serve as coatings for optoelectronic applications due to its high optical transparency.[5] Brown et al.[6] reported that low loss planar optical waveguide based on PSQ material for optical communication. However, the brittleness of PSQ restricts its practical application. Rubber particles are often used to toughen thermosetting resins, but usually sacrifice transparency and thermal stability of the resin.[7] On the other hand, the insulation property is usually reduced by the remaining of metal ion catalyst during the modification. It is highly desirable for PSQ to improve toughness with no loss of optical, electrical, and thermal properties.

Hydroxyl-terminated polydimethylsiloxane (PDMS) was used to toughen PSQ-based resin because of its good miscibility with PSQ and higher mobility to promote plastic deformation in the entire network. Zhu and coworkers have reported the toughening of a PSQ-based resin by incorporation of PDMS chains into the network.[7–10] However, since the coupling reaction of PDMS and PSQ was catalyzed by potassium acetate, the residual ions would affect the insulation property of the resultant silicone. There was no toughening effect if simply mixing and cocuring the two components, and the toughened system would be opaque when the domain size of the rubber particles were larger than 400 nm.[11]

In the present work, we report a simple method to prepare insulated and transparent film of PMSQ prepolymer toughened by hydroxyl-terminated PDMS. To improve the toughness, it is necessary to form covalent bonds for crosslinking the toughened PDMS particles and PMSQ. Firstly, incompletely condensed PMSQ prepolymer was synthesized with

large amount of active reaction sites of silanol (Si—OH) groups in PMSQ molecular structure. Then, hydroxyl-terminated PDMS were blended with PMSQ in the ethanol or acetone to form homogeneous solution. Because pH is an important factor affecting the condensation of silanol,[12] a method of vapor incubation is developed to investigate the pH influence upon silanol condensation between PMSQ and PDMS. For the insoluble system of PMSQ and PDMS in acid, base, or water solution, a normal method of simply external acid or base is infeasible. So an incubation method is often applied to study effects such as pH or relative humidity on the composite in order to avoid the film disintegrating from the substrate or the phase separation. Three kinds of environment are constructed: acidic, neutral, and basic by the vapor of acetic acid, water, and ammonia in sealed jars, respectively. PMSQ/PDMS composites were incubated in three vapor environments for 48 h separately, before the thermal curing to form composite films.

EXPERIMENTAL

Materials

Methyltrimethoxysilane (MTMS) was purchased from Shin-Etsu Chemical. Hydroxyl terminated poly-dimethylsiloxane (PDMS) (viscosity from $\sim$ 30 to 50 mm^2 s^{-1}, 20°C), was obtained from Beijing Dingye Industry & Trade (Beijing, China). Other chemicals such as ammonia, acetic acid, ethanol, and Chromium (III) acetylacetonate obtained from Beijing Chemical Reagent (Beijing, China) were used without further purification.

Synthesis of PMSQ prepolymer

PMSQ prepolymer was prepared from hydrolyzing reaction of MTMS according to an acid-catalyzed hydrolysis procedure.[13]

Preparation of PMSQ/PDMS composite

PDMS was dissolved with PMSQ in ethanol to form transparent solution, and then was cast on glass substrates, silicon substrates, or in Teflon molds. The glass or silicon substrates were thoroughly cleaned: the substrates were immersed into the boiling H_2SO_4/H_2O_2 mixture (7 : 3 v/v) for 30 min (caution: this solution is extremely corrosive), followed by rinsing with deionized water thoroughly, and finally dried with a stream of pure N_2. After one half of solvent was evaporated, the solution PMSQ/PDMS was exposed to vapor environment for incubation.

Three different vapor-saturated environments were constructed: acidic, neutral, and basic. Two hundred and fifty milliliters of acetic acid, water, and ammonia were put into three sealed glass jars (20 L) separately. The room temperature was kept at 25°C. After equilibrium in the sealed jar established, concentrated PMSQ/PDMS were put into the sealed jars for 48 h incubation. The incubated composites were blown with a slow nitrogen flow to remove the remains of water, ammonia, or acetic acid molecules. A slow temperature ramping process of thermal curing was necessary to make a void free cured casting plate. The multistep curing temperature process was as follows: 80°C/24 h, 100°C/24 h, 120°C/48 h, and 150°C/48 h. After curing, castings and films were cooled in the oven to room temperature.

Characterization

^{29}Si-NMR was measured using a Bruker 300M NMR spectrometer with chloroform-d as the solvent, and chromium (III) acetylacetonate (1% (w/w)) was used as a paramagnetic relaxation agent. MALDI-TOF MS measurement was preformed on a Bruker Biflex III. α-cyano-4-hydroxycinnamic acid (CHCA) was used as the matrix, and THF was used as the solvent for both the matrix and analyte. Adventitious sodium and potassium were found to be the cationizing agents of the peak positions. FTIR spectrum was obtained by a Bruker Tensor 27 spectrometer with a KBr plate.

The PMSQ/PDMS composite films deposited on glass were measured by a Shimadzu UV-1601 PC spectrophotometer, while the films deposited on silicon were characterized by the atomic force microscopic (AFM). AFM was carried out on a Nanoscope IIIa multimode instrument (Digital Instruments, USA) in a tapping mode. Commercial silicon probes (model TESP-100) with a typical resonance frequency of $\sim$ 300 kHz were used to scan the films. The three point bending test was performed according to ASTM standard D790-92. Flexural properties were measured on an Instron universal material test machine Model 3365 with a crosshead speed of 1 mm/min, and the results reported here were the averages of three successful tests. Current-voltage (I-V) characteristic of film was recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. Thermal gravimetric analysis (TGA) was conducted on a Perkin Elmer Pyris 1 Thermogravimetric Analyzer with a heating rate of 10°C/min and a nitrogen flow of 20 mL/min.

RESULTS AND DISCUSSION

Our group has been engaged in the study of synthesis and properties of PSQ[14] for many years. Recently, we have developed an economic and environmental friendly method to prepare low-molecular-weight PSQ prepolymer.[13] Because the incompletely
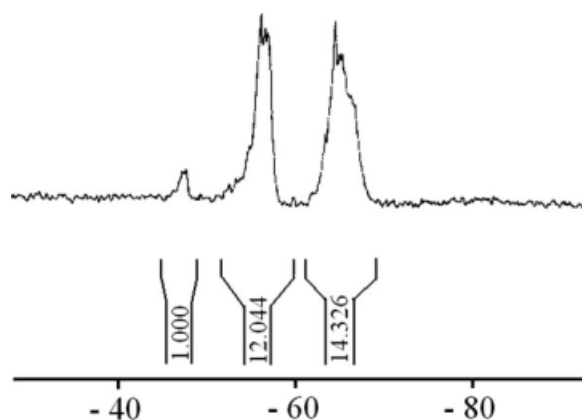
Figure 1 ^{29}Si-NMR spectrum of PMSQ.

condensed silanol groups have a profound influence on properties such as solubility, solution viscosity, and also the reactivity of PSQ, these PSQ prepolymer containing reactive silanol groups have drawn considerable attention in recent years.[15,16] Moreover, the as-prepared PSQ has no halogen or metal ions, and show excellent insulation property.

Figure 1 showed the ^{29}Si-NMR spectrum of the prepared PMSQ prepolymer. Chemical shifts of silicon atoms in silsesquioxane compounds are referred to using the traditional terminology T^n, where n corresponds to the number of oxygen bridges to other silicon atoms. The peaks at -64.5, -54.9, and -47.8 ppm indicate the structure of T^3 (CH$_3$SiO$_{3/2}$), T^2 (O$_{1/2}$Si(CH$_3$)(OH)O$_{1/2}$), and T^1 (O$_{1/2}$Si(CH$_3$)(OH)$_2$) unit, respectively.[17] The ratio of T^1 : T^2 : T^3 unit content determined from their peak areas was 1 : 12 : 14, implying a great number of incompletely condensed silanol groups were contained in the PMSQ prepolymer. In addition, the ratio of silanol to methyl was determined to be 52/100 according to ^{1}H-NMR. D$_2$O was employed to exchange the reactive hydrogen of silanol groups in PMSQ prepolymer.

MALDI-TOF MS was used to study the molecular weight and the detailed structures of PMSQ prepared. Table I summarized the assignment of the main peaks in the mass spectra, and the m/z signals were given by the subtraction of Na$^+$ or K$^+$ mass from the ionized samples. The interpretation of mass spectra was made by comparing the value of molar mass for a possible expected PMSQ formula and the experimentally obtained mass. From the serial of the data, it was speculated that condensation of one methylsilanetriol increased the molecular weight by 76 g/mol which corresponding to the CH$_3$SiOHO repeating unit, and the increase of 134 g/mol contributed to the (CH$_3$Si(O)$_{3/2}$)$_2$ repeating unit in series was also indicated.[18] The peak-to-peak spacing of 18 g/mol resulted from an intramolecular condensation reaction.

General structures for three-dimensional silsesquioxane involve cage, ladder, and random structures. The essential difference among these structures is the degree of silanol condensation. In the cases of fully condensed PMSQ structures, perfect polyhedral of formula, (CH$_3$SiO$_{1.5}$)$_n$ is denoted as T$_n$. Whereas, incompletely condensed products have the general formula T$_n$(OH)$_x$(OCH$_3$)$_y$.[19] A small quantity of methoxyl groups (Si—OCH$_3$) which was not hydrolyzed still exist in the synthesized PMSQ. For example, Scheme 1 showed the proposed structure corresponding to the peak of $m/z = 648$ g/mol. For the molecules b, c, d, e, and f in Scheme 1, two dangling Si—OH groups in close proximity were apt to react intramolecularly to form a more stable Si—O—Si bridge. Stronger intense $m/z = 630$ g/mol peak was observed compared with that of the $m/z = 648$ g/mol peak shown in Table I.

Figure 2 showed the FTIR spectrum of PMSQ. The Si—OH broad absorption is in the region of 3200–3400 cm^{-1}. Also, the Si—OH stretching vibration at 930 cm^{-1}, a fingerprint of uncondensed Si—OH group, is sometimes referred to as a defect band

TABLE I
Significant Peaks of MALDI-TOF MS Spectrum of PMSQ

m/z	Intensity	Structure, T$_n$(OH)$_x$(OCH$_3$)$_y$	m/z	Intensity	Structure, T$_n$(OH)$_x$(OCH$_3$)$_y$
572	Very strong	$n = 8, x = 4$	782	Strong	$n = 11, x = 5$ $706 + 76$
586	Very weak	$n = 8, x = 3, y = 1$	796	Weak	$n = 11, x = 4, y = 1$ $720 + 76$
630	Very strong	$n = 9, x = 3$ $648 - 18$	822	Middle	$n = 12, x = 2$ $840 - 18$
648	Middle	$n = 9, x = 5$ $572 + 76$	840	Strong	$n = 12, x = 4$ $706 + 134$ or $858 - 18$
706	Very strong	$n = 10, x = 4$ $572 + 134$	858	Strong	$n = 12, x = 6$ $782 + 76$
720	Weak	$n = 10, x = 3, y = 1$ $586 + 134$	916	Middle	$n = 13, x = 5$ $840 + 76$ or $934 - 18$
764	Weak	$n = 11, x = 3$ $782 - 18$	934	Middle	$n = 13, x = 7$ $858 + 76$
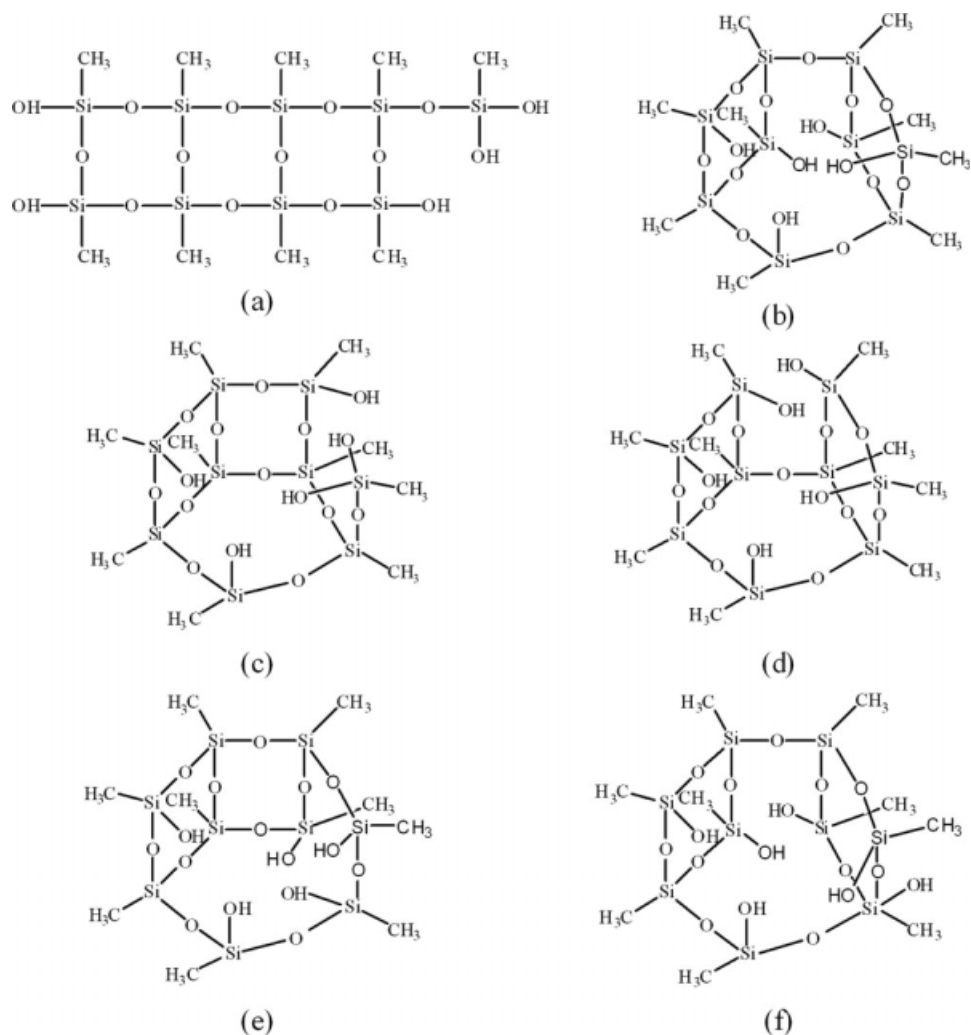
Scheme 1 Some proposed structures consisted in the PMSQ for $m/z = 648$ Da.

within the context of network structure.[20] Si—O—Si stretching absorption bands are in the region of 1000–1200 cm^{-1}. For cage structures, there is a strong Si—O—Si asymmetric stretching absorption in the higher frequency around 1150 cm^{-1}. While for the ladder structures, there is a strong Si—O—Si symmetric stretching absorption in the lower frequency around 1050 cm^{-1}.[21]

In a word, characterization of as-prepared PMSQ prepolymer demonstrated that the series of silsesquioxane with cage and ladder structures contained a great number of reactive silanol groups. The more silanol groups there were in the PMSQ prepolymer, the more likely the reaction was between PMSQ and PDMS in the subsequent processing.

Since interfacial adhesion is of importance for toughening, forming covalent bonds to link toughened phase with the matrix would increase the interfacial adhesion. Hydroxyl-terminated PDMS of low molecular weight was chosen as the rubbery second phase to provide more reactive sites with PMSQ pre-

polymer. The molecular weight of PDMS used is about 700–2000, as measured by MALDI-TOF MS.

The increase of toughness mostly sacrifices the modulus. Rubber toughening in a polymer often results in degradation of its thermal resistance, because usually the rubbers are less thermally stable. To minimize the compromise on thermal resistance for a toughened system, PDMS was chosen as the rubbery second phase for the thermal stability.[9] PDMS content was determined by examining the modulus and thermal stability of the composites.

Tensile properties were determined using an Instron 3365 tensile tester. The test pieces, with a gauge length of 24 mm, of each sample were analyzed at a speed of 10 mm/min. The results illustrated that a higher PDMS content exhibited a higher tensile strain, and thus PDMS toughened the network effectively. The tensile strain was from 3.8% of the pure PMSQ to 24.6% of composite containing 60% PDMS. However, the Young's modulus was decreased accordingly from 368.8 MPa of the pure PMSQ to
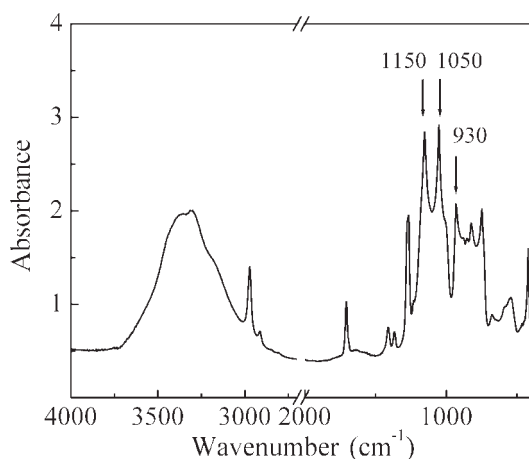
Figure 2 FTIR spectrum of PMSQ.

30.5 MPa for the composite containing 60% PDMS. TGA results showed that the PDMS segment reduces the thermal stability of the network as compared to the pure PMSQ after curing. The weight remaining of the system was about 80% at 800°C when PDMS content was up to 40%. Considering the decrease of modulus and thermal stability and the increase of toughness, the optimal ratio of PMSQ to PDMS was 6 : 4 in the study.

The PMSQ/PDMS deposited on glass were incubated in three different vapor environments for 48 h respectively, and then were underwent a multistep thermal curing process. Visible spectroscopy was used to characterize the transparency of the composite films, and the results were shown in Figure 3.

As shown in Figure 3, after incubation in acidic and neutral vapor, the composite films showed excellent transparency in the visible light range. However, after incubation in the basic vapor, the transmittance of the film was much lower than that of the others. The PMSQ/PDMS clear solution became translucent when incubated in the basic environment, and gelation was then occurred quickly. The gelation time at the room temperature was less than 1 h which was determined by the time when the solution could not flow when the container was tilted. However, pure PDMS solution of the same concentration did not form gels at the same condition for more than 24 h.

Previous work has demonstrated that it is difficult to form gels from hydrolytic condensation of methyltrimethoxysilanes.[12] The conformational difficulty in getting all three groups to participate in the network is one of the reasons. And the intramolecular cyclization reactions of ladder and cage structures in PMSQ also lead to difficult gelation. However, as pH is higher than the isoelectric point (IEP), the silanol condensation mechanism was the attack of deprotonated silanol on the neutral silanol which

accelerate the gelation greatly.[22] Since great number of silanol existed in the PMSQ synthesized, the gelation is taken place rapidly when catalyzed by the ammonia vapor. However, the pure PDMS solution of the same concentration did not form gels in the basic vapor for more than 24 h, indicating the silanol activity of hydroxyl PDMS is much weaker than that of PMSQ. In the basic vapor, the rapid gelation rate of PMSQ/PDMS composite account for the dramatically increasing of the deprotonated silanol concentration in PMSQ.

No gelation was observed for the PMSQ/PDMS system incubated in the acidic and neutral environments, and therefore transparent castings or films formed after thermal curing. The thermal-cured composites after incubation in the neutral and acidic vapor were characterized for the further study. After thermal curing, the toughness of these composites was determined by the flexural modulus, and the results were shown in Table II. The pure PMSQ was too brittle to do the test. After curing, gel formed in the basic vapor became a porous monolith of which modulus could not be determined.

As shown in Table II, the flexural strength of specimen incubated in the acidic environment was much higher than that in the neutral vapor. The flexural modulus of the composite increased from 67.5 to 160.4 MPa. Morphologies of the composite films were studied to interpret the reason of the toughness increasing.

Atomic force microscope (AFM) can be used to investigate the phase shift due to the reflections of different modulus.[23–26] AFM images of PMSQ/PDMS composite films prepared in different vapors were shown in Figure 4.

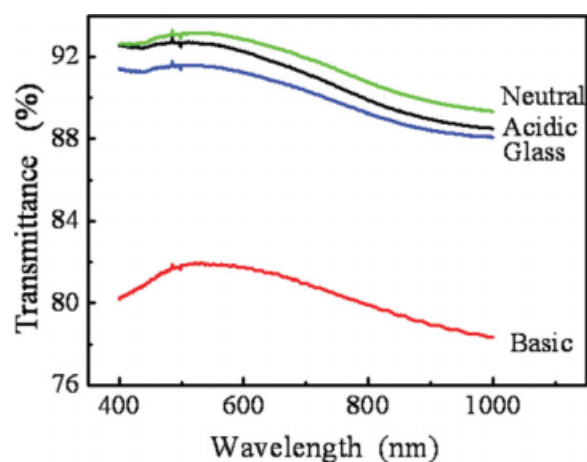Some grain domains appeared in the film after incubation in the acidic environment in Figure

Figure 3 Visible spectra of PMSQ/PDMS films incubated in acidic, neutral, and basic vapors (clean glass slide as the substrate). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Flexural Modulus of Cured Specimens after Incubation in Neutral and Acidic Environments

Environment	Flexural strength (MPa)	Flexural modulus (MPa)
Neutral	4.1 ± 0.2	67.5 ± 2
Acidic	6.2 ± 0.2	160.4 ± 2

4(a,b), while the phase separation was not observed for the film incubated in the neutral vapor [Fig. 4(c,d)]. In Figure 4(b), some light bulge displayed in the phase image could not be seen in the height image. In the phase image, the black (negative) part indicated a crosslinked PMSQ matrix domain because of the difference in the Young's modulus between "hard" crosslinked resin matrixes and "soft" rubber particle domains.[25] The size of silicone rubber domain was about 100 nm. It was the elastic rubber particles dispersed in the matrix that toughens the PMSQ.

When pH is lower than the isoelectric point (IEP) of silanol, the mechanism of the silanol condensation is the attack of the neutral silanol on the protonated silanol. In the acidic atmosphere, the protonation of silanol promote the condensation rate of silanol in both PMSQ and PDMS molecules. For comparison, after PDMS one component incubation in the same condition, the molecular weight was investigated. However, there was no evident indication from the MALDI-TOF MS spectrum that the molecular weight of PDMS increased. It suggested that the silanol end groups of PDMS react mostly with PMSQ prepolymer instead of its self-condensation. These flexible PDMS chains incorporated into PMSQ network significantly increased the toughness of cured resin. Instead of using metal catalyst, the condensation of PDMS and PMSQ catalyzed by the acidic vapor establish chemical bonds between two phases. When the particles are attached to the matrix by covalent bonds, the toughness is generally much improved.[27] If the chain length exceeds a certain limit, however, even chemical bonding at the ends of the chains cannot prevent phase separation. Upon thermal curing in the subsequent process, these long chain PDMS segments precipitate from the resin matrix to form rubbery particles. The chemical bonds at the ends of these segments provide strong adhesion of the
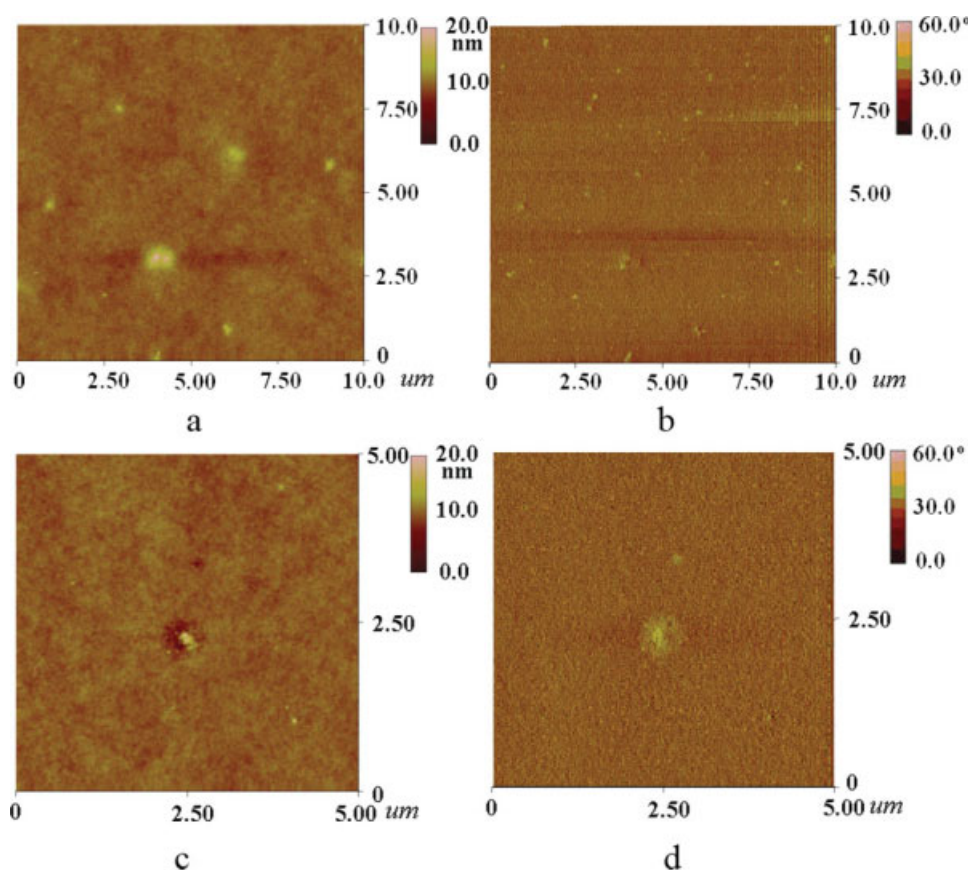

Figure 4 AFM images of PMSQ/PDMS films after incubation in different vapors: Acidic (a, b), and neutral (c, d). (a), (c) and (b), (d) are height and phase images, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
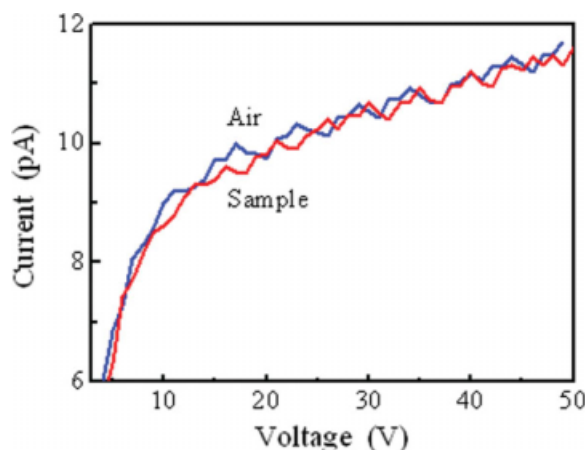
Figure 5 I-V curves of air and PMSQ/PDMS films after incubation in acidic vapor. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

particles to the matrix. Thermal curing process elevates the crosslinking degree of PMSQ and PDMS system to form a network structure. While in the neutral environment, saturated water restricts the condensation of Si—OH. PMSQ/PDMS rigid network structures with high crosslinking density are formed through thermal curing with almost no coupling reaction in advance. Because of the existence of the separated PDMS rubber particles in the silicone crosslinked network, the cured composite incubated in the acidic atmosphere have higher toughness than that prepared in the neutral atmosphere.

Furthermore, AFM result also showed that the size of rubber particle was about 100 nm. That was the reason why films obtained from the acidic incubation are highly optical transparent in the visible light spectra.[11] Because of the smooth morphology of the composite, the film incubated in the neutral vapor showed a higher transmittance than that in the acidic vapor as shown in Figure 3.

Because there was no metal-containing salts catalyst the whole preparation procedure, the resultant composite film exhibited excellent electrical insulation. The current versus voltage curve of cured PMSQ/PDMS casting prepared from the acidic environment was shown in Figure 5. The curve of the casting was almost superposed with that of the reference air, indicating that the as-formed casting has an excellent electrical insulation.

The thermal-cured PMSQ synthesized in this report had a weight remaining of 93% at the temperature of 800°C, while the pure PDMS only had a weight remaining of 6%. Therefore, the PDMS segment degraded the thermal stability of the network as compared to the pure resin. The weight remaining of the composite was 85% at 800°C. PDMS was incorporated into the PMSQ matrix through the silanol condensation. Because of the formation of the network or ladder structure, the thermal stability of the composite was improved compared with the system of methyl-terminated PDMS and PMSQ. After cured at the same condition, the weight remaining of the blend was determined to be 58%.

CONCLUSION

Incubation method was employed for the PMSQ and PDMS blend solution in an acidic vapor before thermal curing. Flexible PDMS rubber particles were formed through the silanol condensation between PMSQ prepolymer and PDMS accelerated by the acidic vapor. Compared with the film incubated in the neutral vapor, the phase separation improved the toughness of PMSQ. Because the average size of the particles was about 100 nm, the film had good transparency. Gelation of PMSQ/PDMS composite occurred in the basic vapor leading to formation of an opaque composite with a poor mechanical property. The insulation of PMSQ/PDMS films was also well retained, and weight remaining of the network was 85% at 800°C.

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