

Surface Science and Stability of Networks Prepared from Hydroxy-Terminated Polydimethylsiloxane and Methyltriethoxysilane

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Polydimethylsiloxane (PDMS) hybrid networks have been prepared by the reaction of PDMS(OH)₂, average molecular weight 26×10^3 , 43.6×10^3 and 58×10^3 , and methyltriethoxysilane (MeTEOS, 10–60 wt%) using a dibutyltin dilaurate or dibutyltin diacetate catalyst. By hydrolysis and homo- and co-condensation, MeTEOS forms a siliceous domain (MeSD) and acts as a crosslinker for the PDMS domain. Kinetic studies showed that high MeTEOS and catalyst concentrations and reduction of free surface area favor fast gelation and efficiency in converting MeTEOS to the MeSD. Under the water-sparse conditions utilized, cure was slow and substantial evaporative loss of MeTEOS occurred. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

As an alternative to coatings which prevent marine fouling by release of toxicants ('antifouling coat-

ings'), polydimethylsiloxane (PDMS) elastomeric coatings provide control by minimizing fouling adhesion strength ('fouling release' coatings).^{1–4} These PDMS coatings are room-temperature vulcanizing (RTV) elastomers which rely on sol-gel cure chemistry as described by Ulrich⁵ and Mark.⁶ In this approach, alkoxy silane hydrolysis and homocondensation produce a siliceous domain (MeSD), while crosslinking is effected by co-condensation of alkoxy silane or alkoxy(hydroxy)silane species with PDMS(OH)₂. This chemistry is basically the same as that used to prepare organic-inorganic 'hybrid' materials,⁷ but the hydrolysis and condensation reactions occur under water-sparse conditions. With a view toward examining cure kinetics, surface chemistry and the nature of the siliceous phase formed in ambient-temperature cure, we describe herein a series of networks with PDMS [$M_n(26–58) \times 10^3$] prepared by cure with methyltriethoxysilane.

EXPERIMENTAL

Materials

All materials were used as received. Silanol end-capped polydimethylsiloxanes (PDMS)(OH)₂ (United Chemical Technologies, Inc.) were obtained with viscosities and molecular weights of 1000 cS (26×10^3), 3500 cS (43×10^3), and 8000 cS (58×10^3), according to the manufacturer's data. Methyltriethoxysilane (MeTEOS) and dibutyltin dilaurate were purchased from Aldrich Chemical Company.

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Network synthesis

Preparation of films for evaluation of wettability

For each PDMS(OH)₂ molecular weight (MW), four levels of MeTEOS were utilized based on total weight of reactants (10, 15.6, 25, and 40 wt% for MW = 26 × 10³ and 43.6 × 10³, and 15.6, 25, 40 and 58.5 wt% for MW = 58 × 10³). Dibutyltin dilaurate catalyst comprised 1 wt%. At room temperature in air, measured amounts of PDMS(OH)₂ and MeTEOS were mixed in a glass vial (i.d. 1.9 cm) with a mechanical stirrer for about 5 min, the catalyst was added and the mixing was continued for another 90 min. The viscous material was then cast on an FEP (tetrafluoroethylene-hexafluoropropylene copolymer) substrate or dip-coated on glass slides (22 mm × 50 mm × 0.15 mm). Samples were subsequently cured at 50–60 °C for 20 h, and stored at room temperature. Alternatively, cure was effected at ambient temperature as shown in the kinetic studies described below.

Preparation of samples for cure kinetics

Measured amounts of PDMS(OH)₂ and MeTEOS were mixed with a magnetic stirrer for about 5 min in either a 10 ml vial (i.d. 1.9 cm, 4–5 g material) or a 50 ml beaker (i.d. 2.9 cm, 15 g material) followed by the addition of a measured amount of catalyst. The reactants were allowed to gel at room temperature in the container, and the progress of the reaction was monitored by measuring the mass of the mixture with a standard analytical balance.

Characterization

Dynamic contact angles were measured with a Cahn dynamic contact-angle analyzer (DCA-312), which is a Wilhelmy plate-type instrument. Unless noted otherwise, water was used as the probing liquid; it was purified with a Barnstead NANOpure ultrapure water system. Each measurement consisted of three cycles, the second and the third of which usually converged. The advancing and receding contact angles obtained in the last cycle are reported.

Stability of surface wettability was estimated by immersing representative samples in either aqueous NaCl (0.5 M) or NANOpure water containing NaN₃ (5 mM) for a period of 22 days, and monitoring water contact angles as a function of immersion time. Stability to mass loss was estimated by immersing samples in NANOpure water and weighing dried samples at 4 h intervals.

²⁹Si NMR magic-angle spinning (MAS) spectra were acquired using a Bruker MSL-200 operating at 39.8 MHz for silicon. Typical spectra were recorded using single-pulse excitation with a recycle delay of 240 s, 200 acquisitions, and MAS speeds ranging from 2.0 to 2.5 kHz. All spectra were acquired at ambient temperatures and externally referenced to octakis(trimethylsiloxy)sil-sesquioxane (Q8M8, downfield peak at 11.9 ppm).

RESULTS AND DISCUSSION

Surface properties

A survey of materials prepared with varying PDMS molecular weights and initial concentrations of MeTEOS was carried out. Under conditions of 50–60 °C cure, all MeTEOS-derived compositions cured into nonflowing solids when cured in a container. Three compositions with low percentages by weight of MeTEOS failed to cure to nonflowing films on either FEP or glass substrates. These included 26 × 10³ and 43.6 × 10³ PDMS(OH)₂ with 10 wt% MeTEOS and 58 × 10³ PDMS(OH)₂ with 15.6 wt% MeTEOS.

To evaluate wettability, advancing and receding contact angles were measured and are listed in Table 1, each value being the average of measurements on four different specimens. In evaluating surface wettability, a high receding contact angle, θ_{rec} , and low hysteresis ($\theta_{\Delta} = \theta_{\text{adv}} - \theta_{\text{rec}}$) are taken as indicators of a high PDMS surface area fraction.^{8,9} The wettability of the films depends on the molecular weight of PDMS macromonomer and the initial weight fraction of MeTEOS. Results for 26 × 10² and 43.6 × 10³ PDMS(OH)₂ are similar, with θ_{adv} decreasing, θ_{rec} increasing, and

Table 1 Contact angles (deg) of networks from PDMS(OH)₂ and MeTEOS

PDMS(OH) ₂ (MW)	MeTEOS (initial wt%)	θ_{adv}	θ_{rec}	θ_{Δ}
26 × 10 ³	15.6	115 ± 1	92 ± 2	23 ± 3
26 × 10 ³	25	109 ± 2	93 ± 1	16 ± 3
26 × 10 ³	40	104 ± 2	95 ± 1	9 ± 3
43.6 × 10 ³	15.6	113 ± 2	91 ± 1	22 ± 3
43.6 × 10 ³	25	108 ± 2	93 ± 1	15 ± 3
43.6 × 10 ³	40	103 ± 1	95 ± 1	8 ± 2
58 × 10 ³	25	108 ± 3	81 ± 1	27 ± 4
58 × 10 ³	40	114 ± 1	88 ± 1	26 ± 2
58 × 10 ³	58.5	104 ± 3	88 ± 1	16 ± 4

hysteresis therefore decreasing with increasing weight percentage of initial MeTEOS. For 58×10^3 PDMS(OH)₂ the results are less systematic, and hysteresis and receding contact angles are not as good as those achieved by using lower-MW PDMS(OH)₂.

A set of samples based on 43.6×10^3 PDMS(OH)₂ cured with 25% MeTEOS was used to investigate the effect on surface properties of immersion in a salt solution. Contact angles as a function of immersion time are shown in Table 2. Within experimental error, the surface tension for the 0.5 M NaCl solution (72.5 dyne cm⁻¹) is the same as the surface tension for water (72.5 dyne cm⁻¹), while the surface tension for the 5 mM NaN₃ solution is about 4% lower (69.8 dyne cm⁻¹). Contact angles for water on the 43.6×10^3 PDMS/25% MeTEOS material just before immersion in the NaCl or NaN₃ solutions were $\theta_{adv} = 106^\circ$ and $\theta_{rec} = 96^\circ$. (These values are slightly different from those listed in Table 1 and may reflect the fact that these samples had been

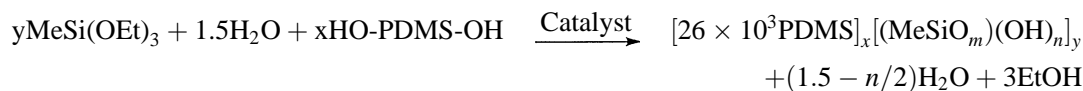
Surface roughness is known to increase advancing and decrease receding contact angles^{8,9}. The first stage of this process may be a kind of nano-swelling caused by the interaction of water with near-surface siliceous domains. The use of a salt solution, particularly NaN₃, as a probing liquid causes somewhat greater changes in receding contact angles than the use of water as a probing liquid.

Kinetics for reactions using methyltriethoxysilane

The kinetics of network formation of the PDMS(OH)₂/MeTEOS system was investigated. The variables examined included the ratio of reactants, the concentration of catalyst and the surface-to-volume ratio of the reactants. Effects of these factors were observed before and after gelation.

Network formation is illustrated in Eqn [1] using 26×10^3 PDMS and MeTEOS as starting materials.

The formula for the product shows the molecular



kept in air for four weeks before the immersion. The effect of cure time on contact angles is discussed in a separate section of this paper (see Fig. 3.) When the 5 mM NaN₃ solution was used as the probing liquid, the contact angles were $\theta_{adv} = 107^\circ$ and $\theta_{rec} = 95^\circ$ before immersion. In comparison, when 0.5 M NaCl solution was used the contact angles were $\theta_{adv} = 106^\circ$ and $\theta_{rec} = 88^\circ$.

Data in the upper portion of Table 2 are for samples which were aged in NaCl solution. The sample was removed and θ_{adv} and θ_{rec} were evaluated with water as a probing liquid (data on left-hand side) and the salt solution (data on right-hand side). The corresponding data for aging in a 5 mM NaN₃ solution are shown in the lower portion of Table 2. During the immersion, there was an increase in θ_{adv} for all probing liquids of about 4–7° and a decrease in θ_{rec} of 2–8°.

The observed decrease in θ_{rec} for water during immersion and the accompanying increase in hysteresis are interpreted in terms of a combination of increasing surface roughness, increasing hydrophilic character due to hydrolysis and the expression of hydrophilic sites at the surface. Surface roughness was not evaluated for these samples, but mass loss during water immersion of samples cured in a similar manner was observed (*vide infra*).

weight of the PDMS macromonomer and the ratio of PDMS to MeSD in terms of subscripts x and y . Water is consumed in hydrolysis and produced in condensation, and $2m + n = 3$. Equation [1] ignores water produced by the crosslinking reaction, i.e. condensation of PDMS(OH)₂ with any methylsilyl hydroxy- or alkoxy-containing species. This is a good approximation for networks with a high-MeSD fraction. The ratio of m to n , i.e. of Si–O to Si–OH in the MeSD, has two limits: considering only hydrolysis, $n = 3$ ($m = 0$), the MeSD would be methylsilicic acid-like [MeSi(OH)₃], while at the other limit, $m = 1.5$ and the MeSD is MeSiO_{1.5}. ²⁹Si NMR spectroscopy (*vide infra*) suggests that the stoichiometry of the MeTEOS/PDMS compositions is at an intermediate level. In terms of mass loss, ethanol dominates mass-wise the volatile reaction products, the ratio of m to n is a second-order consideration, and weighing the reactant mixture proves to be a convenient means of following the reaction. The short residence time of ethanol in PDMS (hours) compared with long cure time (weeks) justifies following cure by monitoring the mass loss of ethanol. (To determine the residence time of ethanol in a PDMS matrix, a mixture of ethanol (16 wt%) in PDMS (8000 cS) was prepared in a 50 ml beaker, and the mass loss of the mixture

Table 2 Effects of immersion on surface properties of self-reinforced networks: contact angles (deg) as a function of time^a

Time (days)	Immersed in 0.5 M NaCl solution				Immersed in 0.005 M NaN ₃ solution			
	Probing liquid = water		Probing liquid = 0.5 M NaCl soln.		Probing liquid = water		Probing liquid = 0.005 M NaN ₃ soln	
	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}
0	106	95	106	88	106	97	107	95
2	110	93	108	91	112	95	108	88
6	111	93	111	91	114	93	109	87
9	112	93	113	92	114	93	112	89
22	113	93	110	85	113	91	112	87

^a The values shown are the average of two runs.

was monitored. The mass loss process is first order with respect to ethanol concentration. Thus, the residence time of ethanol in a PDMS matrix is on the order of hours at most, and is independent of concentration.) Related work suggests that residence time is little affected by the increasing viscosity of the matrix. (The diffusion of a tracer out of a high-molecular-weight polymer is only slightly faster than the diffusion of the same tracer out of a network of the same polymer; see, for example Ref¹⁰.)

Water is shown twice in Eqn [1] to emphasize its role in hydrolysis and as a product of condensation. The net water used and produced is zero if the reaction proceeds to completion ($m = 1.5$).

Gel time

Gel time was determined empirically as the

moment when there was no observable flow of the reactants following an inversion of the vessel. Gelation has been investigated phenomenologically as well as theoretically.¹¹ By the phenomenological approach viscosity is followed as a function of time; Fig. 1 shows a plot for a typical system, 66.0% PDMS(OH)₂, 33.0% MeTEOS and 1.0% dibutyltin dilaurate, in air at ambient temperature, in a 10 ml vial (i.d. 1.89 cm) stirred with a spindle (No. 7 Brookfield). The viscosity increased slowly in the first 600 min, then rapidly at about 630 min. This pattern of rapid increase in viscosity at the gel point is usual for thermosetting systems, but the actual gel time depends on variables such as the relative weight-fraction of reactants and processing conditions. For example, when stirred magnetically the same system described above displayed a gel time of about 100 min.

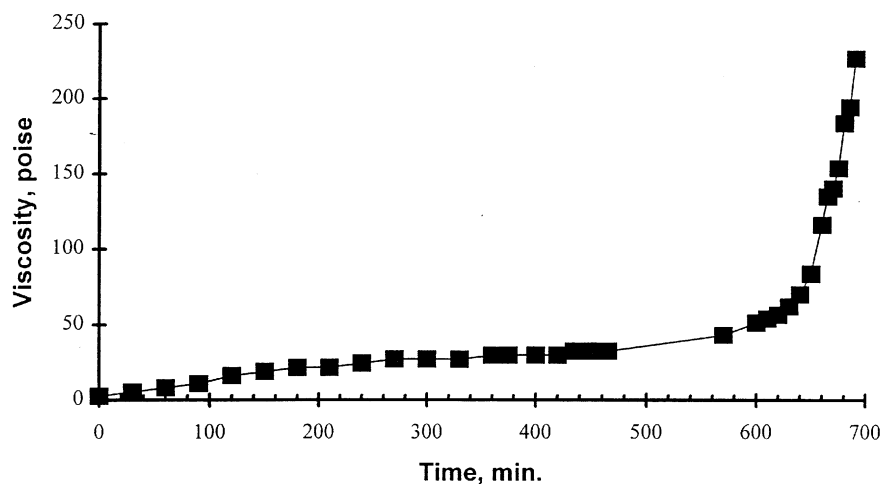


Figure 1 Viscosity as a function of time before gelation. The system, comprising 66.0% PDMS(OH)₂, 33.0% MeTEOS and 1.0% DBTDL in a 10 ml vial was stirred with a No. 7 spindle (Brookfield viscometer).

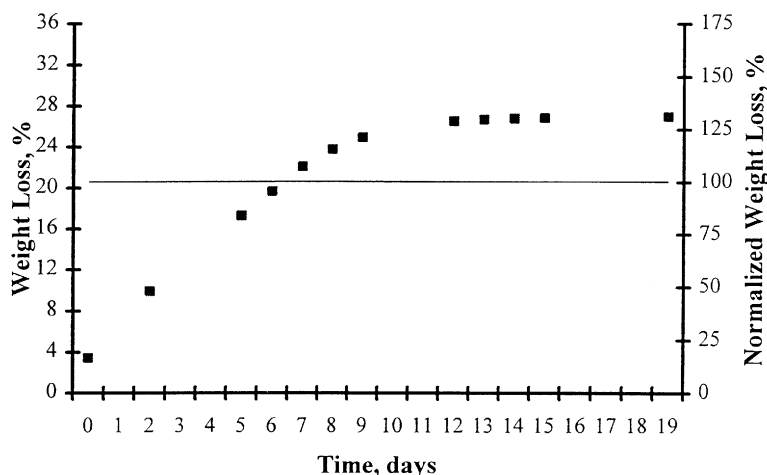


Figure 2 Mass loss as a function of time for the system comprising 65.9 %PDMS(OH)₂, 33.1 % MeTEOS and 1.0 % DBTDL, in a 10 ml vial, magnetically stirred. Weight is expressed as a percentage of the total weight of reactants. The scale on the right shows values normalized with respect to the theoretical maximum loss as ethanol.

Kinetic Study on 26×10^3 PDMS(OH)₂-MeTEOS: mass loss

For kinetic study, a representative composition consisting of 65.9 wt% 26×10^3 PDMS(OH)₂, 33.1 wt% MeTEOS and 1.0 wt% DBTDL was allowed to react in a 10 ml vial stirred magnetically at room temperature. The gel time was 100 min. The mass loss as a function of time is shown in Fig. 2. A calculated mass loss was determined on the basis of Eqn [1], assuming that the siliceous domain had the stoichiometry MeSiO_{1.5}. With this assumption, the calculated net loss of mass is 20.6% of the initial weight of reactants, as indicated by the horizontal line in Fig. 2. The scale on the right of Fig. 2 shows the measured mass loss normalized with respect to the calculated maximum. (A good first approximation is to assume the mass loss during the cure is totally in the form of ethanol, thus the ratio between the current loss and the calculated maximum gives the extent of reaction). The time of gelation is represented by day 0 in Fig. 2. The mass loss increases steadily for about one week after gelation, then the rate of increase drops gradually and levels off after about two weeks. The total mass loss at two weeks was 26.6%, which exceeded the calculated value of 20.6%, indicating that either MeTEOS or some volatile siloxane material, or both, were also lost from the system during cure.

The 26×10^3 PDMS(OH)₂ used in this study contains about 8 wt% low-molecular-weight spe-

cies, most of which can be removed by extraction with acetone (T. Ho and K. J. Wynne, unpublished results). In an attempt to detect volatile species in PDMS(OH)₂, only 0.3% mass loss was detected under ambient temperature and pressure after two weeks. The contribution from the PDMS starting material to excess mass loss is therefore negligible.

The excess mass loss is due to volatility of MeTEOS and the weight fraction of the siliceous domain in the hybrid network is reduced accordingly. The mass loss measurements indicate the ratio of actual (8.9%) to calculated (15.7%) mass of siliceous domain is 0.57. If the presence of SiOH is neglected, the stoichiometry of this material is $[26 \times 10^3 \text{ PDMS}] [(\text{MeSiO}_{1.5})_{37.9}]$.

Solid-state ²⁹Si NMR spectroscopy

A PDMS-MeTEOS sample was prepared for solid-state ²⁹Si MAS NMR spectroscopy in order to determine composition by a method independent of mass loss. The initial composition was 67.1 wt% 26×10^3 PDMS(OH)₂, 31.8 wt% MeTEOS and 1.0 wt% DBTDL. An intense, narrow peak at -22.3 ppm is due to silicon atoms in the PDMS domain. A peak at -67.2 ppm is assigned to silicon atoms in the MeSD (A peak at -72.7 ppm is an MAS sideband associated with the -22.3 ppm peak for the PDMS phase). In prior work on MeTEOS-based gels peaks have been assigned in the range 62-64 ppm to T³ (MeSiO₃) and at 53-57 ppm to T²

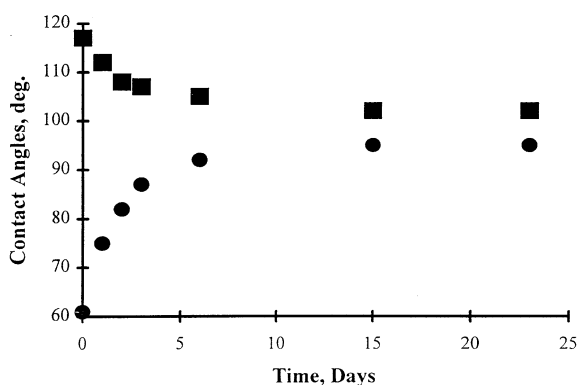


Figure 3 Advancing and receding contact angles of water on a film during cure for the system comprising 65.9% PDMS(OH)₂, 33.1% MeTEOS and 1.0% DBTDL. ■ θ_{adv} (advancing); ● (θ_{rec} (receding)).

[MeSiO₂(OH)]¹². The weak intensity of the peak we observe does not allow an unambiguous assignment (T² vs T³), but it is clear from the irregular shape of this peak that multiple species are present.

Integrating the intensity of these peaks gives a ratio of 20:1 for Si_{PDMS}:Si_{MeSD}. Without volatilization of MeTEOS a ratio of 10:6:1 is calculated. The NMR measurements indicate the ratio of actual (4.5%) to calculated (15.4%) mass of siliceous domain is 0.29. If the presence of SiOH is neglected, the stoichiometry of this material is [26 × 10³ PDMS] [(MeSiO_{1.5})]_{19.4}. The ²⁹Si MAS NMR data confirm the high evaporative mass loss of MeTEOS and suggest that the MeSD is composed of T² and T⁵ species.

Kinetic study on 26 × 10³ PDMS(OH)₂–MeTEOS: contact angles

Contact angles for water on this material during cure as a function of time are shown in Fig. 3. The

change in contact angles shows a pattern parallel to the change in weight, i.e. a faster rate of change occurs in the first week, then a slower rate of change, and finally a leveling off to a final value. As for all thermosets, a characteristic of PDMS hybrid networks is the continuance of crosslinking after gel formation.¹³ The increase in the extent of reaction reduces the mobility of the gel constituents, i.e. the PDMS chains and the siliceous domains. The reduction in mobility at the molecular level enhances the stability of the morphology which favors PDMS chains at the surface. This accounts for the rather large increase of *ca* 35° in θ_{rec} during cure (Fig. 3). The small decrease (*ca* 10°) in θ_{adv} during cure is opposite to the change expected. A decrease in surface roughness may account for this observation.

Effects of catalyst concentration

Effects of catalyst concentration on the kinetics of curing are summarized in Table 3. With catalyst concentration above 0.5 wt%, the mass loss leveled off after 10 days with a total mass loss of 29.0%. With catalyst concentration below 0.5 wt%, the mass loss leveled off after 18 days with a total mass loss of 30.5%. Thus, the gel time and mass loss increase as the catalyst concentration decreases, while the rate of cure decreases with decreased catalyst concentration.

Effects of reactant ratios

When the reactant ratio was changed from 65.9% PDMS(OH)₂ and 33.1% MeTEOS to 83.1% PDMS(OH)₂ and 15.9% MeTEOS (both with 1% DBTDL catalyst) the gel time increased from 100 min to 270 min. As shown in Fig. 4 for 83.1% PDMS and 15.9% MeTEOS, mass loss is rapid in the first three days, then much slower. The total mass loss was 15.5%. The ratio of the weight fraction of siliceous domain in this network

Table 3 Effects of catalyst concentration on the kinetics of the reactions

	Run 1	Run 2	Run 3	Run 4
DPMS(OH) ₂ (wt%)	66.63	66.56	66.33	66.11
MeTEOS (wt%)	33.25	33.21	33.10	32.99
DBTDL (wt%)	0.12	0.23	0.57	0.90
Gel time (min)	250	200	150	120
Mass loss (%)				
At gelation	5.77	4.09	2.78	1.90
At 3 days	24.44	24.06	24.73	24.63
At 10 days	30.52	30.12	28.94	28.97
At 11 days	30.58	30.19	28.97	28.98
At 18 days	30.74	30.37	—	—

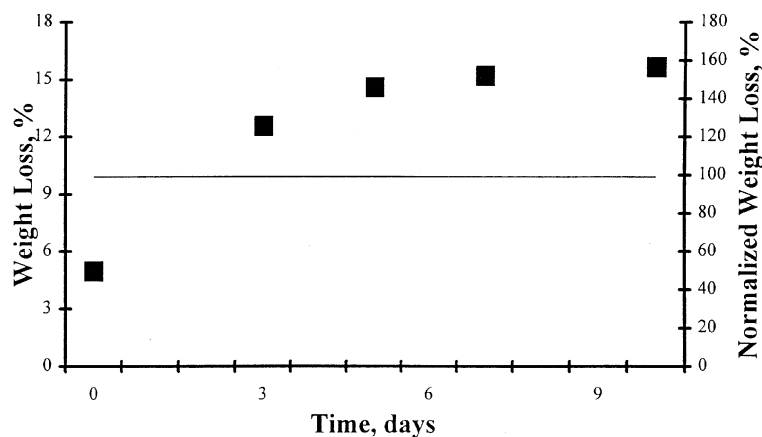


Figure 4 Mass loss as a function of time for the system, comprising 83.1% PDMS(OH)₂, 15.9% MeTEOS and 1.0% DBTDL, in a 10 ml vial, magnetically stirred. Weight is expressed as a percentage of the total weight of reactants. The scale on the right shows values normalized with respect to the calculated loss as ethanol.

(0.47%) to the calculated value (6.7%) is 0.07, compared with 0.57 for 65.9% PDMS(OH)₂ and 33.1% MeTEOS. A similar reduction in mass fraction of siliceous domain was observed when the concentration of the catalyst was 0.1 wt%. Compared with 66.5% PDMS(OH)₂ and 33.4% MeTEOS, a 82.5%–17.4% system showed a longer gel time (140 h vs 4.2 h) and a lower efficiency in forming siliceous domains (the ratios for the actual

to the calculated weight fractions for the siliceous domain were less than 0.01 and 0.11, respectively).

Effects of free surface area

When the reaction vessel was changed from a 10 ml vial to a 50 ml beaker, the free surface increased by a factor of 2.3, and more vigorous stirring was possible with a larger stir bar. The reaction was carried out with 61.5% PDMS(OH)₂, 37.6%

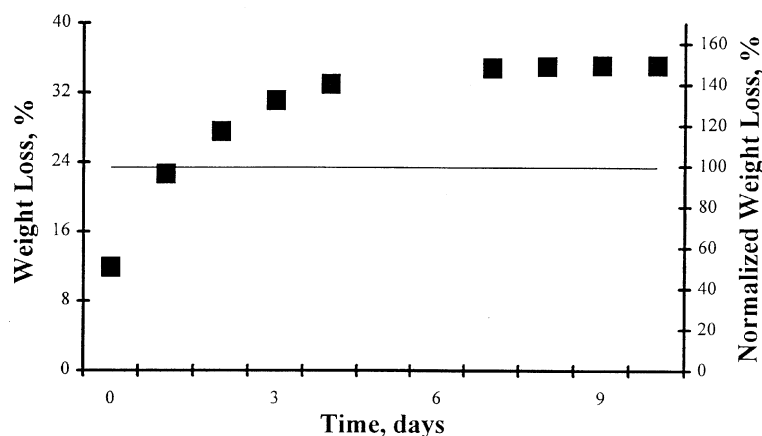


Figure 5 Mass loss as a function of time for the system comprising 61.5%PDMS(OH)₂, 37.6% MeTEOS, and 0.9% DBTDL, in a 50 ml beaker, magnetically stirred. Weight is expressed as a percentage of the total weight of reactants. The scale on the right shows values normalized with respect to the theoretical maximum loss as ethanol.

MeTEOS and 0.9% DBTDL, and the mass loss is shown as a function of time in Fig. 5. The gel time was 90 min. The mass loss at gelation was 11.8%. The mass loss increased rapidly in the first four days, then gradually leveled off after six days. The final mass loss was 35.0%, and the ratio of the actual weight fraction of siliceous domain to the calculated value was 0.22 (i.e. 4.0 wt% siliceous domain vs 18.5% calculated). Thus, the larger free surface and more vigorous stirring enhanced the rate of evaporation of MeTEOS, causing lower efficiency in forming a siliceous phase, and a faster rate of mass loss.

In summary, rapid gelation and low MeTEOS loss are favored by the use of a high MeTEOS concentration and a high catalyst concentration and the reduction of free surface area for the reactants in conjunction with faster stirring. With optimized conditions, the gel time (less than 2 h) is satisfactory and the efficiency in converting MeTEOS to a siliceous domain is 0.57.

Mechanical strength

Young's modulus was evaluated for films prepared with 65.9% 26×10^3 PDMS(OH)₂ and 33.1% MeTEOS. The cured material contained 8.9% siliceous domain and exhibited a modulus of 0.7 MPa and a strain-to-break of $150 \pm 40\%$. The corresponding value for a commercial RTV (GE RTV 11), which contains *ca* 30% CaCO₃ filler, is 1.8 MPa and $212 \pm 8\%$ (both obtained with $0.7 \text{ mm} \times 5 \text{ mm} \times 17 \text{ mm}$ strips at a strain rate 0.5 min^{-1}). Thus, the mechanical strength of the PDMS–MeTEOS materials is modest.

Stability in water

The stability in water of a network prepared using 65.9% 26×10^3 PDMS(OH)₂, 33.1% MeTEOS and 1% dibutyltin dilaurate was evaluated by immersing a thick film in nanopure water and periodically monitoring the mass of the sample. The rate of mass loss was 2% per week. Another sample with a similar starting composition but lower catalyst concentration (0.3%) exhibited a rate of mass loss of 1% per week. The suprisingly high rates of weight loss for these materials has shifted our attention to networks utilizing a different silicicous-phase precursor.

CONCLUSIONS

Polydimethylsiloxane (PDMS) hybrid networks have been prepared by the reaction of PDMS(OH)₂ and MeTEOS using a dibutyltin dilaurate or dibutyltin diacetate catalyst. Initial studies of wettability as measured by contact angles ($\theta_{\text{adv}} = 106^\circ$ and $\theta_{\text{rec}} = 96^\circ$) were encouraging. Kinetic studies showed the reaction rate is dependent on catalyst concentration and on processing conditions. However, evaporative loss of MeTEOS is a major problem under the water-sparse conditions used in preparation of films. This evaporative loss leads to a low MeSD content in films which compromises mechanical properties. Future work is aimed at control of SD composition using alkoxy-silanes which are far less volatile.¹⁴

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