Reinforcement of Poly(dimethylsiloxane) Elastomers by Chain-End Anchoring to Clay Particles

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Received February 17, 1999; Revised Manuscript Received July 12, 1999

ABSTRACT: Difunctional hydroxyl-terminated and vinyl-terminated poly(dimethylsiloxane) (PDMS) precursors with similar molecular weight distributions were used to synthesize end-linked networks in bulk with appropriate tetrafunctional cross-linkers. Composite PDMS elastomers from the same precursors were also synthesized with low concentrations of montmorillonite nanosize clay particles. For unfilled networks, larger amounts of tetraethyl orthosilicate (TEOS) cross-linkers than conventionally used led to optimal networks with higher moduli and lower soluble fractions. In the montmorillonite−PDMS elastomeric composites, enhancement of the modulus was obtained only for nonoptimal networks formed with the hydroxyl-terminated precursor chains but not with the vinyl-terminated chains. These results indicate that the reinforcement in these elastomers can be attributed to the anchoring of the hydroxyl end group to the silicate filler that dramatically reduces the soluble fraction and binds pendent chain ends. The modulus of the optimal networks could not be enhanced by clay reinforcement.

Introduction

Networks synthesized with the stoichiometrically required ratio ($r = 1$) of ethoxy groups in tetrafunctional alkoxysilane cross-linkers to hydroxyl chain ends of hydroxyl-terminated poly(dimethylsiloxane) (PDMS) precursor chains are conventionally regarded as model networks. The cross-linking reaction involved here is that of an alkoxy-functional condensation reaction using a tin catalyst.[1] The networks prepared at or near stoichiometric conditions have a molecular weight between cross-links, M_c, as deduced from modulus measurements, close to the number-average molecular weight of precursor chains, M_n.[2,3] However, these networks still have 5% or greater of soluble fraction, which implies they still contain a significant amount of defects or pendent chains not contributing to their elastic properties. Another cross-linking system used to synthesize PDMS networks is the hydrosilylation reaction of vinyl-terminated PDMS end-linked with tetrafunctional hydridosilane using a platinum catalyst.[1] We have previously shown that optimal networks of this type were obtained using a ratio of cross-linker functions to chain ends much greater than required by stoichiometry ($r_{opt} = 1.7$).[4,5] This may be due in part to a side reaction that consumes the cross-linkers[6] and to kinetic limitations to achieve a high extent of reaction at the lower values of r.[7] The optimal networks formed at r_{opt} have smaller soluble fractions (typically smaller than 1%), higher modulus, and minimum swelling in good solvents. To our knowledge, no systematic study of the effect of r on the properties of networks synthesized from OH-terminated chains cross-linked with TEOS has been performed. In a limited study,[8] it has been shown that use of double the stoichiometric amount of cross-linker ($r = 2$) led to a smaller soluble fraction; however, the effect on the mechanical and swelling properties of the networks was not investigated.

PDMS networks are often used in practice with fillers such as silica particles to enhance their elastic properties or thermal stability.[1] The fillers have a large surface area where polymer chains adsorb chemically or physically. Recently developed fillers such as in-situ precipitated silica[9] and exfoliated (or delaminated) silicate[10] showed appreciable modulus enhancement (reinforcement) at much smaller volume ratio, ϕ, of filler to polymer than conventional fillers. For example, swelling in a good solvent was reduced to 60% its original value when a network was filled with montmorillonite clay particles at ϕ values as low as 1−4%.[10] Because of the inverse relation between swelling and modulus, this represents an appreciable reduction of the amount of fillers needed for these types of nanosize particles in comparison to conventional fillers to achieve a certain level of reinforcement. The great ability of reinforcement of the in situ precipitated silica and that of the exfoliated silicate is attributed to their large surface-to-volume ratio. A polymer/filler interface is believed to consist of chemisorbed and/or physisorbed polymer chains on the surface of the filler. The adsorption is affected by the chemical and physical structures of the polymer molecules and those of the surface of the filler. In the case of silica or silicate reinforced PDMS elastomers, the exact nature of the surface interaction leading to reinforcement is still unclear.

In this work, effects of network imperfections and of precursor chain ends on clay reinforcement of PDMS networks are investigated. Both commercial polydisperse PDMS and anionically synthesized hydroxyl-terminated and vinyl-terminated PDMS are used with a broad range of cross-linker-to-precursor ratios.

Experimental Section

Materials. Four kinds of PDMS precursor chains were used: commercially available hydroxyl-terminated as well as vinyl-terminated polydisperse PDMS and anionically synthesized lower polydispersity PDMS with both type of chain ends. The commercial precursors were products of Gelest, Inc., and were used as received. The precursors were characterized using gel permeation chromatography (GPC), and the calibration parameters obtained by Lapp et al.[11] were used. The molecular weight and the polydispersity index of the four kinds of precursor chains used are listed in Table 1.

The synthesized precursor chains were prepared by polymerizing hexamethylcyclotrisiloxane (D_3) in toluene, using water as an initiator, dimethyl sulfoxide (DMSO) as a pro-

10.1021/ma990218+ CCC: $18.00

Table 1. Characteristics of PDMS Precursors Used in Network Syntheses

end group	source	M_n (g/mol)	PDI
hydroxyl	commercial	20.0K	1.98
hydroxyl	anionic	17.7K	1.30
vinyl	commercial	18.6K	1.97
vinyl	anionic	18.4K	1.29

moter, and benzyltrimethylammonium bis(*o*-phenylenedioxy)-phenylsiliconate as a catalyst.[5] After polymerization, a batch was separated into two portions. One portion was cooled in an ice bath and washed with deionized water to be hydroxyl-end-capped; the other portion was vinyl-end-capped by addition of vinyldimethylchlorosilane. The end-capped precursors were dissolved and reprecipitated with toluene and methanol and then dried in a vacuum oven at 60 °C for 3 days. By this method, hydroxyl-terminated and vinyl-terminated PDMS precursors with almost identical molecular weight distribution were obtained.

For experiments of filled PDMS networks, montmorillonite (SO4682, Southern Clay), modified by ion-exchanging the sodium ions of Na^+−montomorillonite with dimethyl ditallow ammonium bromide,[10,12] was used as fillers. A single silicate layer has a size of 1 nm in thickness and 100−1000 nm in length and width when exfoliated.

Synthesis of Unfilled PDMS Networks. Two series of hydroxyl-terminated PDMS networks were synthesized in the bulk using tetraethyl orthosilicate (TEOS) as a cross-linker. One series of networks was synthesized using the commercial PDMS with *r* varying from near stoichiometry to large excess ($r = 0.9-16.7$) and the other using the anionically synthesized PDMS with *r* varying from 1.0 to 10. Stannous 2-ethylhexanoate was carefully measured and added as a catalyst in the extent of 0.6 g/100 g of chains. A third series of networks was also synthesized with the commercial PDMS using the catalyst in the extent of 1.2 g/100 g of chains to determine the effects of catalyst concentration. The well-stirred mixture of PDMS, TEOS, and catalyst was allowed to cure at 35 °C under vacuum in a polypropylene vial for at least 24 h.

To compare networks prepared from hydroxyl-terminated chains with networks prepared from vinyl-terminated chains, a model network was prepared from the anionically synthesized vinyl-terminated precursor chains following the method of Patel et al.[4] The model network was synthesized in the bulk using tetrakis(dimethylsiloxy)silane (A_4) as a cross-linker with $r_{opt} = 1.7$. The mixture of precursors and A_4 was rotated overnight. A 0.0022 g sample of *cis*-dichlorobis(diethyl sulfide)-platinum(II) was dissolved in 1 g of toluene and added as a catalyst in the extent of 20 μL/g of chains. The well-stirred mixture of PDMS, A_4, and the platinum catalyst was allowed to cure at 35 °C under vacuum in a polypropylene vial for 72 h.

Synthesis of Filled PDMS Networks. The modified montmorillonite silicate clay was mixed with the polymer before cross-linking to prepare a nanocomposite mixture. In a polypropylene vial, the silicate and a small amount of dispersing aid to be discussed below were added to the PDMS precursors and stirred gently. The volume fraction of the silicate was varied from 0 to 1%. When the volume fraction of the silicate was increased beyond 1%, phase separation occurred, and at even higher concentration, the polymer did not cross-link. Burnside and Gianellis[10] reported results for up to 5% in silicate but show a leveling off of property enhancement for filler content above 1%. Distilled water was added as a dispersing aid in the case of hydroxyl-terminated PDMS. Attempted network synthesis using just water as a dispersing aid was unsuccessful for vinyl-terminated PDMS. In this case, a buffer solution (pH = 7) was used instead of water because the addition of water to the ammonium group in the silicate creates a basic condition suspected to prevent the hydrosilylation cross-linking reaction from occurring.[13] The amount of the dispersing aid was 0.5−1.0 wt % of the silicate amount. This is known to give the best condition for exfoliation.[12] The mixture was sonicated for 2 min with an ultrasound probe (Sonics and Materials VibraCell). After sonication, the cross-linker and the catalyst were added to the polymer−silicate mixture. The whole mixture was mechanically stirred and then cured. The ratio of cross-linker functions to chain ends was varied over a wide range.

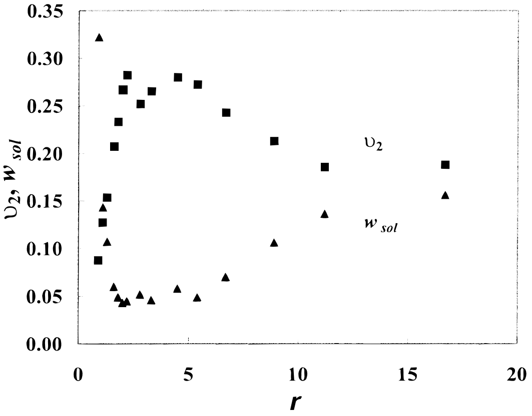


Figure 1. Plot of polymer volume fraction υ_2 (■) and soluble fraction w_{sol} (▲) versus *r* of networks from hydroxyl-terminated PDMS using commercial precursors (PDI = 1.98) with a tin catalyst at 0.6 g per 100 g of chains.

Swelling Experiments. The weight of PDMS network samples, m_{unex}, was measured before swelling. The networks were allowed to swell for 3 days in toluene with daily change of toluene to permit maximum soluble components extraction. The samples were then put in a series of methanol/toluene mixture to deswell with increasing methanol ratio. They were then dried in a vacuum oven, and their weight after extraction, m_{ex}, was measured. The soluble fraction w_{sol} was calculated by the equation

$$w_{sol} = \frac{m_{unex} - m_{ex}}{m_{unex}} \qquad (1)$$

The networks were then left in toluene to reswell to reach equilibrium swelling, and their swollen weight, m_s, was recorded. The polymer volume fraction in the swollen networks υ_2 was calculated by the equation

$$\upsilon_2 = \left[1 + \left(\frac{m_s - m_{ex}}{m_{ex}}\right)\left(\frac{\rho_2}{\rho_1}\right)\right]^{-1} \qquad (2)$$

Here ρ_1 and ρ_2 are the densities of the solvent and of the polymer, respectively.

Mechanical Experiments. The elastic modulus of PDMS networks at small deformation was investigated. Young's modulus was measured with a dynamic mechanical analyzer (DMA). A Perkin-Elmer system 7e dynamic mechanical analyzer was used in this work. Young's modulus was measured at room temperature. The instrument was operated in the extension mode at small strains of 0.5−1% and in the temperature range 20−60 °C. The modulus of each sample was constant and independent of strain in these ranges.

Results and Discussion

Unfilled Networks. The values of υ_2 and w_{sol} for networks from hydroxyl-terminated precursors are plotted versus *r* in Figures 1 and 2. As expected, there is a close correlation between the values of υ_2 and w_{sol}. The smaller w_{sol} is, the greater υ_2 is for each series of networks. In each case, networks synthesized around stoichiometry had quite high soluble fractions. Increasing *r* from unity drastically decreased w_{sol} and increased υ_2.

In the networks made of fairly polydisperse commercial PDMS (Figure 1), the maximum υ_2 (0.28) and

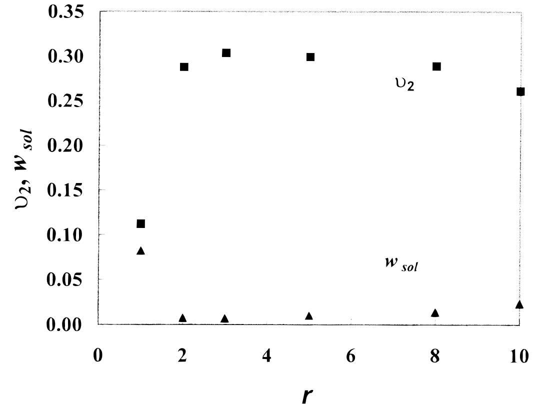


Figure 2. Plot of v_2 (■) and w_{sol} (◆) versus r of networks from hydroxyl-terminated PDMS using anionically synthesized precursors (PDI = 1.30) with a tin catalyst at 0.6 g per 100 g of chains.

Table 2. Soluble Fraction and Swelling of Hydroxyl-Terminated PDMS Networks

			v_2	
M_n (g/mol)	r	w_{sol} (%)	in toluene	in benzene
20.0K (commercial)	2.2	4.5	0.28	0.32
17.7K (anionic)	3.0	0.7	0.30	0.34
18.5K[a]	1.0	6.0		0.23
18.5K[b]	1.0	7.4		0.21

[a] Data from ref 2. [b] Data from ref 3.

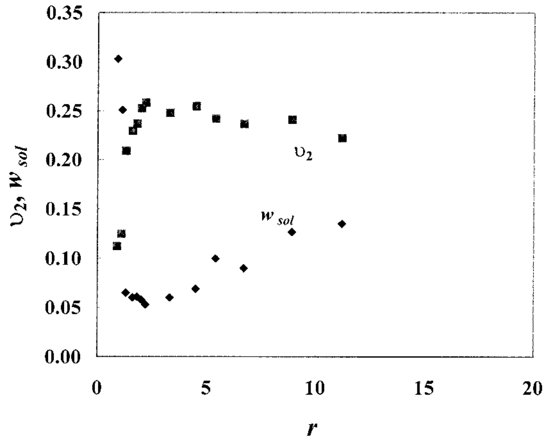
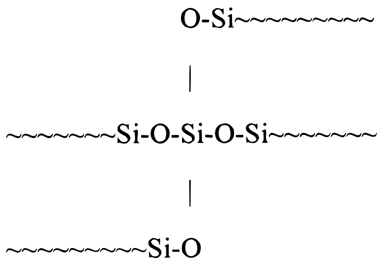


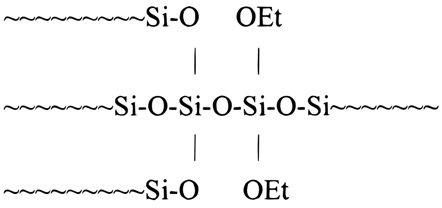
Figure 3. Plot of v_2 (■) and w_{sol} (◆) versus r of networks from hydroxyl-terminated PDMS using commercial precursors (PDI = 1.98) with a tin catalyst at 1.2 g per 100 g of chains.

the minimum w_{sol} (4.5%) listed in Table 2 were obtained around $r = 2-4$. Though using the catalyst in the extent of 1.2 g/100 g of chains rather than 0.6 g/100 g increased v_2 slightly around $r = 1$, it led to greater values for the minimum w_{sol} and a decreased maximum for v_2 between $r = 2$ and 6 (Figure 3). Tests showed that using the catalyst in the extent of 0.3 g/100 g of chains did not lead to network formation. Thus, the catalyst in the extent of 0.6 g catalyst per 100 g of chains was used thereafter. Increasing the value of r beyond 5 gradually decreased v_2. As seen in Figure 1, there is an apparent plateau in the values of v_2 between $r = 2$ and 5 with a steep slope below $r = 2$ and a gentle slope for $r > 5$. A similar curve of v_2 versus r (Figure 2) was obtained for the networks made from the anionically synthesized PDMS with a narrower molecular weight distribution. We note that for these networks minimum soluble factions of less than 1% are obtained, and higher values of v_2 are achieved. Also, the plateau of optimal networks as a function of r is much wider. These results are quite different from those for networks from vinyl-terminated PDMS synthesized by hydrosilylation which showed rather sharp peaks at around $r = 1.7$.[4,5] A probable explanation of this difference follows.

Scheme 1



Scheme 2



Three types of condensation reactions could be involved in the hydroxyl-terminated chain system:

$$\sim\sim Si(Me)_2OH + (EtO)_3SiEt \rightarrow \sim\sim Si(Me)_2OSi(OEt)_3 + EtOH \quad (3)$$

$$\sim\sim Si(Me)_2OH + \sim\sim Si(Me)_2OH \rightarrow \sim\sim SiOSi\sim\sim + H_2O \quad (4)$$

$$(EtO)_3SiOEt + (EtO)_3SiOEt \xrightarrow{H_2O} \equiv SiOSi\equiv + 2EtOH \quad (5)$$

Reaction 3 occurs between a hydroxyl group at a chain end and an ethoxy group of TEOS. This is regarded as the main reaction in this system which forms the matrix. In an ideal situation, all chains and stoichiometric amount of TEOS would be consumed to form a perfect network with junctions shown in Scheme 1 and ethoxy-terminated chains being formed as intermediates. Reactions 4 and 5 are likely side reactions. Chain polycondensation through reaction 4 reported in some research[14] is less likely to have occurred in this work due to relatively low temperature and in the presence of excess TEOS. An example of reaction 5 is the synthesis of silica gel from TEOS under acidic condition.[15] Similar polycondensation of pure TEOS was confirmed in our experiments under the same conditions of tin catalyst and room temperature. This implies that not only hydroxyl-terminated chains but also ethoxy-terminated chains can react with TEOS through a reaction similar to (5), thus incorporating additional TEOS as shown in Scheme 2.

The incorporation of excess TEOS in the network is confirmed from a mass balance of network formation in this work. For example, w_{sol} increased from 0.7% to 2.3% when r increased from 3 to 10 in the networks using anionically synthesized PDMS (Figure 2 and Table 3). The increase in w_{sol} (1.6%) is smaller than the

Table 3. Soluble Fraction and Swelling of Anionically Synthesized Hydroxyl-Terminated PDMS Networks

r	w_{sol} (%)	v_2 in toluene	r	w_{sol} (%)	v_2 in toluene
1.0	8.2	0.12	5.0	1.0	0.30
2.0	0.8	0.29	8.0	1.4	0.30
3.0	0.7	0.30	10.0	2.3	0.28

Table 4. Properties of Networks from Commercial Hydroxyl-Terminated PDMS

r	w_{sol} (%)	E' (Pa) $\times 10^{-5}$	$G_{e,corr}$ (Pa) $\times 10^{-5}$	v_2 in toluene
0.8	35.6	0.5	0.21	0.06
0.9	6.5	2.5	0.85	0.16
1.0	6.0	3.1	1.1	0.19
1.2	4.8	4.4	1.5	0.23
1.6	4.5	5.7	1.9	0.24
2.2	4.0	6.6	2.2	0.27
3.0	3.9	7.0	2.4	0.28
5.0		6.2		
10		5.9		
15	8.3	5.0	1.7	0.22

increase in TEOS (4.1%) in the formulation of the networks. Even though all precursor chain ends can be linked with TEOS, additional TEOS is incorporated in the network and does not become a part of the soluble materials. This explains the wide plateau followed by a gentle slope observed in Figure 2.

The r_{opt} giving maximum v_2 and minimum w_{sol} for the commercial PDMS is located beyond $r = 2$. This value is much greater than unity that has been conventionally regarded to form model networks. In other words, doubling the amount of cross-linker is necessary to achieve tighter networks. The primary cause for the need of this excess cross-linker must be the effective incorporation of TEOS in the network backbone as stipulated above. Backbone biting by excess TEOS is unlikely here because v_2 does not increase beyond the plateau value.

In the networks made of anionically synthesized PDMS, maximum v_2 (0.30) and minimum w_{sol} (0.7%) were obtained at, around, $r = 3$ as listed in the second row of Table 2. Here again r_{opt} is much larger than unity. The networks obtained at r_{opt} have minimal amount of inelastic pendent structures since w_{sol} is less than 1% and the degree of swelling is at a minimum. These networks can be regarded as the tightest model networks that can be produced with this molecular weight of precursor chains. The values of $v_2 = 0.30$ and $w_{sol} = 0.7\%$ are close to those of model networks obtained by hydrosilylation of the corresponding 18.4K vinyl-terminated PDMS precursors in this work ($v_2 = 0.27$ and $w_{sol} = 0.8\%$). These results are also similar to the results from previous work[4] using vinyl-terminated precursors of molecular weight 18.5K that led to a model network with $v_2 = 0.29$ and $w_{sol} = 0.3\%$.

The networks synthesized at r_{opt} were swollen also in benzene. As expected, the v_2 values in benzene are larger than in toluene (Table 2) because benzene is a worse solvent of PDMS than toluene.[4] The v_2 values of networks from the commercial PDMS as well as from the anionically synthesized PDMS are much larger than those of conventional networks with r around unity[2,3] listed in the third and the fourth rows of Table 2.

Data for the Young's modulus of a series of PDMS networks synthesized with the commercial hydroxyl-terminated chains are shown in the second column of Table 4 and are plotted as a function of r in Figure 4.

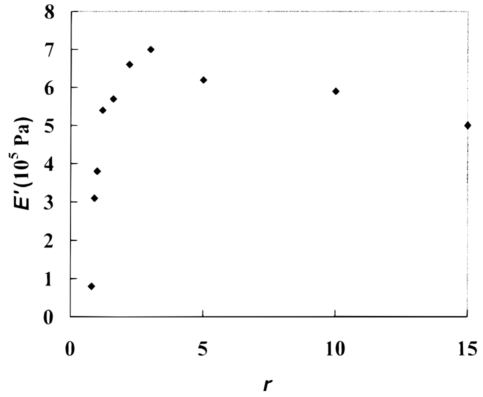


Figure 4. Plot of E' versus r of networks from the commercial hydroxyl-terminated PDMS.

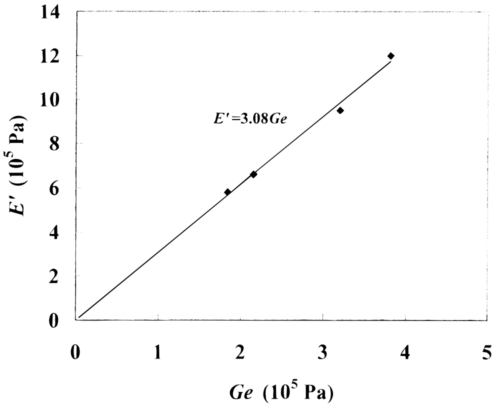


Figure 5. Plot of E' versus G_e of networks from the vinyl-terminated PDMS networks. The line represents a least-squares regression of the data points.

The network synthesized using $r = 3$ showed much greater modulus than the networks synthesized around stoichiometry. This result is consistent with the results of the swelling experiments. Because of the release of gases (such as EtOH) during the curing of these networks, networks cured between the parallel plates of rheometer will contain many gas bubbles. It was therefore impossible to obtain the shear modulus G' of these networks, and the Young's modulus was obtained on a mechanical spectrometer with samples cured open to the atmosphere to allow the release of the gas formed.

The Young's modulus E' is theoretically related to the shear modulus by the equation

$$E' = 2G'(1 + v) \tag{6}$$

Assuming a Poisson ratio v equal to 0.5, a value generally accepted for elastomers, one has[14]

$$E' = 3G' \tag{7}$$

A test for the validity of eq 7 was performed. The Young's modulus E' of vinyl-terminated PDMS networks with known G_e obtained on a Rheometrics RDAII were measured with a Perkin-Elmer DMA. A plot of E' measured on the DMA versus G_e obtained with the RDA is shown in Figure 5, and a slope of 3.08 was obtained by a least-squares regression. This is very consistent with the theoretical value of 3 in eq 7, and the Young's modulus data were converted into shear modulus using eq 7.

The modulus measurements were performed prior to the extraction of the soluble fraction. As the soluble

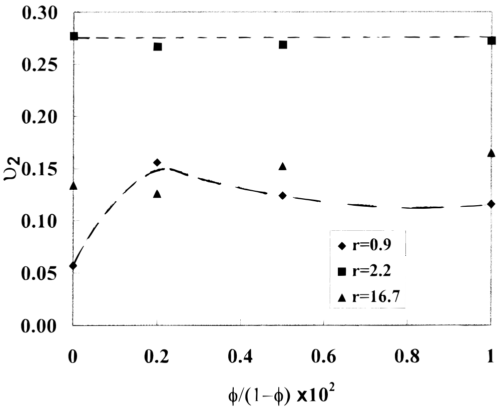


Figure 6. Plot of v_2 versus $\phi/(1 - \phi)$ of silicate-filled networks from hydroxyl-terminated PDMS using commercial precursors. The dashed lines are guides to the eye.

fraction decreases the value of the modulus, a small correction to obtain the modulus of the networks after extraction is necessary especially for imperfect networks with large soluble fractions. We calculated therefore a corrected value of the modulus of dry networks after extraction using the relation[17]

$$G_{\mathrm{e,corr}} = \frac{G_{\mathrm{e}}}{(1 - w_{\mathrm{sol}})^{1/3}} \qquad (8)$$

The results are given in the third column of Table 4. The modulus of the networks synthesized from hydroxyl-terminated chains at r_{opt} is close to that obtained for model networks from vinyl-terminated PDMS of similar molecular weight in this and previous works.

Filled Networks. The values of v_2 for four different series of networks are plotted versus $\phi/(1 - \phi)$ in Figures 6–9. The use of $\phi/(1 - \phi)$ rather than ϕ is to account for the small clay content in the networks. For the networks from commercial hydroxyl-terminated chains (Figure 6), the v_2 values increased when the networks were synthesized using $r < r_{\mathrm{opt}}$ and filled with the silicate. The increase reaches a maximum with as low an amount of silicate as $\phi = 0.2\%$. The structure of the silicates in the networks is likely to be a mixture of different amount of aggregated, intercalated, and exfoliated layers[10] with the optimum structure occurring at this very low concentration of silicates. For networks synthesized using $r = r_{\mathrm{opt}}$, on the other hand, the values of v_2 did not change upon the addition of the filler. When the networks were synthesized using $r > r_{\mathrm{opt}}$, v_2 exhibited a minor increase relative to that for networks synthesized using $r < r_{\mathrm{opt}}$. The same trend was observed for the networks from anionically synthesized hydroxyl-terminated chains (Figure 7). Most important, the values of v_2 of the filled imperfect networks never exceed those of unfilled optimal networks.

For the networks from commercial vinyl-terminated chains, the v_2 values did not change as ϕ increased regardless of the value of r used (Figure 8). For the networks from anionically synthesized vinyl-terminated chains (Figure 9), the v_2 values slightly increased as ϕ increased for the networks using $r < r_{\mathrm{opt}}$; however, the extent of the increase was marginal. The v_2 values decreased somewhat as ϕ increased for the networks using $r = r_{\mathrm{opt}}$. This might be due to lower homogeneity of the composites formed with vinyl-terminated chains compared to that of hydroxyl-terminated chains.

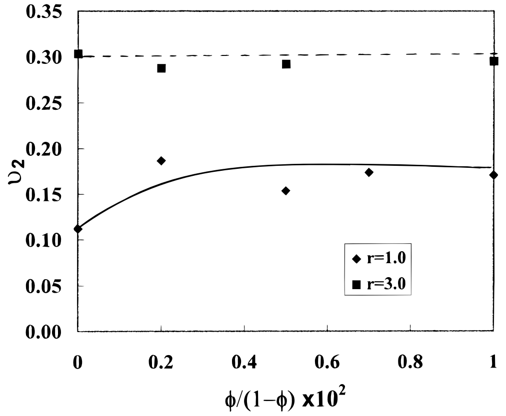


Figure 7. Plot of v_2 versus $\phi/(1 - \phi)$ of silicate-filled networks from hydroxyl-terminated PDMS using anionically synthesized precursors. The lines are guides to the eye.

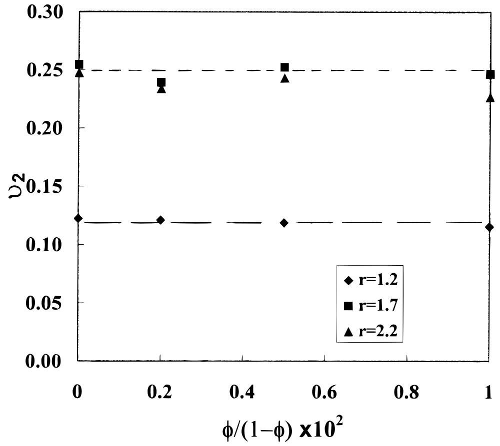


Figure 8. Plot of v_2 versus $\phi/(1 - \phi)$ of silicate-filled networks from vinyl-terminated PDMS using commercial precursors.

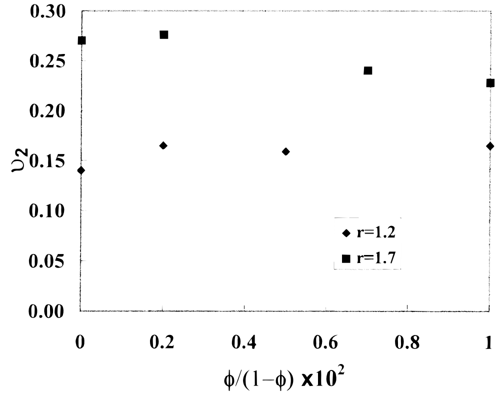


Figure 9. Plot of v_2 versus $\phi/(1 - \phi)$ of silicate-filled networks from vinyl-terminated PDMS using anionically synthesized precursors.

The swelling results are plotted in normalized form as $V_{\mathrm{o}}/V_{\mathrm{f}}$ of each series of networks versus $\phi/(1 - \phi)$ in Figure 10. Here, V_{o} is the polymer volume fraction in a swollen unfilled network, and V_{f} is the polymer volume fraction in a swollen filled network. An effect of similar magnitude to that presented by Burnside and Giannelis[10] is observed only for the imperfect networks synthesized from hydroxyl-terminated chains. Reinforcement was not observed for the optimal networks synthesized from hydroxyl-terminated chains. *These results imply that, for reinforcement of these PDMS networks by the silicate to occur, the presence of free*

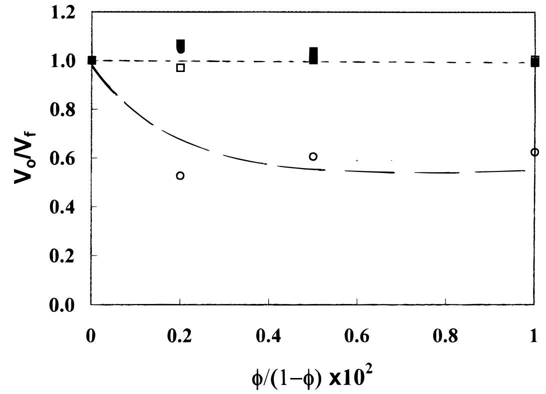


Figure 10. Plot of V_o/V_f versus $\phi/(1-\phi)$ of silicate-filled networks. Circle and square symbols represent the networks synthesized from hydroxyl-terminated and vinyl-terminated chains, respectively. Open symbols represent imperfect networks. Filled symbols represent the optimal or model networks. The lines are guide to the eye.

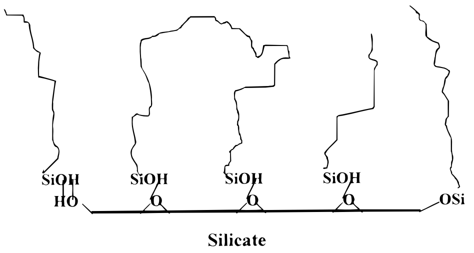


Figure 11. Schematic adsorption of hydroxyl-terminated PDMS chains to a silicate layer.

chains in the soluble fraction and of pendent chains in the network is essential. The bonding (adsorption sites) between PDMS and the silicate thus appears to be formed mainly at chain ends and not along the chain backbone. If adsorption along the chain backbone were comparable in strength to that at chain ends, the optimal networks would have also showed strong reinforcement with the clay fillers.

To qualitatively explain these results, we refer to the accepted existence of silicate oxygen groups on the surface of the clay and of hydrogen groups along the edge of these clay particles.[18] Both the oxygen atoms and the hydroxyl groups can hydrogen bond with the hydroxyl groups at the PDMS chain ends (schematically shown in Figure 11). It is likely that the hydroxyl group at the end of pendent chains binds strongly to the surface of the silicate and thus reinforces the networks by turning pendent inelastic chains into elastic chains. Since the silicate was mixed with PDMS chains before the addition of the cross-linker (TEOS), the proposed mechanism of enhancement implies the weaker hydrogen bond between the silicate and the hydroxyl group is replaced by a covalent bond between TEOS and the hydroxyl group in the presence of the catalyst. When TEOS is present in large enough excess ($r = r_{\mathrm{opt}}$) to form optimal networks, all the hydroxyl group are end-linked to TEOS, and the network cannot be reinforced by the silicate at these very low loadings. In less than optimal conditions, free chains that would have been part of the soluble fraction remain anchored to the silicate and become effective elastic chains. This is evident by the dramatic decrease in soluble fraction for $r = 0.8$ as fillers are added (see Table 5). Furthermore, pendent chains may also tether their free end and become elastic chains.

For the networks synthesized from vinyl-terminated chains, reinforcement was not observed regardless of their imperfection. These results imply that end groups of PDMS chains play a major roll in the reinforcement of PDMS networks by the silicate. The adsorption of vinyl groups to a silicate surface, if any occurs, is known to be appreciably weaker than that between a hydroxyl group and the silicate.[19] No possibility of hydrogen bonding exists in this case. The fact that no reinforcement was observed for the networks synthesized from vinyl-terminated chains supports that adsorption along chains is not significant in PDMS−silicate composites.

Table 5. Properties of Silicate-Filled Networks from Hydroxyl-Terminated PDMS

r	ϕ	w_{sol} (%)	E' (Pa) $\times 10^{-5}$	$G_{\mathrm{e,corr}}$ (Pa) $\times 10^{-5}$	v_2 in toluene
0.8	0	35.6	0.5	0.21	0.06
0.8	0.002	9.7	2.0	0.68	0.13
0.8	0.005	6.4	2.8	0.96	0.17
0.8	0.010	7.5	2.3	0.78	0.15
2.2	0	4.0	6.6	2.2	0.27
2.2	0.005	4.4	6.3	2.1	0.26

In summary, the above experimental results indicate that the modulus reinforcement in PDMS−silicate composites can be attributed to the hydroxyl-terminated chain anchoring onto the silicate. This converts free chains in the soluble fraction and pendent chains in the network into effective elastic chains. Our conclusion is supported by earlier investigations of the interface between PDMS chains and silica particles. Girard et al. studied the kinetic of adsorption of hydroxyl-terminated and trimethyl-terminated PDMS chains (M_w = 40K−500K) to silica surface at several silica concentrations and temperatures.[20] The amount of polymer adsorbed was measured by microanalysis of carbon content after extraction by a solvent. The adsorption of hydroxyl-terminated chains was greater than that of trimethyl-terminated chains. Patel et al.[19] investigated the end-group effect on adsorption of PDMS chains of both low (M_w = 1K) and high (M_w = 50K) molecular weight to silica surface by Fourier transform infrared spectroscopy (FTIR) and showed the order of adsorption as

$$\mathrm{OH}- > \mathrm{H}- > \mathrm{CH_3}- > \mathrm{CH_2}=\mathrm{CH_2}-$$

Though the difference of adsorption became smaller for the chains with high molecular weight, end groups having a high affinity for the surface adsorbed to a greater extent. The superiority in adsorption of the hydroxyl groups was attributed to a hydrogen bonding to the hydroxyl groups on the surface.[19] They concluded from the Scheutjents−Fleer self-consistent mean field model[21] and a Monte Carlo simulation that the chains with end groups having the highest affinity (namely, OH−) adsorbed primarily as loops; that is, the chains adsorbed to the surface at their chain ends. These results lend support to our conclusion on the mechanism of enhancement in imperfect PDMS elastomers from hydroxyl-terminated chains.

Data for Young's modulus of filled PDMS networks synthesized with the commercial hydroxyl-terminated chains are shown in the fourth column of Table 5. Young's modulus E' is converted to shear modulus G_e using eq 7. A correction to G_e for soluble fraction using eq 8 is applied, and the results are shown in the fifth column of Table 5. The values of the modulus increased 4-fold relative to that of the unfilled network by reinforcing the imperfect networks (synthesized using $r = 0.8$) with a concentration of 1% of clay particles. We

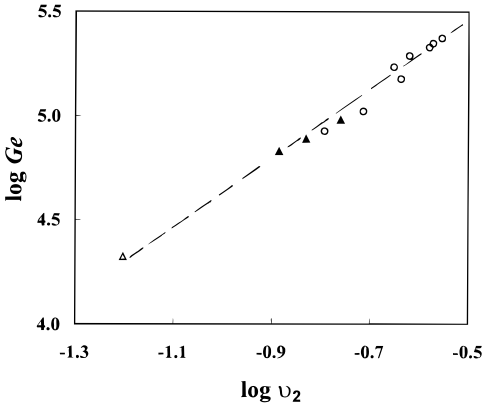


Figure 12. Relationship between G_e and υ_2 for networks from hydroxyl-terminated PDMS swollen in toluene. Filled symbols represent the filled networks. Open symbols represent the unfilled networks. Triangles and circles represent data from networks synthesized using $r = 0.8$ and $r = 2.2$, respectively. The slope of the best-fit line is 1.75.

note that at $\phi = 0.01$ the modulus decreased relative to that at $\phi = 0.005$. We suspect that this is due to a decrease in the extent of exfoliated and intercalated silica layers relative to aggregated layers. This is supported by the fact that the soluble fraction is greater and that phase separation occurred at higher concentration of fillers. No enhancement was observed for the optimal networks (synthesized using $r = 2.2$). Consistent with the results from the swelling experiments, the modulus of the filled networks never exceeded the modulus of the optimal networks.

Swelling data from Table 5 plotted as log G_e versus log υ_2 are shown in Figure 12 as filled symbols along with data from Table 4 for unfilled networks represented by unfilled symbols. For the networks synthesized using $r = 0.8$, υ_2 and G_e increased as a function of filler concentration for the three concentrations examined. All the data points from the filled networks fell reasonably well on the line that represents a least-squares regression of the data points of the unfilled networks. This indicates that the bonding between the filler and the polymer chain increases υ_2 and G_e in the same fashion as would additional cross-linkers. Thus, the reinforcement can be attributed to an increased number of elastic chains obtained by reducing the soluble fraction and by converting pendent chains in the unfilled network into elastic chains. Once a chain end is adsorbed onto the silicate, it acts as an effective cross-link and can trap entanglements that also act as effective cross-links. For the networks synthesized using the close to optimum value of $r = 2.2$, υ_2 and G_e did not change with filler content as free hydroxyl end groups would not be available for adsorption on the silicate. The slope of the best-fit line through the data is 1.75. This indicates that toluene acts as a better solvent in these networks than in the previously studied networks from vinyl-terminated chains.[4,22] The reason for this difference is not clear but could be due to the presence of hydroxyl and ethoxy moieties in the networks and the fact that in the present series of networks the chemical constitution of the networks is varying due the different extent of TEOS incorporation into the networks.

Conclusions

Use of larger amounts of cross-linkers than conventionally used leads to networks of hydroxyl-terminated PDMS precursor chains that have higher modulus (larger number of elastic chains) and a smaller equilibrium swelling in toluene. Networks synthesized with an optimum amount of TEOS cross-linkers have values of υ_2, w_{sol}, and G_e close to those of vinyl-terminated PDMS "model" networks obtained by hydrosilylation. These networks have values of υ_2 that are greater than those of conventional networks synthesized at or near stoichiometric conditions and are comparable to those of filled networks. From the point of view of increasing modulus and reducing swelling, the use of optimum amounts of cross-linkers in this system is a simple and as effective method as introducing fillers.

In PDMS/silicate composites with low concentration of fillers, enhancement of the properties of PDMS network elastomers in terms of higher modulus and lower swelling in a good solvent is obtained only for networks formed from the hydroxyl-terminated precursor chains. Furthermore, when the ratio r of ethoxy cross-link ends to hydroxyl chain ends is such that it leads to very small soluble fractions and, as a consequence, small amounts of defects (optimal networks), no enhancement of the properties is observed. These results indicate that the reinforcement in these elastomers can be attributed to the anchoring of the hydroxyl end group to the silicate filler and that the mechanical properties of the optimal networks cannot be superseded without further chemical modification of the system. The relationship between modulus and swelling for the silicate-filled networks is similar to that of the unfilled networks. Thus, the modulus enhancement through tethering can be regarded as essentially due to an increase in the number of effective elastic chains.

Acknowledgment. We thank E. Giannelis for useful discussions. We also thank S. Burnside for the modified montmorillonite clay and E. Manias and H. Chen for help in the preparation of the elastomer/clay nanocomposites. H.T. is grateful to the Japan Energy Corporation for supporting his study at Cornell. This work was supported by NSF Polymers Program, Grant DMR-9706066.

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MA990218+