

# Synthesis, Structure, and Properties of Poly(dimethylsiloxane) Networks Reinforced by *in Situ*-Precipitated Silica–Titania, Silica–Zirconia, and Silica–Alumina Mixed Oxides

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## SYNOPSIS

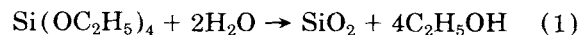
Several novel fillers, specifically silica–titania, silica–zirconia, and silica–alumina mixed oxides, have been successfully precipitated into poly(dimethylsiloxane) (PDMS) networks using a sol–gel approach. The resulting filled networks were found to have very good mechanical properties. In comparison with networks filled only with silica, these materials had good extensibilities as well as high strengths. Filler particle diameters were generally several hundred angstroms, but were found to decrease with increase in crosslink density of the networks. The distributions of particle size were relatively narrow, and there was very little particle aggregation. The presence of *in situ* silica–titania and silica–zirconia mixed oxides can also increase the onset temperature for degradation of the PDMS. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(dimethylsiloxane) (PDMS),  $[-\text{Si}(\text{CH}_3)_2\text{O}-]_x$ , is the most important and by far the most widely used siloxane polymer.<sup>1–3</sup> It has long been known to be a high-performance material because of its extremely low glass transition temperature ( $-125^\circ\text{C}$ ) and high thermal stability compared with those of other elastomers. PDMS elastomers are seldom used in the unfilled state, however, because of their relatively low inherent strengths.<sup>4–6</sup> As a result, almost all applications require that these elastomers be reinforced by fillers in order to improve their mechanical properties.<sup>7–9</sup> As has been done for many years, such reinforcing fillers have been mechanically blended into polymers prior to their crosslinking into network structures. This blending process, however, is a time-consuming and energy-intensive process, and there are problems in controlling the structure of the resulting material.

It can be particularly difficult to control the degree of particle dispersion,<sup>7–11</sup> and this frequently results in inhomogeneous distributions of particles that are badly agglomerated.

For these reasons, a novel reinforcement technique which can generate reinforcing particles within a polymer matrix has recently been developed.<sup>12–21</sup> The most important reaction for doing this is the acid- or base-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS). Silica ( $\text{SiO}_2$ ) is thus generated, as shown by the equation



The concept of such *in situ* precipitations is novel, and of practical importance because the resulting particles provide the same highly desirable reinforcing effects obtained in the usual filler-blending technique.<sup>12–21</sup> The major potential practical advantages of filling a network in such a manner include (1) avoidance of the difficult blending process, (2) control of particle size and distribution, and (3) control of particle agglomeration.

Previous studies of such *in situ*-generated fillers have concentrated on silica, because it is the most widely used and most effective filler available. Silica

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Table I Molecular Weights of the PDMS Chains

Petrach Designation	Quoted $M_n$ (g mol <sup>-1</sup> )	GPC Results		
		$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	$M_w/M_n$
PS 343.8	43,600	28,000	48,300	1.75
PS 343	26,000	22,100	34,600	1.57
PS 342.5	18,000	15,600	27,900	1.79
PS 341	4,200	5,900	12,250	2.07

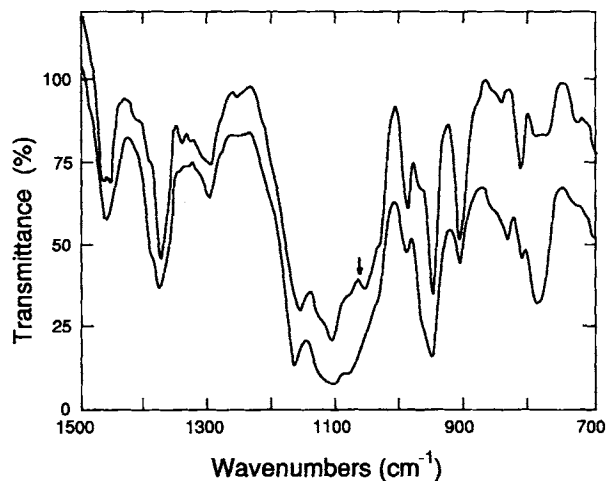
has some disadvantages, however, such as losses in reinforcement at high temperatures and decreases in maximum extensibility of the elastomer.<sup>18,22</sup> For this and other reasons, several other fillers have been *in situ* precipitated into PDMS, including titania (TiO<sub>2</sub>),<sup>23-25</sup> alumina (Al<sub>2</sub>O<sub>3</sub>),<sup>26</sup> and zirconia (ZrO<sub>2</sub>).<sup>27</sup> These fillers have also been incorporated in PDMS elastomers by industry, in the usual blending technique. Generally speaking, different fillers can offer different advantages in reinforcement applications. For example, although titania provides only mild reinforcement in polysiloxane elastomers, it gives substantial improvements in weather resistance and heat stability. Similarly, aluminum oxide is primarily used for improving thermal conductivity, abrasion resistance, and flame retardancy. It is thus of considerable interest to try

to find a filler which possesses a combination of such advantages. The present investigation was therefore undertaken in order to develop a series of novel binary fillers, specifically silica-titania, silica-zirconia, and silica-alumina mixed oxides. The goal was to *in situ* generate fillers with —Si—O—Ti—O—, —Si—O—Zr—O—, and —Si—O—Al—O— bondings, within PDMS networks. The resulting materials will be characterized with regard to reinforcement effects, structure, and thermal stability.

## EXPERIMENTAL

### Materials

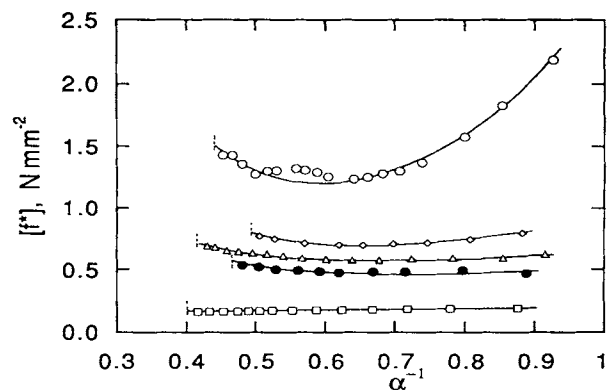
The polymers utilized, four hydroxyl-terminated PDMS samples having quoted number-average molecular weights corresponding to  $M_n = 4.2, 18.0, 26.0,$  and  $43.6$  kg/mol, respectively, were obtained from the Hüls America Company. Actual values of the weight-average molecular weight  $M_w$ ,  $M_n$ , and polydispersity index  $M_w/M_n$  were determined using a Waters 746 gel permeation chromatography (GPC) instrument, and are listed in Table I. TEOS was supplied by the Petrach Systems Company, and stannous octotatate was obtained from the Pfaltz and Bauer Company. All other chemicals, including titanium *n*-butoxide, aluminum tri-*sec*-butoxide, zirconia *n*-propoxide, hydrochloric acid (HCl), ethanol, propanol, and isopropanol, were obtained from the Aldrich Company. Two fumed silica samples having primary particle sizes of 4 and 7 nm were supplied by the Degussa Corporation.



**Figure 1** FTIR spectra of solutions obtained from tetraethoxysilane (TEOS) and aluminum tri-*sec*-butoxide. Part (a) shows the spectrum for the initial mixture of TEOS and aluminum tri-*sec*-butoxide, and part (b) the spectrum after the reaction of TEOS and aluminum tri-*sec*-butoxide in the presence of water and acid. The arrow shows the new peak of interest with regard to Si—O—M—O bonding.

### Preparation of the *In Situ*-Filled PDMS Networks

A sequential two-step sol-gel approach was used to prepare these filled PDMS networks. In this technique, an unfilled PDMS network was first prepared by the usual end-linking reaction.<sup>12</sup> The next step



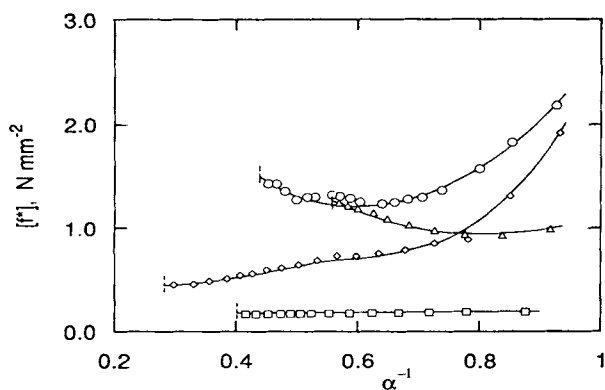
**Figure 2** Stress-strain isotherms at 24°C for an unfilled poly(dimethylsiloxane) (PDMS) network and PDMS networks filled with *in situ*-precipitated silica-titania mixed oxides, represented as the dependence of the nominal stress or modulus on reciprocal elongation. The quoted number-average molecular weight  $M_n$  of the PDMS employed was 18,000 g mol<sup>-1</sup>. In this figure and the others showing mechanical properties, the vertical dashed lines locate the rupture points of the samples. The values of the wt % filler employed were (□) 0.0, (●) 10.5, (Δ) 13.0, (◇) 15.5, (○) 21.4.

involved the swelling of the networks in a solution containing solvent and the ceramic precursors. These starting solutions were prepared by reacting TEOS and the other desired metal alkoxide. Since TEOS is extremely slow to hydrolyze compared to the other metal alkoxides, hydrolysis of a mixture of these two alkoxides generally causes phase segregation. As a consequence, a physical mixture of two oxides is obtained, rather than a covalently bonded mixed oxide. The preparative technique, therefore, utilized an initial formation of polymerizable species from the TEOS (by partial hydrolysis) before reaction with the other alkoxide.

For *in situ* generating the silica-titania mixed oxide, titanium butoxide was introduced into the partially hydrolyzed TEOS solution with vigorous stirring at the chosen ratio of TEOS to titanium butoxide. For *in situ* generating silica-zirconia mixed oxides, zirconium propoxide was used instead of titanium butoxide, with 1-propanol as solvent. Finally, the starting solution for *in situ*-generating silica-alumina mixed oxide employed aluminum tri-*sec*-butoxide, and the solvent was isopropanol.

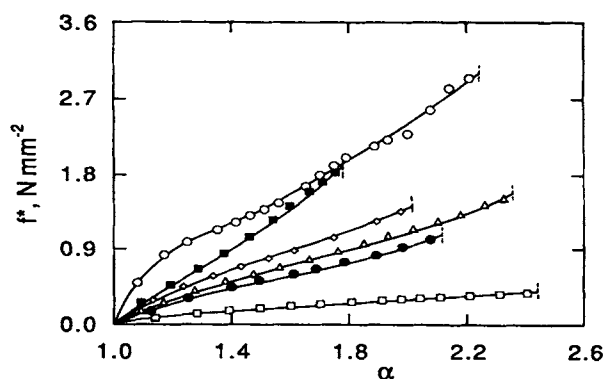
Some of the starting solutions were studied by Fourier transform infrared (FTIR) spectroscopy to search for evidence for —Si—O—M—O— bonding.

The prereaction steps were followed by a base-catalyzed sol-gel conversion of the mixed precursors to generate the reinforcing filler *in situ* by the fol-



**Figure 3** Stress-strain isotherms at 24°C for an unfilled PDMS network and PDMS networks filled with various fillers. The quoted  $M_n$  of the PDMS utilized was 18,000 g mol<sup>-1</sup>, and the types and values of the wt % filler were (□) 0.0, (◇) 19.5 titania, (○) 21.4 silica-titania mixed oxides, (Δ) 22.4 silica.

lowing procedures. The sample sheets were first weighed and then immersed in the chosen starting solution for the desired period of time. The swollen sheets were then placed in 2 wt % diethylamine aqueous solution, and the hydrolysis and condensation of the solution were permitted to occur at room temperature for the desired period of time. After the reaction, each sheet was dried and weighed. The difference in weights before and after the precipitation reaction was used to calculate the amount of filler introduced into the network. The amounts of mixed oxides thus introduced were generally between 10 and 22 wt %.



**Figure 4** Stress-strain isotherms at 24°C for PDMS networks filled with *in situ*-precipitated silica-titania mixed oxides and silica, represented as the dependence of the nominal stress on elongation. The quoted  $M_n$  of the PDMS employed was 18,000 g mol<sup>-1</sup>, and the values of the wt % filler were (□) 0.0, (●) 10.5, (Δ) 13.0, (◇) 15.5, (■) 22.4 silica, (○) 21.4.

**Table II** Ultimate Properties of PDMS Networks Filled with Si-Ti Mixed Oxides

Polymer $M_n$ (g mol <sup>-1</sup> )	Filler Comp. <sup>a</sup>		Wt % Filler <sup>b</sup>	$a_r$ <sup>c</sup>	$(f/A^*)_r$ <sup>d</sup> (N mm <sup>-2</sup> )	$10^3 E_r$ <sup>e</sup> (J mm <sup>-3</sup> )
	SiO <sub>2</sub>	TiO <sub>2</sub>				
18,000	60	40	0.0	2.41	0.37	0.30
	60	40	10.5	2.08	0.99	0.57
	60	40	13.0	2.33	1.48	1.03
	60	40	15.5	1.98	1.33	0.74
	60	40	21.4	2.21	2.87	1.92
26,000	60	40	0.0	3.58	0.15	0.20
	60	40	9.7	2.16	0.93	0.58
	60	40	13.9	1.95	1.22	0.60
	60	40	19.4	2.23	1.71	1.05
18,000	100	0	22.4	1.75	1.78	0.70
18,000	0	100	19.5	3.37	1.48	2.56

<sup>a</sup> Mol % of the two precursors in the reaction mixture.

<sup>b</sup> Silica-titania mixed oxides if not stated otherwise.

<sup>c</sup> Elongation at rupture.

<sup>d</sup> Ultimate strength.

<sup>e</sup> Energy of rupture.

In some cases, portions of PDMS networks were left unfilled, to serve as reference materials.

Additional details on the preparation procedures in general are given elsewhere.<sup>28</sup>

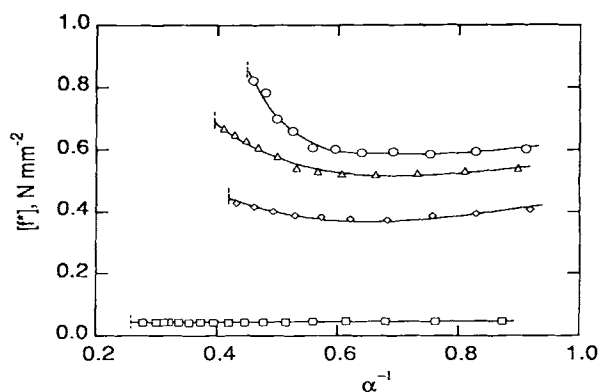
### Preparation of Networks from PDMS Blended with Fumed Silica

Hydroxyl-terminated PDMS with a desired molecular weight was first dissolved in toluene to make a clear, 30 wt % solution. Fumed silica was then mixed

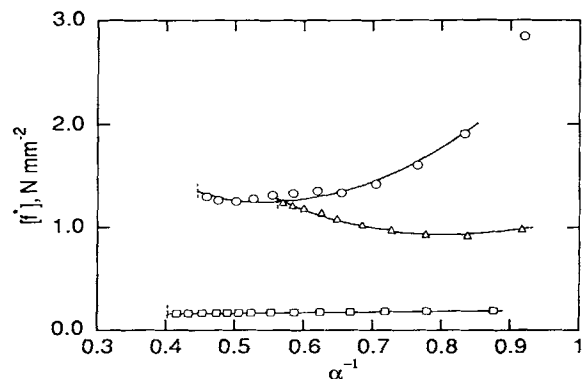
with the resulting solution with vigorous stirring until it again became clear. The solvent was removed by increase in temperature and by exposure to vacuum. After adding TEOS as end-linking agent and stannous octoate as catalyst, the material was allowed to crosslink under a pressure of 5500 psi, at room temperature for 1 day. The crosslinking reaction was then allowed to proceed further, at room temperature for 2 additional days.

### Transmission Electron Microscopy (TEM)

A piece of sample was glued to a mounting pin using epoxy adhesive. Specimen slices having a thickness



**Figure 5** Stress-strain isotherms at 24°C for PDMS networks filled with *in situ*-precipitated silica-zirconia mixed oxides, represented as the dependence of the nominal stress or modulus on reciprocal elongation. The quoted  $M_n$  of the PDMS employed was 26,000 g mol<sup>-1</sup>, and the values of the wt % filler were (□) 0.0, (◇) 9.8, (△) 14.0, (○) 18.8.



**Figure 6** Stress-strain isotherms at 24°C for PDMS networks filled with different fillers. The quoted  $M_n$  of the PDMS employed was 18,000 g mol<sup>-1</sup>, and the types and values of the wt % filler were (□) 0.0, (△) 22.4 silica, (○) 22.0 silica-zirconia mixed oxides.

**Table III Ultimate Properties of the Unfilled PDMS Networks and Those Filled with SiO<sub>2</sub>-ZrO<sub>2</sub> Mixed Oxides**

Sample (wt %)	$\alpha_r^a$	$(f/A^*)_r^b$ (N mm <sup>-2</sup> )	$10^3 E_r^c$ (J mm <sup>-3</sup> )
22.2	2.18	2.56	1.80
17.0	2.08	1.91	1.42
12.2	2.21	1.50	1.25
0.0	2.41	0.37	0.35

<sup>a</sup> Elongation at rupture.

<sup>b</sup> Ultimate strength.

<sup>c</sup> Energy of rupture.

on the order of 1000 Å were obtained from it using a diamond knife on an ultramicrotome (Dortel-Blum MT-2) at -130°C, with a device controlling delivery of a precise amount of liquid nitrogen. Specimens were collected on copper grids and then examined in transmission with a Philips CM 20 electron microscope operating at 200 kV.

### Stress-Strain Measurements

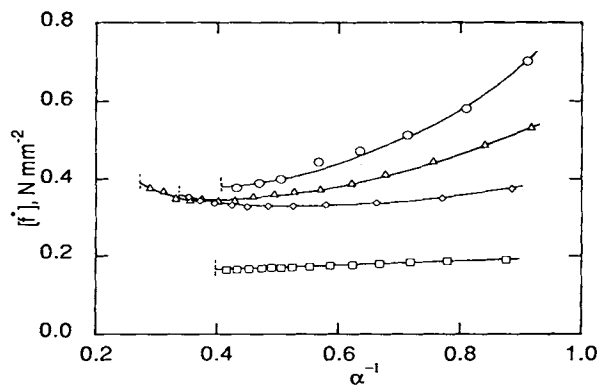
Stress-strain isotherms in uniaxial extension were obtained in the usual manner.<sup>29,30</sup> The force and elongation measurements were made using a sequence of increasing values of the elongation or relative length of the sample,  $\alpha = L/L_0$ . The quantity of primary interest, the reduced nominal stress or modulus, was calculated from the equation<sup>31,32</sup>

$$[f^*] \equiv f^*/(\alpha - \alpha^{-2}) \quad (2)$$

where  $f^* \equiv f/A$  is the nominal stress,  $f$  the equilibrium force, and  $A$  the area of the initial cross section. All measurements were conducted at room temperature and the elongation was generally increased to the rupture point of the sample.

### Thermogravimetric Analysis (TGA)

These experiments were carried out on a Perkin-Elmer (Model TGA-7) thermogravimetric analyzer installed in-line with a PE 7500 professional computer for data acquisition. All samples were studied both in air and in nitrogen. The gases were dried by passing them through a gas purifier before they entered the sample chamber. The samples, typically 5-10 mg, were placed in platinum pans, and weighed directly on the thermogravimetric balance to within  $\pm 0.001$  mg. In the dynamic heating experiments, a



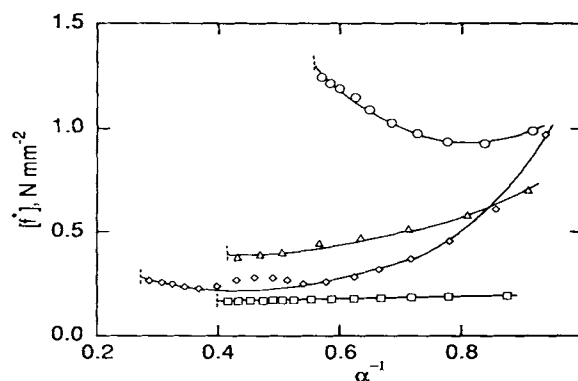
**Figure 7** Stress-strain isotherms at 24°C for PDMS networks filled with silica-alumina mixed oxides. The quoted  $M_n$  of the PDMS employed was 18,000 g mol<sup>-1</sup>, and the values of the wt % filler were (□) 0.0, (◇) 11.7, (△) 15.8, (○) 19.3.

heating rate of 10°C min<sup>-1</sup> over a temperature range 30-800°C was employed.

## RESULTS AND DISCUSSION

### Structure

The results of the spectroscopic structure analysis<sup>28</sup> are illustrated in Figure 1. The FTIR spectrum shown demonstrates the formation of -Si-O-Al-O- bonds in the filled elastomer prepared using the silicate and aluminate precursors. Specifically, a new peak at 1055 cm<sup>-1</sup> appeared in the spectrum of the starting solution, and represents the vibration frequencies of the Al-O bonds in Si-O-Al- bondings.



**Figure 8** Stress-strain isotherms at 24°C for PDMS networks filled with various fillers. The quoted  $M_n$  of the PDMS employed was 18,000 g mol<sup>-1</sup>, and the types and values of the wt % filler were (□) 0.0, (◇) 17.7 alumina, (△) 19.3 silica-titania mixed oxides, (○) 22.4 silica.

**Table IV Ultimate Properties of PDMS Networks Filled with SiO<sub>2</sub>—Al<sub>2</sub>O<sub>3</sub> Mixed Oxides**

Polymer $M_n$ (g mol <sup>-1</sup> )	Filler Comp. <sup>a</sup>		Wt % Filler <sup>b</sup>	$a_r$ <sup>c</sup>	$(f/A^*)_r$ <sup>d</sup> (N mm <sup>-2</sup> )	$10^3 E_r$ <sup>e</sup> (J mm <sup>-3</sup> )
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>				
18,000	70	30	0	2.41	0.37	0.35
	70	30	11.7	2.84	0.96	1.07
	70	30	15.8	3.46	1.28	1.84
	70	30	19.3	2.32	0.80	0.78
26,000	70	30	0	3.58	0.15	0.20
	70	30	10.4	2.78	0.74	0.79
	70	30	14.3	2.69	0.86	0.87
	70	30	17.8	3.01	0.63	0.71
18,000	100	0	22.4	1.75	1.78	0.70
18,000	0	100	17.7	3.50	0.90	1.26

<sup>a</sup> Mol % of the two precursors in the reaction mixture.

<sup>b</sup> Silica-alumina mixed oxides if not specified otherwise.

<sup>c</sup> Elongation at rupture.

<sup>d</sup> Ultimate strength.

<sup>e</sup> Energy of rupture.

## Reinforcement Effects

### Silica-Titania Mixed Oxides

The stress-strain isotherms obtained on the unfilled and filled networks were first represented as plots of modulus against reciprocal elongation, as suggested by the Mooney-Rivlin equation<sup>32-34</sup>

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

where  $2C_1$  and  $2C_2$  are constants independent of elongation  $\alpha$ . Typical isotherms for several networks, including those with silica-titania mixed oxides, are shown in Figure 2. It is readily seen that the moduli of the *in situ*-filled networks were much

higher than those of the unfilled networks. As was the case with the silica-filled PDMS networks, the networks filled with silica-titania mixed oxides also showed an initial decrease in the modulus, followed by an upturn at high elongations. Larger amounts of filler gave larger decreases. The upturn in the modulus at high elongations further demonstrated the desired reinforcing effects. Similar reinforcement effects have been observed in PDMS networks with various crosslink densities.<sup>28</sup>

Figure 3 compares the stress-strain isotherms for networks filled with silica, with titania, and with silica-titania mixed oxides. Compared with the silica-filled PDMS networks, this type of filled PDMS networks had larger extensibilities, and had upturns which occurred at higher elongations. The upturns were smaller, however, because of the lower reinforcement provided by the titanium oxide. Figure 4 shows the corresponding plots of stress against strain, with the area under each curve corresponding to the energy of rupture  $E_r$  (which is the standard measure of elastomer toughness). Values of the ultimate properties thus obtained (specifically the maximum extensibility, ultimate strength, and energy of rupture) are given in Table II

A filler consisting entirely of silica generally increases the ultimate strength but decreases the maximum extensibility. The present silica-titania mixed oxide fillers, however, seem to have less of a detrimental effect on the extensibility, and could thus serve as a good compromise in providing the best balance of these two important properties.

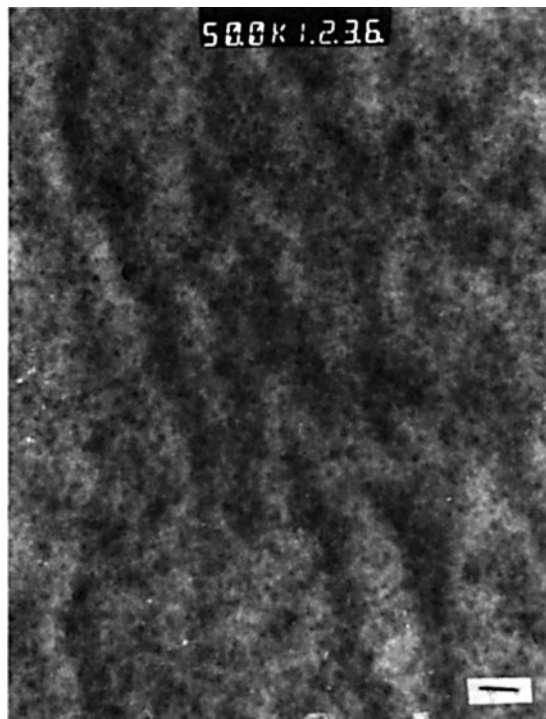
**Table V Ultimate Properties of Some of the PDMS Networks**

Sample (Wt %)	$\alpha_r$ <sup>a</sup>	$(f/A^*)_r$ <sup>b</sup> (N mm <sup>-2</sup> )	$10^3 E_r$ <sup>c</sup> (J mm <sup>-3</sup> )
PDMS	2.41	0.37	0.35
21.4 SiO <sub>2</sub> -TiO <sub>2</sub>	2.21	2.87	1.92
22.4 SiO <sub>2</sub>	1.75	1.78	0.70
19.5 TiO <sub>2</sub>	3.37	1.48	2.56
22.2 SiO <sub>2</sub> -ZrO <sub>2</sub>	2.18	2.56	1.80
19.3 SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	2.32	0.80	0.78
17.7 Al <sub>2</sub> O <sub>3</sub>	3.50	0.90	1.26

<sup>a</sup> Elongation at rupture.

<sup>b</sup> Ultimate strength.

<sup>c</sup> Energy of rupture.



**Figure 9** Transmission electron micrograph for a PDMS network filled with 21.4 wt % silica-titania mixed oxides, at the magnification of 50,000 $\times$ . The  $M_n$  of the PDMS chains was 18,000 g mol $^{-1}$ , and in this and the following three figures, the reference bar corresponds to 1000 Å.

#### **Silica-Zirconia Mixed Oxides**

Typical isotherms for PDMS networks filled with various amounts of silica-zirconia mixed oxides are shown in Figure 5, and Figure 6 compares these isotherms with those for networks filled with silica alone. As expected, the moduli of the *in situ*-filled networks were much higher than those of the unfilled network. The upturns in modulus at high elongations clearly demonstrated the desired reinforcing effects, and the values of the ultimate properties thus obtained are given in Table III. As is readily seen, the silica-zirconia mixed oxides can offer reinforcement similar to that provided by the silica-titania mixed oxides.

#### **Silica-Alumina Mixed Oxides**

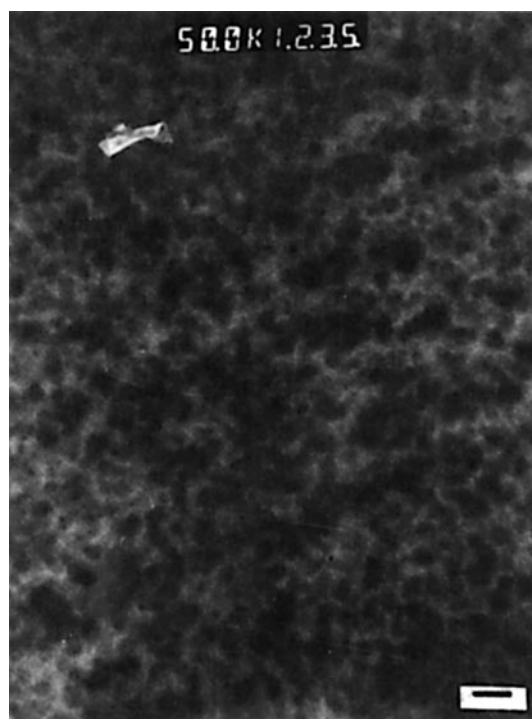
Typical isotherms for PDMS networks filled with different amounts of silica-alumina mixed oxides are shown in Figure 7, and Figure 8 compares the stress-strain isotherms for networks filled with silica, alumina, and silica-alumina mixed oxides. Table IV lists the ultimate properties obtained for these

systems. The moduli of these *in situ*-filled networks are seen to be much higher than those of the unfilled networks, but the reinforcing effects were not as good as those of the other two mixed oxides.

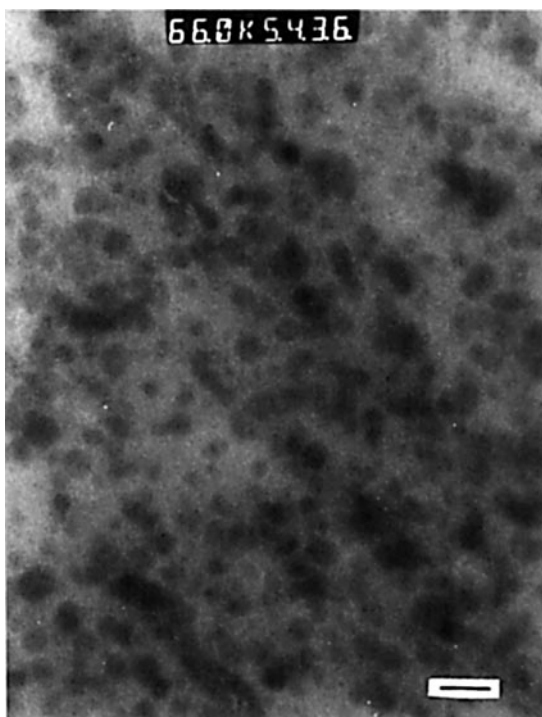
Table V compares the ultimate properties of PDMS networks filled with various fillers, as obtained from both equilibrium and dynamic stress-strain tests. As expected, the ultimate strength and energy of rupture obtained from the dynamic stress-strain tests were higher than those obtained from the near-equilibrium measurements, presumably because of these stresses not having relaxed to their equilibrium values.

#### **Transmission Electron Microscopy**

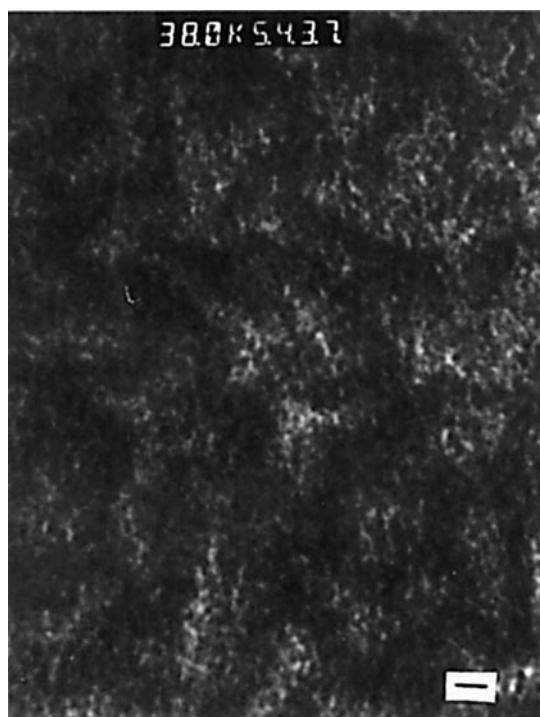
The electron micrographs obtained for the networks filled with *in situ* silica-titania mixed oxides, at a magnification of 50,000 $\times$ , are shown in Figures 9 through 11. Three conclusions can be drawn from these results. First, the silica-titania mixed oxide particles had an average diameter of several hundred angstroms, which is in the range of particle sizes of fillers typically introduced into polymers by the usual blending technique. Second, the distribution



**Figure 10** Transmission electron micrograph for a PDMS network filled with 21.4 wt % silica-titania mixed oxide, at the magnification of 50,000 $\times$ . The  $M_n$  of the PDMS chains was 26,000 g mol $^{-1}$ .



**Figure 11** Transmission electron micrograph for a PDMS network filled with silica-titania mixed oxides, at the magnification of 66,000 $\times$ . The  $M_n$  of the PDMS chains was 43,600 g mol $^{-1}$ .

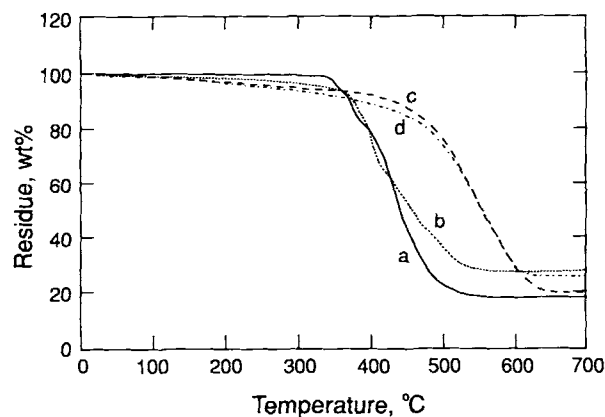


**Figure 12** Transmission electron micrograph for a PDMS network filled with 17.0 wt % silica-zirconia mixed oxides at the magnification of 38,000 $\times$ . The  $M_n$  of the PDMS chains was 18,000 g mol $^{-1}$ .

of particle sizes was relatively narrow, and there was very little of the aggregation of particles that is usually a problem in filler-blended elastomers.<sup>18-20</sup> Third, the particle size increases as the crosslink density decreases (network "pore size" increases). For example, the average diameter of the particles increased from approximately 200 to 300 Å when the  $M_c$  of the PDMS network increased from 18 to 26 kg mol $^{-1}$ . A similar conclusion was reached by Ulibarri and co-workers, and is presumably due to the confining effect of the network pores.<sup>35</sup> Additional information<sup>35</sup> on the growth and reorganization of the *in situ*-precipitated silica-titania particles was obtained by X-ray and neutron scattering measurements. Silica-titania mixed oxides had particle diameters and distributions very similar to those of silica. Compared to them, however, *in situ*-precipitated titania was less well-defined in shape.

The electron micrographs for PDMS networks filled with silica-zirconia mixed oxides are shown in Figure 12. The silica-zirconia fillers were found to have particle sizes and distributions very similar to those of the silica-titania ones. The networks containing silica-alumina mixed oxide particles could not be characterized by TEM.

Some of the structural features elucidated by the electron microscopy can obviously be correlated with the mechanical properties of these materials. The



**Figure 13** TGA thermograms for unfilled and filled PDMS networks obtained under nitrogen. Part (a) is for an unfilled PDMS network, (b) for a network containing 12 wt % blended fumed silica and titania, (c) for a network containing 15.5 wt % *in situ*-precipitated silica-titania mixed oxides, and (d) for a network containing 21.4 wt % *in situ*-precipitated silica-titania mixed oxides.



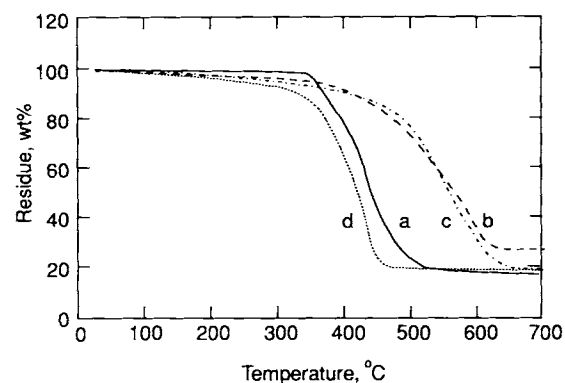
reinforcement provided by these particles is partly the result of the large stresses held by highly extended polymer chains attached to the immobile filler particles. It is thus consistent with strong elastomer-filler attachments. Good dispersion and small particle size are also important because the number of attached elastomer chains is proportional to the filler surface available. *In situ*-generated filler-elastomer systems are also suitable for theoretical studies of reinforcement because of the extremely good filler-particle dispersion obtained. Thus, the use of *in situ*-precipitated mixed oxides can offer an alternative way of changing the interaction between filler surface and polymer networks, with control of filler particle size and its degree of dispersion.

### Thermal Stability Studies by TGA

Analysis of these results is based on the fact that PDMS elastomers are extremely stable thermally at temperatures below 250°C.<sup>4,6</sup> Above 250°C, however, the heat-aging process gradually reduces the PDMS network to a useless material. The changes during heat aging can be caused by a variety of chemical processes,<sup>10</sup> including siloxane-bond exchange, hydrolysis of siloxane bonds, oxidation of hydrocarbon groups, depolymerization or reversion, and condensation of hydroxyl groups.<sup>22,36</sup> Furthermore, the silica fillers blended into siloxane elastomers have deleterious effects that promote this heat aging.<sup>22</sup> The silanol groups (SiOH) on the surface of the filler are acidic and can not only react with SiOH groups at the end of the siloxane skeletal bonds, but can also cause cleavage of Si—O skeletal bonds.<sup>37,38</sup>

### Comparisons between *In Situ*-Precipitated Mixed Oxides and Blended Fillers

Figure 13 presents typical results obtained from TGA measurements under nitrogen, showing per-



**Figure 14** TGA thermograms for unfilled and filled PDMS networks obtained under nitrogen. Part (a) is for unfilled PDMS network, (b) for a network containing 17.0 wt % *in situ*-precipitated silica-zirconia mixed oxides, (c) for a network containing 15.5 wt % *in situ*-precipitated silica-titania mixed oxides, and (d) for a network containing 19.3 wt % *in situ*-precipitated silica-alumina mixed oxides.

cent weight loss over the temperature range 30–700°C. The results are for unfilled PDMS networks, PDMS networks filled with *in situ*-precipitated silica-titania mixed oxides, and PDMS networks mechanically blended with silica and titania. Interestingly, the samples containing *in situ*-precipitated fillers all showed small weight losses at relatively low temperatures, well below the temperature at which the pure PDMS begins to degrade. This could possibly be due to the loss of organic groups not hydrolyzed from the TEOS<sup>39</sup> and titanium butoxide, and the cleavage of siloxane bonds in the chain caused by —OH groups on the surface of the filler.

The other important TGA results for these samples are given in Table VI. Of particular interest is the onset of pronounced degradation, which is presumably due to the formation of volatile cyclic

**Table VI** TGA Results under Nitrogen for the PDMS Networks

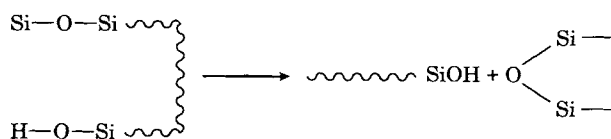
Network	Wt % Filler	Onset of Degrad. (°C)	Temp. for 50% Weight Loss (°C)	End of Degrad. (°C)
1	0	352	440	504
2	20.3% SiO <sub>2</sub>	456	556	603
3	15.0% SiO <sub>2</sub> <sup>a</sup>	398	466	512
4	10.0% TiO <sub>2</sub> <sup>a</sup>	380	446	542
5	19.5% TiO <sub>2</sub>	321	580	605
6	12.0% SiO <sub>2</sub> -TiO <sub>2</sub> <sup>a</sup>	378	460	524
7	15.5% SiO <sub>2</sub> -TiO <sub>2</sub>	476	558	622
8	21.4% SiO <sub>2</sub> -TiO <sub>2</sub>	468	557	604

<sup>a</sup> Silica and/or titania mechanically blended into the networks.

**Table VII Comparisons among Some of the TGA Results**

Network	Wt % Filler	Onset of Degrad. (°C)	Temp. for 50% Weight Loss (°C)	End of Degrad. (°C)
1	0	352	440	504
2	15.5% SiO <sub>2</sub> -TiO <sub>2</sub>	476	558	622
3	21.4% SiO <sub>2</sub> -TiO <sub>2</sub>	468	557	604
4	17.0% SiO <sub>2</sub> -ZrO <sub>2</sub>	403	565	613
5	19.3% SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	344	418	452

oligomers. This degradation occurred at relatively low temperatures for unfilled PDMS networks and for PDMS networks mechanically blended with silica and titania. The presence of *in situ* mixed oxide filler significantly increased the onset temperature for the degradation. For hydroxyl-terminated PDMS, one of the mechanisms for the formation of cyclics involves the hydroxyl chain ends "biting" into the chain.<sup>35,40</sup>



Since the presence of *in situ*-precipitated filler retards the depolymerization process, it appears that the hydroxyl groups on the surface of the filler can hydrogen bond with those at the ends of the polymers, resulting in the deactivation of the depolymerization process. Blended silica and titania fillers did not increase the degradation temperature nearly as much as did the *in situ*-precipitated mixed oxides. It seems that the hydroxyl groups on the surface of these fillers have less ability to deactivate the hydroxyl groups on the PDMS chains.

#### Comparisons Between Different Mixed Oxides

Figure 14 shows the results obtained from TGA measurements under nitrogen for unfilled PDMS networks and PDMS networks filled with *in situ*-precipitated silica-titania, silica-alumina, and silica-zirconia mixed oxides. Table VII lists the most important data obtained from this figure. As in the case of silica-titania fillers, the silica-zirconia ones also significantly increased the degradation onset temperature. Surprisingly, the presence of silica-alumina mixed oxide actually decreased the degradation onset temperature. It would be worthwhile to study the mechanisms of this accelerated degradation.

## CONCLUSIONS

A series of novel fillers, specifically silica-titania, silica-zirconia, and silica-alumina mixed oxides, have been *in situ* precipitated into PDMS networks through a sol-gel approach. The elastomeric networks filled by these novel particles have very good mechanical properties. At least in some cases, these novel fillers can offer not only high modulus, but also high extensibility. Filler particle diameters are typically several hundred angstroms, but depend on the crosslink density of the network. The distribution of particle size is relatively narrow, and there is very little particle aggregation. The presence of *in situ* silica-titania and silica-zirconia mixed oxides can also increase the onset temperature of degradation of the PDMS elastomer.

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