Sol–Gel Preparation of Composites of Poly(dimethylsiloxane) with SiO$_2$ and SiO$_2$/TiO$_2$, and Their Mechanical Properties

Jianye WEN* and James E. MARK

*Department of Chemistry and Polymer Research Center,
The University of Cincinnati,
Cincinnati, OH 45221–0172, U.S.A.*

ABSTRACT: Composites of poly(dimethylsiloxane) (PDMS) with silica and silica-titania mixed oxides have been successfully prepared using the sol–gel hydrolysis and condensation of tetraethoxysilane (TEOS). In the study of the hydrolysis and sol–gel transition reaction, it was found that co-condensation between TEOS and PDMS was the dominant reaction under the chosen conditions, and that most of the PDMS was thereby incorporated in the SiO$_2$ network. The presence of PDMS during the sol–gel reaction was found to greatly shorten the gelation time of the system. The most striking change in mechanical properties of composites with high inorganic content is the marked improvement in impact strength, arising from the existence of energy-absorbing ductile processes. In the case of high PDMS content, the thermal stability of polymer can be improved by the presence of the *in-situ* precipitated ceramic phases.
KEY WORDS   Sol–Gel Reactions / Composites / Poly(dimethylsiloxane) / Silica / Titania / Mixed Oxides / Electron Microscopy / Impact Strength / Thermal Stability /

Sol–gel reactions have been extensively studied for over two decades as a method to prepare ceramic precursors and inorganic glasses at relatively low temperatures.[1–6] This method can be divided into two steps: hydrolysis of metal alkoxides to produce metal hydroxides, followed by polycondensation of the resulting hydroxyl groups to form a three-dimensional network. The reactions are generally catalyzed by the presence of an acidic or alkaline medium. The hydrolysis reaction replaces alkoxide groups with hydroxyl groups. Subsequent condensation reactions involving the silanol groups produce siloxane bonds (Si–O–Si) plus the by-products alcohol (ROH) or water (under most conditions, condensation commences before hydrolysis is complete). Both the hydrolysis and condensation steps generate low-molecular-weight by-products such as ethanol and water. These small molecules must be removed from the system, and such removal would lead, in the limit, to a tetrahedral SiO$_2$ network.

The sol–gel evolution of the TEOS network can proceed in different ways depending on the reaction conditions, such as pH, composition, solvent, and catalyst. The nature of the catalyst and, in particular, the pH of the reaction have a very pronounced effect on the hydrolysis and condensation reactions and the structure of the resulting inorganic network. In brief, under acidic conditions, the hydrolysis rate of TEOS is high but the condensation rate is extremely low, which results in long gelation times. As a result, acid-catalyzed hydrolysis with low water-to-Si ratios tends to produce weakly-

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* Present address: *Department of Chemical Engineering, Virginia Polytechnic & State University, Blacksburg, VA 24061–0211.*

branched "polymeric" sols (linear or chain molecules).[7] This will result in the formation of high-density, low fractal dimension structures. In contrast, a basic environment tends to produce more of a dense-cluster growth leading to dense, colloidal particulate structures due to a high condensation rate. Regardless of the structure of the solution species, gelation occurs when a network is formed throughout the entire volume. The gel consists of interpenetrating solid and liquid phases; the liquid prevents the solid network from collapsing and the solid network prevents the liquid from escaping.[8] Condensation reactions continue to occur after the initial network is formed.

Sol–gel techniques have attracted more and more interest because of the potential for developing new ceramics or glasses. The main advantage of the process is the fact that relatively low temperatures are sufficient for this type of processing of ceramics. As a result, there has been increasing interest in incorporating organic materials into these sol–gel-derived oxides.[9–16] The organically-modified glasses made in this way, which have been termed "ceramers" by Wilkes[10] and "ormosils" and "ormocers" by Schmidt,[11] are of considerable interest because of their potential for providing unique combinations of properties which can not be achieved by conventional methods. For example, the mechanical properties and optical characteristics of glasses can be greatly modified by incorporating organic materials into the inorganic network.

In the last few years, poly(dimethylsiloxane) (PDMS)–SiO_2 and $–SiO_2/TiO_2$ composites have been studied by Wilkes,[10,12,13] Kohjiya,[14] Parkhurst,[15] Sun,[16] and Mackenzie.[17,18] It was found that PDMS can be successfully incorporated into a hybrid network, with the properties of the resulting materials being highly dependent on composition, molecular weight and structure of the polymer, and on processing history. However, most of these studies have focused on the systems with less than 30 wt% of inorganic component in the final product, with relatively little experimental data for higher inorganic contents. It could also be useful to study organically-modified glasses with the inorganic phase as the major component. Also, there are apparently no studies of the influence of polymer on the kinetics of the sol–gel process. Finally, little has been done on the impact strength of these materials, which is a measure of their ability to withstand the application of a sudden load and is an inverse measure of brittleness.

For these reasons, the present study focused on a series of PDMS–SiO_2 and $–SiO_2/TiO_2$ composites having inorganic contents ranging from 30 to 100 weight percent. Nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and shear modulus tests on the gels as a function of time were used to study the hydrolysis and sol–gel reactions. Scanning electron microscopy (SEM) and impact-strength measurements were used to characterize the mechanical properties of the resulting composites. The thermal stability of the PDMS present in the ceramic matrix was studied using thermogravimetric analysis. The results of these various techniques were used in concert to document the properties of this class of inorganic/organic hybrid materials.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF), titanium n-butoxide, glacial acetic acid, ethanol, and hydrochloric acid (HCl) solution were all obtained from the Aldrich Chemical Company, and used without further purification. Tetraethoxysilane (TEOS) was purchased from the Petrarch Systems Company, and the hydroxyl-terminated PDMS samples were obtained from the Hüls America Company. The values of number-average molecular weight M_n, weight-average molecular weight M_w, and polydispersity index M_w/M_n were determined using

Petrach designation	Quoted M_n g mol^{-1}	GPC results		
		M_n g mol^{-1}	M_w g mol^{-1}	M_w/M_n
PS 341	4200	4700	12000	2.50
PS 340.5	1700	2350	4465	1.90
PS 340	500	344	408	1.20

a Waters 746 Gel Permeation Chromatography (GPC) instrument. The results are given in Table I.

Synthesis

The desired amount of distilled water, hydrochloric acid, and ethanol were first mixed in a beaker and then added with vigorous stirring to a flask which contained the desired amount of TEOS and hydroxyl-terminated PDMS.[19] The molar ratio of H_2O to TEOS was 2 to 1 in all formulations, and the reactions were carried out at 80°C for 2 h. The solution was then poured into a Teflon® mold, which was partially covered to avoid too-rapid evaporation of the solvent during the hydrolysis and sol–gel reactions. Depending on the sample composition and size, the drying period varied from one week to several months. The final products were then extracted with THF at 50°C for 5 days, with four renewals of THF, to determine the sol fraction of the sample.

In the case of the PDMS–SiO$_2$/TiO$_2$ combinations, there is the problem of the great difference in the reactivities of TEOS and titanium butoxide. As a result, the titanium compound generally reacts rapidly with water and precipitates out of the reaction mixture before it can react with the TEOS. This difficulty was overcome by using a step-wise polymerization process, the first step of which was the procedure described above. In the second step, the chemically-controlled condensation (CCC) method proposed by Schmidt[20] was used to incorporate Ti into the PDMS/

TEOS system. Specifically, the solution from step one was mixed with titanium butoxide and glacial acetic acid under vigorous stirring at room temperature. The water needed for the co-condensation of TEOS–PDMS–Ti(OBu)$_4$ was thus generated *in-situ*, by the condensation esterification of ethanol and glacial acetic acid.

Characterization

NMR Measurements. The hydrolysis reaction of TEOS was monitored by NMR (Bruker AC 250) at 250 MHz with tetramethylsilane (TMS) as an internal reference, and CDCl$_3$ as solvent. All NMR experiments were run under ambient conditions.[19]

GPC Measurements. The change of PDMS molecular weight during the reaction was monitored by GPC (Waters model 746), with toluene as solvent.

Scanning Electron Microscopy (SEM). The fracture surfaces of some of the samples were observed by SEM. The samples were mounted in suitable sample holders to display the fracture area, coated with gold, and then examined with a Cambridge Stereoscan 90B scanning electron microscope.[19]

Shear Moduli as a Function of Time. The condensation and sol–gel transition of TEOS and PDMS-modiffed TEOS systems were investigated by mechanical tests in which the change of shear modulus of the system with time was monitored. The basic apparatus, which was first used by Saunders and Ward,[7] is shown schematically in Figure 1. The inside of the glass tube was roughened to improve adhesion with the solution to be gelled, which was placed into it over a pool of mercury. An air pressure P was applied to the top of the gelling solution, giving a shearing stress at the tube wall, but not so large so as to cause slippage. Under these conditions, the shearing stress and strain are proportional to one another, and the modulus is given by

$$G = PR^2/4L(\Delta L) \qquad (1)$$

where ΔL is the displacement of the center of
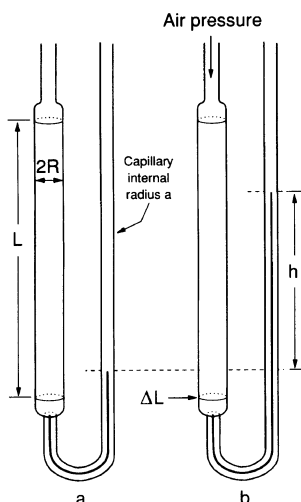
Figure 1. Mechanical property apparatus with the gel first undeformed (a), and then deformed downward (b) by application of pressure directly above it.

the gel meniscus. Since ΔL is so small, a volume displacement is best measured instead, through the change in height of the mercury column in the capillary. This volume is given by

$$\Delta V = \pi P R^4 / 8LG = \pi a^2 h \qquad (2)$$

and thus

$$G = P R^4 / 8 L a^2 h \qquad (3)$$

This formula is valid for $L > R$.

Impact Tests. The impact strengths of the samples were determined by the Charpy pendulum impact test (Zwick 5102B Charpy Pendulum Impact Tester) and by the falling-weight impact test. In the Charpy test, an un-notched specimen with dimensions 50 mm × 4 mm × 6 mm was placed between supports 40 mm apart and struck at the center by a swinging pendulum. The impact strength of the specimen was determined from the energy given up by the pendulum in breaking the test sample (as determined from the decrease in the maximum height of the swinging pendulum head after impact), and from the cross-sectional area of the sample. In the falling-weight impact test, the sample (typically 35 mm-diameter disks with thickness 2.5 mm) was clamped over
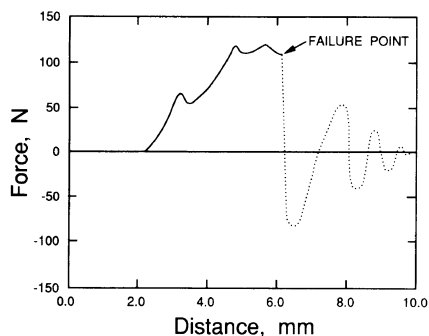
Figure 2. Typical plot of force against distance obtained from the falling-weight impact test.

a 19 mm diameter hole in the sample housing. The sample was then dropped from a height of 3.0 feet onto a 0.25 inch-diameter hemispherical dart at a speed of 142.0 inch per second. The dart is attached to a quartz piezo-electric washer-transducer that sends a charge to an amplifier. The charge was converted into a voltage for recording by a Nicolet model 3091 digital oscilloscope. The impact data were analyzed using a plot of force *vs.* distance, as illustrated in Figure 2, to obtain the impact energy.[19]
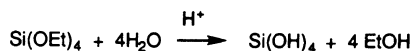
Thermogravimetric Analysis (TGA) Measurements. These experiments were carried out on a Perkin-Elmer (Model TGA-7) thermogravimetric analyzer installed in-line with a PE 7500 professional computer for data acquisition. All samples were studied in nitrogen which had been dried by passing it through a gas purifier before it entered the sample chamber. The samples, typically weighing 5—10 mg, were placed in platinum pans and were weighed directly on the thermogravimetric balance to within ± 0.001 mg. In the dynamic heating experiments, a heating rate of $10°C \min^{-1}$ over a temperature range of 30—800°C was employed.[19]

RESULTS AND DISCUSSION

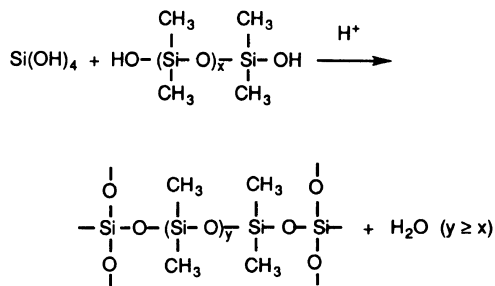### The Hydrolysis and Condensation

The basic reaction scheme for the PDMS–TEOS system is shown schematically below:

Hydrolysis

$$Si(OEt)_4 + 4H_2O \xrightarrow{H^+} Si(OH)_4 + 4\ EtOH$$

Co-condensation

$$Si(OH)_4 + HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O)_{\overline{x}}\ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH \xrightarrow{H^+}$$

$$-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O)_{\overline{y}}\ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-\ +\ H_2O\ (y \geq x)$$

In addition to the co-condensation shown above, reactants could also undergo *self-condensation* which would increase the molecular weight of the PDMS. According to previous studies, if TEOS can hydrolyze immediately so that PDMS chains react with hydrolyzed TEOS from the beginning of the reaction, co-condensation will be the dominant reaction for PDMS–TEOS systems. This can be achieved if acid catalyst and moderate temperature (around 70°C) are used.[15,21] Therefore, similar reaction conditions were used in this study. Also, NMR, GPC, and solvent extraction experiments were carried out in order to confirm that co-condensation is the dominant reaction in this study.

The NMR spectra of the TEOS/H₂O/HCl system before reaction and then 10 min after reaction show a dramatic decrease in the intensity of the silanol proton peak. This confirms that the TEOS hydrolyzed immediately after the addition of the H₂O and HCl, as shown in the first step of this scheme. The polymer molecular weight for various reaction conditions was compared by GPC before reaction and 2 h after reaction. The results are given in Table II and Figure 3(a). The results in the table show that the molecular weight of the PDMS increased instead of decreased after 2 h of reaction. This increase, which was apparently due to self-condensation, was

Table II. Changes in PDMS molecular weight and pholydispersity index under various conditions

Sample No.	Before reaction		20 min at 80°C		2 h at 80°C	
	M_n	M_w/M_n	M_n	M_w/M_n	M_n	M_w/M_n
1[a]	2350	1.90	2385	1.90	2450	1.90
2[b]	5900	2.07	6060	2.04	7400	1.79
3[b]	2350	1.90	2460	1.91	2800	1.88
4[c]	2350	1.90	2440	1.78	2880	1.96

[a] No HCl catalyst present. [b] Concentration of HCl aqueous solution was 0.55 M. [c] Concentration of HCl aqueous solution was 1.1 M.
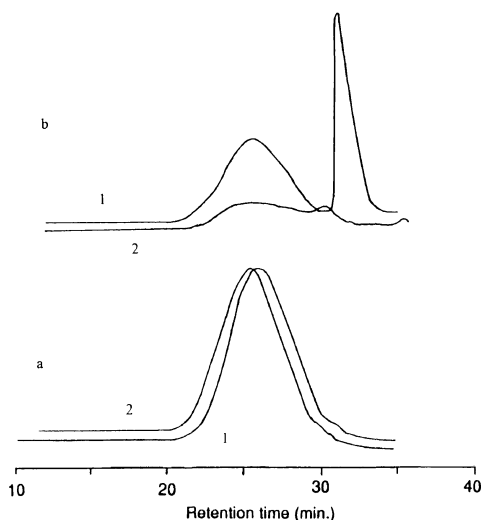
Figure 3. Peak intensity shown as a function of retention time obtained from GPC measurements. Part (a), PDMS in the presence of HCl: (1) before the reaction, and (2) after 2 h at 80°C; Part (b), PDMS/TEOS = 25/75: (1) before the reaction, and (2) after 2 h at 80°C.

generally small (less than 20%), but became more significant as the concentration of acidic catalyst was increased. In the presence of TEOS, hydrolyzed TEOS and partly-hydrolyzed TEOS were immediately produced. As a result, PDMS chains more likely reacted with hydrolyzed TEOS instead of with one other, and the PDMS self-condensation became less important. This analysis is confirmed by the results shown in Figure 3(b).

The effect of solvent extraction on the

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Table III. THF extraction of PDMS–SiO$_2$ composites

TEOS	M_n	Reaction time	Wt% PDMS in	Residual PDMS	Sol fraction
Wt%	PDMS	min	final product	Wt%	Wt%
65	1700	120	65	96.2	2.5
65[a]	1700	120	65	94.9	3.3
65	1700	20	65	93.7	4.1
65	4200	120	65	92.6	4.8
85	1700	120	38	96.7	1.3
85[a]	1700	120	38	96.0	1.5
85	1700	20	38	94.9	1.9
85	4200	120	38	92.1	3.0

[a] The molar ratio of TEOS/HCl was 1/0.02, instead of the usual value of 1/0.04.

PDMS-modified TEOS glasses is described in Table III. It was found in all cases that most of the PDMS was incorporated in the TEOS network, with less than 8 wt% being soluble, as unattached polymer. As expected, the exact amount of extract depended on the reaction conditions (including reaction time) and on the molecular weight of the polymer. The above experimental results all clearly demonstrated that co-condensation was the dominant reaction under these reaction conditions, and that the majority of PDMS was incorporated in the silica network.

### The Influence of PDMS on the Sol–gel Transition of TEOS

The properties that undergo the most dramatic changes at the gel point are the modulus G and the viscosity. The measurement of modulus as a function of time, however, is the more elegant and informative way to look at the gelation process.[22] The technique employed here, compression shear modulus tests, can give reliable results without damaging the gel. The experimental results are shown in Figures 4 through 6 and in Table IV.[19] They are best interpreted by the following analysis.

At the functional-group level, three reactions are generally used to describe the sol–gel process[18]:

Hydrolysis
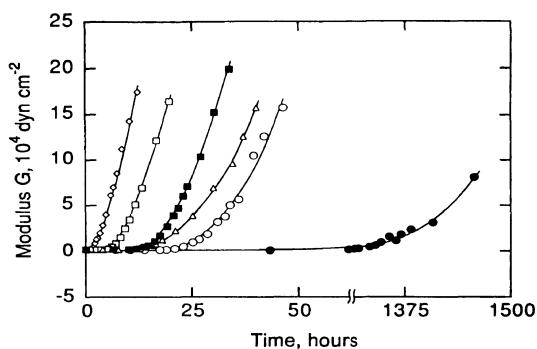
Figure 4. Dependence of shear modulus on time. Sample composition was TEOS/H$_2$O/HCl $= 1/1/0.04$ (molar ratio). The weight percent (relative to TEOS plus PDMS) and molecular weight of the PDMS were: ($\Diamond$) 35 and 4200 g mol^{-1}, ($\square$) 25 and 4200 g mol^{-1}, ($\blacksquare$) 15 and 4200 g mol^{-1}, ($\triangle$) 15 and 1700 g mol^{-1}, ($\bigcirc$) 15 and 500 g mol^{-1}, and ($\bullet$) 0.
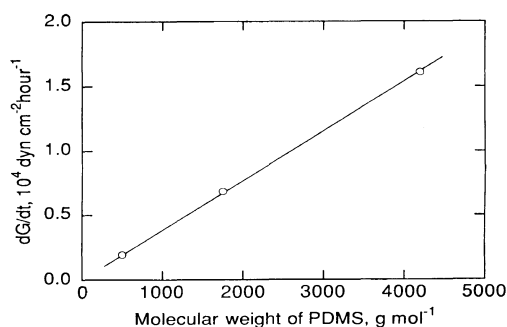
Figure 5. Effect of the molecular weight of the PDMS on the maximum value of dG/dt. The molar ratio of TEOS to PDMS was 1 to 0.022.

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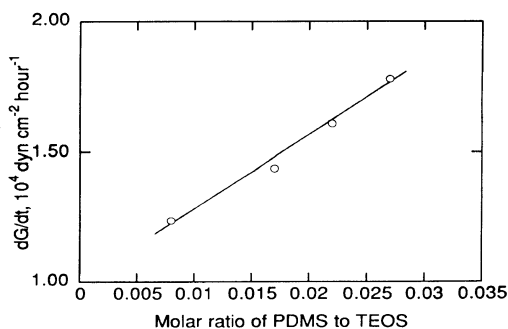
Figure 6. Effect of the molar ratio of PDMS to TEOS on the maximum value of dG/dt. The molecular weight of the PDMS was $4200\,\mathrm{g\,mol^{-1}}$.

Table IV. Gelation times and modulus evolution rates for PDMS–TEOS systems

| Wt% TEOS	M_n PDMS	TEOS/PDMS[a] (molar ratio)	Gelation time[b] h	dG/dt 10^4 $\mathrm{dyn\,cm^{-2}}$
100	0	1/0.000	1350	0.0636
95	500	1/0.022	306	0.195
85	500	1/0.140	18	0.782
65	500	1/0.224	4.5	0.772
85	1700	1/0.022	26.5	0.687
75	1700	1/0.041	9.5	0.744
65	1700	1/0.066	5.2	0.907
85	4200	1/0.008	16.2	1.238
75	4200	1/0.017	8.0	1.441
70	4200	1/0.022	5.1	1.611
65	4200	1/0.027	2.5	1.781

[a] Molar ratio: $\mathrm{TEOS/H_2O/ethanol/HCl} = 1/2/2.5/0.04.$
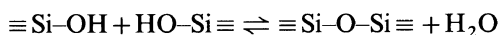[b] The gelation time is defined by the absence of flow in a solution-containing tube.

$$\equiv \mathrm{Si\text{–}OR} + \mathrm{H_2O} \rightleftharpoons \equiv \mathrm{Si\text{–}OH} + \mathrm{ROH}$$
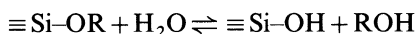
Esterification
Alcohol condensation

$$\equiv \mathrm{Si\text{–}OR} + \mathrm{HO\text{–}Si} \equiv \rightleftharpoons \equiv \mathrm{Si\text{–}O\text{–}Si} \equiv + \mathrm{ROH}$$
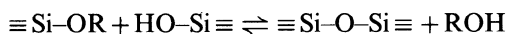
Water condensation

$$\equiv \mathrm{Si\text{–}OH} + \mathrm{HO\text{–}Si} \equiv \rightleftharpoons \equiv \mathrm{Si\text{–}O\text{–}Si} \equiv + \mathrm{H_2O}$$

As discussed above, under acidic conditions the hydrolysis rate of TEOS is high but the condensation rate is extremely low, and this results in 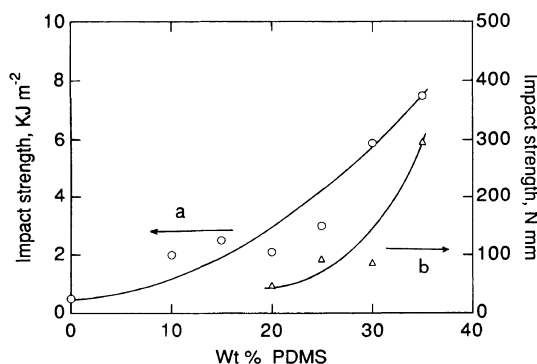long gelation times. For example, as the data in Table IV show, it would take two months for gelation of TEOS under the described reaction conditions. However, it was found from the shear modulus tests (Figures 4 through 6) that the presence of PDMS can dramatically shorten the incipient gelation time from 2 months to days or even hours, depending on the molecular weight and amount of PDMS used. For example (as shown in Table IV), the gelation time was only one hour for a sample with high molecular weight and a large amount of PDMS, compared to two months for TEOS alone. For these systems, the gelation time decreased as the molecular weight increased, or as the amount of PDMS increased, as shown in Figure 4. The reaction of the TEOS with the much higher molecular weight PDMS apparently greatly shortens the time required for the formation of larger branched species required in the gelation process.[23–25] As shown in Figures 5 and 6, the time dependence dG/dt of the modulus is also influenced by the presence of the PDMS. Specifically, it is increased significantly with increase in both the molecular weight of the PDMS and the amount present. The flexibility introduced by the polymer chains facilitates the condensation processes that increase the degree of cross linking in the network structure.

Impact Tests

Since most PDMS–$\mathrm{SiO_2}$ and –$\mathrm{SiO_2/TiO_2}$ composites prepared in the past have had PDMS as the major component, they were rubbery and unsuitable for impact-strength measurements.[19] Some of the composites in the present study, however, had PDMS contents sufficiently low to give composites having the brittleness required in such testing. Figures 7 and 8 show the dependence of the impact strength on the molecular weight of the PDMS and the amount of PDMS present in the PDMS–$\mathrm{SiO_2}$ system, respectively. As can readily be seen, the higher the molecular weight or the larger the amount of PDMS introduced, the higher the impact strength. A similar

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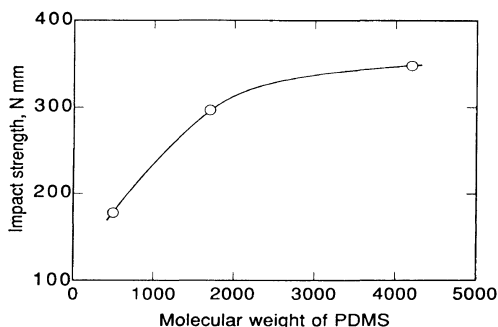
Figure 7. Dependence of impact strength on molecular weight of PDMS for PDMS-modified SiO$_2$ glasses. The impact strengths were obtained from the falling-weight impact test.

Figure 9. SEM micrograph of the fracture surface of a PDMS-modified SiO$_2$ glasses having low PDMS content, at a magnification of 106 ×.

Figure 8. Dependence of impact strengths on amount of PDMS for PDMS-modified SiO$_2$ glasses. The impact strengths were obtained from: (a) the Charpy pendulum impact test, (b) the falling-weight impact test.

analysis can be applied to PDMS–SiO$_2$/TiO$_2$ system.

The impact strength of a material measures its ability to withstand the application of sudden load (or "impact"), which results in fracture. Pure inorganic glasses have an internal strength much greater than the surface strength because fracture arises from the enalrgement of pre-existing surface flaws. These materials are thus very brittle, with correspondingly low impact strengths. Once started, fracture in glasses is thought to spread very rapidly because of the absence of grain boundaries to interrupt its progress.

The PDMS–SiO$_2$ composites apparently have some phase-separated PDMS, even though OH-terminated PDMS was successfully incorporated into the SiO$_2$ network by chemical bonding. This PDMS component can behave as an elastomeric phase because its glass transition temperature is far below room temperature. When the material is subjected to an impact test, the PDMS component can absorb a great deal of energy and thus delay the growth of cracks and fracture. In this way, considerable toughening of silica can be achieved. Increasing the molecular weight presumably facilitates the phase separation because of the decrease in polymer solubility with increase in molecular weight. Increasing the amount of PDMS would increase the number or size of the phase-separated domains helping to absorb the impact energy.

The observation of fracture surfaces can also provide a useful test of these conclusions.[26] Figure 9 shows a typical fracture surface obtained by SEM for a sample with low PDMS content. The smooth fracture surface is associated with completely brittle failure,[27] with no evidence of effective resistance to either initiation or propagation of cracks. Rather different behavior is shown by the sample with high PDMS content, as is illustrated in Figure 10. The sample fractured from right to left, at first in a brittle manner but then with considerable ductility. This is shown by the
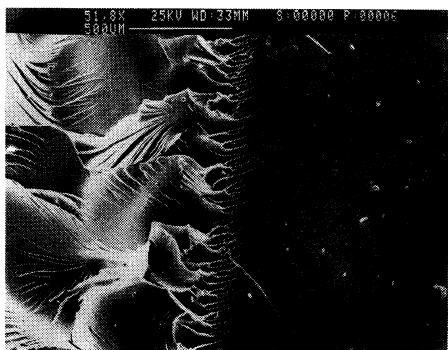
Figure 10. SEM micrograph of the fracture surface of a PDMS-modified SiO$_2$ glass having high PDMS content, at a magnification of 52 ×.
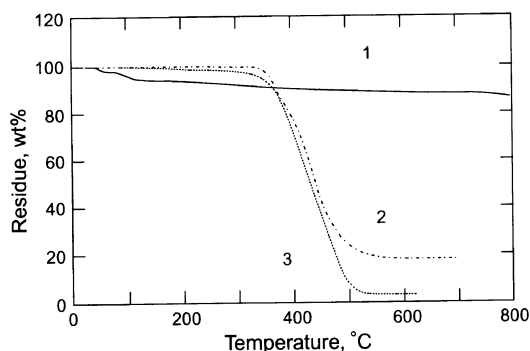
Figure 11. TGA thermograms for PDMS uncross-linked chains, PDMS network, and SiO$_2$ glass. Each curve is labeled with the designation used in Table V.

pronounced whitening or shearing in evidence in the left portion of Figure 10. The material had relatively low resistance to crack initiation, but good resistance to crack propagation because of the energy-absorbing mechanism introduced by the PDMS.

Thermogravimetric Behavior

Thermogravimetric analysis can be used not only to study the thermal decomposition and stability of materials, but also to give important structural information. Figures 11 through 13 show the TGA thermograms for the PDMS–SiO$_2$ composite. The preparative details and the TGA results for these samples are summarized in Table V. Sample compositions (represented as the weight percent of PDMS in the final product) are shown in column four and the total weight loss at 800°C in column five. The last column is the weight percent loss, assumed to come entirely from the PDMS.

Figure 11 shows the TGA thermograms for PDMS uncross-linked chains, PDMS networks, and SiO$_2$. The catastrophic degradation (marked weight loss), which was presumably due to the formation of volatile cyclic oligomers, commenced at about 350 and ended at 500°C for both PDMS chains and for PDMS networks. The initial weight loss of about 6%

Table V. Preparative details for PDMS-modified glasses

Sample No.	Wt% of TEOS	TEOS/HCl[a] (molar ratio)	Wt% of PDMS in final product	Wt% loss at 800°C	Wt% loss of PDMS
1	100	0.04	0	11	0
2	0	0.00	100	3	97
3[b]	0	0.00	100	17	83
4	85	0.04	38	12	32
5	75	0.04	54	15	28
6	60	0.04	70	39	56
7	75	0.02	54	13	24
8	75	0.10	54	17	31
9	85	0.10	38	15	39
10[c]	85	0.04	38	16	42
11	71.5[d]	0.04	60	19	32
12	81.5[d]	0.04	47	20	43

[a] Molar ratio of TEOS to water was 1 to 2. [b] PDMS chains were endlinked with TEOS as crosslinker and stannous octoate as catalyst.[28] [c] Molecular weight of PDMS was 4200 g mol^{-1}. [d] Ratio of PDMS to TEOS and titanium butoxide.
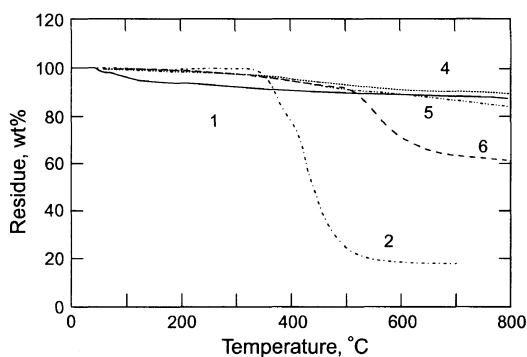
Figure 12. TGA thermograms for PDMS-modified SiO₂ glasses with different PDMS contents. Each curve is labeled with the designation used in Table V.
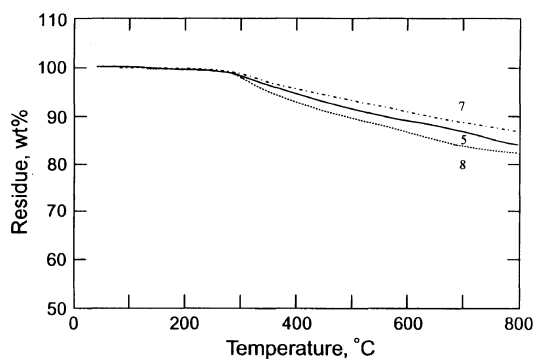
Figure 13. TGA thermograms for PDMS-modified SiO₂ glasses prepared using different amount of HCl catalyst. Each curve is labeled with the designation used in Table V.

below 150°C for the SiO_2 may result from the residual solvent entrapped within the pore structure and from any adsorbed species such as water. Figure 12 shows the TGA thermograms for the PDMS-modified glasses with different PDMS contents. Unlike the case of the SiO_2 glasses, there was no initial weight loss before 150°C for the PDMS-modified SiO_2 glasses. This could be due to their having more condensed structures, preventing solvent entrapment. Also, there was no catastrophic degradation when the PDMS content was less than 55 wt%, as in Samples 4 and 5. The total weight loss at 800°C was less than 40% of the PDMS, as shown in Table V. For Sample 6, which had 70 wt% PDMS, the catastrophic

degradation commenced at about 500°C, which was much higher than the 350°C observed for the pure PDMS network. This is consistent with the conclusion that the PDMS chains are chemically bound to the silica network, giving them increased heat resistance. Figure 13 presents the TGA thermograms for the samples prepared using different HCl (catalyst) contents. It was found that the presence of HCl decreased the onset temperature of degradation, but increase in its amount increased the extent and rate of weight loss.

CONCLUSIONS

Poly(dimethylsiloxane) (PDMS)–SiO_2 and –SiO_2/TiO_2 composites have been successfully prepared using a sol–gel process. The hydrolysis and sol–gel transition reaction of the PDMS–SiO_2 system have been studied by nuclear magnetic resonance, gel permeation chromatography, solvent extraction, and shear modulus tests. It was found that co-condensation between TEOS and PDMS was dominant under the chosen reaction conditions, and that the majority of the PDMS was incorporated in the SiO_2 network. The addition of PDMS was found to shorten the gelation times in these systems, and to increase the rates of increase in modulus of the network structure. The impact strengths and the fracture surfaces of these materials were investigated, with the finding that the addition of PDMS greatly increases their impact strengths and ductility.

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