

Articles

Modification of an Inorganic-Organic Hybrid Composite: Effect of Ethylamine

Anthony B. Brennan* and Thomas M. Miller

Department of Materials Science and Engineering, University of Florida,
Gainesville, Florida 32611

Received June 25, 1993. Revised Manuscript Received December 20, 1993*

Changes in the physical properties of a sol-gel-derived, poly(tetramethylene oxide)/silica hybrid composite as a function of aging in a strongly basic solution of 70% ethylamine in water were monitored. Characterization of the *in situ* modified inorganic phase was carried out using mechanical tensile testing, dynamic mechanical spectrometry, thermogravimetric analysis, swelling studies, and small-angle X-ray scattering experiments. It appears that syneresis, followed by ripening of the original polysilicate phase produces a more sharply phase-separated composite. There are significant and systematic changes in the mechanical and damping characteristics associated with the change in morphology. Additionally, the fractal nature of the system is transformed from a mass fractal to a surface fractal as a result of this solution-induced inorganic modification.

Introduction

A variety of "hybrid" organic-inorganic polymer networks have been prepared utilizing the sol-gel process.¹⁻⁵ These processes usually involve the traditional hydrolysis and polycondensation of metal alkoxides in the presence of a solvated organic polymer. Our effort has been directed toward the structure/property relationships of hybrids derived using triethoxysilane end-capped PTMO and tetraethoxysilane (TEOS).

It is well-known that the structures generated by such a sol-gel process are defined by the processing conditions such as the water-to-alkoxide ratio, catalyst, solution pH, and solvent. It is also recognized that the polymerization process is the equivalent of a step growth polymerization process. Since the average functionality, i.e., alkoxides per molecule, is greater than 2, the resultant polymer will be a network. However, research on acid-catalyzed TEOS has shown that there is a significant portion of nonreacted alkoxides and/or silanol groups present after gelation of the polysilicate network.^{6,7} The reaction mechanisms responsible for these "defects" also result in the formation of polysilicate domains composed of extended, lightly cross-linked, inorganic chains.⁸⁻¹⁰ Since the hybrids discussed

in this work are the product of the single-stage hydrolysis and condensation of TEOS, it is expected that the polysilicate domains generated at the ends of the PTMO will possess similar, extended morphologies.⁸ Consequently, a high degree of interaction between the PTMO and polysilicate chains is expected and observed in these composites.

The morphology of these hybrids has been described as microphase separated, in that short-range, periodic, electron density fluctuations are observed in the small-angle X-ray scattering profiles.¹¹ The morphological model developed for these hybrid composites proposes that three regimes exist: predominantly PTMO-rich domains, amorphous, polysilicate domains, and regions consisting of a mixed phase system of both the organic and inorganic chains.^{11,12} An interdomain spacing of 10-20 nm has been determined using small-angle X-ray scattering and is a function of the relative volume fraction of polysilicate and the processing variables. In particular, it was found that the initial structures formed under acidic conditions resembled a mass fractal dimension using a Prosd analysis of the scattering profile. The same composition polymerized under basic conditions became more sharply phase separated, yet remained optically transparent and was more surface fractal in character.¹³ This difference is important and will be discussed again at the conclusion of this work.

Another issue that needs to be addressed in these systems is the presence of pores within both the polysilicate

* To whom correspondence should be addressed.

• Abstract published in *Advance ACS Abstracts*, February 1, 1994.

(1) Schmidt, H. J. *J. Non-Cryst. Solids* 1985, 73, 691.

(2) Sur, G. S.; Mark, J. E. *Eur. Polym. J.* 1985, 21, 1051.

(3) Huang, H. H.; Orlor, B.; Wilkes, G. L. *Macromolecules* 1987, 20, 1322.

(4) Mauritz, K. A.; Storey, R. F.; Jones, C. K. *Multiphase Polymers: Blends and Ionomers*; Ultracki, L. A., Weiss, R. A., Eds.; ACS Symp. Series, 1989; p 401.

(5) Landry, C. J. T.; Coltrain, B. K.; Brady, B. K. *Polymer* 1992, 33, 1486.

(6) Brinker, C. J.; Drotning, W. D.; Scherer, G. W. *Mater. Res. Soc. Symp. Proc.* 1984, 32, 25.

(7) Glaser, R. H.; Wilkes, G. L.; Bronniman, C. E. *J. Non-Cryst. Solids* 1989, 113, 73.

(8) Keefer, K. D. *Mater. Res. Soc. Symp. Proc.* 1984, 32, 15.

(9) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Assink, R. A.; Kay, B. D.; Ashley, C. S. *J. Non-Cryst. Solids* 1984, 63, 45.

(10) Brinker, C. J.; Scherer, G. W. *J. Non-Cryst. Solids* 1985, 70, 301.

(11) Wilkes, G. L.; Brennan, A. B.; Huang, H. H.; Rodrigues, D. E.; Wang, B. W. *Mater. Res. Soc. Symp. Proc.* 1990, 15, 171.

(12) Huang, H.; Glaser, R. H.; Wilkes, G. L. *ACS Symp. Ser.* 1987, 360, 354.

(13) Rodrigues, D. E.; Brennan, A. B.; Betrabet, C.; Wang, B. W.; Wilkes, G. L. *Chem. Mater.* 1992, 4, 1437.

and PTMO phases. Using BET analysis, Motoyuki et al. have shown that sol-gel-derived poly(vinylpyrrolidone)/silica hybrids possess pores of approximately the same size but much fewer in number than dried silica gel also produced by the sol-gel processing of TEOS.¹⁴ Undoubtedly, the size, distribution, and surface properties of the pores in these hybrids are determined by the initial processing variables and the stoichiometry of the reactants. However, to our knowledge, there have been no reports concerning the modification of existing gel structures using secondary processing. Similarly, there have been numerous examples of modifications made to existing networks by the *in situ* precipitation of silica or titania into the pore structures of organic polymer films using the sol-gel process.^{3,15}

It is possible that one could potentially generate novel membranes by controlling the physical and chemical properties of these pore structures. It was also anticipated that the interactions between the inorganic and organic components of these hybrid composites would also vary with changes in the pore structures. This being the case, one could possibly develop a useful model for studying the role of interfaces in composite structures. With these two ideas in mind, the goal of this work was to examine the change in the network structure/property behavior of a PTMO/silica hybrid induced by systematic modification of the polysilicate phase. This was accomplished by aging the hybrid in a basic solution during which time it was expected that conditions of high solubility for the silica could be created and the morphology manipulated. The aqueous based solution of 70% ethylamine in water was chosen as the aging solution.

Experimental Section

Materials. A nomenclature detailing the conditions under which each gel was synthesized was previously described in detail for these composites.¹⁶ Based on this system, the hybrids synthesized for use in this study are designated TEOS(40)-PTMO(2K)-100-0.014 HCl. Procedures explaining the synthesis of the triethoxysilane end-capped PTMO oligomers have been given elsewhere.¹² The initial sol-gel processing of TEOS and PTMO oligomers was carried out in a cosolvent system of isopropyl alcohol and tetrahydrofuran (Fisher Scientific, HPLC grade). Both solvents were used as received.

Gel Synthesis. The synthesis of the six TEOS(40)-PTMO(2K)-100-0.014 HCl hybrids studied in this experiment was carried using the following procedure. Briefly, 9 g of PTMO, 12 mL of isopropyl alcohol, and 3 mL of THF were stirred in a parafilm covered 50-mL Erlenmeyer flask for 20 min. After 20 min, 6 g of TEOS was added to the PTMO/solvent mixture via a hypodermic needle. This resulted in a solution containing 40 wt % TEOS and 60 wt % end-capped PTMO, with respect to one another. This is denoted by the (40) immediately following the term TEOS in the hybrid designation. Continuing, this new mixture was then covered with parafilm and stirred an additional 7 min. After this 7 min had elapsed, a mixture of 0.225 g of 10 N HCl and 2.475 g of deionized water was added to the PTMO/solvent/TEOS solution. These amounts resulted in a molar ratio of water:ethoxy of 1:1 (100% of the water required for complete hydrolysis) and acid:alkoxy of 0.014:1. These numbers are also used in the sample designation. This solution was again covered with parafilm and stirred for an additional minute. The sol was subsequently poured into six polystyrene Petri dishes which were then covered immediately to reduce solvent evaporation. The

covered petri dishes were then left at room conditions (23 ± 1 °C, ~50% relative humidity) for 4 days to gel.

The petri dishes were then left uncovered for 2 days to exhume any residual alcohol or solvent. These materials were optically transparent indicating no macrophase separation had occurred. The petri dishes containing the samples were then covered and stored for 6 days at ambient conditions before experimentation.

Gel Standardization. Each gel was extracted and dried prior to testing and modification to ensure that all samples were equivalent. The hybrids were soaked in THF for 22 h. This process swelled the cross-linked network and helped remove any residual organics.¹⁷ The gels were removed from the THF and dried in a vacuum oven at 40 °C (28 in.Hg) for 15 h. Next the gels were soaked in deionized water for 24 h. Again the gels were dried in a vacuum oven at 40 °C (28 in.Hg) for 15 h. Samples treated in the manner described are referred to as *standard gels*.

Gel Equilibration. Each gel, after standardization, was placed in a Pyrex petri dish containing 60 mL of a solution of 70% (wt/wt) ethylamine in water (Eastman Chemical). After 1 h, one of the gels was removed from the ethylamine solution, shaken off, and immediately placed in a Pyrex petri dish containing 60 mL of deionized water. The pH was monitored hourly at which time the water was changed. The water extraction was continued for 8 h at ambient conditions. The gel was then placed in a vacuum oven at 40 °C (28 in.Hg) for 15 h. The four remaining gels in the ethylamine solution were removed at time intervals of 4, 7, 13, and 25 h. Each gel was then extracted in water and dried as just described. The hybrids treated in this manner are identified as *equilibrated*.

Characterization Methods. Tensile strength and elongation were measured at ambient conditions using an Instron Model 1122 equipped with a 1000-lb load cell. The crosshead rate was 2.54 mm/min. Dog-bone-shaped specimens were cut using the Type M-III ASTM die described in ASTM test D638M-84. The initial width of the test section was 2.5 mm with a grip-to-grip distance of 25 mm. The average sample thickness was 0.25 ± 0.01 mm, and two to four samples were tested for each exposure time reported.

Dynamic mechanical spectrometry was performed using a Seiko DMS 200(FT) interfaced with a Seiko Rheostation Model SDM/5600H. All experiments were carried out from -150 to 200 °C at a heating rate of 0.75 °C/min in a dry nitrogen atmosphere maintained by a minimum flow rate of approximately 200 mL/min. All spectra presented are those obtained at 1 Hz.

A Seiko TG/DTA 320 interfaced with the same Rheostation was used to conduct thermogravimetric analysis. All tests were performed over the range 25-1000 °C with a heating rate of 10 °C/min in a dry air atmosphere maintained at a flow rate of approximately 100 mL/min.

Swelling behavior was measured using disks punched from the gels (TEOS(40)-PTMO(2K)-100-0.014 HCl) using a No. 6 cork borer. The diameter-to-thickness ratios of the samples were 26:1, 30:1, and 31:1. On the basis of these dimensions, it is reasonable to assume that each can be considered an infinite plate. Each sample was standardized as described above (Materials) prior to exposure to the ethylamine solution. The percent mass uptake of ethylamine solution was continuously monitored as a function of time for a period of 13 days. Upon removal from the ethylamine solution, these gels were deswelled in water and then vacuum dried at 40 °C (28 in.Hg) for 15 h. The swelling behavior of these gels in THF was then monitored as a function of time for 24 h.

Small-angle X-rays scattering data was acquired using a Siemens Kratky camera employing a M. Braun position-sensitive detector from Innovative Technology, Inc. A linear regression analysis was performed on the raw data to determine the slope as necessary for the Porod analysis. The smoothed data were not available for inclusion with this paper.

Results and Discussion

Gel Preparation. The structure/property relationship of the PTMO/silica hybrids is strongly dependent upon

(14) Motoyuki, T.; Chow, T. Y.; Ohnaka, T.; Samura, H.; Saegusa, T. *Polym. Bull.* 1992, 29, 653.

(15) Mauritz, K. A.; Warren, R. M. *Macromolecules* 1989, 22, 1730.

(16) Huang, H.; Orler, B.; Wilkes, G. L. *Polym. Bull.* 1985, 14, 557.

(17) Brennan, A. B.; Wilkes, G. L. *Polymer* 1990, 32, 733.

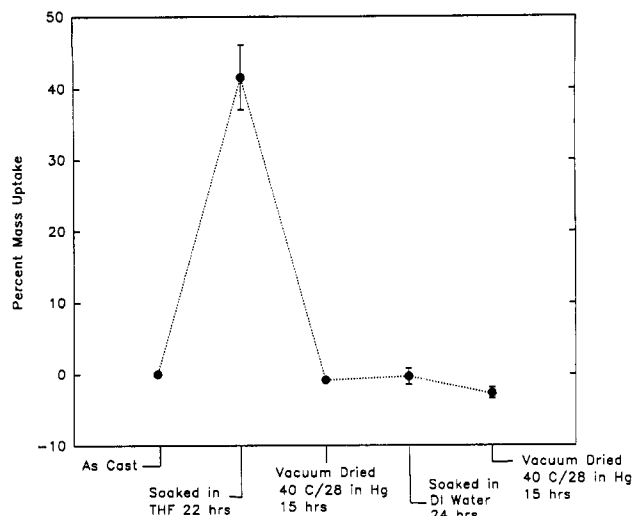


Figure 1. Mean value of the percent mass uptake of the six TEOS(40)-PTMO(2K)-100-0.014 HCl gels during the standardization process.

Table 1. Recorded pH Values during Deswelling in Water

ethylamine exposure time (h)	pH during deswelling in water for x h								
	1	2	3	4	5	6	7	8	9
as-cast									
1	10	9.5	9.5	9.5	9	6.5	6.5	6.5	
4	9.5	9.5		9.5	8.5	8.5	8.5	7.5	6.5
7	9.5	9.5	9.5	9	8.5	7.5	6.5		
13	10.5	10	8.5	9.5	7	6.5			
25	11	10	9.5	8.5	7	6.5			

processing conditions and age.¹⁸ Therefore, to characterize the structural changes induced by the ethylamine solution, it was first necessary to achieve a benchmark structure. The procedures described above, i.e., gel synthesis and standardization, served this purpose.¹⁷ After the mass of the gels was monitored at each step in the standardization process, it was determined that there was effectively no THF soluble material in the as-cast gel. The results are illustrated in Figure 1 as the mean value of percent mass uptake of the gels at each stage of the extraction process. It can be seen that essentially no decrease occurred in the mass of the THF swollen gel after vacuum drying. Similarly, virtually no increase in mass is evidenced when the dried hybrid is exposed to water. The larger decrease in mass observed after swelling with water and subsequent drying indicates that there may have been some further hydrolysis and condensation of the inorganic phase. A sixth gel was not dried or standardized. This gel was designated the *as-cast* gel throughout this publication.

The exposure times listed throughout this paper refer to time of immersion in the ethylamine solution. However, it is important to point out that the actual time at a high pH (e.g., pH > 8.5) is significantly longer in some cases. As described previously, samples removed after 1, 4, 7, 13, and 25 h of immersion in the ethylamine solution were then placed in Pyrex petri dishes containing approximately 100 mL of deionized water. The pH of this water was measured every hour and then replaced with fresh deionized water. The variation of pH as a function of time for each series of gels is listed in Table 1 for the 9-h deswelling period. The pH of the water solution is close

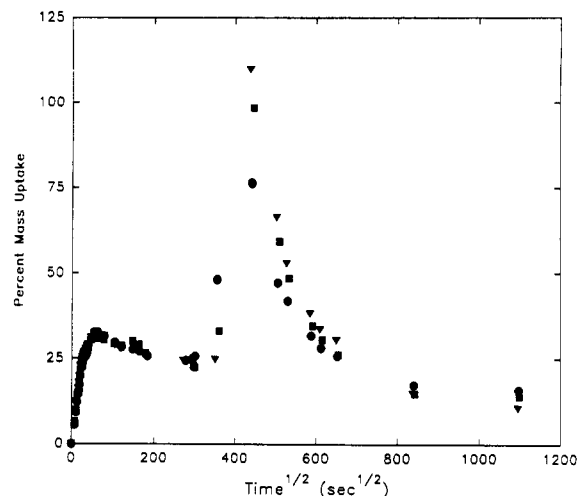


Figure 2. Absorption profile of three standard TEOS(40)-PTMO(2K)-100-0.014 HCl gels exposed to the 70% (wt/wt) ethylamine in water solution (each represented by a different symbol).

to neutral after a period of ca. 5–7 h for all the gels. The recorded pH values of 8.5 for at least the first few hours after removal from the ethylamine solution indicate that the actual exposure time to a strongly basic solution is not limited to the original 1, 4, 7, 13, and 25 h.

The overall absorption profile of a standard gel (TEOS(40)-PTMO(2K)-100-0.014 HCl) over a period of 13 days is graphically illustrated in Figure 2. The percent mass uptake of solvent as a function of the square root of time is linear up to 1 h. Recall that the percent mass uptake of the large gels when exposed to deionized water for 24 h during the standardization process resulted in a negligible percent increase in mass (Figure 1). This suggests that the significant absorption over the first hour is attributable to the uptake of ethylamine through the high surface area polysilicate phase. During the next ca. 22 h the gels deswell slightly. Beyond the initial deswelling in the first 24 h, there is a sharp increase in solvent uptake. The maximum percent mass uptake of 100% occurs after approximately 60 h of immersion. The gels then begin to deswell in a nonlinear manner over the next 6–8 days. The final swollen state at 13 days is on the average 13.5%. Upon removal from the ethylamine solution, deswelling in water, and drying, the gels soaked for 1 h are usually turbid, while those soaked for 25 h are usually optically transparent. The intermediate soaking times of 4, 7, and 13 h exhibit a progressive shift toward transparency, respectively. This turbidity is not a surface defect but rather a bulk property.

The linearity of the ethylamine solution uptake versus square root of time plot (Figure 2) suggests Fickian diffusion of the solvent into the gel. The turbidity that develops in the gel soaked for 1 h indicates a phase-separation process has occurred during soaking and deswelling. This could be due to an enlargement of the pore structure or a migration of the PTMO phase away from the polysilicate domains. This will be discussed in more detail later. The deswelling which occurs after the diffusion process is complete, i.e., after the first hour of immersion in ethylamine, is most likely due to the process of syneresis, followed by ripening of the polysilicate phase. The syneresis process, as described by Brinker and Scherer,

(18) Wilkes, G. L.; Huang, H. H.; Glaser, R. H. *Silicon Based Polymer Science*; Zeigler, J. M., Gordon, Fearon, G. W., Eds.; ACS Advances in Chemistry Series; American Chemical Society: Washington, DC, 1990; p 207.

(19) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979; pp 40–54.

Table 2. Thermogravimetric Analysis

ethylamine exposure time (h)	% ROI	
	run 1	run 2
as-cast	20.5	20.7
1	21.2	21.1
4	21.0	21.0
7	20.8	20.9
13	20.9	20.8
25	20.8	21.0
312 (13 days)	5.5 ± 0.2	

Table 3. Mechanical Properties

ethylamine exposure time (h)	av elastic modulus (MPa)	av stress at break (MPa)	av elongation at break (%)
as-cast	24	5.7	22
1	110	8.7	7.7
4	87	9.6	10
7	73	7.7	10
13	57	6.3	10
25	42	9.1	18

involves the condensation of silanols and/or alkoxides to form siloxane bonds.¹⁰ The net effect of syneresis is a reduction in pore volume and increase in network density of the polysilicate phase. In conjunction with the syneresis process is the ripening process proposed by Iler, whereby the polysilicate network continues to densify while it ages in the high-pH solution.¹⁹ The mechanism through which this occurs has been described in terms of a growth process that occurs between two neighboring silicate particles experiencing conditions of high solubility. These processes become more apparent when the mechanical properties of these modified hybrids are presented shortly.

The next phase of the swelling profile (Figure 2) implies that the structural change which occurs after 25 h of exposure to the ethylamine solution must be dominated by significant dissolution of the polysilicate phase. It is well established that the solubility of amorphous silica at 25 °C increases from 180 ppm at pH 9.5 to 876 ppm at pH 10.6.¹⁹ The pH of the 70% (wt/wt) ethylamine solution is 12.5. Therefore, on the basis of the massive expansion the gels experience after ca. 2 days in ethylamine, it is reasonable to assume the polysilicate is solubilized.

Further support for the dissolution of the polysilicate phase by day 13 was obtained by swelling the three samples that had been exposed to the ethylamine solution (and deswollen in water) in THF for 24 h. During the first 30 min of exposure to THF, the gels increased in mass. However, for the remaining 23.5 h the percent mass uptake remained a constant $96.9 \pm 5.07\%$. This value is compared to the percent mass uptake of THF during the standardization procedure prior to their exposure to the ethylamine solution, $46.1 \pm 1.36\%$. This difference clearly suggests that the polysilicate domains, which function as cross-link sites, have been significantly dissolved.

The extent of dissolution of the silica phase leading to a reduction in the polysilicate phase can be evaluated in terms of silica content by TGA. The percent residue on ignition (% ROI) of each gel is listed in Table 2 according to immersion time in ethylamine. It is apparent that the % ROI remains constant at $20.9 \pm 0.1\%$ even after 25 h in the ethylamine. Thus, the swelling and deswelling that occurs in the first 25 h does not cause complete dissolution and subsequent extraction of the polysilicate. However, the % ROI of the sample immersed for 13 days clearly demonstrates a reduction of silica content in the gel from 20.9% to $5.5 \pm 0.2\%$.

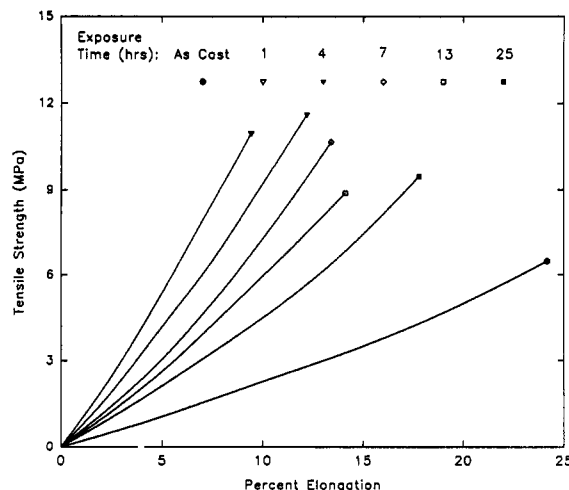


Figure 3. Typical tensile stress vs percent elongation for the TEOS(40)-PTMO(2K)-100-0.014 HCl as-cast and equilibrated gels (symbols are for ease of identification only).

As we have stated, an analysis of the mechanical behavior of the gels can provide further insight into structural changes induced by exposure to the ethylamine solution. Typical tensile strength versus percent elongation responses are plotted in Figure 3 as a function of exposure time to the ethylamine solution. The measured values for the elastic modulus, stress at break, and percent elongation at break are listed in Table 3.

The elastic modulus increases sharply from 24 to 110 MPa after 1 h of immersion in ethylamine. It then decays to a low of 42 MPa after 25 h of immersion in the ethylamine. The modulus of the gel exposed for 25 h is significantly lower than that of the 1-h gel, yet it is still nearly twice that of the as-cast gel. In terms of the syneresis process, the increase in the 1-h modulus can be explained as an increase in the stiffness of the polysilicate network resulting from the additional condensation induced by the catalytic nature of the ethylamine solution. Brinker and Scherer described the aging process in terms of a ripening of the sol–gel-derived polysilicate structure.^{10,20} This is a solution process whereby mass transport of the more soluble phase to the less-soluble phase increases the density of the structure. The change in the polysilicate morphology caused by aging is illustrated in Figure 4. Inherent in this process is the formation of pore structures which have a significant effect on physical and mechanical properties of the gel. It is most likely that the turbidity of the gels soaked for 1 h in ethylamine may be due to an insoluble phase that is retained in the pores of the silicate structure. Along with the developing pore structure, under the basic conditions of this experiment, the skeletal structure densifies as is indicated by the thicker lines (Figure 4). As the gels are aged for longer times, i.e., 25 h, this insoluble phase continues to diffuse out and the pore size is reduced by further condensation of the polysilicate structure, which causes shrinkage. A reduction in the pore volume explains the deswelling and shift towards transparency that occurs between 1 and 25 h of immersion in the ethylamine (Figure 2). The changes in pore structure explain the swelling behavior and optical properties of the gels in the first 25 h. However, the decrease in modulus after the first hour requires an

(20) Brinker C. J.; Scherer, G. W. *Sol Gel Science: The Physics and Chemistry of Sol–Gel Processing*; Academic Press: San Diego, CA, 1990.

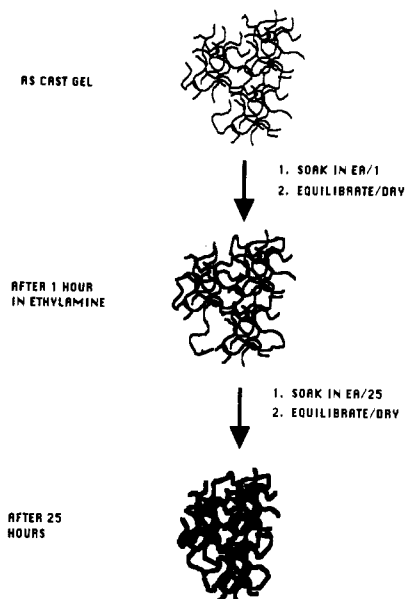


Figure 4. Illustration of the aging process which results in a conversion from the initially linear polysilicate structures to more ramified clusters which begin to "sinter" into fibrils and create pores.

examination of the effect of syneresis on the overall network, i.e., the polysilicate and PTMO phases.

The contribution of the PTMO phase to the modulus depends upon the initial extent of reaction of the chain ends with the TEOS monomer during the initial processing of the gel. Similarly, physical entanglements may form along the length of the PTMO chains as solvent evaporation and gelation occur. Therefore, entanglements may be between PTMO chains or PTMO chains and the polysilicate chains. The dynamic mechanical behavior of these PTMO/silica hybrids yields information about the extent of phase mixing between the PTMO and polysilicate phases.^{17,18} Thus, the dynamic mechanical analysis of these materials is presented here.

The storage modulus for gels equilibrated after 1, 4, 13, and 25 h of immersion in ethylamine is plotted as a function of temperature (frequency = 1 Hz) in Figure 5. As a reference, the storage modulus of the as-cast gel is included in Figure 5 and is typical of an acid-catalyzed gel prepared in aprotic solvents.¹² The key features of the storage modulus response to temperature are the onset of the T_g at 180 K, the rubbery modulus and the increase in the modulus near 400 K. The increase in the rubber modulus near 400 K is due to additional condensation of nonreacted alkoxides, i.e., syneresis, as previously reported for these materials. The absence of this characteristic increase in the storage modulus at higher temperatures supports the argument that syneresis is the dominant process in the first 25 h of exposure to the ethylamine solution. The storage modulus at 298 and 348 K is listed for each gel in Table 4, where it can be seen that the storage modulus is inversely proportional to immersion time in ethylamine in a manner similar to the elastic tensile modulus (Table 3). An explanation of this trend requires an examination of the $\tan \delta$ response.

The as-cast gel exhibits a very broad loss dispersion extending from 180 to 320 K (Figure 6). The shape and magnitude of this $\tan \delta$ peak are related to the molecular

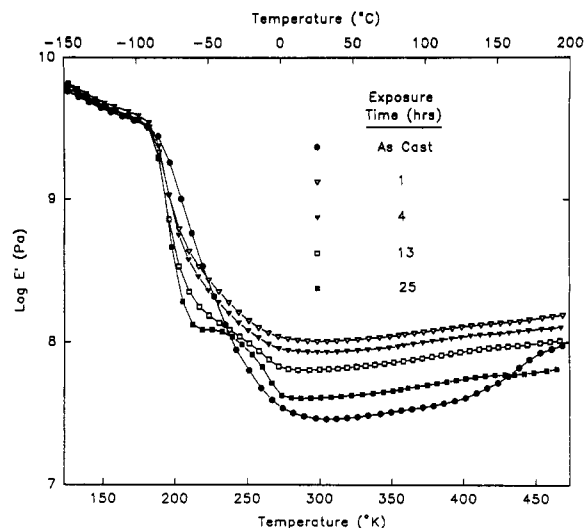


Figure 5. Dynamic mechanical spectrum of the log storage modulus as a function of temperature for the TEOS(40)-PTMO-(2K)-100-0.014 HCl as-cast and equilibrated gels.

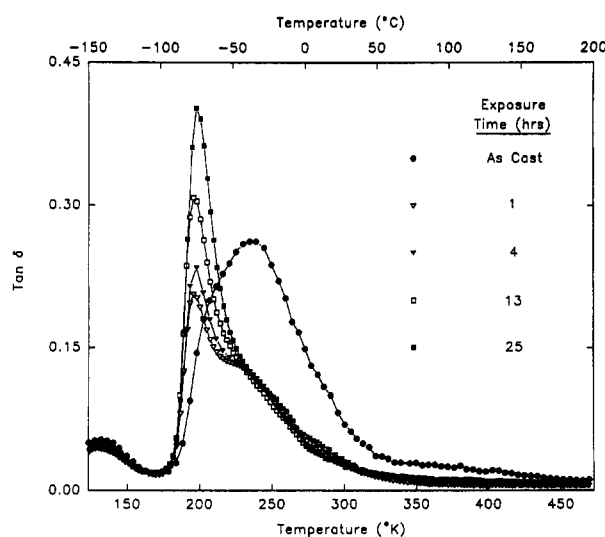


Figure 6. Dynamic mechanical spectrum of the $\tan \delta$ response as a function of temperature for the TEOS(40)-PTMO-(2K)-100-0.014 HCl as-cast and equilibrated gels.

Table 4. Dynamic Mechanical Storage Modulus

ethylamine exposure time (h)	storage modulus (MPa), 1 Hz	
	298 K	348 K
as-cast	29.0	32.2
1	101	110
4	85.4	91.7
13	64.3	71.8
25	40.7	45.3

motions of the PTMO phase as previously described.^{17,18,21} The lower temperature portion of the broad dispersion are indicative of free PTMO chains, and the higher temperature portion are indicative of entanglements or at least interactions of a restrictive nature between the PTMO chains and the polysilicate chains. The lower temperature segment of the $\tan \delta$ peak which extends from 180 to 300 K decreases in magnitude from 0.28 for the as-cast gel to 0.18 for the gel immersed in the ethylamine solution for 1 h. The temperature at which the maximum $\tan \delta$ is measured is 50 K lower for the 1-h gel compared with the

Table 5. SAXS Analysis: Porod Exponent

ethylamine exposure time (h)	Porod exponent
as-cast	-1.42
1	-2.02
3	-2.08
7	-2.10
13	-2.07
25	-2.10

as-cast gel, i.e., 190 versus 240 K. Interestingly, the T_g of no-TEOS-added, end-capped PTMO is on the order of 190 K. This indicates that the system undergoes a phase separation process. The increasing time of exposure to ethylamine does not cause shifts along the temperature axis but does significantly increase the magnitude of the $\tan \delta$ to a value of 0.43 for the 25-h gel.

The magnitude of the higher temperature shoulder of the $\tan \delta$ relaxation, ca. 230–300 K, does not change after the initial decrease measured following 1-h immersion in the ethylamine solution. Thus, it appears that the first hour of exposure of these gels to the ethylamine solution initially tightens the overall network, thereby reducing the molecular motion as expected for a syneresis process. However, over the next 24 h the increase in molecular motion in the PTMO phase indicates that the network density is decreasing. Therefore, we propose that increasing exposure time to the ethylamine solution (up to 25 h) results in a significant and systematic reduction in PTMO chain restriction. This occurs as the result of a phase-separation process induced by the conditions of high solubility experienced by the polysilicate phase. Such a reduction in PTMO/polysilicate interaction should also manifest itself in a change in network cross-link density. Efforts are currently underway to apply the concepts of rubber elasticity theory to confirm such changes.

The final evidence for change in the polysilicate structure as described is a Porod analysis of the small-angle X-ray scattering data from these gels as a function of immersion time in the ethylamine solution. Silicate particles produced by the sol–gel process display dilational symmetry and/or self-similarity over a range of magnifications and are thus categorized as fractal particles.⁹ The Porod analysis, i.e., $\log I(s)$ versus $\log s$, where $I(s)$ is the intensity of scattered radiation and s is the scattering vector, for these systems has been described in detail elsewhere.¹³ The slope of the $\log I(s)$ versus $\log s$ plot is a measure of the fractal nature of the scattering phase(s). A scattering particle is said to be a mass fractal if the Porod exponent, x , has the limits defined by $0 > x > -2$ for smeared data, i.e., the incident beam originates from a source possessing an infinite slit geometry. The mass fractal behavior is due to the lower dimensions of the scaling particle relative to the scattering volume. Thus the mass scales with the characteristic length according to the relationship $M \propto (\text{length})^D$. Whereas for a surface fractal, the surface area of the particle is proportional to the Porod exponent. A surface fractal dimension is given by $x = D_s - 6$. For smeared data, a Porod exponent that is defined by the limits $-2 > x > -3$ is said to be a surface fractal. The Porod exponent values for the as-cast and ethylamine solution exposed gels are listed in Table 5. The trend is that initially the scattering behavior can be characterized

by mass fractal particles. However, after treatment with the ethylamine, the $\log I(s)$ versus $\log s$ plot becomes significantly more negative, indicating that the particles have become more surface fractal in nature. This behavior is in complete agreement with the response of two-stage sol–gel processing of TEOS as described by Brinker et al.⁹ It confirms our discussion of the syneresis process in these hybrid composites and the resultant behavior.

Conclusions

The results just presented demonstrate that by exposing the original acid-catalyzed hybrid composite to a strong ethylamine solution for no more than approximately 25 h, the nature of the interaction between the PTMO and polysilicate phases is significantly altered. These changes in mechanical properties manifest themselves in an initial increase in the modulus and shifting of the T_g closer to that of the no TEOS added, end-capped PTMO processed under the same sol–gel conditions. Similarly, the increased low temperature loss dispersion centered at approximately -80 °C suggests an enhanced contribution from unrestricted PTMO chains. These changes in mechanical behavior may be attributed to a transformation of the predominantly linear inorganic structures which exhibited a high degree of mixing with the PTMO chains to more highly branched, ramified clusters, which formed as the network ripened in the high pH solvent. This change in morphology is confirmed by a change in the Porod exponent from a mass fractal to that of a surface fractal upon soaking in the ethylamine solution. These domains continue to interact with the elastomer, as is evidenced by the overall increase in modulus of these optically transparent 25-h exposed materials over the as-cast gels. Nevertheless, the composite network now behaves more like a polymer matrix reinforced with a second phase of discrete particles which exhibit fewer but more intense interactions with the polymeric phase.

These initial results suggest that it may indeed be possible to manipulate, *in situ*, the morphology and hence the degree of interaction between the organic and inorganic phases in these hybrid networks. This can be done by controlling both the pH of the modifying solution and the kinetics of diffusion which dictate the localized pH within the composite. Therefore, the possibility now exists of swelling the less-restricted PTMO phase with a selected monomer. Subsequent polymerization of the absorbed phase would create a four-phase composite exhibiting tailorable properties depending upon the monomer selected. Similarly, selective dissolution of the PTMO phase could be induced, resulting in a new composite now possessing the same polysilicate structure yet a different matrix. Results soon to be published show such materials are significantly tougher and possess pH sensitive pore structures. The expected benefit of these IPNs are enhanced separations, controlled release, and biomaterials.

Acknowledgment. Financial support from a duPont Young Faculty Investigator Award (A.B.B.) is gratefully acknowledged. The authors also thank Dr. David Rodrigues for the collection of the small-angle X-ray scattering data.