

An Organic/Inorganic Single-Phase Composite

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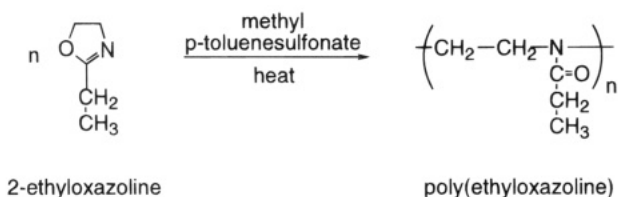
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A composite of essentially equal volumes of poly(ethyloxazoline) and silica was prepared by hydrolyzing the silica precursor tetraethyl orthosilicate in a solution of the polymer in an organic solvent. Characterization by several instrumental and chemical techniques indicated that the composite consisted of only one phase. From this evidence we conclude that it was a molecular semi-interpenetrating network. In composites made with other ratios of these components, some characteristics changed abruptly as silica content was increased from <15 to >25 volume %. We postulate this concentration range to be the silica percolation threshold. A sharp increase in surface area above ~85 volume % silica is interpreted to reflect the presence of insufficient polymer to fill the voids normally found in silica made by the sol-gel technique.

Introduction

Our original goal in this effort was to prepare a composite of an organic polymer and an inorganic glass in which the molecules of each component were intimately entwined within those of the other. Such a structure would be a molecular interpenetrating or semiinterpenetrating network, depending on whether the polymer were cross-linked or linear, respectively, and would consist of only one phase. A schematic representation is shown in Figure 1.

In previous reports,¹⁻⁴ we described the successful synthesis of such a composite consisting of poly(ethyloxazoline) (PEOX) as the organic polymer and silica as the inorganic glass. PEOX derives its name from the monomer from which it is made:⁵



In those previous reports, we also described the results of characterization of the composite that showed it to consist of only one phase. Concurrently with and subsequent to our reports, there have also been other reports (for example, refs 6-14) of composites akin to

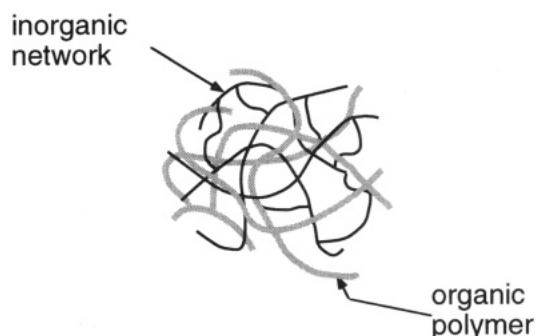


Figure 1. Schematic representation of goal molecular organic/inorganic semiinterpenetrating network. Polymer is represented by shaded line; inorganic component by solid line.

that we originally described. In this paper, we review our original, and some additional, supporting evidence for the single-phase structure and present some further interesting observations on the change in its characteristics with change in the ratio of PEOX to SiO₂.

Experimental Details

Intermediates. All materials were obtained from laboratory supply houses and used mostly as received. Some of the tetraethyl orthosilicate (TEOS) that was not obtained as high-purity grade was distilled before use. Some of the PEOX had been obtained as a sample from Dow Chemical Co.

Solutions. TEOS was added at room temperature to a 30 wt % ethanol solution of PEOX in the proportions required for the particular composition. Water acidified with HCl was then added with magnetic stirring. Mole ratios of 5:1 water to TEOS and 0.05:1 HCl to TEOS were used. A stoichiometric equivalent (2:1 mole ratio) of water to TEOS generally gave

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insufficient hydrolysis and condensation reactions in a reasonable time period. Except for low ratios of TEOS to PEOX, the polymer partly precipitated after addition of the TEOS but redissolved in 1–2 min after addition of the acidified water, which started the exothermic hydrolysis and condensation reactions. During the course of the studies, several other formulations of the same ingredients had been used before this procedure was selected.

In the resulting solution, the water reacts with the ethoxysilane group to form silanol, which then self-condenses to siloxane. The catalyst provides reasonable rates of reaction and the low pH needed for predominantly linear chain growth.¹⁵ The solution was left to stand in a closed container for at least 2 h, and often overnight, to be certain hydrolysis was close to complete before processing further. Without this aging, some of the TEOS and low molecular weight hydrolysis and condensation products were lost by evaporation, leading to lower ratios of silica to polymer than intended. Whether or not there is an optimum aging period was not investigated. We did find that final product characteristics are very sensitive to processing conditions, possibly including aging time. However, we kept all conditions the same within each set of samples.

The compositions in which methyltriethoxysilane (MTEOS) was used in place of a portion of the TEOS were made in essentially the same fashion described for those compositions using TEOS alone, except that the PEOX was dissolved in acetone rather than ethanol. The solutions with the higher levels of MTEOS became hazy on aging for 2 h.

A control PEOX/SiO₂ 33/67 weight ratio composite sample was made in which there was no possibility for intertwining of the molecules of each component. A ~30% Ludox dispersion containing 2 weight parts of 7 nm silica particles was added to a 20% solution containing 1 weight part of PEOX in water. Coatings and disks were made by letting the water evaporate as described next.

Formed Products. The solid composite products were made by evaporating the solvent from these solutions.

Disks of ~1–5 mm thickness were made by letting the solution slowly evaporate in loosely covered Teflon jars either at room or elevated temperature. As is characteristic of monolithic objects made by sol-gel process,¹⁵ these disks were generally warped and cracked, even though evaporation rates were kept very slow in an attempt to prevent these problems.

Coatings were made by drawing the solutions down on glass or plastic panels with doctor blades of 5–50 mil thickness and letting the solvent evaporate. Evaporation at room or elevated temperature was relatively fast, and coatings were obtained in minutes to hours or overnight, depending on solvent and temperature. The coatings of high SiO₂ concentration generally cracked and flaked. Those of lower SiO₂ concentration were smooth and uniform.

All the disks and coatings were transparent. For characterization other than hardness, the disks and coatings were generally broken up or ground to powders before measurements were made.

The compositions made with MTEOS were cast into dialysis bags for evaporation of the solvent at room temperature. When the gels were partially dry, the bags were removed by dampening with glycerol water, and the gels left to dry further.

Characterization and Testing. Elemental analysis for light elements was done by Microanalysis, Inc. Si was measured by inductively coupled plasma (ICP) on a Perkin-Elmer Model ICP/6500 analyzer. Oxygen could not be accurately measured because of the presence of Si. It was therefore assumed to be the difference between 100% and the total of the other measured elements.

Hydrolysis and condensation of TEOS gives three different types of functional species: unreacted ethoxysilane, silanol, and siloxane ($\equiv\text{SiOC}_2\text{H}_5$, $\equiv\text{SiOH}$, and $\equiv\text{SiOSi}\equiv$). The amounts of each of these and the polymer species were determined from the elemental analyses. Standard stoichiometric calculations

of the type normally used for elements in unknown compounds were used, except that the amounts of the species rather than of the elements were the unknowns. The sums of the amounts of each element in each of these species were equated to the measured amount of that element. This procedure gave a number of simultaneous equations which were solved for the amounts of the various species. In this manner, errors in analysis were smoothed out over all the species.

For the combination of PEOX and SiO₂, the number of equations is larger than the number of unknowns. Therefore, a least-squares method was used in the solution of the simultaneous equations. In those cases in which the resulting species contents did not add up to 100%, the calculated values were normalized to 100%. The deviations were generally less than 3% absolute but as high as 15.6% for silica itself. These deviations could be due to either error in analysis or the presence of unknown species not included in the arithmetic calculations. In either case, error was again smoothed out among all the species, and the resulting values at least gave some indication of the ratios of species. A sample calculation is given in the Appendix.

Attempts had also been made to determine the content of the three types of Si functional groups (alkoxysilane, silanol, siloxane) by Raman and ²⁹Si solid-state nuclear magnetic resonance (NMR) spectroscopy, but unsuccessfully. Such a determination would have been helpful both in following the course of the reaction and in characterizing the final product. Raman bands can be assigned to individual molecular species containing various combinations of these three functional groups,¹⁵ but they are characteristic of the species as a whole and not of the individual functional groups. We confirmed this species dependence with a set of several model compounds in which only the functional groups in question were different. No specific assignments could be made to these functional groups themselves that would permit tracking them through the reaction. Essentially the same situation exists for solution ²⁹Si NMR. This technique was not even tried for tracking the concentration of the three functional groups during hydrolysis and condensation of TEOS, because the solution spectra contain innumerable peaks representing individual molecular species. Although these peaks can be grouped by Q_n structure (the number of other Si atoms attached through O to the Si atom in question), the difference between alkoxysilane and silanol cannot be distinguished. In solid-state ²⁹Si NMR, broad peaks representing the Q_n structures were obtained. These signals could not be resolved into components representing the three separate functional groups. ¹⁷O NMR was not attempted for this purpose because the uncertainty of success by this method did not warrant the extensive effort and time required to obtain the spectra and synthesize the enriched precursor.

Transmission electron micrographs (TEM) were obtained on a Hitachi H600 transmission electron microscope at magnifications up to 300 000. Microtomed sections were ~600–800 Å thick and viewed without staining. The visual image of one section that was stained with OsO₄ was no different from those that were not stained.

Differential scanning calorimetry (DSC) scans were obtained on a DuPont Instruments 910 differential scanning calorimeter from –50 to 250 °C at a programmed temperature rate of 20 °C/min under N₂. The instrument was calibrated against In. The first heating cycle gave a very large and broad endotherm starting at ~50–100 °C, which was attributed to evolution of solvents, reactant, adsorbed water, and products arising from further condensation of incompletely condensed inorganic species. This endotherm masked any other events in the region. For this reason, a second heating cycle was always run. The results reported were based on this second cycle. In some cases, a third cycle was run for confirmation of the results. Cooling between cycles was done by rapid quench in solid CO₂. T_g was determined both by the computer software in the instrument and by a manual procedure. In the manual procedure, the flat portions of the DSC trace before and after its inflection were extended, and a bisecting line drawn between the extended lines. The point at which this bisecting line intersected the inflection portion of the DSC trace was considered to be its midpoint and the T_g. The difference in

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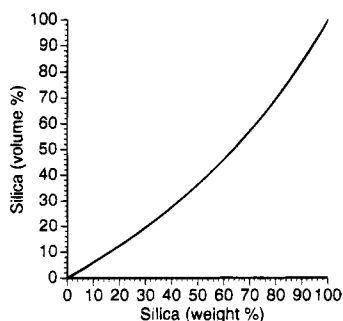


Figure 2. Relationship between weight and volume fraction based on densities of PEOX and SiO₂ as measured by He pycnometry.

heat capacity before and after T_g was taken as the ordinate distance between the two extended flat portions of the DSC trace at the T_g .

Some few dynamic mechanical analysis (DMA) traces were obtained on a Perkin-Elmer Model DMA7 instrument at a frequency of 1 Hz and temperature rate of 5 °C/min over the range -70 to 160 °C. However, this technique was not pursued because meaningful trends over the whole PEOX/SiO₂ composition range could not be derived. The higher SiO₂ content compositions were too brittle for preparation of the necessary free-standing film samples for measurement. From the sparse results obtained (not shown), it appeared that DMA tracked DSC, except at a somewhat higher temperature. Attempts at dielectric analysis (DEA) were unsuccessful because of interference by the HCl catalyst.

Thermogravimetric analysis (TGA) scans for ash content were obtained on a DuPont Instruments 951 thermogravimetric analyzer at a programmed heating rate of 20 °C/min in an air atmosphere.

Small-angle X-ray scattering (SAXS) scans were obtained on a Kratky small-angle diffractometer and wide-angle X-ray scattering (WAXS) scans on a Philips wide-angle powder diffractometer. In both instruments, Cu K α radiation was used. For SAXS, brittle samples had to be held in position with MMM Scotch Magic Tape 810. Scans were also taken of the tape to determine background in these cases.

X-ray powder diffraction patterns were also taken on Beamline X3A1 of the National Synchrotron Light Source at Brookhaven National Laboratory. Targets were 1-mm thick powder samples. An incident wavelength of 0.6535 Å selected by a silicon (111) monochromator was used. Background was measured and subtracted.

Atomic force microscopy (AFM) was done on a Digital Instruments Nanoscope 2. The solutions were spin coated on Si wafers.

Raman spectra were obtained on a Nicolet Model 910 Fourier transform (FT) Raman spectrophotometer with 1.06 μ m Nd:YAG laser. IR spectra were obtained on a Nicolet Model 800 FTIR spectrophotometer.

Solid-state ²⁹Si NMR spectra were acquired on Chemagnetics CMX360 and Bruker CXP300 spectrometers with magic angle spinning. Operation was both in single-pulse and proton-silicon cross-polarization modes.

Skeletal density was measured by He pycnometry in a Micromeritics AccuPyc 1330 helium pycnometer. This instrument gives the actual solid density to the extent that there are no microscopic closed pores that the helium cannot penetrate. These density measurements permitted interconversion of weight and volume percent (Figure 2):

$$V_i = W_i d_o / (W_o d_i + W_i d_o)$$

$$W_i = V_i d_i / (V_o d_o + V_i d_i)$$

where V is the volume fraction, W the weight fraction, and d the density; i and o stand for inorganic and organic, respectively.

Surface area was measured by the standard N₂ Brunauer, Emmett, Teller (BET) method in a Micromeritics accelerated surface area and porosimetry (ASAP) 2400 instrument.

Hardness of compositions covering the whole range of PEOX/SiO₂ ratios was measured on monolithic pieces on a Vickers tester. The pieces were mounted in potting compound, and their surfaces ground flat on a grinding wheel before measurement. In this measurement, hardness, in gigapascals, was taken as the force exerted by the stencil divided by the area of its indentation. These measurements were used to determine the effect of SiO₂ content on hardness.

The amount of material extracted by solvent was derived from the elemental analysis of samples before and after boiling in the solvent for 2 h.

Whether or not the composites flowed in the melt was determined by compressing chips of the composite to a film in a Carver press at 250–350 °C under 230–2300 kg of force for 1–3 min.

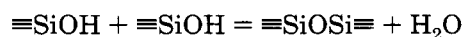
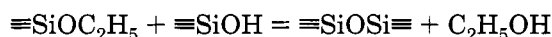
Melt viscosity was measured at 300 °C on a Rheometrics RMS-800 dynamic mechanical spectrometer. The sample, precompressed into a disk ~1-mm thick, was placed between two 25-mm-diameter parallel disk plates, one on the motor shaft, the other on the torque transducer shaft. This assembly was housed in an oven to control temperature and provide a nitrogen atmosphere. The magnitude of the transducer torque response and its phase relative to the motor-imposed fixed amplitude oscillation over a series of discrete frequencies gave viscous and elastic moduli and the derived complex viscosity.

Results

In our initial effort to make this type of structure, we tried TEOS in combination with seven different polymers covering a range of polymer type, polarity, solubility, molecular weight, crystallinity, and melting point and/or glass transition temperature (T_g). These polymers were poly(ethylene oxide), PEOX, poly(isobutylene), poly(methyl methacrylate), poly(vinylpyridine), the polycarbonate of 4,4'-isopropylidenebisphenol, and poly(vinyl alcohol). They were all used in an amount that would give an equal volume of the polymer and the SiO₂ formed from the TEOS, assuming each component had the density in the composite that was reported in the literature for its solid density. This assumption generally translated into a weight ratio of around 33 polymer to 67 silica. Our subsequent density measurements showed that the resulting volume ratios were close to, but not exactly as, intended (see Figures 2 and 8).

Of the polymers tried in the initial attempts, only the PEOX gave immediately successful results in that no separate phases could be detected by TEM. For this reason, most of our investigations were on composites of silica with this polymer. Some of the other polymers subsequently gave the desired single-phase structure after the preparation conditions were altered somewhat, and we have since made composites from larger ranges both of polymers and inorganic components (Table 1).

The results of the elemental analysis of the original 33/67 PEOX/SiO₂ composition (see Experimental Details) show that this particular sample contains a significant amount of unhydrolyzed ethoxysilane and/or uncondensed silanol groups or strongly adsorbed ethanol or water, respectively. The method does not permit distinction between the respective unreacted groups and the adsorbed free molecules:



Because of these unreacted or adsorbed groups in the

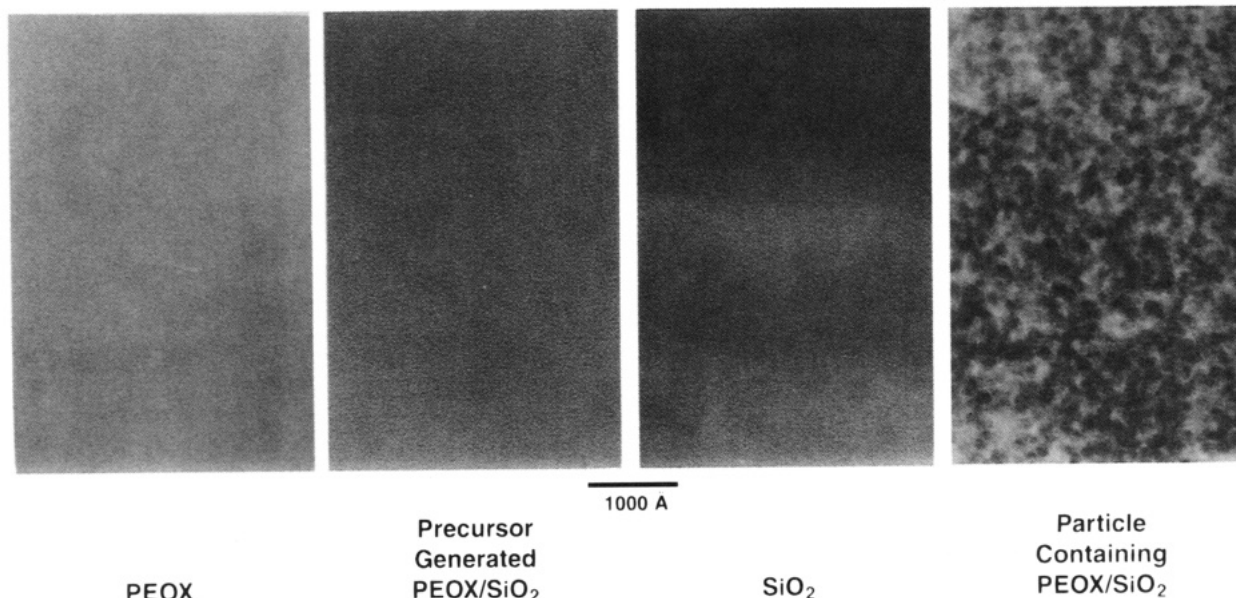


Figure 3. TEM of precursor-generated composite, its components, and particle-containing composite control. The scale bar represents 1000 Å.

Table 1. Some Other Successful Polymer and Inorganic Components

polymers	inorganics
amides	silica
poly(ethyloxazoline)	titania
poly(acrylamide)	zirconia
poly(6-aminocaproamide)	alumina
acrylics	aluminum phosphate
poly(methyl methacrylate)	
poly(hydroxyethyl acrylate)	
poly(hydroxyethyl methacrylate)	
acrylic ester copolymers	
vinyls	
poly(vinyl alcohol)	
ethers	
poly(ethylene oxide)	
ionics	
poly(sodium styrenesulfonate)	
poly(tetrabutylammonium styrenesulfonate)	
styrenesulfonate)	
poly(<i>N</i> -methyl-4-vinylpyridinium styrenesulfonate)	

composites, polymer content is lower and silicon species content higher than intended. Accordingly, there are several arbitrary ways to determine silica content, illustrated with this 33/67 PEOX/SiO₂ composition:

	%
total Si species from simultaneous equations	72.0
total Si species from N analysis only	72.4
SiO ₂ from Si and N analysis assuming only PEOX and SiO ₂	66.4
SiO ₂ from Si analysis only	54.6
SiO ₂ from ash content: pyrolysis	55.2
TGA	55.1

As can be seen and as would be expected, these different methods give widely different values. The first

two represent the actual composition containing the incompletely condensed silica species. The third represents the composition that would result from complete condensation of the silica. It comes closest to the intended composition. The last two represent the amount of the potential fully condensed SiO₂ present in the composition containing the incompletely condensed silica species. In relating characteristics to composition, the third method reflecting the intended composition was used in most cases.

The composite made from PEOX and TEOS in proportion intended to give a 33/67 PEOX/SiO₂ weight ratio was a brittle, transparent, colorless, or at most slightly yellowish, glass. Sample shape reflected that of the container in, or surface on, which it was prepared. TEM micrographs were featureless at magnifications up to 300 000, indicating that there was only one phase down to a scale of ~20 Å. The micrographs had the same appearance as those of the two separate components (Figure 3), except that the micrograph of the silica alone had a corrugated pattern known as chattering, which is a common phenomenon arising from the microtoming of a brittle, glassy structure. TEM of the control composite containing dispersed SiO₂ particles, on the other hand, showed the presence of the second phase particulates (Figure 3). A sample of the precursor-generated composite was unaffected by immersion in tetrahydrofuran and in water, both of which are good solvents for the polymer. A small sample of this composite burned to a white, opaque ash when held in a Bunsen burner flame. The ash retained the shape and size of the original sample. Its opacity was at least partly due to crazing that was visible in an optical microscope. The crazing was probably caused by explosive release of PEOX combustion products.

AFM supported the results obtained with TEM. Top views of the surfaces of spin-coatings of the 33/67 weight ratio PEOX/SiO₂ precursor-generated composite and of its components showed random features essentially similar to one another (Figure 4). It is very difficult to determine molecular features in these amorphous materials by this AFM technique. There is no regular

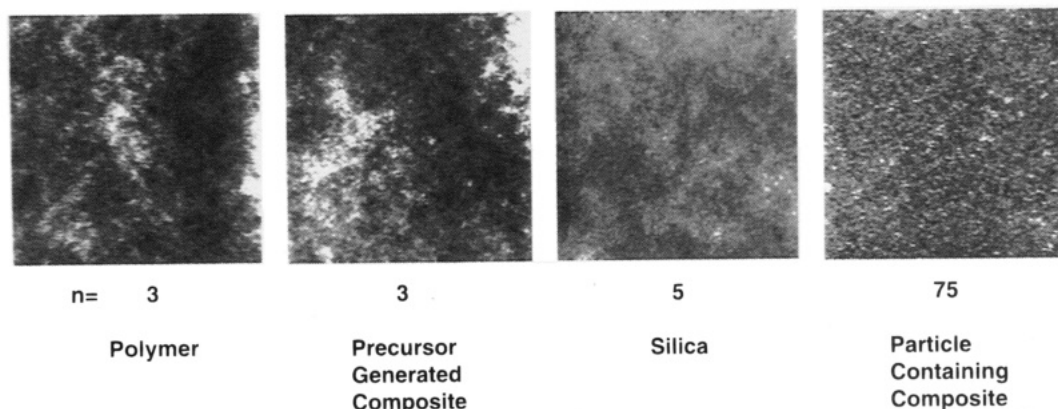


Figure 4. AFM top view of surfaces of 33/67 weight ratio PEOX/SiO₂ spin-coated precursor-generated and particle-containing composites and the precursor-generated components covering an area of 5 × 5 μm. The *n* values designate the height in nanometer.

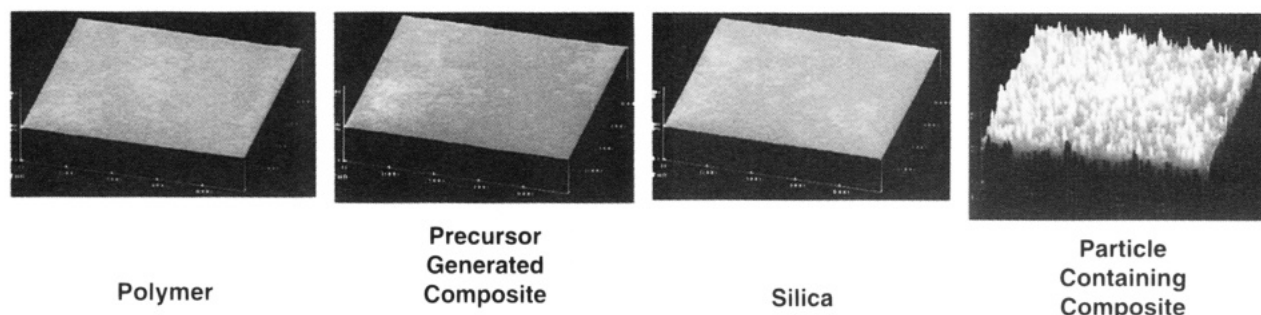


Figure 5. AFM topographic view of same surfaces as in Figure 4 covering the same area. Height is 75 nm.

Table 2. Constancy of Deviations in AFM Surface Height at Various Magnifications

material	measurement range (Å)	av height (Å)	deviation (noise?) (Å)
PEOX	3000	1.93	0.26
	1500	1.81	0.24
	150	1.78	0.26
SiO ₂	3000	2.54	0.31
	1500	1.89	0.30
	300	1.16	0.17
	150	0.86	0.11
precursor-generated composite	3000	2.66	0.31
	1500	2.11	0.28
	300	2.34	0.29
	150	3.42	0.41
particle-containing composite	3000	82.83	8.30
	1500	86.31	8.67
	300	68.07	9.15
	150	29.03	5.46

structure, such as a crystalline lattice deduced from other measurements, that can aid the eye in interpretation. We interpreted the features shown by the micrographs to be nothing more than surface roughness. This interpretation was supported by the fact that deviations in height were essentially the same at all magnifications (Table 2). Also, topographic views of the surfaces (Figure 5), showed all three of them to be about the same and that features in the top view were due to roughness. At higher magnification, some differences could be seen in the topographic views (Figure 6). The composite was rougher than the PEOX, which was rougher than the SiO₂. The sharpness of the composite edges resembled that of the SiO₂ more than that of the PEOX. A top view taken in tapping mode of a 50 nm square of the precursor-generated composite at even higher magnification still showed surface roughness but also had a fibrous texture of the right dimensions to be

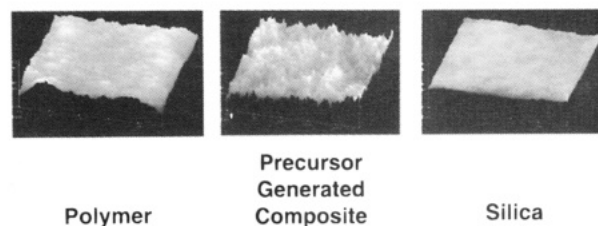


Figure 6. Higher magnification AFM topographic views of spin-coated surfaces of 33/67 weight ratio PEOX/SiO₂ precursor-generated composite and of its components. Area covered is a 250 nm square. Height is 5 nm.

the individual chains or molecules (Figure 7). There is no distinguishing feature to permit designation of the individual threads as being one component or the other. The particle-containing composite control had distinctly different features from the other three materials both in the top and topographic views (Figures 4 and 5).

Having obtained what appeared to be the goal structure, other tests were run to confirm these initial results. Also, a range of compositions from pure PEOX to pure SiO₂ was made to determine scope. The glasses containing a high silica content tended to be brittle. This brittleness increased with increasing silica content.

Elemental analysis showed that condensation to siloxane groups was incomplete throughout the series of PEOX/SiO₂ compositions just as it was in the 33/67 PEOX/SiO₂ composition. The same incomplete condensation is also true for pure silica generated by the sol-gel process. There is typically at least one nonbridging group per Si atom which leads to its high surface area.¹⁵ In line with this incomplete condensation, the He pycnometer density values of the composites as a function of their Si species content agreed well with those calculated from the measured He pycnometer

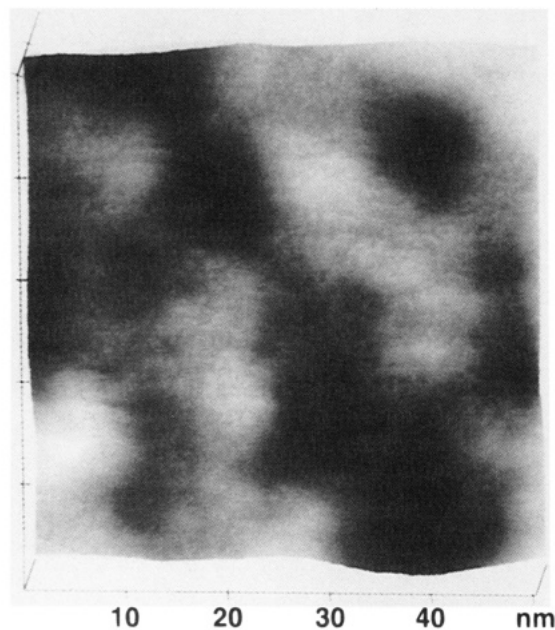


Figure 7. AFM top view of spin-coated surfaces of 33/67 weight ratio PEOX/SiO₂ precursor-generated composite taken in tapping mode. Area covered is a 50 nm square. Height is 2 nm.

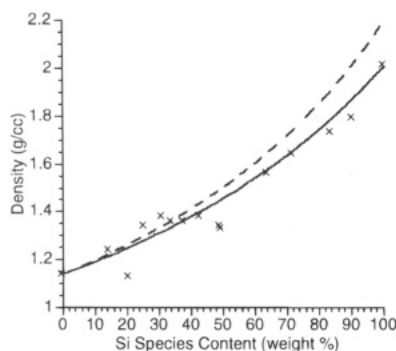


Figure 8. Densities of PEOX/SiO₂ composites as a function of composition. (x) measured; (-) calculated from measured component densities, (- -) calculated from literature density value for fully condensed SiO₂. Both drawn curves are second-order polynomial best fits of the calculated points. For the measured composite values, the weight percent of Si species was calculated by subtraction of the amount of polymer derived from N analysis.

density of SiO₂ (2.01 g/cm³) made by the sol-gel process (Figure 8) but lay slightly below those calculated from the literature value (2.2 g/cm³) of fully condensed SiO₂. As expected, the incompletely condensed Si species have slightly lower density than fully condensed SiO₂. Measured and literature values for PEOX were the same (1.14 g/cm³).

As is generally true¹⁵ for silica made by the sol-gel process, surface area of the pure SiO₂ component was high. This surface area decreased down to <1 m²/g as SiO₂ content decreased to ~80–90 wt % and remained at that low level for the rest of the compositions of lower SiO₂ content (Figure 9).

The SAXS scans of all of the precursor-generated composites, regardless of SiO₂ content, were featureless (Figure 10). Because of brittleness and physical form, those samples with higher SiO₂ content, had to be taped on to the instrument target holder. This tape gave an upturn in the scattering curve at low 2θ values, but there were no features additional to that upturn due to

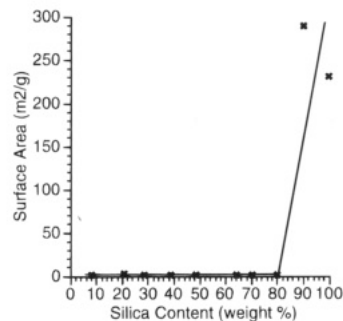


Figure 9. Surface area of PEOX/SiO₂ precursor-generated compositions measured by N₂ BET method.

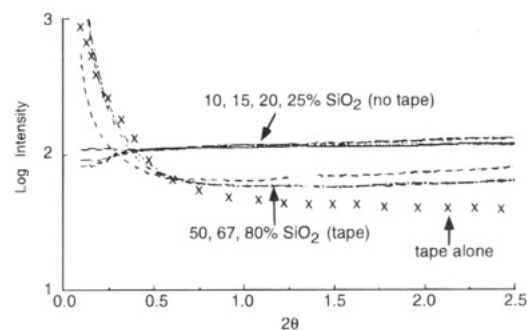


Figure 10. SAXS scans of precursor-generated PEOX/SiO₂ compositions. The x's trace curve of tape alone. Curves with upturn at low 2θ were of composites taped to holder. Curves with no upturn were of composites in film form that required no tape.

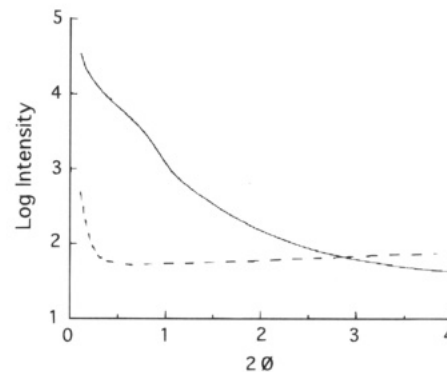


Figure 11. SAXS scans of 33/67 weight ratio PEOX/SiO₂ precursor-generated (- -) and particle-containing (-) composites.

a second phase in the composite. The composite containing particulate SiO₂, on the other hand, showed scattering over a range of 2θ values centered ~0.7–0.8, indicating the presence of a scattering second phase (Figure 11).

The WAXS scans had the characteristic bands seen in amorphous materials (Figure 12). The position of the dominant band, indicative of intermolecular distance, was about the same as that of the SiO₂ alone down to a SiO₂ content of ~30 wt %, and increased below this content (Figure 13).

From the X-ray powder diffraction patterns taken on the synchrotron, the distances between atoms can be derived. By appropriate mathematical analysis, the number of atomic pairs having a given distance between them can be determined, thus giving a distribution of the number of atom pairs as a function of their separation distances (*r*). This distribution is called the pair density function (PDF). It yields a reliable measure of

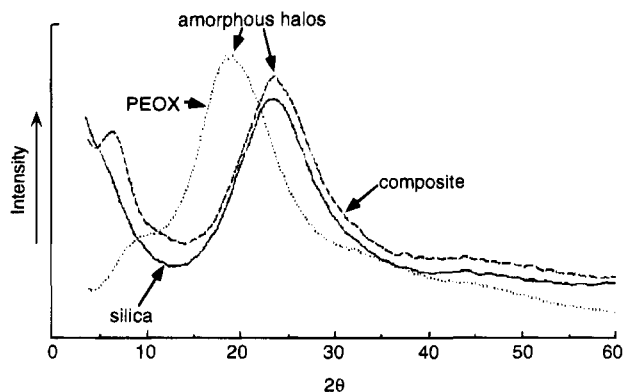


Figure 12. WAXS scans of PEOX, PEOX/SiO₂ precursor-generated composite, and SiO₂. Intensity scale is different for the different scans.

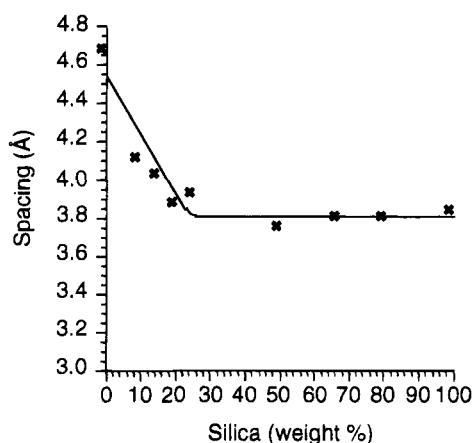


Figure 13. Intermolecular spacing of PEOX/SiO₂ precursor-generated compositions from WAXS scans.

atomic pair density for r in the range 1–100 Å. This function can also be calculated for both single- and two-phase systems. For the precursor-generated 33/67 PEOX/SiO₂ composite, this PDF corresponded to that calculated for a single-phase structure but not to that calculated for a two-phase structure. On the other hand, this function derived for the particle-containing composite corresponded to that calculated for a two-phase and not a single-phase structure. Details of this analysis will be described in a forthcoming paper by Rosenfeld and Harlow, who analyzed and gathered the data, respectively.

In DSC, the composites having SiO₂ content above ~30 wt % did not have the T_g shown by the polymer (Figures 14 and 15). Below this level, there was a T_g (Figure 15), which increased slightly with increasing SiO₂ content. In this range, the differences in the heat capacities before and after the T_g decreased with increasing SiO₂ content. SiO₂ itself has a T_g of ~1000 °C, which is beyond the temperature range covered by the instrument. The particle-containing composite control had a T_g , albeit a broad one, even though its SiO₂ content (67 wt %) was well above the critical ~30 wt % level (Figure 14).

In Raman spectra, there was a continuous displacement of the carbonyl band from 1642 cm⁻¹ toward longer wavelengths as SiO₂ content was increased (Figures 16 and 17). Band area also decreased. Again, there was a change in curve slope, as seen in the other composite characteristics, but at somewhat higher SiO₂ content of ~40–50 wt % SiO₂. We have no explanation

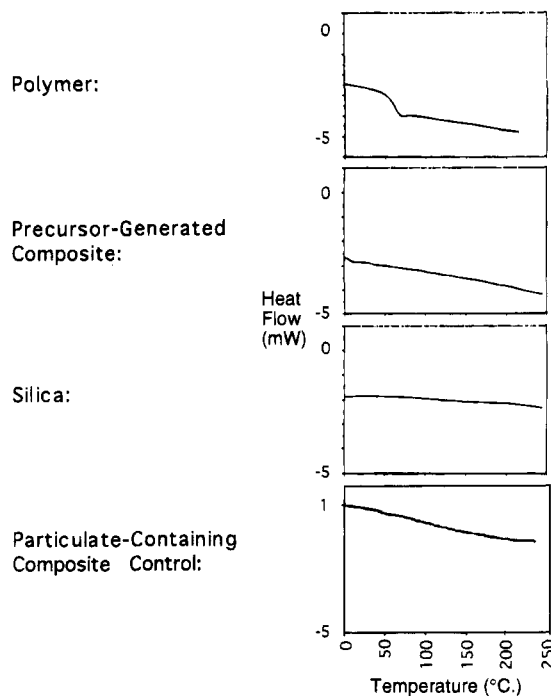


Figure 14. DSC of 33/67 PEOX/SiO₂ composites, PEOX, and SiO₂.

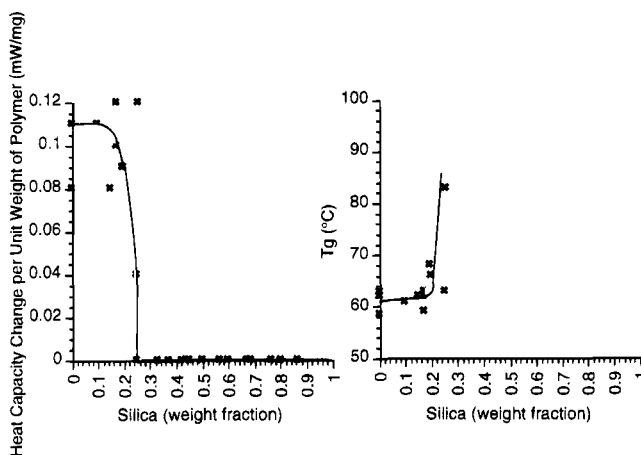


Figure 15. Characteristics of DSC scans of precursor-generated PEOX/SiO₂ compositions. Changes in heat capacity (left graph) and T_g (right graph) with change in SiO₂ content.

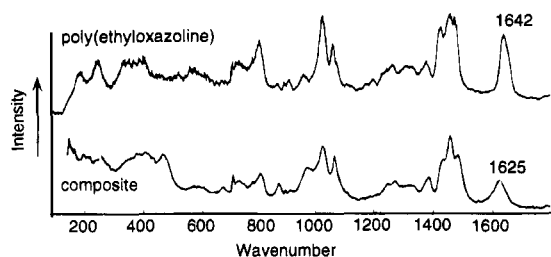


Figure 16. Raman spectra of PEOX and PEOX/SiO₂ 33/67 composites. Carbonyl band marked with wavenumber.

for the continuous band shift and area change. We expected, a priori, separate bands for the free and hydrogen-bonded carbonyls, the latter band shifted from the first, but each at a constant given wavenumber as SiO₂ content increased. The unbonded carbonyl band intensity was expected to decrease and the hydrogen-bonded one to increase, both in accordance with their individual scattering cross sections, with the increase in SiO₂ content. We had seen such behavior in a

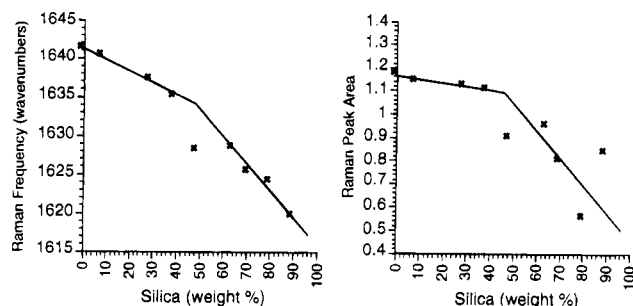


Figure 17. Relation of PEOX carbonyl band displacement (left curve) and area (right curve) to SiO_2 content in precursor-generated composite.

polyacrylamide/ SiO_2 composite of corresponding structure. However, in contrast to these expectations, there was only one band at any given SiO_2 content and a continuous shift in its wavenumber and decrease in area as the SiO_2 content increased. It is conceivable that this apparently single carbonyl band may actually be a combination of the two expected, unbonded and hydrogen bonded, but very closely spaced bands that vary in intensity as SiO_2 content is changed, thus giving the appearance of a shift and area change. However, attempts to instrumentally resolve the single band into two were unsuccessful, and the phenomenon of continuous change in wavenumber remains unexplained.

Displacement of the PEOX carbonyl band in the infrared (IR) spectrum of the composition containing 67 wt % SiO_2 was about the same as it was in the Raman spectrum of the same composition.

NMR relaxation times of ^{29}Si in the solid composites were significantly increased (>6000 s for Q_3 , even longer for Q_4)³ over those¹⁶ of sol-gel SiO_2 alone, indicating either some type of constraint of the SiO_2 molecular motion or exclusion of O_2 (a relaxation agent) in the composites. In either case, the presence of proximate PEOX is indicated. The long relaxation times made it difficult to obtain meaningful spectra having correct ratios of Q_3 and Q_4 (Figure 18). In proton-silicon cross polarization spectra, Q_4 was emphasized over Q_3 . Our explanation of this inversion of Q_4/Q_3 ratio compared to that in sol-gel SiO_2 alone¹⁷ is that the PEOX chains are close enough (<5 Å) to the SiO_2 that their protons provide the cross-polarization. Neither of these NMR phenomena are definitive proof of the single-phase structure, but they are both certainly in the right direction.

The composites containing more than ~ 30 wt % SiO_2 were resistant to extraction of the polymer component when digested in four different boiling solvents that dissolve PEOX (Figure 19). Below this SiO_2 content, the composites dissolved.

Hardness changed very little as SiO_2 content was increased from 0 to $\sim 30\%$ (Figure 20). Beyond that level, hardness increased sharply with SiO_2 content.

Attempts to form the composites by melt compression showed that compositions below ~ 30 wt % SiO_2 could be pressed to films, whereas those above this level of SiO_2 did not even soften. Measurement of melt viscosity showed a large initial increase with SiO_2 content, a

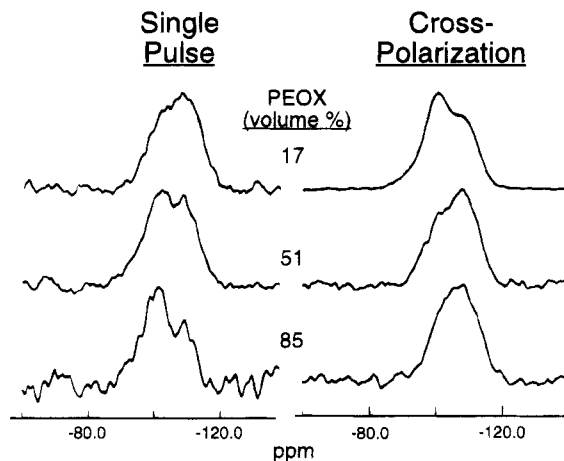


Figure 18. NMR solid-state ^{29}Si spectra with magic angle spinning of three composites of different PEOX/ SiO_2 ratios acquired in both single-pulse and proton-silicon cross-polarization modes.

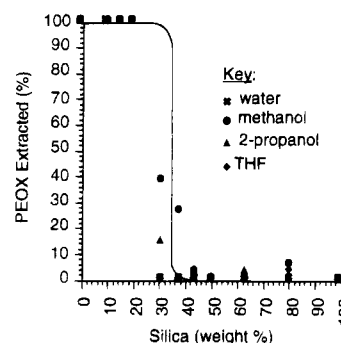


Figure 19. Solvent extraction of PEOX/ SiO_2 precursor-generated composite compositions.

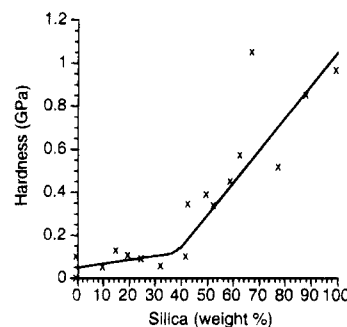


Figure 20. Hardness of PEOX/ SiO_2 precursor-generated composite compositions.

leveling off with further increase in SiO_2 until $\sim 40\%$, and intractability at higher levels (Figure 21).

Composites were made with the combination of MTEOS and TEOS to give ~ 50 vol % each of PEOX and total Si species but with varied amounts of the methyl-substituted silica to reduce connectivity of the network. Hardness of these compositions decreased with methyl substitution (Figure 22) and extrapolated to the value for pure polymer at ~ 0.7 mole fraction of MTEOS. The DSC traces showed no indication of a T_g .

Discussion

The challenge in preparing a single-phase molecular organic/inorganic semiinterpenetrating network structure arises from the inherent incompatibility of the two widely different types of components and the cross-

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(17) Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C. Press: Guelph, Canada, 1983; pp 384-5.

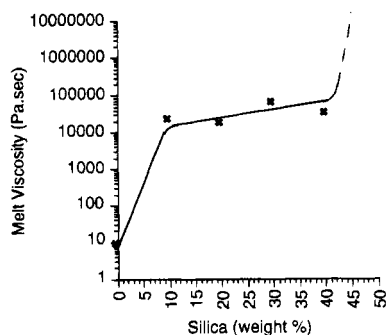


Figure 21. Melt viscosity of 33/67 PEOX/SiO₂ precursor-generated composite.

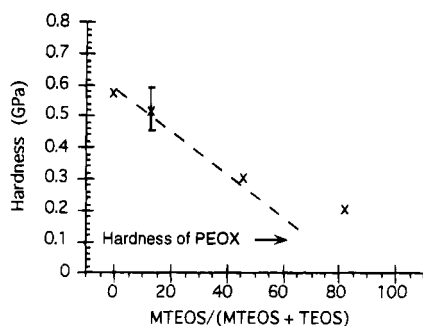


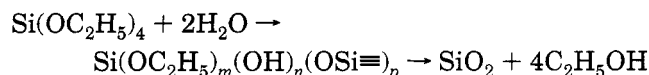
Figure 22. Hardness of precursor-generated composites containing methyl substitution on the silica network. The error bar represents the typical spread of hardness values found on one specimen. The dashed line is drawn by eye through the results for the composites containing ~50 vol % Si species, ignoring the last point which represents a sample containing 57 vol % Si species.

linked nature of the inorganic component. Obviously, this type of composite structure could not be made by any type of mixing of the preformed components themselves. One of these components would have to be generated in place within the other. The sol-gel process is well suited to such a procedure. In the sol-gel process, a metalloorganic precursor for the inorganic component is hydrolyzed with water under the influence of a catalyst, and the resulting hydroxyl groups self-condense to give the inorganic network. Conducting this process, then, in a solution containing the polymer provides the opportunity for intimate molecular mixing.

It is well-known¹⁵ that, in the case of silica, the structure of the network depends on the pH of the solution. Acid conditions tend toward an open, more linear type of network. Basic conditions give more highly branched clusters or even particulate growth. On this basis, acid conditions would better provide the openness of the SiO₂ network required for interpenetration of the polymer.

We postulated that to obtain the desired molecularly intertwined structure, the polymer would have to become kinetically entrapped in the developing inorganic network. Accordingly, the rate of network formation would have to be commensurate with the rate of evaporation of the solvent and volatile byproducts. The mesh size¹⁵ of the inorganic component at the point of its network formation would have to be small enough to prevent the polymer molecules from escaping and associating into a separate phase. Also, all ingredients would have to be mutually compatible at the point at which the network forms and preferably up to that point during the evaporation process.

Although hydrolysis of TEOS is faster than condensation of the resulting silanol groups in an acidic environment, the two steps overlap. The overall reaction can be depicted from a functional group standpoint as



with ethoxysilane (m) continually decreasing, silanol (n) increasing and then decreasing, and siloxane (p) continually increasing. The reaction never goes completely to SiO₂; there always being some residual silanol and, perhaps, as in the case of our original composition (see Appendix), even some ethoxysilane. As the solvent evaporates, the concentrations of the reactants in the sol-gel component, and thus their reaction rates, increase. This increase in rate permits the reaction to proceed to the point of complete network formation and entrapment of the polymer before phase separation occurs.

The characteristics of the initially successful 33/67 PEOX/SiO₂ sample were consistent with this composite consisting of a single phase. The sample was transparent, featureless in TEM, and resistant to solvent extraction. The ash resulting from pyrolysis gave no indication of gross voids of the type that would have resulted from second phase PEOX domains. No evidence of a separate polymer phase was seen in DSC, SAXS, IR, Raman spectroscopy, or AFM. In a sense, all this evidence was negative. It showed the absence of any second phase. However, one measurement did give positive, and thus even much stronger, evidence for a single-phase structure in which the chains of each component are intimately entwined within those of the other. This measurement was the X-ray powder diffraction patterns acquired on the synchrotron and the pair density functions derived therefrom. Because these measurements and functions are of atomic resolution, they provide proof of the intimate molecular mixing. The measured functions corresponded to the calculated single- and two-phase structures for the precursor-generated and particle-containing composites, respectively. Further support for the single-phase structure was also obtained from the additional compositions in which the ratio of PEOX to SiO₂ ranged from one pure component to the other.

In this series of compositions having varied PEOX/SiO₂ ratios, the featureless SAXS scans showed that there was no separate phase present at any ratio. On the other hand, DSC gave indication of polymer thermal events below ~30 wt % SiO₂. Although not necessarily suggesting a separate PEOX phase, evidence from WAXS, solvent extractability, hardness, and melt flow also showed a difference between the compositions containing less than ~30 wt % SiO₂ and those containing more than this amount.

Our interpretation of these results is that the SiO₂ exists as disconnected oligomers at low concentration. At ~25–35 wt % (order of magnitude ~15–25 vol %) SiO₂, the oligomers are at their percolation threshold, and above this concentration form a connected continuous network. Similar silica percolation thresholds have also been postulated for other composites prepared from TEOS.^{14,18} In our composites, we conclude from the evidence cited above that at all compositions, both below and above the percolation threshold, these materials

exist as single-phase structures in which the PEOX molecules are intimately intertwined with those of the SiO₂ oligomers or network. We do not imply that the combination is a true solution of thermodynamic stability even though there is evidence for hydrogen bonding between the two components. However, in our postulate of molecular entrapment, this composite should have characteristics similar to those of a true solution in some regards, such as the single-phase structure.

The percolation threshold occurs at a much higher SiO₂ concentration than would be expected, for it is possible to make pure SiO₂ gels and aerogels, in which percolation has obviously occurred, containing only <1 vol % solids.¹⁹ The skeleton of the network in these gels is sparse and compliant, but increasingly rigid in gels of increasingly higher density, thus higher effective SiO₂ content.

On this basis, the ~25–35 wt % SiO₂ composition for the composites might be regarded as a “rigidity threshold” rather than a percolation threshold. In other words, a network exists and, at this point, is sufficiently robust to constrain fully the mobility of the polymers. That such is not the case is shown by the fact that composites containing <25–35 wt % silica dissolve completely (Figure 19). Thus, they have no continuous silica network, i.e., they are below a percolation threshold. The failure to percolate at such high silica content is probably a kinetic phenomenon. The organic polymers inhibit diffusion of SiO₂ oligomers, thus keeping them nearly stationary, favoring their growth by diffusion of monomers, and preventing network formation.

Our explanation of the behavior of T_g in these single-phase composites is based on the generality that the T_g of an intimate combination, such as a solution, is intermediate between those of the two components in proportion to their relative fractions. Even though this PEOX/SiO₂ combination is not a true thermodynamically stable solution, according to our postulate, the intimacy of the component molecules should provide much the same effect on T_g as that found in a true solution. Thus, there should be a T_g at all component ratios. In this type of structure, however, there is an additional factor. The inherent T_g of the SiO₂ component itself changes as its structure changes with component ratio. At low SiO₂ content, below the percolation threshold, the SiO₂ oligomers are probably either liquid or have very low T_g . Thus, they do not confer much restraint on the PEOX molecules, and there is only a slight increase in T_g with increased SiO₂ content. Above the percolation threshold, the SiO₂ becomes increasingly rigid as its network is built up, and its T_g increases accordingly. The upturn in the T_g curve (Figure 15) is in agreement with this postulate. At some point above network formation, the combined T_g of the composite becomes high enough that it is above the range of the DSC instrument and the decomposition temperature of the PEOX and is thus not detectable. If two phases were present, the T_g of each component would remain

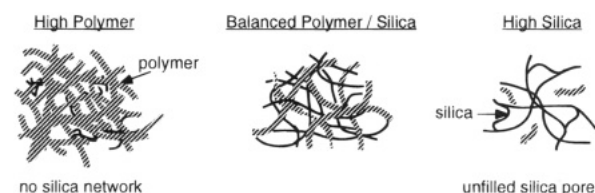


Figure 23. Schematic representation of precursor-generated PEOX/SiO₂ composites above and below SiO₂ percolation threshold and PEOX void-filling threshold. Polymer is represented by shaded line, silica by solid line.

constant or, at most, change slightly toward one another over the whole range of component ratios. In that case the T_g of the PEOX, or close to it, would be detected at any concentration in the composite. Consistent with this statement is the T_g of the two-phase control sample (Figure 14).

Because of the molecular dispersion, there is no scattering of small-angle X-ray even in the SiO₂-deficient region. Above the percolation threshold, the SiO₂ exists as a continuous network, and its interchain distance remains relatively constant in the WAXS. The further decrease in PEOX content as SiO₂ content is increased permits further silanol condensation without altering the basic linear chain distance. In this concentration region also, the continuous SiO₂ network holds the PEOX tightly enough that it cannot be extracted by solvent and does not flow when heated. Extraction and flow and even dissolution can occur, however, in compositions below the percolation threshold in which PEOX is not so held.

At very high SiO₂ contents, above ~80–90 wt %, there is not enough PEOX to fill the voids normally formed in SiO₂ made by the sol-gel process, and the composites consequently have high surface area. Below this SiO₂ concentration, there is no void space between the two components and there is essentially no surface area. Our view of the structure of these single-phase composites is shown schematically in Figure 23.

There is probably also a PEOX percolation threshold. However, it is difficult to identify. At high silica content, the network has enough rigidity to resist the compressive capillary forces generated as the solvent evaporates. The dried gel thus retains porosity resulting from the space formerly occupied by solvent molecules, even though there are too few PEOX molecules present to interfere with silanol condensation. The PEOX molecules may still percolate through accessible open pore space even at a small volume fraction because of their linearity and length. Accordingly, the existence of porosity in composites containing >80% silica does not necessarily indicate failure of the PEOX to percolate.

In those compositions in which the methyl group decreases the connectivity of the silica network, the siloxane rings in the silica network are expected to become larger and consequently less rigid. The hardness data reflect this clearly. At a constant silicon species content, the hardness drops toward that of the pure polymer as the MTEOS content approaches ~70 mol %. This dependence of rigidity on connectivity is consistent with several published reports. Glaser et al.²⁰ showed that the character of MTEOS/TEOS gels varied from rigid to rubbery to liquid as the MTEOS content

(18) Mauritz, K. A.; Storey, R. F.; Jones, C. K. In *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; pp 401–17.

(19) Hrubesh, L. W.; Tillotson, T. M.; Poco, J. F. In *Better Ceramics Through Chemistry IV*; Zelinski, B. J. J., Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1990; pp 315–9.

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Table 3. Effect of the Amount of Water Used To Hydrolyze the TEOS

species	wt % of each species	
	2/1 mole ratio water/TEOS	5/1 mole ratio water/TEOS
$\begin{array}{c} \text{---CH}_2\text{CH}_2\text{N---} \\ \\ \text{CH}_2\text{CH}_2\text{C=O} \\ \\ \text{Si}_{0.25}\text{OC}_2\text{H}_5 \\ \text{Si}_{0.25}\text{OH} \\ \text{Si}_{0.25}\text{O}_{0.5} \end{array}$	28.0	29.6
$\text{Si}_{0.25}\text{OC}_2\text{H}_5$	11.5	0.0
$\text{Si}_{0.25}\text{OH}$	24.5	11.0
$\text{Si}_{0.25}\text{O}_{0.5}$	36.1	59.4

increased. Fahrenholtz and Smith²¹ examined the surface area of xerogels made from MTEOS/TEOS and found that it dropped from ~ 800 to < 1 m²/g as the mole percent of MTEOS rose between 60 and 70%. Schwertfeger et al²² prepared aerogels from a similar system, methyltrimethoxysilane/tetramethoxysilane, and found that they collapsed if the mole percent of MTMOS exceeded $\sim 80\%$. Despite the loss of rigidity on addition of MTEOS, the DSC results indicate that the silica network was apparently still rigid enough to suppress the glass transition of the PEOX at the concentrations of MTEOS and component ratios used.

In summary, the goal of a single-phase organic/inorganic composite structure appears to have been reached. From the existence of only a single phase, we conclude that these composites are molecular organic/inorganic semiinterpenetrating networks. This single-phase structure exhibits a SiO₂ percolation threshold at ~ 25 – 35 wt % SiO₂ and a PEOX void-filling threshold at ~ 80 – 90 wt % SiO₂. Characteristics change sharply at the concentration at which the SiO₂ percolates. Disruption of the SiO₂ network with methyl substitution decreases hardness, but does not interfere with the single-phase nature of these composites.

As shown in Table 1, we have also made these single-phase structures with other polymers and inorganic components. Conditions are quite critical and affect the phase structure and characteristics of the product composites significantly. Some illustrative effects for $\sim 33/67$ PEOX/SiO₂ composite are shown by the dependence of the species formed on the amount of water used (Table 3) and by the fact that the presence or absence of a T_g was dependent on pH (not shown).

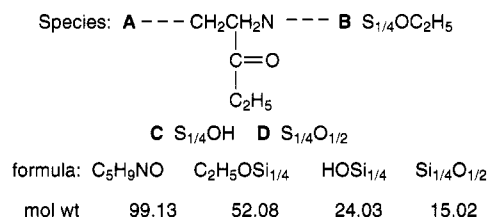
As implied by the range given for the percolation threshold, it does not occur at a single exact concentration. From other of our studies not reported herein, we have found the threshold concentration to be dependent on synthesis conditions, the nature of the composite components, and the particular property being measured. Such behavior would be expected for this type

of chemistry, for inorganic network formation and its manifestation in the composite are affected by these factors.

Acknowledgment. Professor D. N. Theodorou of the University of California at Berkeley helped in interpretation of the WAXS scans. Dr. R. L. Harlow collected the synchrotron data and Dr. H. D. Rosenfeld did the analysis and interpretation of these data. Dr. D. B. Chase obtained and interpreted the Raman spectra. Dr. F. C. Wilson obtained the SAXS and WAXS scans. Dr. D. J. Coulman obtained and helped in interpretation of the AFM scans. Mr. C. H. Hales wrote the computer program for solving the simultaneous equations for silica and PEOX species analysis. Drs. A. J. Vega and G. C. Campbell obtained the solid state NMR spectra and provided their interpretations.

Appendix

The method for calculating the amount of each species from the elemental analysis is illustrated by an example of PEOX/SiO₂ of intended 33/67 weight ($\sim 50/50$ volume) ratio. The weight amounts of the possible species present on hydrolysis and condensation of the TEOS precursor are designated by the letters **A**, **B**, **C**, and **D**.



Found: C, 22.25; H, 4.70; N, 3.90; Si, 25.5; O, 43.65 (by difference).

$$\text{For C: } 5\mathbf{A} + 2\mathbf{B} + 0\mathbf{C} + 0\mathbf{D} = 22.25/12.01 = 1.85$$

$$\text{For H: } 9\mathbf{A} + 5\mathbf{B} + 1\mathbf{C} + 0\mathbf{D} = 4.70/1.008 = 4.66$$

$$\text{For N: } 1\mathbf{A} + 0\mathbf{B} + 0\mathbf{C} + 0\mathbf{D} = 3.90/14.01 = 0.28$$

$$\text{For O: } 1\mathbf{A} + 1\mathbf{B} + 1\mathbf{C} + 0.5\mathbf{D} = 43.65/16.00 = 2.73$$

$$\text{For Si: } 0\mathbf{A} + 0.25\mathbf{B} + 0.25\mathbf{C} + 0.25\mathbf{D} = 25.5/28.09 = 0.91$$

Derived mole values: **A**, 0.282; **B**, 0.220; **C**, 1.02; **D**, 2.40.

$$\text{Weight \%: } \mathbf{A}, 0.282 \times 99.13 = 27.95$$

$$\mathbf{B}, 0.220 \times 52.08 = 11.46$$

$$\mathbf{C}, 1.02 \times 24.03 = 24.51$$

$$\mathbf{D}, 2.40 \times 15.02 = 36.05$$

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