

Organic/Inorganic Hybrid Network Materials by the Sol–Gel Approach

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Organic/inorganic hybrid materials prepared by the sol–gel approach have rapidly become a fascinating new field of research in materials science. The explosion of activity in this area in the past decade has made tremendous progress in both the fundamental understanding of the sol–gel process and the development and applications of new organic/inorganic hybrid materials. In this review, a brief summary of the research activities in the field of organic/inorganic nanocomposite materials and a general background of the sol–gel chemistry are first given. The emphasis of this report, however, is placed on the synthesis, structure–property response, and potential applications of the organic/inorganic hybrid networks that possess chemical bonding between the organic and inorganic phases, particularly those systems that were developed in our laboratory since 1985.

Introduction

The sol–gel process, which is mainly based on inorganic polymerization reactions, is a chemical synthesis method initially used for the preparation of inorganic materials such as glasses and ceramics. Its unique low-temperature processing characteristic also provides unique opportunities to make pure and well-controlled composition organic/inorganic hybrid materials through the incorporation of low molecular weight and oligomeric/polymeric organic molecules with appropriate inorganic moieties at temperatures under which the organics can survive. The organic/inorganic hybrid materials made in this way, which have been termed “ceramers” by Wilkes et al.¹ and “ormosils” or “ormocers” by Schmidt et al.,² are normally nanocomposites and have the potential for providing unique combinations of properties which cannot be achieved by other materials. For the past decade, organic/inorganic nanocomposites prepared by the sol–gel process have attracted a great deal of attention, especially in the fields of ceramics, polymer chemistry, organic and inorganic chemistry, and physics. The preparation, characterization, and applications of organic/inorganic hybrid materials have become a fast expanding area of research in materials science. The major driving forces behind the intense activities in this area are the new and different properties of the nanocomposites which the traditional macroscale composites and conventional materials do not have. For example, unlike the traditional composite materials which have macroscale domain size of millimeter and even micrometer scale, most of the organic/inorganic hybrid materials are nanoscopic, with the physical constraint of several nanometers, typically 1–100 nm, as the minimum size of the components or phases. Therefore, they are often still optically transparent materials although microphase separation may exist. Through the combinations of different inorganic and organic components in conjunc-

tion with appropriate processing methods, various types of primary and secondary bonding can be developed leading to materials with new properties for electrical, optical, structural, or related applications.

Organic/inorganic hybrid materials prepared by the sol–gel process can be generated using different synthetic techniques by incorporating various starting inorganic and organic components with varied molecular structure:

(1) Hybrid networks can be synthesized by using low molecular weight organoalkoxysilanes as one or more of the precursors for the sol–gel reaction in which organic groups are introduced within an inorganic network through the $\equiv\text{Si}-\text{C}-$ bond.^{2–5}

(2) Organic/inorganic hybrid network materials can also be formed via the co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between inorganic and organic phases.^{1,6–7}

(3) A hybrid material can also be synthesized through the in situ formation of inorganic species within a polymer matrix.^{8–15} Specifically, inorganic species, generally in the form of particles with a characteristic size of a few hundred angstroms, can be generated in situ within the polymers by first swelling cross-linked, ionomeric, or crystalline polymeric host with a compatible solution containing metal alkoxides followed by the promotion of the sol–gel reaction of the inorganics. Various inorganic particles with extremely homogeneous particle size have been prepared in this manner within elastomeric or plastic matrixes.^{16–29} The concept of such “in situ” generation of fillers is novel and of practical importance in terms of elastomer reinforcement.^{11,12,30}

(4) Starting from the opposite direction of (3), organic/inorganic composites can be obtained by either the infiltration of previously formed oxide gels with polymerizable organic monomers or the mixing of polymers with a single or mixture of metal alkoxides in a common solvent. In the first approach, the impregnation of porous oxide gels with organics is followed by an in situ

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polymerization initiated by thermal or irradiation methods.^{31–33} In the second approach, polymers can be trapped within the oxide gel network if the hydrolysis and condensation of metal alkoxide are carried out in the presence of preformed polymers.^{34–42} Optically transparent composite materials can be obtained if there is no macro- or microphase separation during both the gel forming and drying process.

(5) Similar to approach (4), organics can also be simply impregnated or entrapped as a guest within inorganic gel matrixes (as a host). This approach has been extensively used in the incorporation of enzymes, proteins, and various organic dyes such as luminescent dyes,⁴³ photochromic dyes,⁴⁴ and nonlinear optical (NLO) dyes⁴⁵ into an inorganic network. The main driving force behind the intensive research activity in preparation of these types of materials is the development of new optical and bioactive materials in the application of photophysical, electrical, biotechnical, and nonlinear optical (NLO) devices.^{43,46–51}

(6) Hybrid networks can also be formed by interpenetrating networks and simultaneous formation of inorganic and organic phases. By using triethoxysilane $R'Si(OR)_3$ as the precursor with R' being a polymerizable group such as an epoxy group, an organic network can be formed within the inorganic network by either photochemical or thermal curing of such groups, as Schmidt has demonstrated in 1984.^{4,52,53} Novak and Grubbs⁵⁴ also developed an interesting convenient method to form inorganic/organic simultaneous interpenetrating networks (SPINs), where both inorganic glass and polymer formation occur concurrently. These transparent composites are synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization (aqueous ROMP) of cyclic alk-enyl monomers and the hydrolysis and condensation of metal alkoxides.

(7) Other new synthetic strategies have also been developed in recent years.^{55–63} For example, by employing polymerizable monomers as the cosolvent such that all mixture components contribute either to the silica network or to the organic polymer to avoid large scale shrinkage, a “nonshrinking” sol–gel composite materials can be obtained.^{56,57} A different kind of inorganic/organic nanocomposite material has been developed by exploiting the unique intercalation and self-assembling characteristics of layered ceramics, particularly those based on the 2:1 layered silicates.^{58–62} These 2:1 layered silicates consist of two-dimensional layers formed by sandwiching two SiO_2 tetrahedral sheets to an edge-shared octahedral sheet. Single chains of the polymer alternately stacked with the layers of the host can be obtained by intercalative polymerization of various monomers in the silicate galleries. Researchers⁶³ are also exploring novel processing strategies to produce organic/inorganic composite biomimetically—taking inspiration from the fact that biological systems fabricate complex multicomponent, multiphase materials using assembly, and processing strategies that are unique but reproducible.

The incorporation of organic/oligomeric/polymeric materials into organic/inorganic networks by the sol–gel process makes it possible to optimize selected properties independently. Specifically, the introduction of organic groups into an inorganic network leads to new structure–property variation, thereby promoting new potential

applications for the resulting composite materials. As examples:

(1) Flexibility can be introduced by the incorporation of organic/oligomeric/polymeric materials into the inorganic networks.

(2) New electronic properties, such as conductivity, redox properties, etc., can be achieved by introducing conductive polymers along with transition-metal alkoxides.

(3) By incorporating organic dyes or π -conjugated polymers into the inorganic networks, the optical properties can be systematically altered in both the linear as well as nonlinear optical properties (NLO).

Even though many of the network systems are comprised of components having very different refractive indexes, the resulting material can often be prepared optically transparent due to the small scale lengths over which phase separation may exist. As a result, these composite materials can find applications in many fields which are far beyond the scope of application of traditional composite materials and this is one important reason for the strong interest in the application of organic/inorganic hybrid materials. To date, the number of commercial sol–gel hybrid products is still comparatively small, but the promise of new technological uses remains. Some potential applications for these materials are as follows:

(1) Scratch and abrasive-resistant hard coatings and special coatings for polymeric materials, metal, and glass surfaces.^{64–74}

(2) Electrical and NLO materials.^{42,43,47,48,75,76}

(3) Adhesives and contact lens materials.^{65,77}

(4) Reinforcement of elastomers and plastics.^{8,12,25–27,60–62}

(5) Catalyst and porous supports, adsorbents.^{5,36}

(6) Tunable solid-state lasers^{78,79} and chemical/biomedical sensors.^{80,81}

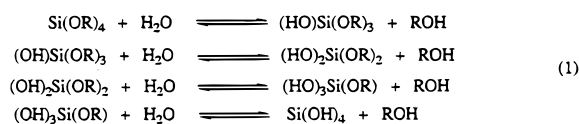
On the basis of the connection between the inorganic and organic phases, the organic/inorganic composite materials can be also conveniently divided into two general classes: those with chemical bonding between the two phases and those without.⁸² *Following a brief introduction to the sol–gel chemistry, this review principally addresses the synthesis, structure–property response, and applications of organic/inorganic nanocomposites with chemical bonding between the organic and inorganic phases, with some emphasis on the research carried out in our laboratories that was initiated in 1985.* As can be imagined, it is impossible to completely review this field and omissions to the other workers has not been by design but is due to space limitations. In this regard the interested reader is referred to some other recent reviews^{49,82–91} to allow a complete view of the history and recent development of organic/inorganic hybrid materials.

General Background of Sol–Gel Chemistry

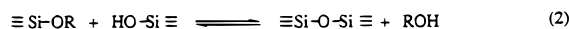
Considering the key role of the sol–gel reaction in the preparation of organic/inorganic hybrid materials, it is difficult to understand their preparation without a basic knowledge of the sol–gel process. Over the past 2 decades numerous studies have been carried out in the field of sol–gel chemistry, and great progress has been made in understanding the reaction mechanisms although many questions remain. However, a brief review of the most basic sol–gel chemistry, especially

Scheme 1

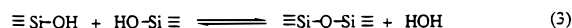
Hydrolysis



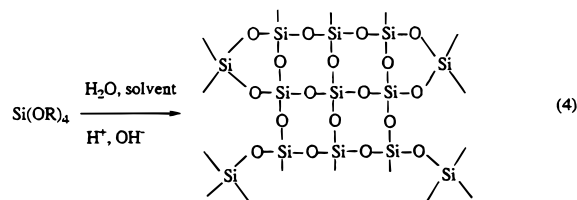
Alcohol Condensation (Alcoxolation)



Water Condensation (Oxolation)



Overall Reaction



that related to the preparation of organic/inorganic composites, is still appropriate here. Interested readers may refer to other studies and reviews for a more complete understanding of the entire sol-gel field.⁹²⁻¹⁰⁰

As stated earlier, the sol-gel reaction is a method to prepare pure ceramic precursors and inorganic glasses at relatively low temperatures. The reaction is generally divided into two steps: hydrolysis of metal alkoxides to produce hydroxyl groups, followed by polycondensation of the hydroxyl groups and residual alkoxy groups to form a three-dimensional network. The general scheme can be represented in Scheme 1 with silicone alkoxide as the example.

The sol-gel process generally starts with alcoholic or other low molecular weight organic solutions of monomeric, metal or semimetal alkoxide precursors M(OR)_n , where M represents a network-forming element such as Si, Ti, Zr, Al, B, etc., and R is typically an alkyl group ($\text{C}_x\text{H}_{2x+1}$) and water. Generally, both the hydrolysis and condensation reactions occur simultaneously once the hydrolysis reaction has been initiated. As can be seen from Scheme 1, both the hydrolysis and condensation steps generate low molecular weight byproducts such as alcohol and water. These small molecules must be removed from the system, and such removal would lead, in the limit, to a tetrahedral SiO_2 network if the species were silicon. The removal of these byproducts also contribute to the high shrinkage that occurs during the classical sol-gel process.¹⁰⁰

Both hydrolysis and condensation occur by nucleophilic substitution (S_N) mechanisms which involve three steps: nucleophilic addition (A_N), proton transfer within the transition states, and removal of the protonated species as either alcohol or water. For non-silicate metal alkoxides, generally no catalyst is needed for hydrolysis and condensation because they are very reactive. In the case of silicon based metal alkoxides, the hydrolysis and condensation reactions typically proceed with either an acid or base as catalyst. Therefore, the structure and morphology of the resulting network strongly depend on the nature of the catalyst, in particular, the pH of the reaction. In the case of the

Table 1. Electronegativity (χ), Coordination Number (N), and Degree of Unsaturation ($N - Z$) for Some Metals

alkoxides	χ	N	Z	$N - Z$
$\text{Si(OPr}^i)_4$	1.90	4	4	0
$\text{Sn(OPr}^i)_4$	1.96	6	4	2
$\text{Ti(OPr}^i)_4$	1.54	6	4	2
$\text{Zr(OPr}^i)_4$	1.33	7	4	3
$\text{Ce(OPr}^i)_4$	1.12	8	4	4
$\text{Al(OPr}^i)_3$	1.61	6	3	3

common silicon alkoxides, since the hydrolysis rate is high under an acidic environment relative to that of condensation, acid catalysis promotes the development of more linear or polymer-like molecules in the initial stages. For a pure metal alkoxide system, this will result in the formation of high-density, low fractal dimension structures. On the other hand, base catalysis results in a higher condensation rate. Therefore, this environment tends to produce more of a dense-cluster growth leading to dense, colloidal particulate structures.^{98,100-102} In addition to the pH of the reaction, the size of the alkoxy group can also influence the hydrolysis and condensation reactions through a steric or leaving-group stability effect. For example, species such as tetramethoxysilane (TMOS) tends to be more reactive than tetraethoxysilane (TEOS).

Mixed-metal alkoxide systems are also of great interest because of the potential properties and applications they provide. In the case of different metal alkoxide combinations, the structure and morphology of the resulting network depend not only on the nature of catalyst but also on the relative chemical reactivity of metal alkoxides. The great difference in their reactivity can often cause phase separation.¹⁰³ Therefore, the control of the reactivity of metal alkoxides is necessary in order to be able to tailor the structure of the resulting materials. The hydrolysis and condensation reactions in the sol-gel process generally start with the nucleophilic addition of hydroxylated groups onto the electrophilic metal atoms which results in an increase of the coordination number of the metal atom in the transition state. As described by Sanchez and Ribot, the degree of reactivity of a given metal or semi-metal atom of an alkoxide is not due only to the electrophilic nature but rather is more a function of degree of unsaturation.⁸² The extent of unsaturation is given as $(N - Z)$, where N is the coordination number of the atom in the stable oxide network and Z is the oxidation state. Table 1 lists the electronegativity and the degree of metal unsaturation for a few metal alkoxides. It is noted that silicon has a low electrophilicity and zero degree of unsaturation. Therefore, silicon alkoxides are less reactive. On the other hand, non-silicate metal alkoxides, including elements such as Ti, Zr, Al, and B with higher unsaturation, all have much higher reactivity than silicon. They are so sensitive to moisture, even in the absence of a catalyst, that precipitation of the oxide will generally occur as soon as water is present. For example, the hydrolysis and condensation rates of titanium butoxide are much faster than that of tetraethoxysilane (TEOS). As a result, titanium butoxide generally reacts rapidly with water and precipitates out of the reaction mixture before it can coreact with the TEOS into a network. The sequence of reactivity is expressed as follows:^{103,104}



There are several ways to control the coreactivity of two or more metal alkoxide species to avoid unnecessary phase separation. Chemical additives, such as glycols, organic acids (acetic acid), β -dicarbonyl ligands (ethyl acetoacetate (EACAC)), have often been used as chelating ligands to slow the hydrolysis and condensation reactions of non-silicate metal alkoxides.^{105,106} After forming a complex with the chelating ligand, the species between metal and chelating agent is less easy to hydrolyze.¹⁰⁷ However, the chelating ligand will normally remain which alters the structure of the final network. Chemically controlled condensation (CCC), a procedure proposed by Schmidt and Seiferling,¹⁰⁸ has also been used to control the difference in reactivity of various metal alkoxides. Specifically, hydrolysis of a fast-reacting alkoxide species is slowly initiated by the controlled release of water from the esterification of an organic acid with an alcohol. Once the fast-reacting alkoxide has been partially hydrolyzed and condensed, water is added to complete the overall reaction and to incorporate the slower reacting alkoxide. Another useful method was used by Parkhurst et al.¹⁰⁹ to incorporate titanium butoxide into TEOS-based silica gel. In this procedure, the TEOS species is allowed to partially hydrolyze and condense in the presence of an acid catalyst and water. Then, fast-reacting titanium butoxide is added. Once introduced, it quickly hydrolyzes and at least partially condenses into the preexisting immature TEOS-based network rather than precipitating as titania.

Synthesis and Properties of Organic/Inorganic Nanocomposites

Both small organic moieties and polymeric/oligomeric species can be chemically bonded with inorganic components to produce organic/inorganic hybrid network materials. In this section, such hybrid materials with functionalized polymeric/oligomeric species as the organic component are reviewed first, with emphasis on the work from our laboratories. Following this, the incorporation of small organic groups is discussed.

Hybrid Materials Incorporating Polymeric/Oligomeric Species

A new range of material properties can be produced by combining the features of the inorganic sol-gel alkoxide moieties with those of oligomeric/polymeric species. The resulting composites can vary from soft and flexible to brittle and hard materials depending on the chemical structure of the organic components and the overall composition ratio of organic to inorganic. Modification of the structure of inorganic components also has a profound effect on the properties of the resulting composite materials although the majority of the research concern the sol-gel processing of silica.

Many polymeric/oligomeric species have been successfully incorporated within inorganic networks by different synthetic approaches. The chemical bond between inorganic and organic phases can be introduced mainly by three approaches: (1) functionalize oligomeric/polymeric species with silane, silanol, or other functional groups that can undergo hydrolysis and condensation with metal alkoxides; (2) utilize already existing functional groups within the polymeric/oligomeric species; (3) use alkoxysilanes ($R'Si(OR)_3$) as the

Table 2. Oligomers/Polymers Used in the Preparation of Organic/Inorganic Hybrid Materials

oligomers/polymers	phase connection	ref
poly(dimethylsiloxane) (PDMS)	chemical bond	1, 6, 7, 109, 110–122
poly(tetramethylene oxide) (PTMO)	chemical bond	6, 7, 123–132
poly(methyl methacrylate) (PMMA)	chemical bond	3, 133
polystyrenes	no chemical bond	31–33
polyoxazolines (POZO)	chemical bond	134
	no chemical bond	135
polyimides	chemical bond	166
	no chemical bond	130, 136–139
polyamide	no chemical bond	140
poly(ether ketone) (PEK)	no chemical bond	141
poly(ethylene oxide)	chemical bond	158
poly(butadiene)	chemical bond	142
epoxy	no chemical bond	116, 143
polycarbonate	chemical bond	5, 144
poly(vinyl alcohol)	no chemical bond	34
poly(methyloxazoline)	no chemical bond	35, 37
poly(ethyloxazoline)	chemical bond	36
poly(vinyl acetate)	chemical bond	38
poly(acrylic acid)	no chemical bond	34, 145, 146
poly(ethyleneimine)	no chemical bond	41
poly(2-vinylpyridine)	chemical bond	147, 148
poly(<i>p</i> -phenylenevinylene)	no chemical bond	39
poly(<i>N</i> -vinylpyrrolidone)	no chemical bond	74
poly(ϵ -caprolactam)	no chemical bond	36
polyurethane	no chemical bond	149, 150
poly(<i>N,N</i> -dimethylacrylamide)	no chemical bond	149, 150
cellulosics	no chemical bond	34
poly(silicic acid esters)	no chemical bond	40
polyacrylics	no chemical bond	57
poly(arylene ether phosphine oxide)	chemical bond	151
poly(oxypropylene)	chemical bond	152
poly(arylene ether sulfone) (PSF)	chemical bond	116
cellulose acetate	chemical bond	153
poly(acrylonitrile)	chemical bond	154
	no chemical bond	39
	chemical bond	155

sole or one of the precursors of the sol-gel process with R' being a second-stage polymerizable organic group often carried out by either a photochemical or thermal curing following the sol-gel reaction. Table 2 lists many oligomers and polymers that have been incorporated into an inorganic network via this method. Table 2 is by no means comprehensive, and only these systems with chemical bonding between organic and inorganic phases will now be presented here.

1. Incorporation of Poly(dimethylsiloxane) (PDMS). As already mentioned, the low process temperature characteristic of the sol-gel reactions makes it possible to incorporate preformed oligomers or polymers that are often functionalized with trialkoxysilyl groups into the organic/inorganic networks via the co-condensation of functionalized oligomers or polymers with metal alkoxides. In 1985, work was initiated in our laboratory to develop novel organic/inorganic hybrid network materials by reacting metal alkoxides with functionalized polymeric/oligomeric species. The first successfully prepared system was that of the PDMS-TEOS system.^{1,6,7} Low molecular weight (500–1700 g/mol) PDMS oligomers terminally functionalized with silanol groups were successfully coreacted into a network with TEOS, using an acid catalyst. The chainlike inorganic structures were promoted by using acidic catalysts. This system was studied later by other researchers^{109,115–122} and PDMS with higher functionality and molecular weight have also been incorporated into the silica networks.¹¹⁵

The backbone of PDMS and the hydrolysis/condensation products of TEOS possess the same nature of chemical bonds (Si–O–Si) which help to make the organic and inorganic components more compatible. PDMS can also be maintained in solution with the reactive sol–gel components during reaction. If hydrolysis of the metal alkoxide is sufficiently rapid so as to provide hydrolysis products of the alkoxide for reaction with the silanol-terminated PDMS, a better dispersion of the functionalized PDMS in the final network can be achieved. Structural analysis by small-angle X-ray scattering (SAXS), dynamic mechanical spectroscopy (DMS), and other techniques did demonstrate that some dispersion of PDMS was achieved by optimizing the reaction conditions even though some degree of localized microphase separation did occur and was influenced by reaction conditions and catalyst.^{6,7} Systematic experiments were carried out to study the effects of the acid content, the content of PDMS, and the molecular weight of PDMS on the structure and properties of this material.^{110–114} Depending on the amount and molecular weight of PDMS used, the final materials could be either flexible or brittle and all showed optical transparency clearly indicating that phase (domain) size was smaller than the wavelength of visible light. As expected, decreasing the PDMS content resulted in a system with higher modulus, but it also led to cracking and greater shrinkage which made it difficult to prepare thick monolithic materials as is also the case for pure sol–gel glasses. Less microphase separation and improved molecular uniformity was achieved with the use of PDMS of lower molecular weight. Of the three factors, however, the mineral acid content of the reacting system was particularly important in determining the structure of the final materials. A model was suggested to interpret the experimental results. At the beginning of the reaction, some self-condensation of the PDMS species was believed to take place, particularly if given sufficient time, because most of the silanol groups arose from the PDMS. As the hydrolysis reaction of TEOS occurs, the dominant type of reaction will shift from self-condensation of PDMS to co-condensation of PDMS and hydrolyzed TEOS because silanol groups are generated from TEOS. Finally, if the silanol functionalities from PDMS species become exhausted, some self-condensation of TEOS occurs. According to this reaction scheme, the relative length of these three reaction periods clearly will determine the structure of the final cast products. High acid content will result in a relatively short first period because the rate of the hydrolysis reaction of TEOS is increased. This suggests that less PDMS will be phase-separated and more will be incorporated into the network of TEOS. The reverse will be true if the first period is relatively long, as is the case for a low acid content. A better overall dispersion of PDMS could be achieved with a higher acid content. However, higher acid content can also promote backbone (–Si–O–) interchange within PDMS chains, i.e., the cleavage of Si–O skeletal bonds, formation of cyclic species, and recombination of PDMS chains. This may also alter the morphology and structure of the final materials by particularly influencing the molecular weight distribution of the initial PDMS oligomers.

Hybrid networks prepared from PDMS and titanium tetraisopropoxide (TIP) was also studied by Joardar.¹²²

In this case, TIP end-capped PDMS instead of silanol-terminated PDMS was used to avoid possible PDMS chain degradation by additional TIP. Hybrid materials synthesized from varying PDMS–TIP compositions and different initial reaction conditions were then subjected to a systematic structure–property relationship study. Compared to the PDMS–TEOS systems, the PDMS–TIP materials showed less phase mixing and were of higher modulus for a comparable ratio of organic to inorganic components. At the 50/50 PDMS–TIP composition there was a rather distinct change in the mechanical properties which signified a morphological change in these materials. It was proposed that connectivity of the titanium oxide domains occurred at the 50/50 PDMS–TIP composition level which resulted in the changes in morphology and mechanical properties. SAXS and electron microscopy studies indicated that the domain sizes of the oxide phase in the PDMS–TIP material were smaller than those in the PDMS–TEOS material of equivalent composition, and these differences may be due to the reactivity difference between TIP and TEOS. Recently, Babonneau¹²¹ prepared hybrid PDMS–oxide gels by cross-linking OH-terminated PDMS with Si, Ti, or Zr alkoxides. This researcher further investigated the influence of the alkoxide nature on the development of OH-terminated PDMS networks by ²⁹Si and ¹H MAS NMR, as well as Ti K edge X-ray absorption for titanium-containing gel. TEOS was found to serve as a cross-linking agent which prevents chain extension, i.e., self-condensation of the functionalized PDMS. On the other hand, titanium or zirconium alkoxides seem to behave mainly as a catalyst for condensation of PDMS and thus leads to the formation of long PDMS chains through self-condensation. In both cases, reactions occur between PDMS and the metal alkoxides during the hydrolysis process.

2. Incorporation of Poly(tetramethylene oxide) (PTMO). While the successful preparation of PDMS–TEOS systems did demonstrate the possibility to prepare organic/inorganic hybrid networks, these composites did not display high tensile strength and elongation which was attributed to remaining loose or dangling PDMS chain ends and the molecular weight “scrambling” or redistribution of PDMS chains caused by higher acid catalyst concentration.^{6,7} The inherently poorer mechanical properties of pure PDMS along with these network defects were believed to lower the tensile strength of the resulting materials. To overcome these problems, hydroxyl terminated PTMO oligomers (650–2900 g/mol) with better mechanical properties were made. However, a different approach was utilized in functionalizing the PTMO oligomers. As mentioned above, a difference in the reactivity of the end groups of the selected oligomer and that of TEOS can result in poor incorporation of the oligomeric component. Therefore, the use of functional groups with reactivity comparable to those that exist on the alkoxide group certainly favors the preparation of hybrid systems with better component dispersion and network development. Often this can be achieved by endcapping the oligomeric or polymeric components with triethoxysilane groups.⁷ For example, oligomers or polymers can be functionalized with triethoxysilane groups by allowing triethoxysilyl isocyanates to react with oligomers or polymers containing pendant amines or alcohols to form urea or urethane linkages, respectively. Triethoxysilane-func-

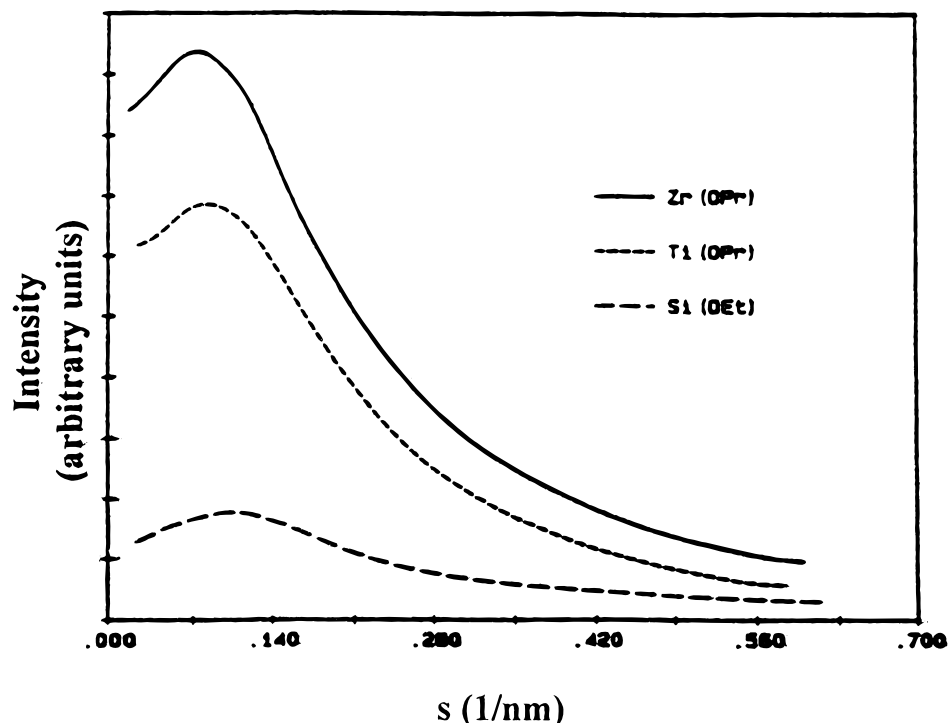


Figure 1. SAXS profiles for Ceramers TEOS(50)–PTMO(2k)–100–0.014–RT, TiOPr(50)–PTMO(2k)–100–0.014–RT, ZrOPr(50)–PTMO(2k)–100–0.014–RT. The sample nomenclature indicates that the material was prepared with 50 wt % of metal alkoxide and 50 wt % of triethoxysilane-functionalized PTMO with M_w of 2000, 100% of the stoichiometric amount of water for the hydrolysis reaction, 0.014 molar ratio of HCl/metal alkoxide, and cast at room temperature into film form from a 2-propanol solution (reproduced with permission from ref 126).

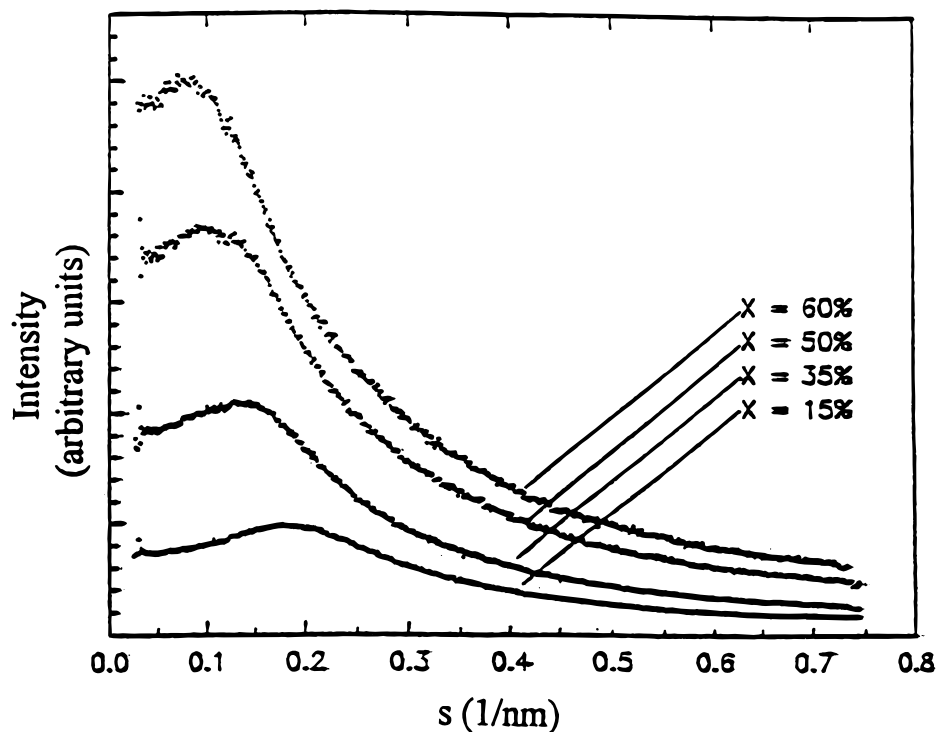


Figure 2. SAXS profiles of PTMO–TiOPr systems (PTMO molecular weight 2000 g/mol) containing varying amounts of TiOPr.

To further strengthen the concept behind the development of the microdomains of rich inorganic regions, Figure 2 shows the SAXS profiles from a series of TiOPr–PTMO hybrid network materials where the variable is that of composition ratio, i.e., the functionalized 2000 g/mol of PTMO molecular weight has been held constant.¹²⁸ The maximum scattering intensity as well as the interdomain spacing was found to systematically increase with an increase in metal alkoxide content. The correlation distance increased from ca. 7

to 17 nm as the initial reactant weight fraction of TiOPr was increased from 15% to 60%. This suggested that, as expected, as the inorganic domains became larger, but connected by the same organic spacer length, the interdomain distance would increase.

On the basis of a variety of related SAXS investigations, a simplified model was proposed and is schematically shown in Figure 3.¹²³ This very general model attempts to visually convey the types of structure present in the PTMO–metal alkoxide hybrid materials

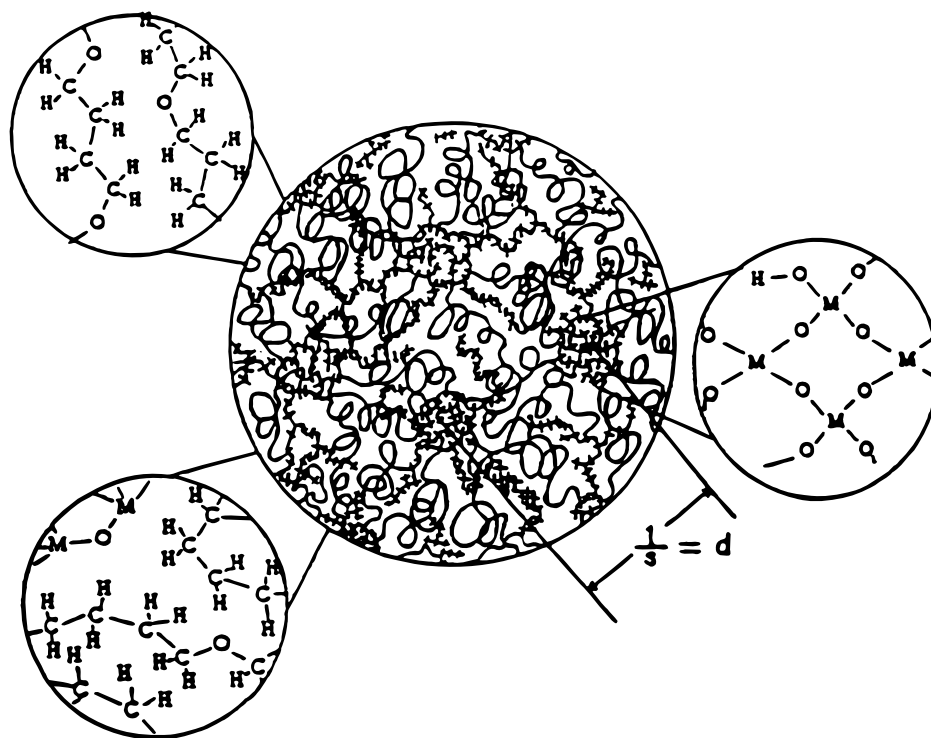


Figure 3. Generalized model of the local morphological structure in PTMO-TEOS hybrid systems, in which $1/s$ is an estimate of the correlation distance where the value of the scattering vector, s , is that at the first interference peak in the SAXS profile (reproduced with permission from ref 123).

when percolation of the inorganic phase is absent.¹²³ The model displays three generalized regimes or phases:

- (1) The regime identified in the upper left circle represents the "lower electron density" organic-oligomeric-rich phases.
- (2) The regime in the right-hand side circle indicates the "higher electron density" inorganic-rich regions.
- (3) The third regime identified in the lower left circle represents the regions in which the two components display some level of mixing.

The correlation length (interdomain spacing) between two inorganic-rich regions can be approximated in terms of $1/s$, where s is the value of the scattering vector at the interference peak. This generalized model suggests the separation of a dispersed inorganic-rich phase chemically cross-linked at the interface with an oligomeric-rich matrix phase except at very high initial inorganic content. The interdomain spacing as well as the intensity of scattering has been found to depend on the nature of metal alkoxide, the molecular weight of oligomeric species, metal alkoxide content, temperature of processing, etc.

All the PTMO-metal alkoxide hybrid networks discussed so far were prepared with 2-propanol (IPA) as solvent. SAXS studies also showed that solvent type influenced the structure of the hybrid systems. When using a *N,N*-dimethylformamide (DMF)-IPA cosolvent system as the reaction medium, the SAXS scattering profiles became much sharper as the DMF content increased, indicating a narrower distribution of either domain sizes or interdomain spacings or both. This was believed to be attributable to the less acidic nature of the mixture when DMF was used as cosolvent which promoted less mixing between the two components.

The chemical stability of PTMO-TEOS and PTMO-TiOPr hybrid materials in neutral and alkaline aqueous solutions has also been investigated.¹⁵⁹ For PTMO-

TEOS hybrids, the aging in 1 M NaOH for 24 h resulted in a better-defined two-phase microstructure because of the solubility of silicon oxide in the highly basic solution. The loss of silicon oxide resulted in a higher PTMO chain mobility to the extent that the PTMO chains could now undergo crystallization at low temperatures. The modulus of the treated network was also lower than untreated hybrids due to the loss of silicon oxide and hydrolysis of the alkali-treated networks. These results also supported the microstructural model proposed above. For PTMO-TiOPr hybrids, little change in the titanium oxide content was observed due to the lower solubility of titanium oxide in 1 M NaOH solutions. However, base treatment resulted in better phase separation between the inorganic and the organic phases which resulted in a higher mobility of the organic phase.

Besides the effects of the molecular weight of PTMO and influence of solvent effects, a substantial "aging effect" has also been noted in some cases.^{7,124} If the ambient temperature cast films are later heated to a higher temperature (ca. 100 °C), the extent of reaction can be increased. Aging can also take place in the time period between gelation and vitrification of the "hard" regions and this aging effect can be easily interpreted by using the concept of the time-temperature-transformation (TTT) cure diagram established by Gillham.¹⁶⁰ Here, the isothermal cure of a system is usually characterized by gelation and vitrification and is complicated by the interaction of the chemical kinetics and the changing physical properties due to network development which influences the diffusivity of the reactive species. At a specific cure temperature, the T_g of the system will increase as the reaction proceeds and this will continue until the system reaches its new T_g which can often be the new higher cure temperature. Thus the cessation of the reaction is not necessarily an

indication that the reaction is complete but only quenched due to vitrification. Subsequent exposure of the system to a higher temperature that surpasses the original T_g can also result in further reaction.

Commenting briefly on acid catalysts, mineral and low molecular weight organic acids have been most used for the preparation of ceramers as well as conventional sol gels. However, the utilization of the polymeric acid catalyst poly(styrenesulfonic acid) (PSS), which is readily available in various molecular weight and degrees of sulfonation, has also been investigated.^{132,161} The results demonstrate that PSS is an effective catalyst for the preparation of PTMO-TEOS hybrid materials that possess comparable properties to the same composition prepared with low molecular weight acid catalysts. An advantage of a polymeric acid catalyst is that it can be used as a rheological modifier to enhance processability yet also minimize fugitive acid moieties that are prominent from low molecular weight catalyst. Clearly, a similar approach could be followed but with a polymeric base catalyst such as a polyamine functionalized chain.

The effect of titanium(IV) tetraisopropoxide ($\text{Ti}(\text{OPr})_4$) on the final properties of PTMO-TEOS hybrid systems was also investigated following the above studies. Due to the large difference in the reactivity of titanium(IV) tetraisopropoxide and TEOS, a new reaction scheme was developed to incorporate titanium(IV) tetraisopropoxide into PTMO-TEOS systems.^{6,7} In this approach, TEOS and triethoxysilane-functionalized PTMO was first partially hydrolyzed and condensed by using a CCC system of glacial acetic acid and 2-propanol (no water). The titanium(IV) tetraisopropoxide is added later to avoid phase separation. With this approach, transparent hybrid materials were produced. The resulting materials develop a higher network density and high modulus, and the ultimate strength is improved with respect to the pure PTMO-TEOS hybrid systems.

Triethoxysilane functionalized PTMO has also been incorporated with titanium(IV) tetraisopropoxide, aluminum tris-*sec*-butoxide ($\text{Al}(\text{OBu})_3$) and zirconium tetra-*n*-propoxide ($\text{Zr}(\text{OPr})_4$) without the presence of TEOS.^{113,162-164} Again, due to the fast reaction rate of these metal alkoxides, the direct addition of water will cause precipitation. Therefore, two new reaction approaches were developed to solve this problem:

(1) Chelating ligands, such as β -dicarbonyl ligand ethyl acetoacetate (EACAC), were first utilized.¹⁶³ The hydrolysis rate of metal alkoxides can be slowed by forming a complex with the chelating ligand so that no precipitation occurs and homogeneous sols or gels can be obtained. The functionalized PTMO species was added later. A drawback of using ligands is that they remain in the final products and may influence the structure-property behavior.

(2) A second approach was also developed by slowly adding water containing an acidified (HCl) alcohol solution to the metal alkoxide systems to avoid precipitation.¹⁶⁴ Transparent hybrid materials can be prepared by these approaches. SAXS and DMS analysis of these systems indicate a microphase-separated morphology similar in nature to that of previously described PTMO-TEOS systems.

Besides the normal solution casting and thermal curing technique, microwave curing processing has also been utilized to promote the sol-gel reaction of PTMO-TEOS, PTMO-TIP, and PTMO-zirconium propoxide

systems. Microwave processing has the ability to potentially promote a higher rate of reaction due to specific interactions with the dipoles of the appropriate functionalized reacting groups. Indeed, it was found that gelation and near final properties of the PTMO-TEOS hybrid systems can be achieved in a matter of minutes.¹⁶⁵ The higher intensity and flat "tail region" from the SAXS scattering curve of microwave-processed PTMO-TEOS hybrid networks also indicated a higher extent of reaction and higher level of phase separation compared to ambient temperature casting or even conventional thermal (convection) cured systems.⁶ The morphology for the ceramers made by microwave processing and thermal curing is nearly identical in that they all display an average correlation length of ca. 10 nm. There is no major change in morphology except that the intensity of scattering increases with the extent of curing and densification as expected. However, for PTMO-TiOPr systems, the differences in these hybrid materials cured thermally and by microwaves were not as great as observed in the PTMO-TEOS systems. The faster reaction rate of the titanium alkoxides was proposed to be the responsible factor.

3. Incorporation of Poly(ether ketone) (PEK).

By utilizing a similar synthetic approach to that for the PTMO-TEOS systems, triethoxysilane-functionalized PEK oligomers ($M_n = 3900$ g/mol) were used to synthesize a hybrid network with TEOS.¹⁵⁸ PEK is an amorphous engineering thermoplastic material with good mechanical properties, thermal stability, and a relatively high glass transition temperature of ca. 150 °C in higher molecular weight form. A major difference between the PEK system and those of the PDMS or PTMO systems is that the high glass transition temperature of PEK can further limit the extent of cure caused by vitrification as gelation and network buildup occur. The gelation and vitrification occurred at low extents of reaction. However, by utilizing thermal postcure treatments at elevated temperature, further network development can be promoted. The final materials still maintain high transparency (but not water white) although local microphase separation does occur.

4. Incorporation of Polyoxazolines (POZO). Chujo et al.¹³⁵ synthesized polyoxazoline-silica hybrid materials by using a comparable synthetic approach. Triethoxysilane-terminated POZO with a molecular weight of 500-2000 was obtained by ring-opening polymerization of 2-methyl-2-oxazoline followed by termination with (3-aminopropyl)triethoxysilane—the same functionalizing agent as was utilized in the PTMO studies already reviewed. These silane-terminated POZOs were then subjected to acid-catalyzed cohydrolysis and condensation with TEOS to produce a homogeneous, transparent, and glassy inorganic/organic hybrid material. It should also be mentioned here that a hybrid without chemical bonding between inorganic and organic phases can also be prepared simply by utilizing the hydrogen-bond interactions between the silanol group and the POZO amide carbonyl group.¹⁶⁶

An important application proposed for this latter hybrid material is the preparation of highly porous silica having micro- or nanoscale pores. This can be readily done by calcination of the hybrids at temperatures between 600 and 800 °C which are below the fusion temperature of metal alkoxide. The organic component

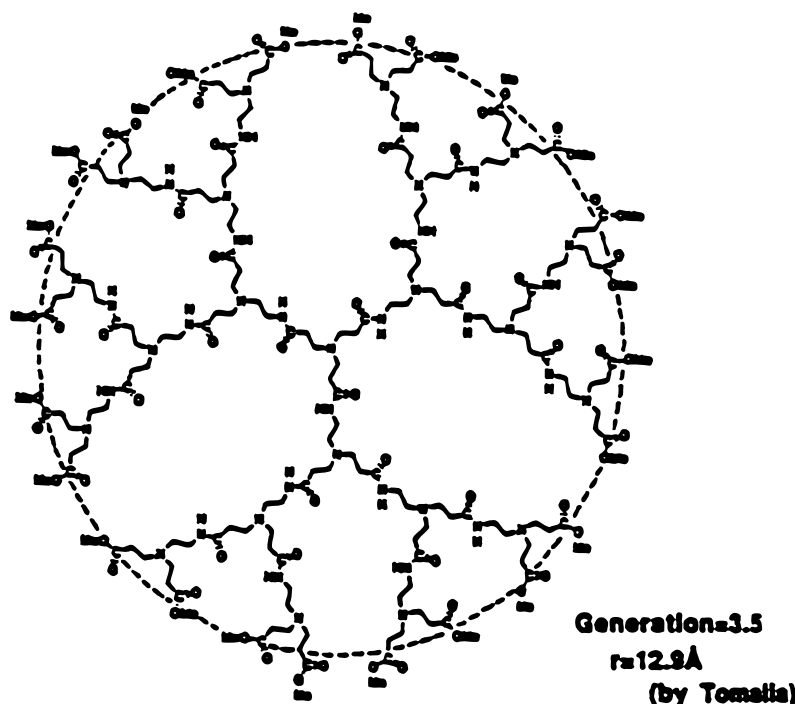


Figure 4. Schematic expression of a starburst detrimer of 3.5 generation (reproduced with permission from ref 168).

is decomposed at these temperatures, leaving behind a porous structure with surface areas varying between ca. 200 and 800 m²/g depending on the composition and molecular weight of POZO.^{36,166} The authors of this review have also obtained highly porous silica with surface area as high as over 1000 m²/g through the calcination of PTMO-TEOS hybrid materials.¹⁶⁷ The influence of molecular weight and content of PTMO, reaction condition, and calcination temperature to the surface area of the resulting porous silica is still underway in our laboratory.

Control of the pore size in silica gels prepared by this hybrid approach can also be achieved by using so-called "starburst dendrimers" as the organic component.¹⁶⁸ These dendrimers, which are prepared with ammonia (core), methyl acrylate, and ethylenediamine, contain an *N*-alkylamide group as the repeating unit and possess a three-dimensional dendritic structure emanating from a central unit via a number of generations as shown in Figure 4. The number of generations determines the size of the dendrimer. In the case of dendrimer with 3.5 generations which has been employed to prepare hybrids, the radius of the dendrimer is ca. 12.9 Å which is found to be very close to the peak of the pore-size distribution curve of porous silica (13 Å).

5. Incorporation of Polyimides. Recent research work on organic/inorganic hybrids has been aimed to improve the properties of polymers with respect to better thermal stability and mechanical strength. So far, polyimides have drawn the most attention in this regard.¹³⁶⁻¹³⁹ Unlike other high-performance polymers, such as Kevlar, polyimides are synthesized from a precursor molecule (poly(amic acid)) which is soluble in some organic solvents. This opens the possibility to produce polyimide-silica hybrid materials through the sol-gel approach.

By utilizing a comparable synthetic approach with PTMO-TEOS systems, Brennan¹³⁰ synthesized polyimide-containing hybrid network systems: titanium tetraisopropoxide (TiOPr)-polyimide in which the poly-

imide was based on 6F-benzophenone tetracarboxylic acid dianhydride (6F-BTDA) and bis(aminopropyl)-tetramethyldisiloxane (BisP). The oligomeric molecular weight ranged from 5000 to 13 000 g/mol. They were functionalized by either (aminophenyl)trimethoxysilane (AMP), (isocyanatopropyl)trimethoxysilane, or hydrosilylation of nadic anhydride. The SAXS behavior of these materials was similar to that of TiOPr/PTMO and TEOS/PTMO hybrid networks in that an interdomain spacing developed caused by a periodic fluctuation in electron density. It is generally believed that the introduction of inorganic components into organic materials can improve their thermal stability based on the fact that these species have good thermal stability and also enhance mechanical strength. Indeed, the hybrid networks described above exhibited relatively good thermal stability. However, thermal weight loss studies also indicated that the thermal stability of these hybrid systems was dependent upon the nature of the particular silane end group used to functionalize the polyimide with the order of thermal stability being (aminophenyl)-trimethoxysilane (AMP) > (isocyanatopropyl)trimethoxysilane > hydrosilylation of nadic anhydride.

Nandi et al.¹³⁷ reported the preparation of molecular level polyimide-silica and polyimide-titania composites by using a so-called "site isolation" method. In this method, metal alkoxide is maintained in isolated pockets in the polymeric matrix, and this can be achieved by prebinding the metal alkoxide precursor (tetraethoxysilane or titanium butoxide) to the carboxylic sites of the polyamic acid formed initially. The authors suggested that the metal alkoxide can be chemically bonded with the precursor polyamic acid through cohydrolysis of carboxylic groups and metal alkoxide. However, they did not confirm the formation of chemical bonding. The polyamic acid precursor was synthesized from 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA). During the final curing step, imidization occurs, leading to ring closure which releases water that can then hydrolyze the metal alkox-

ides to eventually generate the oxides. The rigidity of the polyimide backbone (as evidenced by the high T_g) slows the mobility of the metal alkoxide clusters and prevents agglomeration of large particles. Both TEM and SEM observations indicate the formation of a homogeneous dispersion of SiO_2 (and TiO_2) nanoclusters with a size of about 1.5 nm within the polyimide matrix. As a result, transparent and flexible polyimide-containing organic/inorganic films can be obtained in this way.

Morikawa et al.¹³⁶ also reported the preparation of polyimide–silica hybrid films by the hydrolysis and condensation of a metal alkoxide (TEOS) in a polyamic acid solution, followed by subsequent heating of the resulting film at high temperature. In this method, the polyamic acid was first prepared from PMDA and ODA in *N,N'*-dimethylacetamide (DMAc), and TEOS and water were then added to the solution of polyamic acid. The reaction between TEOS and water resulted in a homogeneous mixture which was then cast onto a glass plate. After this was heated to ca. 270 °C the polyimide–silica hybrid film was obtained. Hybrid films having silica content up to 70 wt % and silica size of approximately 5 μm could be obtained. This method was later modified by the same research group by introducing ethoxysilyl groups as the diamine monomer into the polyimide matrix, to connect the silica particles with the polyimide matrix and using methanol as the solvent, hybrid films containing up to 50 wt % silica with much smaller size (about 0.2–0.08 μm in diameter) were obtained.¹³⁶ In contrast to the other preparation method given above, the hybrid films made in this way show a higher storage modulus, a reduction in the decrease of the glass transition temperature, and low $\tan \delta$ maximum.

The preparation and properties of additional polyimide–silica hybrid systems have also been investigated by several other research groups and only brief remarks will be made about this work here. Mascia and Kioul¹³⁹ studied the compatibility of polyimide–silica ceramers by adding a small amount of (γ -glycidyloxypropyl)-trimethoxysilane (GOTMS) as a coupling agent. Compatibility of the components can be readily achieved by the addition of coupling agent and the morphology of the hybrid films was strongly dependent on the molecular weight of polyamic acid, alkoxysilane solution composition, reaction time, and the type of coupling agent and catalyst. The tensile strength and ductility of hybrid materials was found to increase with the addition of low functionality alkoxysilane and the GOTMS coupling agent. Wang et al.¹³⁸ also studied the morphology, thermal stability, and mechanical properties of polyimide–silica composites. In their studies, an organically substituted alkoxysilane, (aminophenyl)-trimethoxysilane (APTMS), was utilized to provide bonding sites between the polyimide and the silica-like phase. They found that small amounts of APTMS can improve the modulus and strength of the resulting hybrid materials, and the transparency also increased with an increase of APTMS.

6. Incorporation of Acrylate Polymers. Acrylate polymers, including poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and poly(butyl methacrylate) (PBMA), have been utilized to prepare organic–inorganic composite materials. However, in most of the studies, no primary chemical bonding exists between the

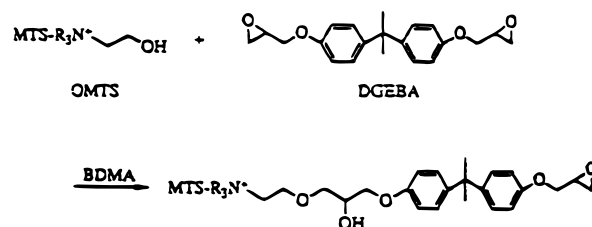


Figure 5. Based-catalyzed oxirane ring-opening reaction between hydroxyl groups of OMTS and DGEBA (reproduced with permission from ref 144).

polymeric component and the inorganic phase for this type of inorganic/organic composites although homogeneous and optically transparent products can be obtained due to the compatibility promoted by strong hydrogen-bonding interactions between the organic and inorganic species. Only a few studies have focused on developing covalent bonding between the two phases. As an example, Wei et al.¹³³ developed an approach that can covalently incorporate acrylate polymers into a silica network. In this approach, the acrylate polymers were first synthesized by group-transfer polymerization (GTP) of allyl methacrylate (AMA) and by copolymerization of AMA with methyl methacrylate (MMA). Then the allyl methacrylate polymers were functionalized by hydrosilylation of the allylic segments to convert allylic vinyl groups to triethoxysilyl groups. Finally, the triethoxysilyl groups in acrylate polymers and TEOS cohydrolyze and condense in the presence of acid catalyst via the sol–gel reaction. With this approach, transparent and monolithic hybrid materials can be obtained at room temperature by a slow evaporation of solvent and small molecule byproducts.

7. Other Systems. Other examples of functionalized oligomers and polymers that have been covalently incorporated into an inorganic network are polystyrenes,¹³⁴ polyamide,¹⁴¹ poly(ethyleneimine),^{147,148} epoxy,^{5,144,169} poly(ethylene oxide),¹⁴² poly(oxypolypropylene),¹¹⁶ poly(arylene ether phosphine oxide),¹⁵² poly(arylene ether sulfone) (PSF),¹⁵³ cellulose acetate,¹⁵⁴ polyacrylics,¹⁵¹ polyacrylonitrile,¹⁵⁵ and polybutadiene.^{116,143} All these oligomers have been incorporated into the inorganic network utilizing terminal functional groups such as triethoxysilane.

While epoxy–inorganic composite can be obtained using epoxy-containing triethoxysilane as the precursor in the sol–gel process, epoxy–silicate nanocomposites consisting of individual mica-type silicate (MTS) layers embedded within a cross-linked epoxy matrix have also been prepared by dispersing an organically modified mica-type silicate (OMTS) in an epoxy and curing at 100–200 °C.¹⁴⁴ In this approach, OMTS is prepared by an ion-exchange reaction from Na–montmorillonite and bis(2-hydroxyethyl)methyl tallowalkylammonium chloride. Following the delamination of OMTS within an epoxy resin (diglycidyl ether of bisphenol-A, DGEBA), the curing is carried out in the presence of nadic methyl anhydride (NMA), benzyltrimethylammonium chloride (BDMA), or boron trifluoride monoethylamine (BTFA). The hydroxyethyl groups of the alkylammonium ions located in the galleries of the OMTS participate in the cross-linking reaction and result in chemical bonding of the epoxy network to the OMTS as shown in Figure 5. The resulting composite exhibits molecular dispersion of the silicate layers with a layer spacing of 100 Å or more in the epoxy matrix which has been verified using X-ray

diffraction and transmission electron microscopy. This nanocomposite exhibits good optical clarity and dynamic modulus reinforcement greater than epoxies modified with comparable conventional filler amounts and may have applications as adhesives, coatings, electronic, or structural materials.

In summary, most of the research efforts in this area have focused on searching for hybrid materials with new properties. The study of structure–property relationships of these new materials has been less emphasized although its importance is obvious. A knowledge of the structure and its relationship to final properties is a powerful tool in designing the synthesis to obtain the desired properties. A typical example is the preparation of new organic/inorganic hybrid network materials with high refractive index.^{152,153} Titanium tetraisopropoxide was chosen as the inorganic component due to its high refractive index. PSF, PEPO, or PEK were chosen as the organic components due to their high refractive index relative to most other organic polymers. The triethoxysilane-functionalized PEPO, PEK, and PSF were incorporated with titanium tetraisopropoxide through the sol–gel process. The refractive index of each of these materials exhibited a linear relationship with titanium oxide content. Also, they have a refractive index and an optical dispersion behavior between that of organic polymers and inorganic glasses. As we have alluded to, the morphology of organic/inorganic hybrid materials can be characterized by a variety of analytical techniques ranging from visual inspection, optical microscopy, SEM, TEM to DMS and small-angle scattering techniques such as SAXS and SANS.^{7,38} The morphological details can be related to reaction mechanisms and ultimately to physical properties. As discussed earlier, for several of the organic/inorganic composites prepared from silane-functionalized polymeric/oligomeric species and metal alkoxide, detailed morphological studies have been carried out on the PTMO–TEOS systems and a general morphological model based on SAXS data has been proposed—recall Figure 3. However, it should be realized that with different chemical structures of the organic species and different reaction conditions will result in hybrid materials with variations to this general model. For example, the influence of reaction conditions on the morphology of hybrid materials was clearly demonstrated by a study of Rodrigues and Wilkes in which a fractal analysis was utilized to analyze the effect of cosolvent systems on the development of the structure of the inorganic phase in PTMO–TEOS hybrid networks. It was observed that PTMO–TEOS hybrid materials reacted in the cosolvent systems of DMF/IPA and THF/IPA displayed different SAXS profiles and the earlier proposed generalized morphological model did not provide sufficient information about the nature of the inorganic phase and the interaction of this phase with the organic component in the various hybrid systems. Therefore, an improved morphological model was proposed to account for the growth of the inorganic phase and its interaction with the organic component through fractal analysis. It was shown in this work that for the PTMO–TEOS hybrids reacted in DMF/IPA, the structure of inorganic components changed from mass fractal to surface fractal with the passage of reaction time. This feature could be attributed to the early attachment of the PTMO chains to the growing polymeric silicate species followed by the

diffusion of smaller secondary silicate species to the primary silicate species located at the chain ends. There was also greater mixing between TEOS and PTMO as the PTMO content was increased based on the broader scattering profiles. In the case of PTMO–TEOS hybrids reacted in THF/IPA, more mixing occurred between PTMO and silicate components. The silicate particles displayed mass fractal behavior and were more open and linear. Recently, Landry et al.¹⁶⁹ proposed two morphological models to describe small-angle X-ray scattering data of organic/inorganic composites based on a triethoxysilane-endcapped bisphenol A epoxide resin (EAS)–TEOS system reacted under slightly basic conditions, and a random trimethoxysilane-functionalized copolymer of poly(methyl methacrylate) (MMA–TMS) with added tetramethoxysilane (TMOS) reacted in an acidic medium. They concluded that for the EAS hybrid materials, the inorganic phase exhibits particle-like characteristics at length scales less than ca. 250 Å which can be described by a noninterpenetrating fractal cluster (NIFC) model, and the organic and inorganic components are bicontinuous at larger distances which can be interpreted by a bicontinuous two-phase (B2P) model. The MMA–TMS composite is better described by bicontinuous organic and inorganic phases with a periodic fluctuation of about 40 Å and the B2P model offers a more accurate picture of the MMA–TMS hybrid morphology.

Clearly, as more control develops for systematically varying the morphology of the hybrid systems, new properties will appear.

Incorporation of Small Organic Moieties

A direct way to introduce smaller organic moieties into a hybrid network through chemical bonding is to use bifunctional or/and trifunctional alkoxy silanes ($R'_n\text{Si}(\text{OR})_{4-n}$, $n = 1-3$, $R = \text{alkyl}$, $R' = \text{organic group}$) as one or more of the precursors for the sol–gel reaction. This approach has been extensively studied by Schmidt and co-workers since the late 1970s and the hybrid materials made in this way have been termed ORMOSILS or later as ORMOCERS.^{2-5,53,65,77,108,170-173} The synthetic route in this approach is quite straightforward—instead of using metal alkoxide as the precursor for sol–gel reaction, alkoxy silanes are used as the only (or one of) the precursors and the organic groups X are introduced into the inorganic network through the $\equiv\text{Si}-\text{C}-$ bond in an alkoxy silane. Trifunctional alkoxy silanes, $R'_3\text{Si}(\text{OR})_3$, are the most common precursors to introduce organic groups because a variety of such silanes are commercially available, while bifunctional alkoxy silanes have to be used in the presence of higher functionality precursors in order to form a three-dimensional network.

The organic/inorganic hybrid materials made by this approach can be viewed more as a molecular type of hybrid network because the organic groups have been chemically bonded with the inorganic component *before the reaction starts*. While these types of hybrid network materials still suffer the same drawbacks as classical sol–gel materials, e.g., generation of large amount of byproducts and shrinkage during the drying process, they have generated considerable interest. By tailoring the structure of the organic group R' , mechanical, optical, or electrical properties of the resulting composite materials can be greatly modified. Some example properties that can be introduced by organic molecules

are mechanical such as flexibility, toughness, optical such as NLO and UV adsorption, and electronic such as conduction and redox properties.^{42,43,47,48,75,76} For example, when triethoxysilyl-functionalized NLO dyes are used as the only (or one of) the sol-gel reaction precursors, the resulting hybrid materials possess NLO response. Organic/inorganic composite materials made in this way combine the optical response of the organic structure with good optical quality, good mechanical property, and environmental stability of inorganic glasses. Depending on the type of organic materials used, second-order and third-order NLO materials, and other optical materials can be obtained. If the R' group is a polymerizable organic group, an organic network can be formed within the inorganic network by either photochemical or thermal curing. For example, by using methacrylate monomers containing trialkoxysilane and TEOS as the precursors of the sol-gel reaction, Schmidt et al. introduced PMMA within the silica network through an in situ polymerization of methacrylate monomers following the hydrolysis and polycondensation of silane functional groups.³ Recently, Schubert et al.¹⁷⁴ synthesized organically modified silica aerogels by base-catalyzed hydrolysis and condensation of alkoxy-silanes (RSi(OMe)₃)/TEOS mixtures, followed by supercritical drying of the alcogels with methanol or CO₂. By the proper choice of the organic groups, the ratio of RSi(OMe)₃/TEOS, and drying condition, aerogels with interesting new properties such as permanent hydrophobicity can be prepared by this approach.

Another area utilizing functionalized low molecular weight organics that has attracted interest from both the academic and industrial section is the preparation of inorganic/organic hard coatings for polymeric materials. Sol-gel coatings made from metal alkoxides already have commercial applications for glass and metal substrates. However, due to the thermal expansion coefficient difference and poor adhesion between sol-gel coating and polymeric materials, the applications of these pure metal alkoxide sol-gel coatings often encounter major difficulties for polymeric substrates. Using organic/inorganic composite as the coating materials can overcome many of these problems because the introduction of organic components into the inorganic network reduces the extent of shrinkage, brings flexibility to the brittle inorganic network, and increases the adhesion between the coating and polymer substrate. Schmidt has developed a series of scratch and abrasive-resistant coating materials which are based on Al₂O₃, ZrO₂, TiO₂, or SiO₂ as network formers and epoxy or methacrylate groups bound to Si via a ≡Si-C-bond.^{66,108,170,175} More recently, organic/inorganic hybrid abrasion-resistant coating materials based on polyfunctional alkoxy-silane and metal alkoxides as the precursors of composite networks have also been developed in our laboratory.^{68-73,176} The polyfunctional alkoxy-silane precursors are obtained by first functionalizing organic molecules with trialkoxysilane groups and then hydrolyzing and condensing the system with or without metal alkoxides to form an inorganic network with organic molecules inside the network. The organic molecules that have been incorporated into the hybrid network by this approach include diethylenetriamine (DETA),⁷¹ 3,3'-iminopropyltri-amine (IMPA),⁷³ 4,4'-diaminodiphenyl sulfone (DDS),⁷⁰ melamine,⁷¹ bis- and trismaleimides,⁶⁸ tris(*m*-aminophenyl)phosphine oxide compound,⁶⁹ re-

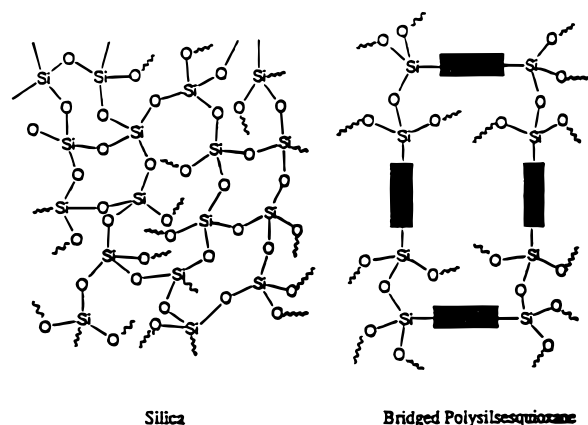


Figure 6. Representation of the chemical connectivities of a silica network and a bridged polysilsesquioxane network. The shaded rectangles correspond to the variable organic species (reproduced with permission from ref 178).

sorcinol,⁷³ glycerol,^{72,73} and a series of diols.^{72,73} The metal alkoxides are tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), titanium butoxide, zirconium propoxide, and aluminum tri-*sec*-butoxide. The adhesion between coating and substrate can be further improved by first treating the polymeric substrate surface with an oxygen plasma or a primer solution of isopropanol containing (3-aminopropyl)triethoxysilane. The resulting coating materials have been applied on several polymeric substrates such as PMMA, polycarbonate, and CR-39 lenses. Because reactive organic groups can be introduced into the inorganic networks, other functional coating materials such as fluorescent coatings and high refractive index optical coatings can also be obtained by this approach.¹⁵²

A final example of inorganic/organic hybrid network materials synthesized with lower molecular weight polyfunctional alkoxy-silane and metal alkoxides as the precursors of the sol-gel reaction extend from the so-called "bridged polysilsesquioxanes" developed by Shea et al.^{177,178} These bridged polysilsesquioxanes are three-dimensional network materials that are assembled by the sol-gel reaction of polyfunctional low molecular weight building blocks as shown in Figure 6. The trialkoxysilane terminated organic spacers can introduce a wide variety of organic functionality, such as arylene, alkylene, alkenylene, and alkynylene groups, into the final network materials. These materials have the potential for the fabrication of NLO materials and high surface area aerogels and xerogels.

Final Remarks

The area of organic/inorganic hybrid network materials prepared by the sol-gel approach has rapidly become a fascinating new field of research in materials science. The explosion of research in the past decade in this field has promoted considerable progress in both the fundamental understanding of the sol-gel process in general and its use in the development and applications of new organic/inorganic hybrid materials. As has been discussed within this review, a very wide range of material properties can be generated by combining the appropriate features of a given inorganic metal moiety with those of appropriately selected organic species. In some cases, these two different types of moieties can be directly bonded to each other to build a hybrid network, while in other cases just strong seconding bonding

interactions promote the miscibility of the different components. It has also been demonstrated in this review that a more complete understanding of their structure–property behavior can be gained by employing many of the standard tools that are utilized for developing similar structure–property relationships of organic polymers. Specifically, use of mechanical, thermal analysis, X-ray scattering, and microscopy methods in conjunction with other standard tools such as NMR can be invaluable in leading to a truer understanding of how these materials function in light of their chemistry and morphological features. Although the number of commercial hybrid sol–gel products is still relatively small, the promise of their use in new technological applications remains high. It is expected that over the next decade, numerous such materials will enter into the marketplace and serve an important function in the ever growing field of materials science.

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