



Silica-Based Sol-Gel
Organic-Inorganic
Nanocomposite Materials:
A Review of Different Material
Technologies

by Sandra K. Young

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Silica-Based Sol-Gel Organic-Inorganic Nanocomposite Materials: A Review of Different Material Technologies

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Abstract

Organic-inorganic nanocomposite materials continue to interest researchers. The idea of combining the properties of organic systems with the properties of inorganic systems in a synergistic fashion is not only desirable but also widely sought in materials. It is the difficulties with which these materials are often met which keep many researchers from entering this field. However, the area of silica-based organic-inorganic nanocomposites is not new and is quickly becoming one of the emerging technologies for new materials. This work represents an overview of the different types of silica-based organic-inorganic nanomaterials.

Acknowledgments

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1. Introduction

Since the initial interest in sol-gel science and technology in the 1970s, a wide variety of research has been performed, including fundamental kinetic evaluations [1, 2], mechanism studies [3, 4], and structural variations of the metal alkoxide from traditional silica to other metals such as aluminum [5], zirconium [6, 7], and titanium [8, 9]. In the mid-1980s, the emphasis began to shift from pure inorganic systems to organic-inorganic composite materials. This report details silica-based sol-gel chemistries and resulting materials. This area of research is becoming so significant that entire books [1, 10] and journal issues [11] are being dedicated to advances in the area. The study of silica-based organic-inorganic composites may be divided into four distinct areas of research: monomers, associations, interpenetrating networks (IPNs), and telechelic polymers.

2. Inorganic-Organic Monomers

In the context of sol-gel chemistry, inorganic-organic monomers are molecules containing a central metal atom, such as silicon, bonded to reactive alkoxy groups and/or organic groups. These monomers, when assembled together, form organic-inorganic siloxane materials. There are two distinctive types of inorganic-organic monomers: organically modified silicate (ORMOSIL) monomers and silsesquioxane monomers. Of the silsesquioxane monomers, there are two distinct types—bridging silsesquioxanes and polyhedral oligomeric silsesquioxane. All of these monomers will be addressed separately.

2.1 ORMOSIL Monomers

In the mid-1980s, considerable research was conducted in the field of ORMOSIL chemistry [12–21]. ORMOSILs are derived from tetrafunctional silicon alkoxides such as tetraethylorthosilicate (TEOS), as shown in Figure 1. Since ethyl groups are commonly used in sol-gel chemistry and many of the silanes available contain ethoxy groups, most of the structures in this report will show ethoxy groups. However, it might be useful to note that there are also methoxy, propoxy, butoxy, and other long-chain hydrocarbon alkoxy groups.

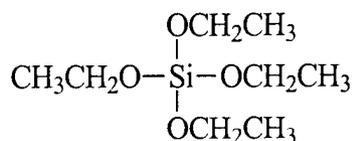


Figure 1. TEOS, a tetrafunctional alkoxy silane.

Organic modification may take place by substitution of an alkyl, aryl, or any moiety, replacing one of the reactive alkoxide groups, as shown in Figure 2. Here, n is representative of the number of organic moieties connected to the silicon atom, and f is representative of the number of reactive alkoxy groups connected to the silicon. For a monofunctional silicon alkoxide ($f = 1, n = 3$), the monomer "terminates" the polymer chain since there is only one reaction site. A difunctional silicon alkoxide ($f = 2, n = 2$) behaves as a "bridging" agent, connecting molecules in a linear fashion. A trifunctional silicon alkoxide ($f = 3, n = 1$) behaves as a "crosslinker," allowing for branching in the network. A tetrafunctional silicon alkoxide ($f = 4, n = 0$) behaves as a "networking" agent, allowing for complete connectivity between all functional arms of the molecule.

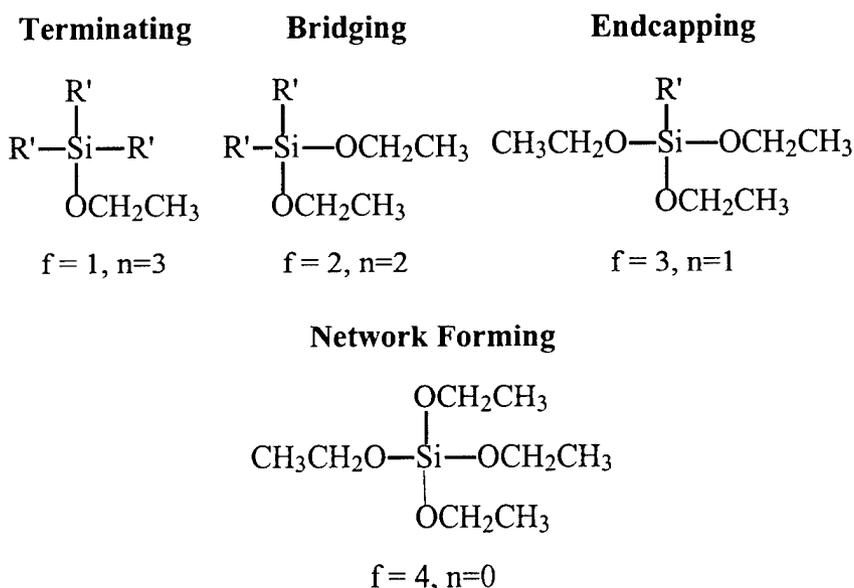


Figure 2. The ORMOSIL functionality spectrum.

Traditional inorganic glasses require temperatures in excess of 1000 °C in order to have densification of the siloxane network [22]. These temperatures prohibit the organic modification of traditional glasses due to the high-temperature instability of the Si-C and C-H bonds. Sol-gel derived glasses, however, do not require high temperatures for formation, making organic modification possible (see Figure 3).

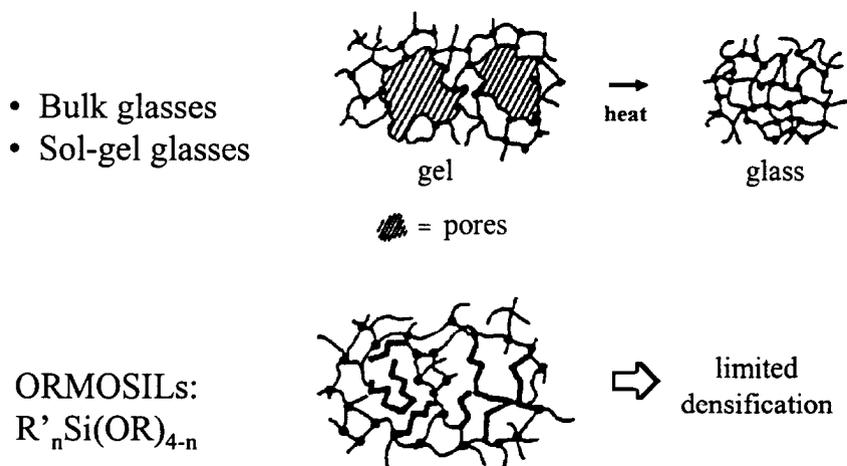


Figure 3. Incorporating porosity in sol-gel networks.

Upon sol-gel polymerization of tetrafunctional silicon alkoxides, network formation and crosslinking is extensive. Careful drying of this highly connected system removes excess water and alcohol, allowing for complete vitrification of the network. With organic modification of the silicon, sol-gel polymerization limits both the crosslinking (by inclusion of monomers of lower functionality) and material densification (by creation of specific free volume or porosity in the sol-gel network). Represented by R, the functional group on an organically modified silicate can be any organic moiety including methyl, vinyl, or benzyl. Figure 4 depicts ORMOSIL connectivity achieved through sol-gel polymerization. It is reasonable to expect that variation of the number and type of organic moieties included on the silicon monomer results in a variety of pore sizes that can be created in the sol-gel network. The pore size corresponds to the physical size of the organic moiety and the excluded volume of the moiety. Due to their organic nature, these pores can attract organic or divert polar gas molecules. In essence, ORMOSILs form precisely defined porous networks, each possessing unique physical and chemical properties.

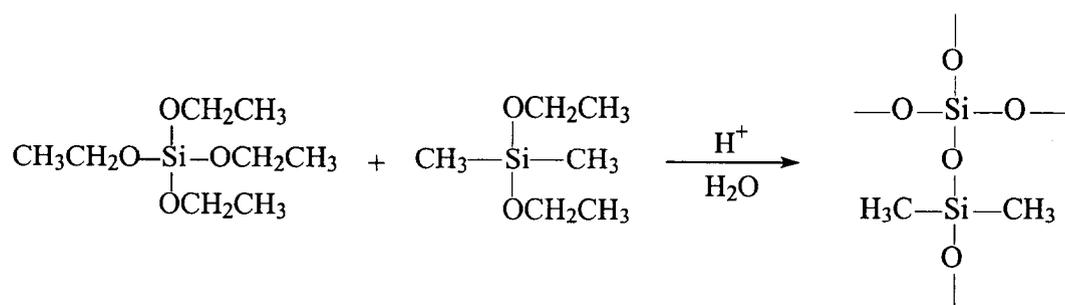


Figure 4. ORMOSIL connectivity through sol-gel chemistry.

2.2 Silsesquioxane Monomers

Similar to ORMOSIL monomers, silsesquioxane monomers are useful for creating sol-gel glasses with controlled porosities. Silsesquioxanes are silica atoms that are covalently bound to organic molecules. These molecules can have two very different structures, as shown in Figure 5.

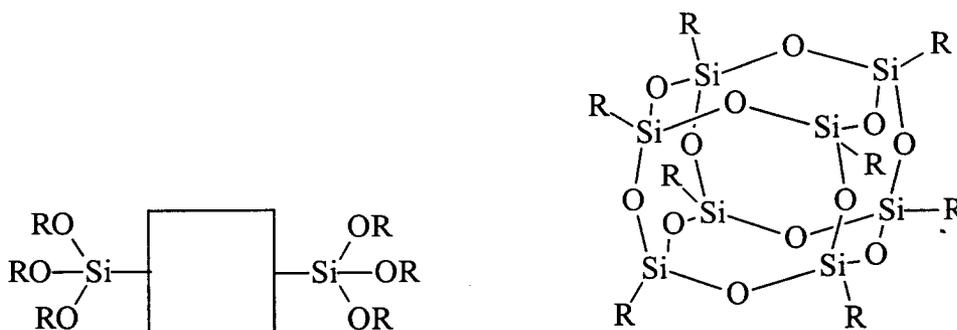


Figure 5. Two basic structures of silsesquioxanes.

Bridging silsesquioxanes contain an organic bridging agent that behaves as a spacer unit and resides between two reactive di- or trialkoxysilane end groups [23–25]. Polyhedral oligomeric silsesquioxanes are cube siloxane structures with eight potentially reactive sites. These materials will be discussed separately in more detail.

2.2.1 Bridging Silsesquioxanes

The general structure of silsesquioxane-type monomers is shown in Figure 6. These bridging units have traditionally been hydrocarbon, containing consecutive methyl or benzyl groups, but can be synthesized to have any kind of organic spacer functionalities. The organic bridging agent can be synthetically developed to resemble a polymer backbone for use as an interface compatibilizer or for use as a material of a specific size that can be burned out to create a specific porosity. Upon initial sol-gel network formation, porosity is limited due to the presence of the bridged organic groups. Limiting porosity through usage of a spacer unit, with its specific organic character, can be beneficial for specific gas or liquid permeation.

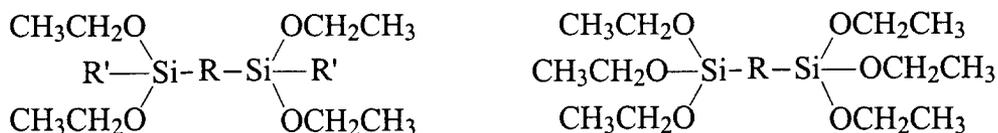


Figure 6. Bridging silsesquioxane monomers.

Lacan et al. [23] synthesized functional bridging-silsesquioxane materials in order to investigate the mechanical properties and gelation process in proceeding from a viscous liquid to a viscoelastic solid. Two silsesquioxane materials were made—an amine-acid chloride organic spacer unit and a methacrylic spacer unit. The results obtained for these two materials were compared to those of a pure TEOS-derived system in order to establish a comparison between mixed organic-inorganic and purely inorganic materials. In the gel state, the amine-acid chloride silsesquioxane material with the short organic chain spacer unit was observed to possess the network with the most strength and greatest elongation. This behavior was expected for the pure inorganic network where the hydrolysis was very fast, resulting in a short gelation time, and the resultant network was ordinarily more viscous. The amine-acid chloride spacer unit between the two silicon alkoxides did not restrict the three-dimensional (3-D) network formation, resulting in increased viscous character through organized network formation.

Silsesquioxanes are often used to create inorganic materials with specific controlled porosities. Shea [26] has investigated the use of alkyl and aryl silsesquioxanes in hybrid organic-inorganic materials in order to control the morphology of the material on a molecular level. The use of these organic spacer units (mono-, di-, and tri- methyl or phenyl, anthracene, and ethynyl groups) allowed for the “engineering” of material pore size by varying the size of the spacer unit. The incorporation of these materials into sol-gel processed films was confirmed by solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, which also indicated that the ethynyl linkage was the most hydrolytically unstable during the sol-gel process, resulting in cleavage of the Si-C bond. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were used to study the silica morphology. Gas sorption porosimetry was used to investigate the pore structure in greater detail. The results from this analysis indicated that the materials showed substantial microporosity with additional mesopores and that the micropore structure was more dependent on the macromolecular structure than on the length of the organic spacer unit. Thermal analysis via differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA) showed the relatively high thermal stability of these materials. These limited porosity systems can be modified to form well-defined porous systems through removal of the spacer units by ozonolysis (see Figure 7) [24, 26]. By removing the spacer units after the network formation, well-defined pores corresponding to the organic spacer were left in the sol-gel network.

Along these same lines, Brinker [27] used organic templates in an attempt to separate the pore size and pore volume. The organic templates (mono-, bi-, and triphenyl groups) were embedded in a dense silica matrix and subsequently removed by thermal oxidation or ozonolysis. The resultant pores mimicked the

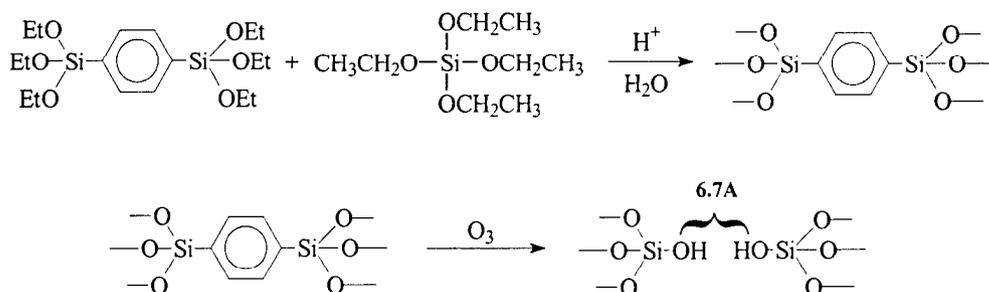


Figure 7. Formation of precise porosity through usage of bridged aryl silsesquioxanes.

size and shape of the organic ligand with no collapse of the surrounding matrix. Adsorption and ellipsometry results indicated that the removal of the biphenyl groups (1) created porosity in the films with a volume fraction approximately equal to that of the template, (2) caused the formation of a continuous network of pores by removal of the template with no creation of mesoporosity, and (3) resulted in the presence of very small pores consistent with the removal of the organic template.

2.2.2 Polyhedral Oligomeric Silsesquioxanes (POSS)

The usage of bulky substituents in polymer chemistry, such as norbornene, adamantane, or fullerene (see Figure 8), to increase thermal and mechanical properties by restriction of chain mobility is becoming commonplace. As an added substituent on the main chain, adamantane, for example, can increase the glass transition by as much as 100 °C [28]. However, with very low incorporations of the bulky substituents, the polymers tend to become very brittle. Some of these substituents can be used as the main-chain polymer. However, as a polymer, norbornene only has a glass transition temperature of 55 °C [29, 30]. In both cases of substituent and polymer, the solubility and pliability of the end polymeric material has decreased significantly. Therefore, the challenge to find a bulky substituent that can not only increase the thermal and mechanical properties but also maintain some of the pliability and solubility that the organic polymer possesses has remained.

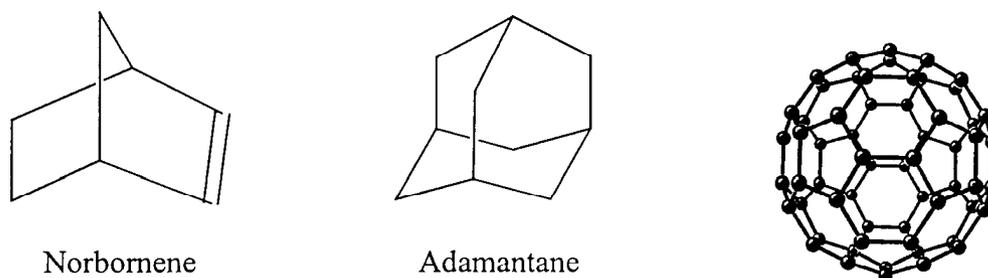


Figure 8. Common bulky substituents.

POSS materials have been studied for the last 15 years as alternative bulky, inorganic, ring-structured substituents to the characteristic bulky organics. The main researchers in the field include the following: Dr. Rich Laine's research group at the University of Michigan at Ann Arbor [28-35], a research group headed by Dr. Joseph D. Lichtenhan at the U.S. Air Force Research Laboratory - Propulsion Directorate (Wright-Patterson Air Force Base, Dayton, OH) [36-42], and Dr. Frank Feher's research group at the University of California at Irvine [43-45]. In addition, Dr. Lichtenhan and Sean Phillips [46] have been involved with the start of the Hybrid Plastics Company, which promotes the usage of POSS molecules in nanocomposite materials. On this website, 56 variations of the POSS molecule are available for utilization in composite materials.

POSS materials can be easily chemically altered to include acrylate arms [35], as shown in Figure 9, or epoxy arms [33, 34], as shown in Figure 10. These chemical modifications can supposedly be controlled. By using specific equivalents of modifier per number of arms, in Figure 9, for example, only four arms are chemically modified. This, while theoretically correct, is unlikely to produce just that four-armed molecule, but also a variety of other multireactive armed species.

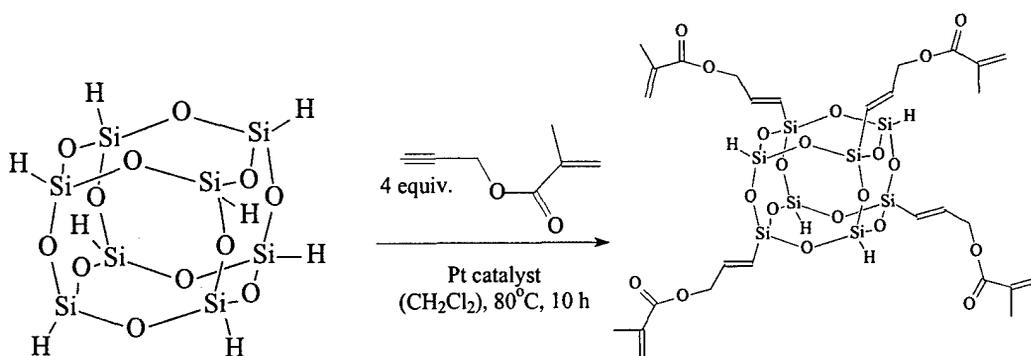


Figure 9. Creating an acrylic-POSS material.

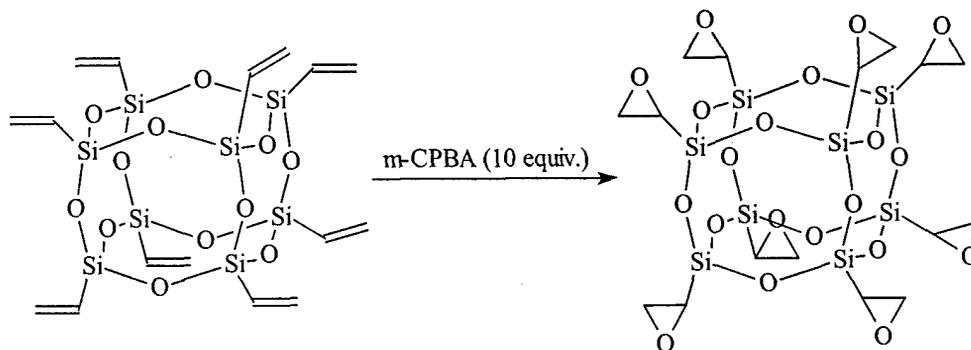


Figure 10. Creating an epoxy-POSS material.

Therefore, in the case where there are eight equally reactive sites on the molecule, it might be more practical to have a complete chemical modification, as is shown in Figure 10 of the epoxy system. However, a POSS material with less-reactive arms, such as the H-Si (silane), as opposed to H-Si-Me₂-O-, may be able to exhibit more control over the reaction because of the slower reaction rate. POSS cubes are characterized via FTIR, ¹H, ¹³C, ²⁹Si NMR, and mass (chemical ionization [CI], electronic ionization [EI], or fast atom bombardment [FAB]) spectroscopies and size exclusion chromatography (SEC).

POSS cubes can then be made into polymeric nanocomposite materials through curing of the POSS molecule. The specific polymer composite structure developed depends on the number of reactive arms involved in the polymerization. Sellinger and Laine [34] reported polymerizing two-arm and eight-arm epoxy POSS cubes. These materials were polymerized using ZnCl₂, BF₃OEt₂ initiators or ethylene diamine as a cross-linking reagent at room temperature in CH₂Cl₂. Confirmation was made that the polymerizations involved only the epoxy arms, not the vinyl arms, by subjecting the original eight-armed vinyl POSS molecules to the same reaction conditions. All POSS-polymers were easily made and had increased stability compared to their acrylate counterparts, but resulted in insoluble polymers.

A more recent study by Lee and Lichtenhan [36] discussed the incorporation of epoxy-POSS molecules as reinforcing agents in epoxy systems. The study varied the level of POSS molecule loading (0%, 5%, and 9%) into diglycidyl ether of bisphenol A (622.76 g/mol). The epoxy-POSS molecules used were monofunctional (1442.06 g/mol—minimum mass), terminating the polymer chain. The glass transition temperature was shown to increase with increasing POSS content, but only by about 7 °C. Isothermal aging and stress relaxation experiments were performed and indicated that POSS-reinforcements slowed down the motion of the polymer chains and, therefore, the time required to reach structural equilibrium was significantly increased with respect to nonreinforced polymers. However, by observing no change in the endothermic transition, it can be suggested that the POSS cages are completely incorporated within the network without the formation of macroscopic phase-separated domains.

Feher and coworkers [43–45] have reported linking silsesquioxane molecules together using silane coupling agents to form a silsesquioxane nanocomposite. By changing the moieties on the silane-coupling agent, the thermal properties of the polymer could be modified. For example, the researchers reported a polymer utilizing a silane-coupling agent with -MeO(SiMe₂O)₂SiMe₂ arms had a T_g = 23 °C, while a polymer utilizing a silane-coupling agent with -MeO(SiMe₂O)_nSiMe₂ arms (n ~ 3.4) had a T_g = 58 °C. While these glass transitions overall were low, it was important that the study showed control of the structure-property relationships.

While this was not an all-inclusive study of the POSS-based nanocomposite materials, it was significant to note that for the epoxy-based systems, the research published was very preliminary work. If considering the potential of the POSS materials with respect to the bulky, organic substituents, these materials have been shown in preliminary studies to increase the thermal and mechanical properties of the polymer. Silanes and siloxanes materials typically have one dimension in the range of 1-100 nm, forming transparent nanocomposite materials. In addition, silane and siloxane materials can be chemically tailored, resulting in a spectrum of chemical and mechanical environments.

3. Organic-Inorganic Associations

Organic-inorganic association systems are those in which there is no covalent bonding between the organic polymer and the inorganic network but exhibit characteristics similar to those which are covalently bonded. This synergistic relationship can occur through two types of associative behavior—hydrogen bonding and association/coupling equilibrium.

A wide variety of polymers contains moieties, which would ideally have the capability for hydrogen bonding. Various polyesters, polycarbonates, polyacrylates, and polyamides possess moieties such as carbonyls, ethers, and amine groups, which have free electrons available for hydrogen bonding. Yet most polymers, when mixed noncovalently with inorganic sol-gel systems, are completely phase separated.

Some polymers do exist (see Figure 11) which possess moieties capable of hydrogen bonding with an inorganic sol-gel network [47-49]. Hydrogen bonding of the sol-gel component with these polymers retards severe phase separation during network densification. Researchers in organic-inorganic associations have utilized the specific polymers that have hydrogen-bonding capabilities in copolymers. The other polymer in the copolymer typically does not have the capability of interacting with an inorganic phase. In these copolymers, the hydrogen-bonding polymer is used as a compatibilizer with the other polymer system. Ideally, the compatibilizing comonomer, which is only a small fraction of the copolymer, will diffuse to the interface of the two immiscible polymer systems and reduce the interfacial tension through favorable interactions. This reduction of interfacial tension creates a stable organic-inorganic composite interface by reducing the dispersed-phase particle size and increasing the adhesion between the two phases.

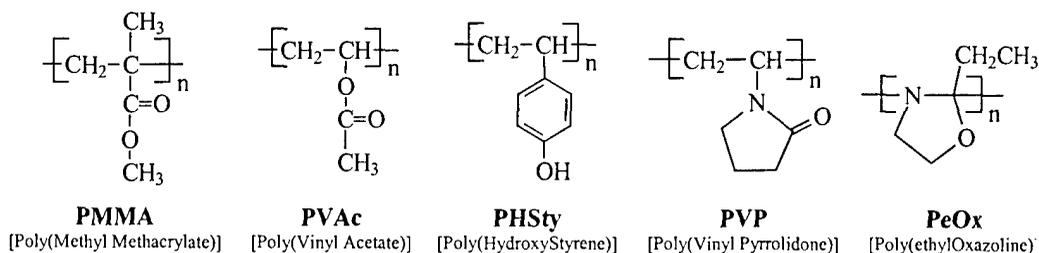


Figure 11. Several polymers that interact with an inorganic phase.

An association/coupling equilibrium occurs between polymer systems which hydrogen bond [50]. Here, there is a dynamic equilibrium between hydrogen-bonded groups and a covalently bound inorganic network producing -C-O-Si- bonds (see Figure 12). The reason for the equilibrium is the hydrolytic instability of -C-O-Si- bonds. Generally, the equilibrium is shifted towards the hydrogen-bonded moieties. Polymers containing carboxylic acid end groups can also undergo this type of association/coupling equilibrium (see Figure 13). The carboxylic acid end groups are acidic enough to catalyze the reaction. The end groups are then involved in the dynamic equilibrium between hydrogen-bonded chain ends and covalently bound chain ends. This in situ behavior also occurs in template systems, where an ionomeric membrane is utilized as a morphological template for in situ sol-gel reactions.

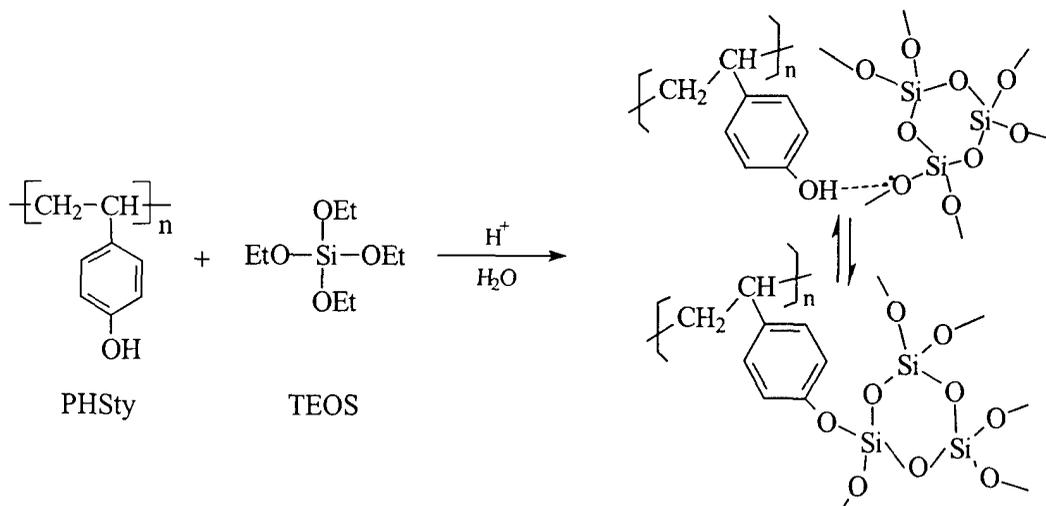


Figure 12. Inorganic association/coupling equilibrium with polymers.

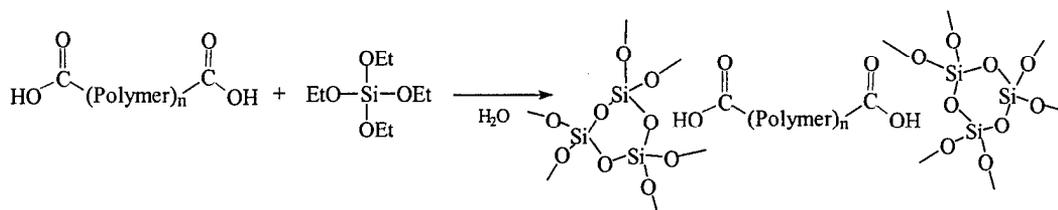


Figure 13. End group in-situ association materials.

4. Organic-Inorganic Interpenetrating Networks

An interpenetrating polymer network (IPN) is any material containing two polymers, each in network form. The three conditions for eligibility as an IPN are as follows: (1) the two polymers are synthesized and/or crosslinked in the presence of the other, (2) the two monomers have similar reaction kinetics, and (3) the resulting two polymers are not dramatically phase separated [10, 51-53]. Of course, these are loosely held guidelines. IPNs that have only one polymer crosslinked (where the polymers are synthesized separately) or where the polymers have vastly different reaction kinetics are still considered to be IPNs. IPNs are distinguishable from blends, block copolymers, and graft copolymers in two ways: (1) an IPN swells but does not dissolve in solvents, and (2) mechanical creep and flow are suppressed [10].

Several kinds of IPN architectures exist (see Figure 14). These systems differ mainly because of the number and types of crosslinks that exist in the system. A noncovalent semi-IPN is one in which only one of the polymer systems is crosslinked. A noncovalent full IPN is one in which the two separate polymers are independently crosslinked. A covalent semi-IPN contains two separate polymer systems that are crosslinked to form a single polymer network. This covalent semi-IPN is similar to a noncovalent IPN because one of the polymer systems can be crosslinked without networking with the second linear system. However, the two systems tend to be networked for better synergistic property development. Examples of covalent semi-IPNs are found almost exclusively in the realm of organic-inorganic composite materials.

4.1 Noncovalent IPN Materials

A wide variety of organic-inorganic noncovalent IPN materials has been formulated in an effort to improve material properties. Inorganic incorporation into polymers ranging from polyacrylates and polyesters to polyimides and nylons has been attempted [54-57]. The problem with the noncovalent systems, which can also be a problem with the covalent systems, is the lack of a

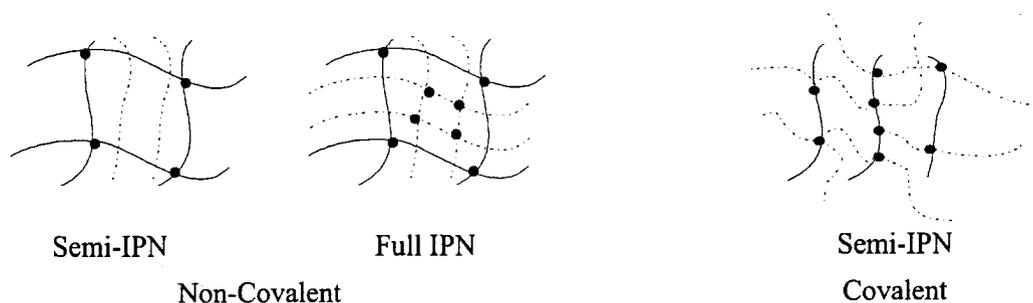


Figure 14. IPN materials.

compatible interface. This problem could stem from several factors, including surface energy phenomena and lack of molecular interactions between phases. Figure 11 shows several polymers that can interact with the inorganic phase. These polymers are proposed to hydrogen bond with the inorganic phase, creating an interface between the two materials. However, the key to having noncovalent organic-inorganic materials is not only utilizing a polymer that can have hydrogen bonding between the two phases but also to have low loading of the inorganic phase. Low loading of the inorganic phase will result in an increase in the overall material properties without sacrificing the interfacial bonding.

4.2 Covalent IPN Materials

A variety of polymers and copolymers has been synthesized incorporating reactive silicon alkoxides along the backbone of the polymer (see Figure 15) [57–63]. Silicon alkoxide incorporation into the polymer backbone can be accomplished with many monomers and through various synthetic means (see Figure 16). For example, silicon alkoxides can be incorporated into a polymer backbone via free-radical polymerization through a vinyl moiety, via a condensation reaction with an organic moiety on the silicon alkoxide monomer, or via a postreaction (such as a hydrosilylation reaction). Through covalent attachment of the reactive silicon alkoxides, polymer-polymer interfacial problems were reduced. However, covalent IPN materials can have similar problems with the interface as the noncovalent materials.

Again, similar to the noncovalent systems, a general lack of cohesiveness between the two phases can exist at molecular weight loadings higher than 10%. This problem with the gross phase separation at the interface is under investigation by researchers. Utilization of a variety of intermolecular bonding forces seems to improve upon the overall separation problems of the material. For example, by utilizing a polymer with a covalently bound silicate material that can also hydrogen bond with the organic polymer backbone creates more opportunities for better interfacial interactions.

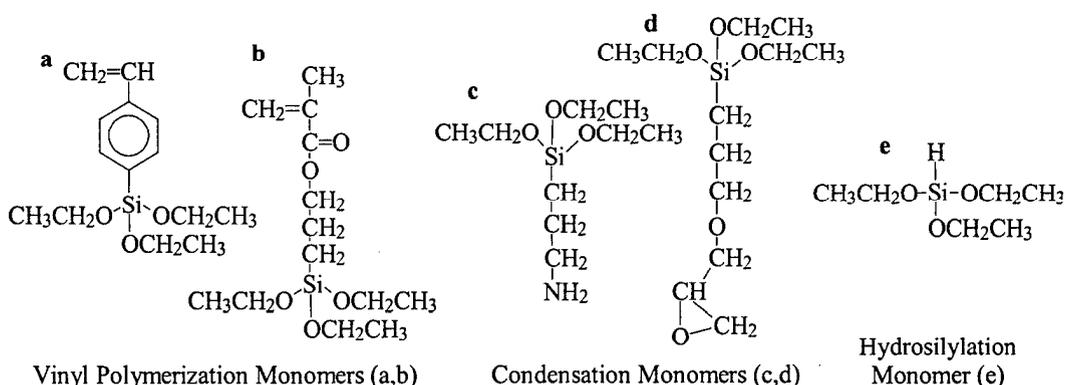


Figure 15. Some monomers utilized in covalent IPN materials.

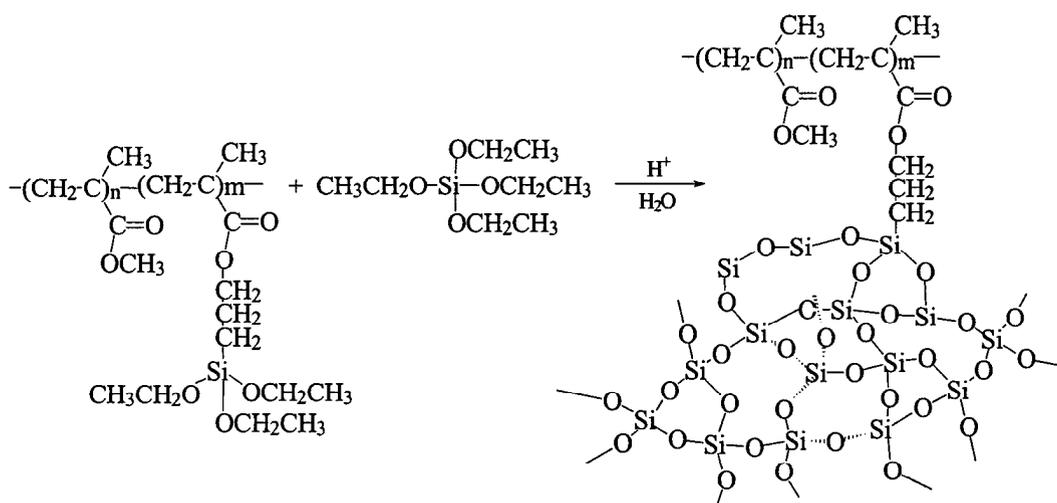


Figure 16. Covalent IPN material synthesis.

5. Organic-Inorganic Telechelic Polymers

The formation of telechelic materials is an alternate method to have covalent bonding between the organic and inorganic phases of the composite material. A telechelic polymer is one containing one or more functional end groups (see Figure 17) that have the capacity for selective reaction to form bonds with another molecule [64]. Telechelic polymers typically contain hydroxyl or carboxylic acid end groups. Composite materials or block copolymers can then be made through these end groups by postreactions. A polymerization could be started at the -OH or -COOH end groups or by changing the end group functionality. Modifying the -OH or -COOH end group through an endcapping reaction with an acid chloride yields a vinyl end group where a free-radical reaction could occur.



Figure 17. Telechelic organic-inorganic polymers.

Organic-inorganic telechelic polymers can be made by many methods, two of which are condensation reactions or condensation/hydrosilylation reactions. In the first method, a condensation reaction can be performed utilizing an ORMOSIL monomer that contains such functionalities as an amine, epoxy, or cyano. Typically, little or no catalyst is needed for these condensation reactions to occur. In the second two-step method, the -OH or -COOH end groups are first endcapped with vinyl groups via a condensation reaction with, for example, acrylic acid for a hydroxyl end group. Then, in a second step, a hydrosilylation reaction is done utilizing the telechelic vinyl-endcapped polymer and a silane monomer. Here, a catalyst is needed. However, the catalyst used is dependent upon the polymer backbone. Certain catalysts used can add at a carbonyl instead of at a vinyl; therefore, catalyst choice is critical.

Tian et al. [65, 66] studied the properties of similar poly(ϵ -caprolactone) (PCL) ceramers for use as a coating material for bone implants and prosthetic devices and as support for enzyme immobilization. TEM analysis showed some degree of co-continuity between the two phases when the composition was 50/50 (PCL/SiO₂). Also studied was the effect of varying the ethanol content, as well as varying the polymer-to-alkoxysilane ratio on the final appearance of the films. The gelation time was observed to be independent of the PCL content, but the final appearance of the films was related to the amount of PCL and ethanol in the system. An increase in the amount of ethanol and a decrease in the amount of PCL lead to an increase in the optical clarity of the films.

6. Summary

A diverse body of research is ongoing in the very important area of organic-inorganic silica-based nanocomposites. No limitations appear to exist for variations of chemical structure and composition of these materials. New materials and possible technology applications are constantly being explored.

The Polymers Branch of the U.S. Army Research Laboratory has a few ongoing projects in the Emerging Materials (EMAT) Program and to the epoxy-composites program related to the type of work described in this technical report. These programs involve simple sol-gel reactions based on ORMOSIL, silsesquioxane, and telechelic polymer technologies. It is likely that technical reports will be submitted regarding these important works in the near future.

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