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REVIEW

# Transparent Organic/Inorganic Hybrid Gels: A Classification Scheme

Anna B. Wojcik* and L. C. Klein
Rutgers-the State University of New Jersey, Ceramics Department, P. O. Box 909, Piscataway, NJ 08855-0909, USA

**An attempt is made to classify transparent organic/inorganic materials synthesized by the sol–gel process. The chemical structures of the hybrids are the main criteria for this classification. Three main types of organic/inorganic gels are distinguished and their basic physico-chemical characteristics are outlined. © 1997 by John Wiley & Sons, Ltd.**

**Keywords: organic/inorganic gels; interpenetrating networks; polymer-impregnated gels; organic-doped gels; sol–gel process**

## INTRODUCTION

In the last decade, sol–gel technology has become a popular way to create organic/inorganic hybrid materials. We use 'hybrid' as the generic term for an organic/inorganic material. An accepted name for many of these materials is 'ormosils' (organically modified silicates)[1] or, more generally, 'ormocers (organically modified ceramics).[2] Another name is 'ceramers' (ceramics modified with polymers).[3] All of these terms refer to organic/inorganic materials where the constituents are covalently bonded to each other. Another broad categorization for organic/inorganic gels is nanocomposites, to emphasize the nanometer level of mixing.[4] 'Nanocomposite' often refers to a hybrid where organic and inorganic constituents are not covalently bonded. The forces acting between the constituents vary from weak to relatively strong.

Some notable attempts to classify hybrids have appeared. For example, Chujo and Saegusa[5] have reviewed organic/inorganic materials prepared by the sol–gel method where the organic constituents are polymers, but not low-molecular-weight radicals or groupings. Sanchez and Ribot[6] divide hybrids gels into two classes: Class I corresponds to hybrids where organic molecules are blended into the inorganic network, whereas Class II includes hybrids where inorganic and organic constituents are linked together via covalent or iono-covalent bonds. Schubert *et al.*[7] concentrate on organic/inorganic hybrids using organofunctional metal alkoxides. Organic/inorganic materials have been classified according to specific optical functions such as second-harmonic generation,[8] nonlinearity,[9] or dye properties.[10] Building on these classifications, we continue to systematize sol–gel hybrids by looking at the structure, methods of preparation and the nature of links between organic and inorganic constituents.

To make the scope of this paper manageable, we will consider optically transparent hybrid gels. The reason for this selectivity is that current applications for these materials are largely in optics, and this parallels our own interests. This limitation means that the majority of the hybrids under consideration are silica-based. Silica finds application in optics due to its low thermal expansion coefficient and good transparency in the UV, visible and near-IR. It happens that silica is most often studied and modified in sol–gel processing, because organosilicon chemistry lends itself to this type of processing.

## THE SOL–GEL PROCESS

The sol–gel process is defined in this context as the hydrolytic process with a silicon alkoxide such as tetraethyl orthosilicate (TEOS). Upon addition of water, TEOS in a co-solvent hydrolyzes and polymerizes to build a silicate network. In time, the system arrives at the sol–gel transition where an irreversible gel exists. In the

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* Present address: Spec Tran Corporation, 50 Hall Road, Sturbridge, MA 01566, USA.

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single- component system, it is known that the result is an oxide skeleton which is porous after the solvent is removed.

The sol–gel process as described occurs at room temperature. Polymers that otherwise are destroyed at ceramic processing temperatures can be incorporated. A natural progression begins to take shape from the single-component sol–gel silica system to the multicomponent ORMOSIL systems. The impetus for the formation of so many combinations of polymers and silica is, in fact, the sol–gel process.

## CLASSIFICATION OF ORGANIC/ INORGANIC HYBRID MATERIALS

Based largely on the chemical structure of the hybrid gels, we divide them into three major groups:

covalently bonded organic/inorganic gels;

organic/inorganic interpenetrating networks; and

polymer-impregnated gels.

Some of these groups contain subgroups, usually differing in method of preparation or special function.

For transparent hybrids, for all practical purposes, the inorganic component is silica. The concept of modifying inorganic networks by using covalent bonding works with silicon, because the Si–C bond is stable and does not undergo hydrolysis under the conditions of the sol–gel process.

## COVALENTLY BONDED ORGANIC/ INORGANIC GELS

In the absence of an organic constituent, a three-dimensional network of inorganic polymer consisting of Si-O-Si units forms in the conventional sol–gel process. In the absence of an inorganic constituent, there are C–C covalent bonds between mers in a polymer backbone, along with weaker van der Waals bonds between polymer chains. However, in a sol–gel process carried out with a precursor containing direct organic/inorganic links, it is possible to form homogeneous materials where all bonds are covalent bonds, C–C, Si–C and Si–O. This class of hybrid gels constitutes organic/inorganic polymers. Undoubtedly, the largest class of inorganic/organic gels is made up of hybrids linked via Si–C bonds that are stable and do not undergo hydrolysis under the sol–gel processing conditions.

### Silanol-terminated polymers

There are several methods of linking polymers covalently to silica. In an early example, silanol-terminated poly(dimethylsiloxane) (PDMS) was co-condensed with TEOS as shown in Scheme 1. The organic/inorganic PDMS chains, containing non-bridging methyl groups and nonlinear Si–O–Si angles, exhibit significant flexibility.[11] However, PDMS with its Si–O–Si backbone does not approach the flexibility of organic polymers that have C–C backbones.

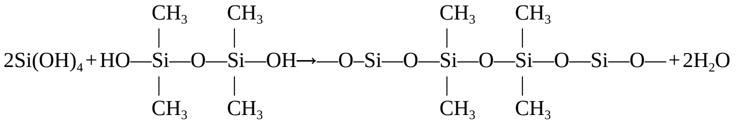
When the functionality (the number of alkoxysilyl groups per oligomeric chain) of PDMS is increased to 6 or PDMS is replaced by poly(tetramethylene oxide) (PTMO), the stiffness and the mechanical strength both improve considerably.[12] When the functionality of the polymeric chain is higher, as it is for polymethacrylate copolymer,[13] the resulting gel is tougher than pure silica xerogel (dried silica gel).

Similarly to PDMS and TEOS, other organic polymers have been functionalized with alkoxysilyl groups and covalently bonded to silica. Polymers that have been coupled with silica are

Hydrolysis of TEOS

$\mathrm{Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH}$

Copolymerization with PDMS



$$\mathrm{2Si(OH)_4 + HO{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}OH \rightarrow {-}O{-}Si{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}Si{-}O{-} + 2H_2O}$$

**Scheme 1.** Covalently bonded organic/inorganic gels: organic/inorganic polymers. Schematic illustration of silica–PDMS hybrid polymer.[11]

PTMO-based polyurethane oligomers,[12,14] polyoxazolines,[15] polyimide,[12] poly(arylene ether ketone),[16] poly(arylene ether sulfone),[17] polystyrne,[18] polyoxopropylene (PPO),[19] polyacrylonitrile,[20] copolymers of methyl methacrylate and allyl methacrylate[13] and cyclophosphazenes.[21]

The final properties of organic/inorganic gels are governed by their microstructure. Cellular structures are observed in PDMS/silica gels when the sol–gel parameters ($H_2O$ and HCl concentrations and temperature) are adjusted to accelerate the gelation process.[22] Some hybrids containing small concentrations of organic polymer are porous. More typically, hybrids are designed to have low porosity. With high concentrations of the organic component, hybrids have low densities, indicating high free volumes characteristic of the organic polymers.[24]

Generally, it is claimed that covalently bonded hybrids combine the flexibility and mechanical properties of the organic polymer chains with the hardness, stiffness and transparency of silica. In detail, the properties of the hybrids are governed by the chemistry, presence of side chains or pendant groups, and length of polymeric chains. Especially important are the concentration and distribution of alkoxysilyl groups attached to the polymeric chain, as they directly affect the rigidity or flexibility of the system.

## Free-radical polymerization

Another method leading to covalent linkage of organic polymer to silica is free-radical polymerization. When an organic radical $R'$ in an organo-substituted silico-ester of formula $R'Si(OR)_3$ contains olefinic moieties, it is possible to build a polymeric network by thermal or photochemical free-radical polymerization of $C=C$ bonds. Epoxide groups are also polymer formers, via photo-induced cationic polymerization or via condensation with curing agents bearing groups such as amine or hydroxyl. Organic polymerization can be carried out simultaneously with condensation of hydrolyzed alkoxysilyl groups.

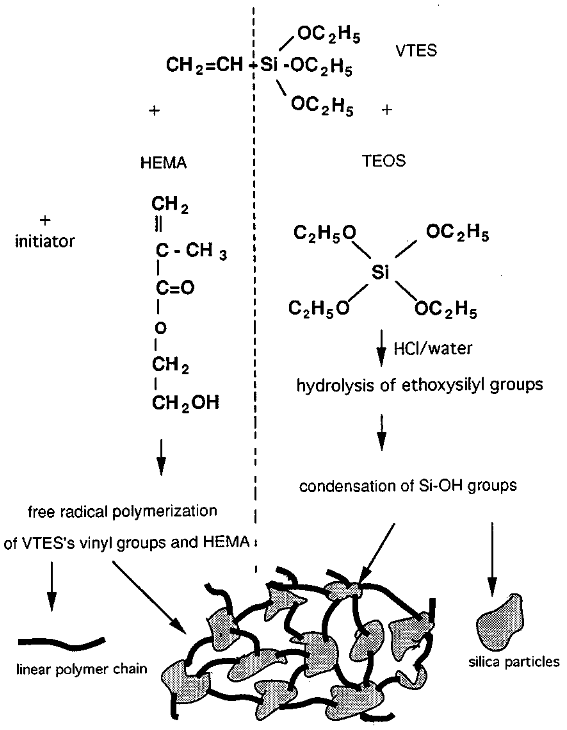
The commonly used organoalkoxysilanes bearing polymerizable $C=C$ bonds are 3-methacryl-oxypropyl trimethoxysilane (MEMO) $CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$ and vinyl trimethoxysilane $CH_2=CH\text{-}Si(OCH_3)_3$ (VTMS) or its ethoxy analog (VTES). Alkoxysilyl groups of these organic/inorganic monomers form Si-O-Si bonds upon condensation or co-condensation with another inorganic precursor, such as TEOS. At the same time, (meth)acryl or vinyl groups are able to polymerize with organic/inorganic monomers or with (meth)acrylic or vinyl monomers. These processes lead to the formation of organic/inorganic polymers and organic/inorganic copolymers.

Reportedly, homopolymerizations of organic/inorganic monomers by the sol–gel process from single monomer systems are difficult.[24,25] For most of the organic/inorganic precursors, gelation times under acidic conditions are quite long. The same is true for two-comonomer systems—organic/inorganic monomer and organic monomer. The reason for the long gelation time is the low concentration of alkoxysilyl groups and steric hindrance from organics in the system. However, the process can be accelerated by photocuring with UV or using a tri-monomer system. An idealized structure of an organic/inorganic copolymer synthesis by co-condensation and copolymerization of the tri-monomer system TEOS–vinyl triethoxysilane (VTES)–hydroxyethyl methacrylate (HEMA) is shown in Scheme 2.

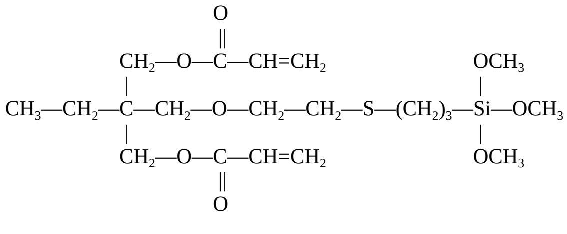
Ellsworth and Novak use soluble oligomers of silicic acid instead of TEOS in a condensation with (meth)acryl trialkoxysilane to increase the silica content of organic/inorganic hybrids and reduce shrinkage.[27] Hoebbel *et al.*[28,29] have used tetramethylammonium silicate ($[N(CH_3)_4]_8Si_8O_{20}.69H_2O$) converted by an ion-exchange process into double-four ring (D4R) oligomers of silicic acid ($H_8Si_8O_{20}$). This oligomer can be stabilized by reaction with functional siloxanes containing polymerizable groups such as vinyl, allyl, hydrido or chloromethyl. The functionalized derivative can be polymerized while preserving silicic acid cages in the structure.

When the organic/inorganic monomer bears two or more olefinic moieties in its structure, the monomer is highly photosensitive, creating very favorable conditions for rapid organic polymerization under UV. A series of diacrylate alkoxysilanes were synthesized by Wolter *et al.* by coupling mercapto-substituted alkoxysilanes to the triacrylate monomers or acrylate resins.[30,31] The resulting organic/inorganic monomer (Fig. 1) can be co-condensed via its alkoxysilyl groups with TEOS, whereas its acrylic groups can be cured by UV, or polymerized thermally. Likewise, diacrylo-trialkoxysilane organic/inorganic monomer from aliphatic triacrylate–glycerol propoxytriacrylate (GPTA) and 3-mercaptopropyl trimethoxysilane was used to synthesize UV-curable coatings for optical fibers.[32]

A subgroup of hybrids containing a covalent link are those where the polymer exhibits specific electronic or electro-optic properties. Examples of these hybrids include nonlinear optics (NLO) polymer/silica gels, organic dye/silica gels and conducting polymer/silica gels. For example, organic dye/silica gels of cyan, magenta and yellow have been synthesized.[33]



**Scheme 2.** Covalently bonded organic/inorganic gels: organic/inorganic polymers. Schematic illustration of the sol–gel polymerization of a three-monomer system: HEMA–VTES–TEOS.[26]



$$CH_3{-}CH_2{-}\overset{\displaystyle CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2}{\underset{\displaystyle CH_2{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH{=}CH_2}{C}}{-}CH_2{-}O{-}CH_2{-}CH_2{-}S{-}(CH_2)_3{-}\overset{OCH_3}{\underset{OCH_3}{Si}}{-}OCH_3$$

**Figure 1** Structure of organic/inorganic monomer obtained by coupling 3-mercaptopropyl trimethoxysilane to trimethylolpropane triacrylate (TMPTA).

The chromophore was linked covalently to the polymeric component via the reaction of an amine, halogen or isocyanate functionality of the polymer, while the silica and polymeric components were covalently bonded via the action of 3-chloropropyl trimethoxysilane. Polymers with conducting properties such as polypyrrole, polyaniline or polythiophene have been covalently incorporated into silica, following their alkoxysilyl functionalization.[34]

## Ormogels

When the organic component is a low-molecular-weight group or radical and not a polymeric chain or network, the hybrid is an ‘ormogel’ (organically modified gel), distinct from an ‘ormosil’. Ormogels are formed from $R'Si(OR)_3$-type organosilanes, where the radical R has a network-modifying effect and is used to introduce new functionalities into the inorganic network. Polymerization of $R'Si(OR)_3$ alone leads to formation of silsesquioxanes of general formula $(RSiO)_{1.5}$, i.e. a silicate framework where each Si atom is linked covalently to an organic radical R.

Bifunctional silanes of formula $R'R''Si(OR)_2$ can also be used to prepare ormogels. Upon polymerization, these organoalkoxysilanes form cyclic species or linear chains, and therefore are not able to crosslink and form networks themselves. They can be used with tetrafunctional silanes (TEOS) to incorporate desirable functionality into the hybrid network. For example, hydrophobicity can be achieved by introducing a methyl, phenyl or fluoroalkyl chain for R.[35,36] There are also ormogels in which the radical R forms a bridge between two Si atoms. A good example of this is arylene- or alkylene-bridged polysilsesquioxanes synthesized from bis(triethoxysilyl) or bis(trichlorosilyl) aryl or alkyl monomers.[37,38] Various aliphatic or aromatic molecules have been used as the organic spacer between two silicon atoms.

## ORGANIC/INORGANIC INTERPENETRATING NETWORKS

The next major class of hybrids is interpenetrating networks, which are characterized by a time factor, i.e. ‘simultaneous’ or ‘sequential’. The terminology of interpenetrating polymer networks (IPNs) is borrowed from organic polymer technology.[39] In some cases, 'semi-sequential' is used to reflect the linear structure of the organic polymer in which a crosslinked inorganic network is formed.

### Sequential organic/inorganic interpenetrating networks

Silica precursors (TEOS and TMOS) are able to solvate some organic polymers. This enables the silica precursor to polymerize in the environment of an organic polymer solution. The number of polymers that form solutions with sol–gel formulations is limited, however. Some initially soluble polymers tend to precipitate during gelation when a change in solvent composition leads to phase separation.

For those select polymers that are soluble, the method is very simple. The polymerization of the silica precursor occurs around the preformed polymer chains or domains. When the organic polymer is formed before the inorganic polymer, these materials fit the description of sequential organic/inorganic interpenetrating polymer networks.

Generally it is found that polymerization of TEOS in the presence of preformed polymers under acidic conditions generates small, well-dispersed silica particles. Depending on the choice of polymer, highly transparent, lightweight materials can be obtained. Among the polymers used to form sequential IPNs, those that give transparent hybrids are those capable of forming hydrogen bonds with hydroxylated $SiO_2$ particles.[40] Strong interactions between silanols, having the character of Brönsted acids, and specific groups on the polymer that are hydrogen acceptors, are responsible for the high degree of two-phase mixing.

Linear polymers with hydrogen-acceptor groups, amide, carbonyl and carbinol, have been used in semi-sequential organic/inorganic IPNs. These polymers are poly(*N*,*N*-dimethacrylamide), poly(2-methyl-2-oxazoline), poly(methyl methacrylate) (PMMA), polyvinylpyrrolidone (PVP), poly(acrylic acid) (PAA) and its copolymers, poly(vinyl acetate) (PVAc), and poly(vinyl alcohol) (PVA).[40–43]

In detail, the properties of the hybrids are functions of the relative fractions of the polymer and TEOS in the sol–gel formulation, along with the chemistry and length of the polymer chain. When TEOS is polymerized in the presence of the polymer, the glass transition ($T_g$) of the polymer increases or becomes undetectable. The density of the hybrid does not follow a mixing rule for the inorganic and organic components, but is suppressed even with high inorganic contents. More or less porous structures with open or closed pores can be formed in these systems.

### Simultaneous organic/inorganic interpenetrating networks

While only a few organic polymers are soluble in sol–gel formulations, many organic monomers are soluble in TEOS. These monomers can be introduced directly into sol–gel formulations. Both ring-opening polymerizations and free-radical polymerizations can be carried out simultaneously with the hydrolysis–condensation of TEOS.

The resulting hybrids have no covalent linkages between the organic and inorganic components. These hybrids consist of interpenetrating systems of organic/inorganic networks. To reflect their dual character and their synchronous polymerizations, they are called simultaneous organic/inorganic interpenetrating polymeric networks (IPNs). This simultaneous route captures insoluble organic polymers within a sol–gel inorganic network.

In the preparation of simultaneous networks, it is important to control the rates of both polymerizations. Systems with the inorganic condensation rate much faster than the organic polymerization rate turn into brittle hybrids that shrink because the polymer content is low, due to evaporation of unreacted monomer. Systems with a fast organic polymerization rate usually show uncontrolled polymer precipitation leading to heterogeneous composites. In practice, the kinetics of polymerization are difficult to control, so the success of the simultaneous approach rests on the careful selection of the monomers and their composition.

The idea of simultaneous interpenetrating networks has been advanced by Novak and coworkers.[27,44–46] Several monomers of acrylate type (free-radical polymerization) or cyclic alkenes (ring-opening metathesis) have been used. They include acrylamide/*N*,*N*′-bisacrylamide monomer systems, 2-hydroxyethyl or hydroxymethyl acrylate, and 7-oxanorbornene and its derivatives. In order to obtain non-shrinking hybrids, tetra-acryloxyethoxysilane was used instead of TEOS. The acrylate monomer liberated due to hydrolysis acted as a cosolvent to solvate the polymerizing silica network. The result was transparent hybrids with no shrinkage. Wojcik and Klein[47] have studied the incorporation of silica with di- and triacrylate monomers, hexanediol diacrylate (HDDA) and glyceryl propoxytriacrylate (GPTA). These simultaneous IPNs are transparent hybrids with good mechanical strength.

## POLYMER-IMPREGNATED GELS

The third major class covers some of the earlier sol–gel hybrids, where mixing on the nanometer scale was achieved by monomer infiltration into a previously formed silica gel. When a xerogel is filled, presumably with monomer, the monomer can be polymerized *in situ*. Interpenetration is achieved when the impregnating monomer polymerizes in the open pores of the rigid, fully crosslinked silica matrix. In the polymer-impregnated gels, some porosity typically remains. Although some copolymers of methyl methacrylate, butadiene and styrene have been used to impregnate silica, the best-known system is still silica impregnated with PMMA. The sequential steps are shown schematically in Fig. 2.[48–51] While this type of hybrid was important at first, it has been surpassed by other methods of hybrid synthesis that are simpler.

## ORGANIC-DOPED GELS

Finally, it should be mentioned that silica gels can be doped with small quantities of organic molecules. Doped gels are prepared either by addition of organics into sol–gel solutions, or by infiltration of the dopant into previously formed xerogels. Although some interactions between the dopant molecules and the inorganic matrix take place, the optical properties or chemical functions of the organics are preserved in the solid state. A number of organics have been used, including organic dyes and chromophores,[10] liquid crystals[52] and active biomolecules, enzymes and proteins,[53] in order to produce specific optically active or bioactive devices for a broad range of optic and electro-optic applications. Suitably doped gels exhibit highly efficient luminescence, photochemical hole burning, photochromism and tunable laser action.[54]

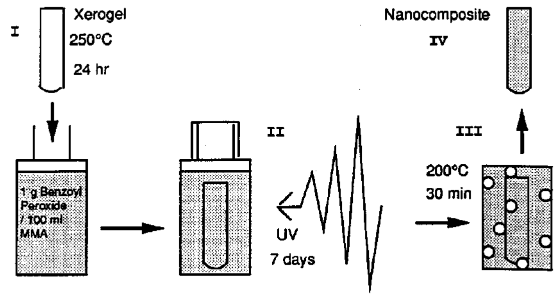


**Figure 2** Polymer-impregnated gels. Schematic of the four steps in the infiltration, polymerization and recovery of net-shape nanocomposites.[51]

It is important to point out that in pure inorganic matrices, activity of the dopant tends to decrease because of thermodynamic incompatibility between the organic and inorganic constituents. Consequently, organic-doped inorganic gels are being replaced by organic-doped hybrid gels, where the hybrid gel may belong to any of the classes. A good example is PMMA–silica composites doped with organic laser dyes, where it was shown that the hybrid host was better than either pure PMMA or pure silica.[55]

## SUMMARY

We see that sol–gel processing has expanded to encompass a range from its core of oxide materials, where the oxide is still the majority component, to hybrids, where the oxide and polymer are present in equal proportions. While attempts have been made to classify organic/inorganic materials according to interactions between the components, it is not always straightforward. Hybrids can be classified generally according to the presence or absence of covalent linkages between the components or the presence or absence of hydrogen bonding/van der Waals bonding. Other classifications reflect the timing of polymerization—whether the polymers react simultaneously or sequentially. The scale of mixing is another means of classifying hybrids according to the subdivision of the microstructure or the distribution of the components. Thermodynamic factors relating to solubility and miscibility and the kinetics of phase separation influence the outcome of the processing. Furthermore, processing of the hybrids may be a one-step or a multi-step process.

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