

Inorganic-Organic Composite Materials Derived from Sol-Gel Processing

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Composite materials incorporate two or more different types of components that are normally immiscible. For example, fiberglass contains an organic polymer matrix that is reinforced by inorganic glass fibers. Such a composite takes advantage of both the strength of the glass and the ductility of the polymer, and thus incorporates the best of both materials. The properties of a composite are determined by the properties of the matrix, the filler, and the phase interface [1]. Optimizing the degree of mixing between the two phases on the molecular level can greatly improve the properties of the composite.

The fundamental obstacle to making organic-inorganic composites lies in the very different processing conditions required for each component: organic compounds decompose under the high temperatures common to inorganic solid state syntheses. Sol-gel processing (the hydrolysis and condensation of metal alkoxides to form a three-dimensional network), however, proceeds readily at room temperature and provides a feasible path to inorganic-organic composites. The growth of these gels is random and statistical, but the structure and morphology of the resulting solid can be controlled using pH and other experimental variables [2-6].

The simplest inorganic-organic composites are those that contain no covalent bonds between the phases. These can be synthesized by precipitating an inorganic phase into a preformed organic polymer or by polymerizing the polymer within the preformed inorganic matrix [7-12]. Mechanical properties such as the elastic modulus and abrasion resistance are improved relative to the pure organic component and vary with the volume fraction of each component. There is little direct evidence of molecular level mixing in these materials, though Scherer reported that no second phase was observable in a TEOS poly(ethyloxazoline)-silica composite even at 3 nanometer resolution [9].

The properties of composites are greatly enhanced by the incorporation of covalent bonding between the phases [11]. For example, poly(methylmethacrylate) was covalently linked to a preformed silica gel [12]. The modulus of rupture of the covalently linked composite increased forty percent relative to the unlinked composite.

Wilkes has conducted detailed studies to determine the effect of covalent bonding and nanoscale mixing of the organic and inorganic phases in several systems [13-18]. Silica was precipitated into oligomers possessing functionalities that enabled them to bond with the inorganic phase. The length of the oligomer and the number and type of potential bonds to the inorganic system proved critical to the properties of the composites. For example, dynamic mechanical measurements showed that triethoxysilyl endcapped oligomers exhibited less phase separation from the silicate than did silanol endcapped oligomers. Small angle X-ray scattering showed that the triethoxysilyl endcapped oligomers exhibited a periodicity in structure while the silanol endcapped oligomers did not. The domain spacing increased with the spacing between triethoxysilyl groups. All data indicate nanoscale mixing of phases. A model was proposed for these composites in which there are regions rich in silica, regions rich in oligomer, and regions in which the two components are evenly dispersed [18].

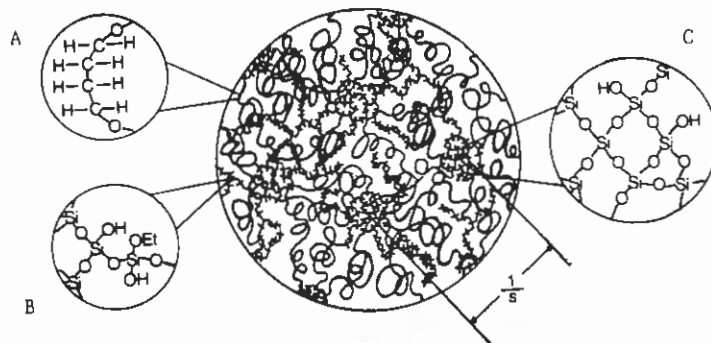


Figure 1. The Wilkes model

Composites made from metal alkoxides other than TEOS have also been studied [19]. Alumina and titania composites were synthesized by employing β -dicarbonyls to mediate the reactivity of these alkoxides [20, 21]. The alumina gel contained extractable side products of the hydrolysis and condensation that adversely affected its mechanical properties. An alternative route to this composite using dilute HCl has been presented [22].

Simultaneous Interpenetrating Networks (SIPN) have been synthesized by means of sol-gel methods [23]. This entails the simultaneous formation of the silica and polymer network such that no phase separation can occur. The use of separate catalysts for the inorganic (F^- , H^+) and organic phases (free radical, ROMP) facilitates phase mixing [24]. Shrinking can be avoided by choosing a metal alkoxide whose corresponding alcohol is itself polymerizable and using this alcohol as the cosolvent [25]. All components are polymerizable, thus neither evaporation nor the attendant shrinkage and fracture occurs.

Practical applications of these materials have been limited. Shea has synthesized aryl-bridged polysilsequioxanes in an attempt to "engineer" regular porosity into the gel [26]. His results have been inconclusive. Packing of the particles seems to be the prime factor that determines porosity. Related studies of alkylene-bridged silsesquioxanes show that greater degrees of condensation lead to greater micro- and mesoporosity. Rigid spacers also seem to be a requirement for microporosity [27].

These polysilsesquioxane gels have been used as confinement matrices for the formation of nanophase materials [28]. The gels were also etched in an oxygen plasma to remove the organic component. A greater percentage of pores in the mesoporous region resulted [29].

In another practical application, Schmidt has used sol-gel processing to fabricate contact lens material [30]. $Si(OR)_3R'$ was treated with $Ti(OR)_4$ and methylmethacrylate to enhance network formation and provide flexibility, respectively. The phases were successfully crosslinked. The resulting material satisfied all the requirements of contact lenses including wettability, scratch resistance, and flexibility.

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