Survey over the State of the Art in the Field of Processing of Inorganic-Organic Composite Materials

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Abstract

Inorganic-organic composite materials by sol-gel processing have gained more and more interest during the past ten years. The sol-gel process allows to incorporate organic compounds or groupings of very different chemical nature. They range from isolated organic molecules like dyes to groupings linked to the inorganic backbone and oligomeric or polymeric organic chains. Synthesis chemistry defines to a great deal structure and properties, since thermal rearrangement after preparation is the exception due to the thermal stability of the inorganic backbone and the limited thermal stability of the organics. Interesting applications are under development in the field of photonic materials, protective coatings, electronic materials, reinforced polymers and elastomers. The field can be considered as one of the most interesting sol-gel areas.

1. INTRODUCTION

Sol-gel processing of inorganic-organic composites has gained increasing significance during the last years. This is based on the unique properties of the sol-gel process for synthesizing inorganic networks or small particles by soft chemistry methods below the decomposition regime of organic groupings or organic polymers. Whereas in the case of "pure" inorganic compositions, in general, higher temperatures have to be employed in order to achieve fully dense final materials (like inorganic glasses or ceramic materials), the presence of organic groupings can reduce the densification temperature remarkably, as shown in various publications [1 - 3]. This principle is already used for a long period for microelectronic purposes. =Si-CH₃ containing sol-gel derived oligomeric systems are used for spin-on processes to be densified at temperatures around some hundred °C. These coatings can be oxidized and densified to SiO₂ glass.

This simple example shows one of the attractive possibilities of the organic modifications: to produce thick and dense layers, which is extremely difficult without organic modification. The combination of organic and/or polymer chemistry with sol-gel chemistry opens an almost endless number of variations due to the variability of organic groupings and organic reactions. As a result of this, numerous types of materials can be synthesized with structural variations, be distinguished by their bonds between the organic and the inorganic phase, by their phase dimensions, by their type of matrix or by their application oriented properties.

2. STRUCTURAL ELEMENTS

The connection between organic and inorganic units is one of the key issues determining structures of sol-gel derived inorganic-organic composites. Various types of bonds or links can be considered.
2.1 Covalent Bonds

Covalent bonds are restricted to elements able to form links to organic groups as well as to inorganic backbones. The most common element therefore (to this end) is Si, which, under ambient conditions, forms stable bonds to oxygen as well as to carbon. This is used in silicones and can be extended into a variety of organic groupings and used in hetero-inorganic backbones (fig. 1).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{Si} & \quad \text{C} \\
\text{Al} & \quad \text{O} \\
\end{align*}
\]

Fig. 1. Model for a covalent link for connecting an oxidic network to organics.

If the environment of the bond can be protected from water, various other bonds can be taken into consideration, e.g. $\equiv \text{Si}-\text{O}-\text{C} \equiv$, $\equiv \text{Sn}-\text{C} \equiv$, $\equiv \text{P}-\text{C} \equiv$ or others. The $\equiv \text{Si}-\text{O}-\text{C} \equiv$ bond is relatively stable even in not hermetically protected environments.

2.2 Coordinative Bonds

Coordinating or chelating ligands can be used for forming bonds between inorganic and organic units in various ways: as chelating agents complexing inorganic network forming precursors like Ti-, Al- or Zr-alkoxides. Therefore, $\beta$-diketones, conjugated organic acids or amines can be used. Examples are alkoxy dicarbonates (a), methacrylates (b) (fig. 2a). Ammine complexes can be used to introduce inorganic ions into organic or organically modified matrices, for example, in form of copper or silver complexes (fig. 2c and d).

\[
\begin{align*}
\text{Al} & \quad \text{O} \quad \text{C} \\
\text{Zr} & \quad \text{O} \quad \text{C} \\
\end{align*}
\]

Fig. 2a/b. Structure model of $\beta$-diketone or methacrylate complexes.
Fig. 2c/d. Structure model of ammine complexes.

These few examples show only the basic principle; complex chemistry provides numerous other possibilities.

2.3 Isolated Molecules and Clusters

Dispersion of isolated molecules within sol-gel matrices is of interest for components with selected functions like special optical properties (non-linear optical properties, lasing properties, for photochemical hole burning (PHB) or others).

Migration of isolated molecules leads to cluster formation. For example, complex structures in d can be reduced, heat treated and chemically converted into Ag halides to form silver halide nanoclusters in sol-gel matrices showing a photochromic behavior [4]. Clusters can be formed by in situ growth reactions from various types of precursors. In ZrO₂ β-dicarbonyl complexes with polymerizable ligands to form an additional organic matrix, ZrO₂ clusters reaching from several up to 50 nm can be grown [5]. CdS or ZnO clusters can be precipitated in methacryloxyxisilane containing solutions, and an inorganic-organic network can be synthesized by sol-gel and polymerization reactions afterwards [6]. By diffusion of alkoxides into elastomers and subsequent hydrolysis nanoscaled precipitates of oxides can be formed within the organic matrix by hydrolysis and condensation [7].

2.4 Structures Formed by Organic Crosslinking of Inorganic Networks

Crosslinking of inorganic backbones by organic reactions can be carried out by groupings able to perform polymerizing, polyaddition or polycondensation reactions Eq. (1a) and (1b) show an example with polymerizing ligands.
Reactive groupings can be directly crosslinked, or organic monomers or oligomers can be used for building up organic chains (e.g. oligomeric acrylates, polydimethyl siloxanes or others).

2.5 Interpenetrating Phases or Networks

Basically, reaction (1a) and (1b) can be used to build up interpenetrating networks, too. However, it is pretty difficult to prove this on the level of molecular structure dimensions. In most cases, phase separation is more likely. Interpenetrating phases containing composites on a nano range have been prepared by infiltrating microporous silica gel with organic monomers like methylmethacrylate and subsequent polymerization. This short overview over structural elements for building up, of course, is not complete. But it demonstrates the potential of chemistry to design structures by means of chemistry.

3. SELECTED EXAMPLES

3.1 General Considerations

Regarding the possibilities provided by chemistry, it is not simple to decide the type of material or reaction to be selected for closer investigation. In addition to this, the sol-gel chemistry leads to changes in material properties by only a few changes of reaction parameters. This is interesting from fundamental aspects, e.g. structure to property relations. To tailor these materials to be suitable for uses as new products, in general leads to stringent conditions defined by a set of very special parameters. To achieve these properties, the numerous possibilities provided by chemistry now act as an obstacle well known already from the problems of inorganic gel structures; only minimal changes in synthesis conditions lead to large variations in gel structures. But in this case, after transformation of these gels into homogeneous glasses, the remaining dominating parameter is only composition. In the case of the inorganic-organic sol-gel derived composites, in general, we remain in the "gel phase", and the result of the influence of the numerous parameters is kept within the structures. In the following examples, the development of material properties for practical use will be emphasized.

3.2 Optical Materials

Due to the recently increasing attention paid to optical materials, sol-gel developments for materials with special optical properties have gained more and more interest. The material developments comprise almost all types indicated in chapter 2.1 - 2.6.

The introduction of organic dye molecules mainly has been carried out from reasons of stability or structural analysis probing. Some interesting results have been reported on the stabilization effect of sol-gel matrices on various optical properties of dyes. Levi et al. got a remarkable stabilization of photochromic dyes [8]. Makishima [9] reported that PHB dyes can be used at higher temperatures in sol-gel matrices. Dunn et al. found surprising stabilization against laser shot decay of lasers dyes in Al₂O₃/SiO₂ sol-gel matrices [10]. Altman et al. showed similar effects in matrices based on methacryoxy silane systems with Rhodamine 6G [11]. Reisfeld and coworkers could show stabilizing effects with a variety of dyes in silica gel matrices, especially after impregnating them with MMA and polymerizing it [12].

Another type of composite was realized by Prasad, using \( \chi^3 \) polymers and reinforcing them with a sol-gel inorganic backbones [13]. From Wilkes et al., diamino diphenyl sulfone-based TiO₂ sol-gel composites with \( n_D \) values up to 1.73 have been reported [14]. TiO₂/SiO₂-polyetethylen glycol composites were developed for matrices for embossing CD
ROMs [15]. Mackenzie recently reported on CdS nanoparticle containing ORMOSILs (ORganically MOdified SILicates) [16]. From Krug et al. new wave guiding systems to be patterned by embossing have been shown [17]. These systems are based on ZrO₂ methacrylate complexes polymerized with methacrylate derivatives (fig. 3.). The materials show less than one dB/cm loss and can be modified by active components.

![Chemical structures](image)

**Fig. 3:** Zr-alkoxide-methacrylate complex structural units as a basis for copolymers with methylmethacrylates and Si-methacrylates [after 17].

Kasemann et al. reported on coatings for glass surfaces with extremely low surface energies. These composites, based on Al₂O₃ and fluorine containing groupings, show surface free energies as low as polytetrafluoroethylene even at very low fluorine contents. The reason is a self-aligning mechanism by a special processing during coating and drying, providing a strong adhesion to the glass surface and a concentration of the fluorine containing groupings in the surface (fig. 4) [18], proved by ESCA profiling. These coatings show an interesting antiadhesive and dust repellent effect on glass surfaces.

![Coating model](image)

**Fig. 4.** Structural model of self-aligned low surface energy ORMOCER coatings (ORgani-
cally MOdified CERamics).
Mackenzie et al. prepared transparent composites by impregnating silica gel by methyl methacrylate and polymerizing it. Tough bulk materials can be optimized by this process [16]. Klein et al. continued the work [19]. Spanhel et al. were able to prepare photoluminescent semiconductor quantum dot doped ORMOCERs by using bifunctional ligands for incorporating the dots in an inorganic-organic matrix (eq. 2). Sanchez, Babonneau et al. could show that a variety of organic dyes can be advantageously dispersed in alkyl modified silicate sol-gel matrices, showing non-linear optical effects [20, 21]. Levy et al. could increase the lifetime of photochromic dyes by incorporating them into sol-gel matrices [22].

\[ x\text{Cd(OEt)}_2 + \text{excess } H_2S \rightarrow x\text{CdS} \downarrow + 2\times\text{EtOH} \quad (2) \]

Cds + L-R \rightarrow \text{CdS}\text{L-R}

\[ x\text{Cd(OEt)}_2 + \text{excess } R \sim S \sim S \sim S \sim R \xrightarrow{\text{reduction}} x\text{CdS} \downarrow + R \sim \text{SH} \]

\[ \text{Cds} + \text{SH} \sim R \rightarrow \text{Cds}\text{SH} \text{R} \]

L= -\text{NH}_2, -\text{NH}(\text{CH}_2)_n\text{NH}_2, -\text{SH} \text{ or carboxylates} \]

These examples show the interesting potential of this group of materials for new optical applications. The structure of this type of materials includes almost all types of composites, ranging from the type of materials with organically modified inorganic backbones, isolated organic molecules in sol-gel matrices, interpenetrating networks up to nanoparticle containing inorganic-organic matrices.

3.3 General Aspects of Incorporation of Sol-Gel Nanoparticles into Organic and Inorganic Matrices

Nanoparticles or colloids with a few exceptions act as intermediates in the sol-gel processes. Growth mechanisms in most cases are difficult to analyse. There are two important hypotheses trying to explain narrow sized distribution from LaMer and Smoluchowski [23, 24]. Sanchez [20], Rinn [25] and Strehlow [26] showed results indicating a model for narrow particle size distributions based on surface energy control by coordinative ligands. If these ligands contain reactive groups, they can be used to crosslink them with organic groups or monomers. Sanchez could show that β-dicarbonyl ligands on Zr alkoxides allow to tailor Zr nanoparticles between several and 50 nm to be incorporated in inorganic-organic sol-gel matrices. Similar results were obtained by Spanhel with Cds.

In situ formation of nanoparticles is of interest for reinforcing elastomers or other organic polymers, too. The change of structure and properties on silicone rubbers could be demonstrated by Mark et al. [27]. Landry et al. prepared SiO\textsubscript{2} containing PMMA, polyvinyl acetate, polyvinyl pyrrolidone, polycryst acetate and polycarbonate polymers. They could show that even above T\textsubscript{g}, high moduli of elasticity could be maintained,
indicating a strong interaction between the organic and the inorganic phase. Calvert showed that the in situ preparation of inorganic particles in polymers leads to interesting effects concerning structures and properties [28, 29].

A completely different approach was chosen by Okato et al. [30], who used clay minerals to prepare rubber clay hybrids, increasing storage modulus and modulus of elasticity remarkably compared to carbon filled species. Fig. 5 shows a structural model of the composite. Even if the clay is not sol-gel derived, the basic surface chemistry, in order to disperse and to peptize the clay, is closely related to the sol-gel colloidal chemistry.

![Fig. 5. Structural model of a clay rubber composite; ———: clay platelets (after 30)](image)

Novak et al. developed systems for in situ formation of SiO₂ nanocomposites claiming to be able to avoid shrinkage completely by this process [31]. The modification of polymeric organic matrices with sol-gel derived inorganic nanoparticles is a fascinating new aspect of polymer chemistry, which can open a completely new field of opportunities. The whole development is at its infancy and the potential cannot be estimated at present.

3.4 Interpenetrating Networks

The question whether an inorganic-organic sol-gel composite can be considered as an interpenetrating network type or not is not easy to be answered. This is partially related to difficulties related to structural analysis, partially a matter of definition. Therefore, composites will be taken into consideration showing at least oligomeric units of both organic and inorganic parts. Parkhurst showed that it is possible to obtain homogeneous composites from polydimethyl siloxane and Ti alkoxides, indicating an interpenetrating network type. Another type is the PMMA filled silica gel, as prepared by Mackenzie, Klein and Reisfeld [16, 19, 12]. Composites prepared by Wilkes et al. with various oligomers (CERAMERS) at least partially can be considered as interpenetrating network type materials [32 - 40]. A model is shown in fig. 6 according to [10].
Other types of composites based on alkoxides and oligomers have been developed by Teoeve and coworkers [41]. These composites, called polycerams, are based on modified polybutadines, polyethylene exode acetanes, substituted polyethylene imuris or related polygatis and SiO₂ derived from silicon alkoxides for low DK purposes as films.

χ² composites developed by Prasad is another example for this type of composites. Mackenzie and coworkers developed so-called "rubbery ORMOSILs" from alkoxy silanes and PDMS, showing surprising properties with respect to elasticity and porosity. Finally, a series of composites developed by Schmidt et al. can be considered as interpenetrating network type of composites [42 - 46].

4. CONCLUSIONS

The combination of sol-gel chemistry with organic polymeric chemistry and the modification of inorganic sol-gel networks with organic functions is one of the most fascinating outlooks of the sol-gel process. The rapid increase of this field in research and industry demonstrates this clearly. The sol-gel process is, with only a few other methods, the only way to prepare this type of materials. Due to the soft wet chemistry, there is the vision to approach biological routes to composite preparation, too.

5. REFERENCES


23. D. Sinclair, V. K. La Mer, Chem. Rev. 44 (1949) 245. oder