

Organically Modified Ceramics by the Sol-Gel Method

John D. Mackenzie

Department of Materials Science and Engineering
University of California, Los Angeles, CA 90024-1595, U.S.A.

Numerous ceramics have now been prepared from liquid solutions at room temperature with the use of metal-organic precursors via the sol-gel method. If organic compounds such as dyes and polymers are added to the liquid solutions, two types of organically modified ceramics can be prepared. Type one is simply a fine mixture of the organic and inorganic components. Type two involves chemical bonding between the two components. A third type can be made by the impregnation of organics into the continuous pores of a porous inorganic gel. Organically modified ceramics based on these three approaches have unique properties and microstructures. Some can exhibit rubbery behavior even when the ceramic oxide content is 80%. Some can be very much harder than organic plastics and yet retain optical transparency. Some are excellent matrices for organic and inorganic nonlinear optical materials. Many sensors have been fabricated as well as ultrafilters. Scientifically and technologically, the organically modified ceramics constitute a new and exciting class of materials for the future. The present status of these new materials and their potentials will be critically reviewed.

1. INTRODUCTION

Engineering materials can be divided into five groups. They are the metals, ceramics, organic plastics, semiconductors and composites. The properties of the first four materials are governed by their chemical bonds, structures and microstructures. When the property of one particular material is unsatisfactory, then one can mix them on a macroscopic scale to obtain a composite with a more acceptable property. There are numerous examples of useful composites such as steel-reinforced concrete, fiber glass-reinforced polymers, etc. On a microscopic scale, some common composites include the use of fine silica powder to strengthen rubber tires and of organic polymers to strengthen concrete. Recently, the development of the sol-gel technique has led to the preparation of nanocomposites. In fact, the sol-gel technique enables one to prepare organic-inorganic hybrid materials which even contain chemical bonds between the organic and inorganic phases. The objective of this report is to present a review of the current status of some organically modified ceramics, the so-called "ORMOCERS." These Ormocers frequently have unique properties which cannot be obtained in other materials and the sol-gel technique is uniquely suitable for their synthesis.

2. THE THREE TYPES OF ORMOCERS

The sol-gel technique is of great interests and importance to users of engineering materials because (a) it can be used to prepare new

materials. which cannot be synthesized by other methods and (b) it permits the fabrication of materials at relatively low temperatures and into complex shapes which are difficult for other processing method such as melting and sintering. Examples of the uniqueness of the sol-gel method are evident in the case of the Ormocers. Ceramics, principally oxide ceramics, can be modified by the incorporation of organics in three general ways as shown in Fig. 1. In the first method, the organic material is simply added to the sol-gel solution and the solution then allowed to form into a gel with continuous pores as shown. This composite is then dried and stabilized by heating to some temperatures not high enough for the decomposition of the organics. The role of the oxide gel is to protect the organic and to enable the fabrication of the organic-inorganic composite into some specific shape such as a film. Theoretically, as a first approximation, any organic can be trapped into any oxide matrix by this method. Because the organic will usually decompose at some relatively low temperatures, below 350°C, say, and the crystallization of oxide gels does not normally occur at temperatures below 350°C, the oxide is likely to be amorphous in these materials [1]. The second method involves the use of a porous oxide ceramic, amorphous or crystalline, with continuous pores. The porous ceramic is immersed in a solution containing the organic, for example a monomer. The solution is impregnated into the pores, and in the case of the monomer, it is caused to polymerize. The pores may or may not be fully filled. An oxide-polymer is now formed. It should be noted that the

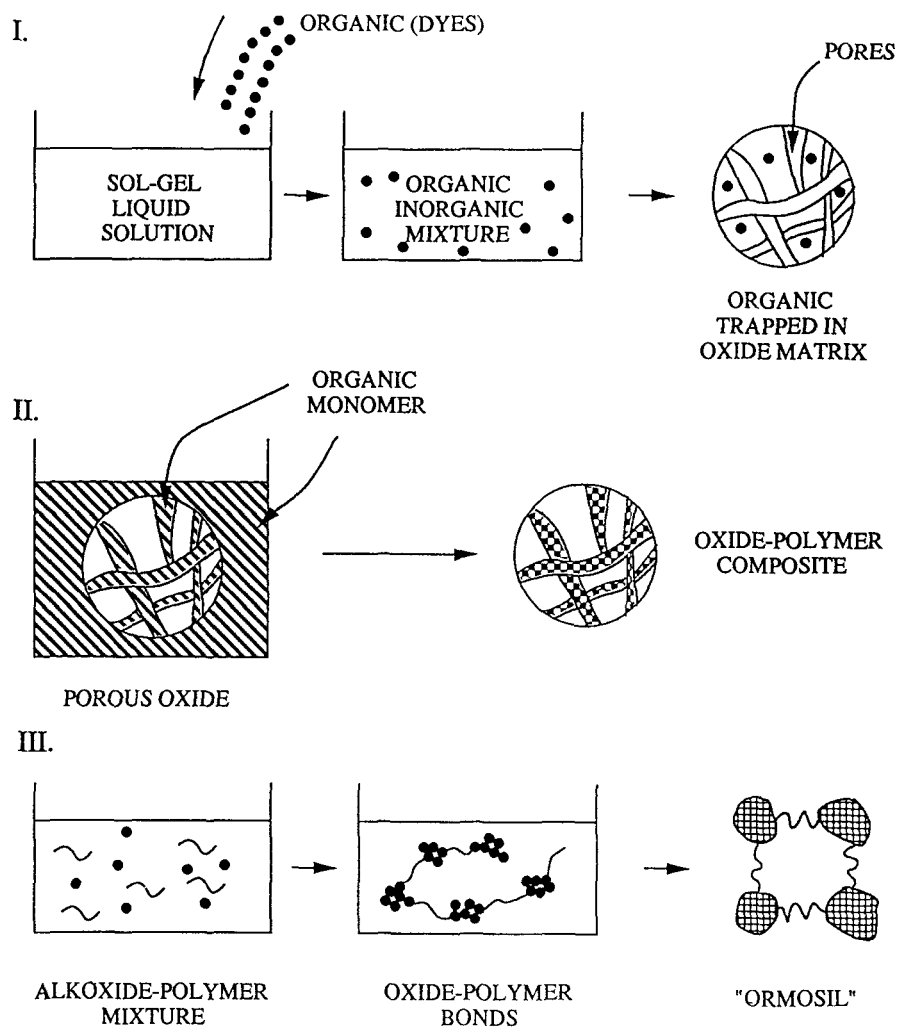


Figure 1. Three general types of Ormocers.

diameters of the pores are usually very small, 10-200Å and both the pore size and size distribution are controllable via the processing method. The third method involves a chemical reaction between the inorganic precursor, for example, a metal alkoxide, and the organic in solution such as a polymer chain. When the gel is formed, inorganic oxide clusters will be bonded to each other by the polymer chains as shown in the figure. This inorganic-organic "compound" gel is still porous and can be used as the starting porous oxide as in Fig. 1-II. Further, other organics can also be added to the solution in III to obtain the sample shown in I. Since many oxides can be

rendered into the gel state and many organics of all types are available, theoretically an infinite number of Ormocers can be synthesized. Although the field is less than ten years old, many interesting examples of Ormocers are already known. Some of these will now be reviewed.

3. TYPE-I ORMOCERS

Because SiO_2 gel is the most widely studied gel easily prepared from a silicon alkoxide such as tetraethoxysilane (TEOS) and many organic dyes are readily available, the dissolution of dyes in a SiO_2 has been the subject of many studies. Since

the earliest work of Avnir, Levy and Reisfeld in 1984 on the incorporation of dyes such as Rhodamine 6G in SiO₂, many organics other than dyes have been used including liquid crystals and enzymes. The potentials for the applications of such Type I Ormocers are enormous. Examples of these materials are shown in Table 1. Undoubtedly many industrial products will eventually be developed. In the mean time, many important scientific as well as technical problems remain to be solved. For instance, many workers ignore the fact that the SiO₂ gel formed at room temperature, and even after drying at 100-200°C, remains highly porous, contains an abundance of OH groups and are mechanically weak. Such gels have been referred to as "silica glass" which conveys the impression that they are like melt-formed oxide glasses and are thus dense and strong. This is certainly not true for the SiO₂ gels. The solution to this porosity problem can be partially solved by impregnating the pores with

other gels or polymers as for the Type II materials. A second serious problem is that there is a lack of knowledge regarding the location of the organics within the gel. What are the proportions of the organics which are completely surrounded by the oxide, partially in the pores and completely in the pores? The size of the organics may be much less than or larger than the average pore diameter. The question of leaching if these Ormocers are subsequently placed in liquids such as alcohols has been raised and is being investigated [13-15]. It appears that leaching does occur in some cases. Since the size of organic molecules are of the same order as the diameter of some pores, it is of interest to inquire if the microstructure of the gel itself can be altered when an appreciable concentration of organics are put into the gelling liquid. Despite these unanswered questions, Type-I Ormocers will be very important engineering materials in the near future.

Table 1
Type-I Ormocers and their potential applications [21]

Entrapped Organics	Potential Applications	Reference
Rhodamine 6G	Dye laser	Avnir [3]
Quinizarin	Optical data storage	Tani [4]
Bixin	Photoconduction	Makishima[5]
Poly-p-phenylene vinylene	Third order NLO	Prasad [6]
n-(4-nitrophenyl)-L-prolinol	Second harmonics	Toussaere[7]
o-phenanthrolin	Chemical sensors	Zusman [8]
Enzymes	Biochemical sensors	Brain [9]
Liquid crystals	Display systems	Levy [10]
Spiropyrane	Photochromics	Levy [11]
Phenoxazinium	Hard colored coatings	Nakazumi [12]

4 TYPE-II ORMOCERS

Prior to the recent development of Ormocers, a number of metal oxides with ultrafine ($< 100\text{\AA}$) pores have already been studied as the inert host for a variety of impregnants. For example, the intercalation of zeolites is well known [16]. Polyfurfuryl alcohol was impregnated into the Vycor-type porous glass and pyrolyzed to obtain electronically conducting samples [17]. Such research had led the present author and his student C.C. Liu to investigate the impregnation of polymethylmethacrylate (PMMA) in porous Vycor glass [18]. More recently, we were able to impregnate a variety of organic polymers into SiO_2 gels to obtain transparent nanocomposites [19-21]. In the case of PMMA, transparent composites can be made from 1 to 99% PMMA [21]. In general the ideal mixture rule for a number of properties rule is applicable. Because the impregnation is almost 100% and because the pore diameters are $< 200\text{\AA}$ and the refractive indices of PMMA and SiO_2 are nearly the same, the transparency frequently exceeds 99% for visible light for samples with a thickness of light for samples with a thickness of 3mm. A comparison of various properties of an Ormocer-II sample with 33% PMMA in SiO_2 with other materials is shown in Table 2. The Ormocer sample has mechanical properties far superior to that of PMMA but its density is significantly less than that of window glass. Despite these attractive features the Ormocer-II is still a brittle solid because the SiO_2 phase is continuous.

If the heat-treatment of a SiO_2 gel is rigidly controlled, very narrow pore size distribution as well as the pore size can be controlled accurately [22,23]. A variety of organics has been impregnated into such SiO_2 gels with pore diameters predominantly of 14, 45 or 90\AA . Some of these materials have been shown to have lasing capabilities. They have also been tested as scintillators and wavelength shifters [24]. The controlled heat-treatment of oxide gels other than SiO_2 to maintain a network of interconnecting pores has been reported for TiO_2 and ZrO_2 in the development of ceramic ultrafilters [25]. These materials are now polycrystalline. The same treatment presumably can be applied to other oxide systems. Thus in the near future, it is anticipated that many polycrystalline porous ceramics will be available for the impregnation of different organics. Pores which still exist after impregnation can be filled by inert gels or polymers. The sol-gel method is highly flexible and porous ceramics can be fabricated into many forms such as fibers, films and spheres. Silica gels, for example, have been fabricated into microspheres in the range of 20 to $70\ \mu\text{m}$ in diameter and impregnated with optically active dyes [26]. The uses of such microspheres as sensors, slow release media for medicines, chemical reactants, fragrances and components of optical display panels have been suggested. It is obvious that opportunities abound for the use of the Type-II Ormocers for many future applications.

Table 2
Comparison of Type-II Ormocer properties with other materials [21]

Material	Density g/cc	Relative Abrasion ($10^{-3}\ \text{mm}^3/\text{cycle}$)	Vickers Hardness (kg/mm^2)	Modulus of Rupture (kpsi)
SiO_2 glass	2.20	12	700	15,500
Soda-lime glass	2.50	---	450	12,000
SiO_2 -33% PMMA	1.85	35	220	12,000
PMMA	1.20	350	20	8,000

5. TYPE-III ORMOCERS

Oxide gels prepared from metal alkoxides frequently involve the hydrolysis and condensation reactions of the precursors such that an oxide network is formed which is predominantly made up of metal-oxygen bonds. There may be some OH groups left after drying. Because of the large amount of continuous fine pores present, the gel is mechanically weak. Further, ionic oxides are well-known to be brittle solids. Thus oxide gels would fracture easily on drying and further heat-treatment. If, however, the three-dimensional network is not entirely made up of M-O bonds but that the continuity is broken up by non-bridging organic groups as shown in Fig. 2, then it is readily seen that the network may now be less brittle, especially if the M-O-M angle is less than 180° . Such considerations have led to the use of precursors such as methyl-trimethoxy silane, $\text{CH}_3\text{Si}(\text{Ome})_3$, for the preparation of modified SiO_2 gels. The gel network is thus permeated by the presence of 25% of non-bridging CH_3 groups. Such materials constitute the Type-III Ormocers. The properties most affected by the presence of such non-bridging organic groups are the mechanical properties.

In 1985, Wilkes *et al* [27] first prepared such inorganic-organic hybrids by reacting TEOS with polydimethyl siloxane (PDMS). The materials were named "Ceramers." Separately, Schmidt also reported the successful preparation of other such materials of which he named "Ormosils" (organically modified silicates)[28]. Since 1985, many organic-inorganic hybrid gels have been prepared with other oxides such as ZrO_2 and TiO_2 [29,30]. In the SiO_2 -PDMS system, when the amount of PDMS is in excess of approximately 20 wt.%, and if the microstructure is carefully controlled, the Ormocer can be actually rubbery [31]. The rubbery behavior is attributed to the ability of the PDMS chains which link clusters of SiO_2 to curl and uncurl under externally applied stress [32]. The chains can distort because the Si-O-Si angle is approximately 150° . Structural evidence has been obtained from ^{29}Si NMR measurements [33]. The SiO_2 -PDMS structure is depicted in Fig. 1-III. The mechanical properties are highly dependent on the ratio of PDMS to SiO_2 , as well as on the processing conditions. At this very early stage of research, the rubbery Ormosils compare favorably with commercial organic rubbers as far as compressive modulus and resilience are concerned. However, the elongation is only of the order of 25% versus the

800% attainable by commercial rubber. Nevertheless, a rubbery Ormosil with 70% SiO_2 should be much more environmentally stable than a purely organic rubber. The replacement of CH_3 groups by phenyl groups can improve the thermal stability of many organic materials. This has been found to be true for the Ormosils as well.

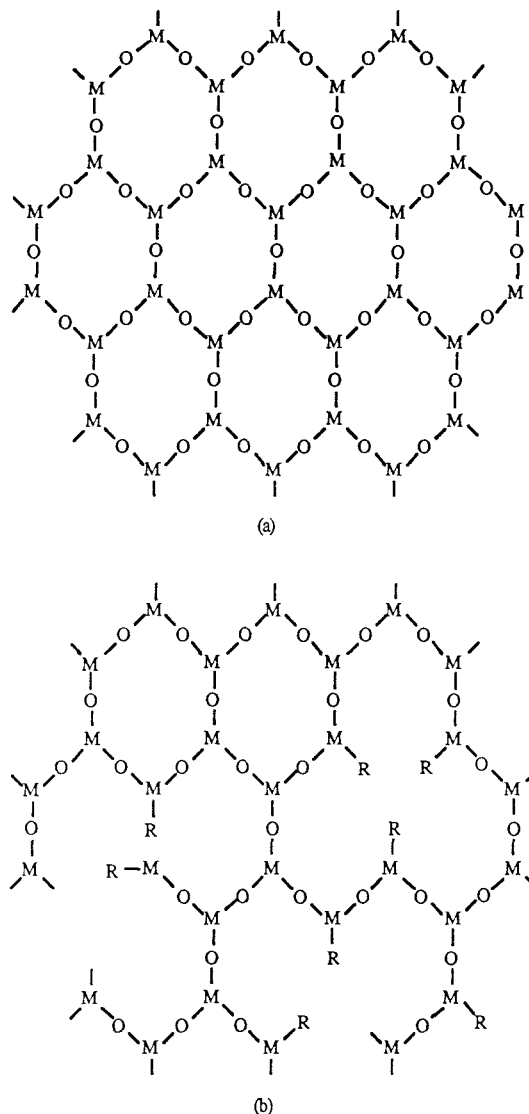


Figure 2. Organic groups in an oxide network to decrease brittleness.

In Fig. 3, the room temperature resilience of some Ormosil samples are compared with that of a commercial rubber after the samples have been heated in air to 150° for long times. The Ormosils appear to be stable under such conditions.

If the PDMS concentration in an Ormosil is less than about 20% and if the sol-gel liquid solution has been subjected to ultrasonic irradiations, the gels are hard, dense and transparent [34]. The Vickers hardness of these low PDMS materials can be as high as 200 Kg/mm² in comparison with the values of less than 25 Kg/mm² for the hardest plastics such as polyethyleneterephthalate (PET) and 500 Kg/mm² for common soda-lime silicate glasses. Such Ormocers compositions are potentially useful hard coatings for organic polymers. Another family of high temperature stable Ormosils are those prepared from TEOS and polyimides [35, 36]. These hybrid materials in film forms have glass transition temperature (T_g) in excess of 400°C. The films are flexible although the SiO₂ content is 70 wt.%. During the process, SiO₂ particles are formed via a phase separation process and are dispersed in the organic matrix. It was suggested that these materials will be important for microelectronics [36]. Because of their lower susceptibility to brittle fracture during fabrication, high optical transparency and yet maintaining sufficient hardness for polishing, the Type-III Ormocers are ideal matrices for optical elements containing semiconductor quantum dots [37, 38] and organic dyes [39, 40]. Superficially, the Type-III Ormocers resemble the polysiloxanes or silicones [41]. However, the processing method, the structures and the concentration of the oxides are different.

6. FUTURE GENERATIONS OF ORMOCERS

The three types of Ormocers described above constitute a new family of engineering materials with potentials for many engineering applications. They can be combined to create even more interesting materials. There is of course a great deal more scientific research necessary together with or before practical developments. Even greater scientific challenges are available if the Type-III Ormocers are prepared such that active organics like dyes are structurally bonded to an oxide network containing active metal ions such as the rare-earth ions. Some research have already been reported on such new systems [42-44]. The transfer of energy between organics and inorganics should be of use to numerous applications and lead to the fabrication of truly

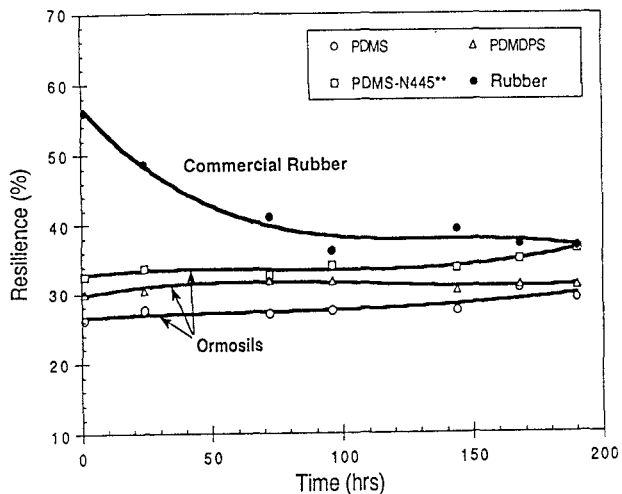


Figure 3. Variation of room temperature resilience of commercial rubber and Ormosils after heating in air and at 150°C for various times.

multifunctional materials. There will be opportunities for creating not only electronic, structural and optical materials but biomaterials as well.

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John D. Mackenzie is the NSG Professor of Materials Science at the University of California, Los Angeles. His research interests are glasses, amorphous solids and sol-gel based materials. He was the founder of the Journal of Non-Crystalline Solids and its Editor-in-Chief for 20 years. Professor Mackenzie is the author of more than 400 publications and was elected to the U.S. National Academy of Engineering in 1976 for his contributions to glass science and technology. He is a Fellow of the American Ceramic Society and the British Royal Society of Chemistry.

