38

ORGANICALLY MODIFIED CERAMICS—MATERIALS WITH "HISTORY" OR "FUTURE"?

H. SCHMIDT

38.1. INTRODUCTION

If one wants to answer the question of the future of a group of materials, one first has to look into its history. The combination of materials with different properties in order to gain new properties is an old objective of researchers concerned with material development. There are numerous examples for composites, and the tendency during the last decade shows that the unit size of the composite phases is decreasing continuously. If the unit size reaches the nanometer range, mechanical mixture of the different components becomes impossible. Other methods like vapor deposition or chemical routes have to be chosen. The sol–gel process is a suitable way to synthesize ceramic precursors like gels with the desired composition at low temperatures. These mostly amorphous materials can have different structures or microstructures, where two extremes are the *polymer type* (Fig. 38.1*a*) and the *colloidal type* (Fig. 38.1*b*). It depends on composition and reaction conditions, which type will be obtained, and which combinations are possible. The low processing temperature allows to incorporate organics, which can have different functions, depending on their type and the way they are linked to the organic network. Figure 38.2 illustrates some general possibilities. Organics can act as network modifiers and network

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Ultrastructure Processing of Advanced Materials.
Edited by Donald R. Uhlmann and Donald R. Ulrich (deceased).
ISBN 0-471-52986-9

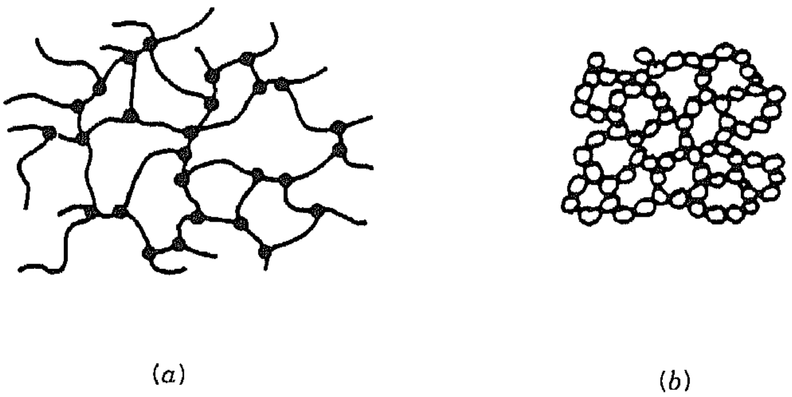


Figure 38.1. Two different types of ceramic gels. (*a*) Polymer type; (*b*) colloidal type.

formers. They can add special functions as a consequence of their chemical nature. Because there exists a large variety of organic groupings, the number of variations is almost endless. In order to bring some systematics into the jungle, it is necessary to develop some rules in the sense of structure to property or component to property relation. The size of organic and inorganic or inorganic and mixed organic–inorganic phases is not included in this structural con-

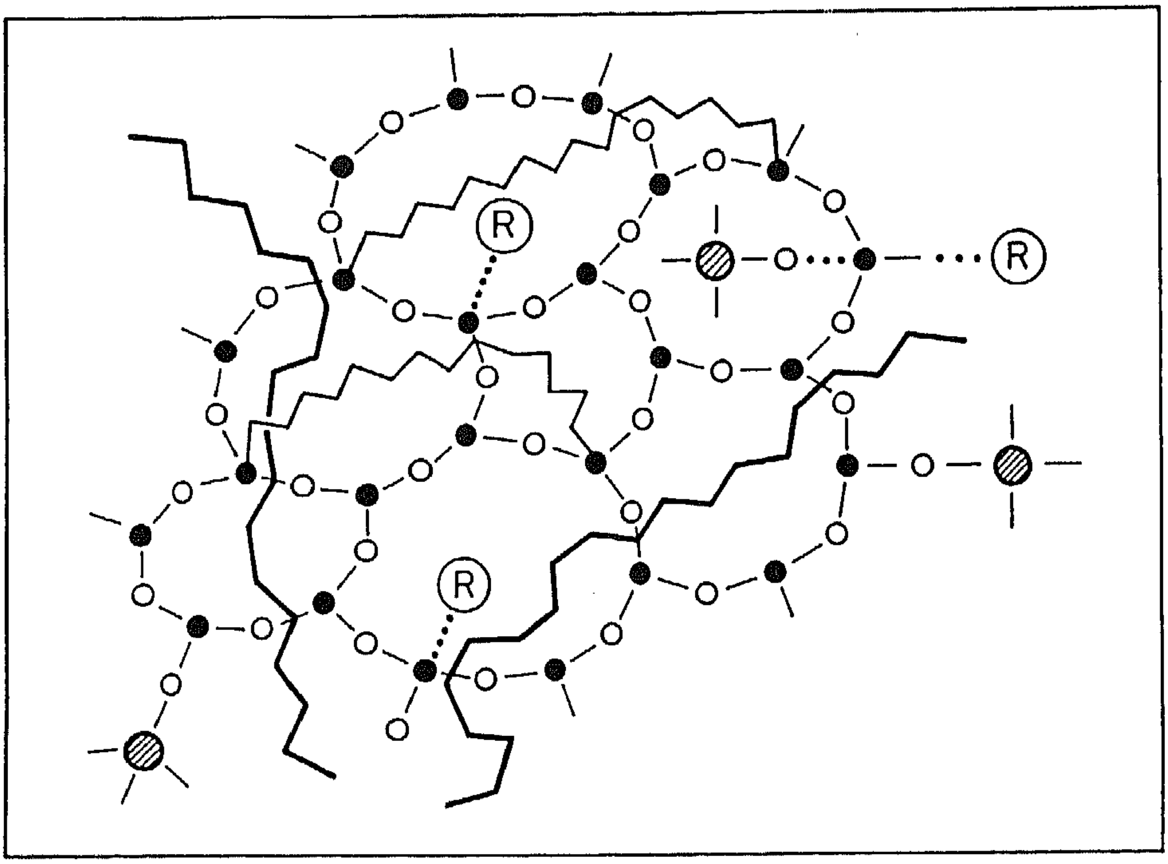


Figure 38.2. Possible structures or organic-inorganic polymers. ○ = O; ● = Si; ○ = inorganic heteroatom; 〰 = organic chain.

sideration. Because the building up process starts with molecules, due to their reactivity differences separation or arrangement effects are possible.

The Si atom offers a convenient method to link organics via a $\equiv$Si—C$\equiv$ bond covalently to an inorganic backbone, if at least one $\equiv$Si—O— bond is present at the same Si atom, because the $\equiv$Si—C$\equiv$ bond is pretty stable under ambient conditions. With other network formers, like Ti or Al, other coupling principles are necessary if a chemical bond to the organic part is desired. Complex formation (e.g., by chelating ligands) is one, ionic bonds (e.g., to organic acid ions) are another possibility.

The sol–gel process plays the dominant role for the synthesis, because it is the most important and a very flexible method to synthesize inorganic polymer networks at low temperatures. For reactions of the organic grouping, the wide knowledge of organic chemistry can be used. However, very often it is necessary to develop new routes, because the simple transformation of known reactions into different media or other reaction conditions very often is not possible. Principles of reactions by sol–gel chemistry are published elsewhere, as well as reactions of organic groups [1–6] and will only be partially discussed in this Chapter.

38.2. GENERAL ASPECTS OF INORGANIC–ORGANIC POLYMERS

The question has to be answered, what are the reasons for investigating or synthesizing organically modified inorganic polymers or inorganically modified organic polymers? There is at least one very simple reason: The scientific curiosity for what comes out by "mixing" together organics and inorganics on a nano or even molecular level. Behind this "simple" one, a lot of other reasons exist like the question, which sizes of the different phases are possible? or can the sizes be tailored? which properties can be obtained? or is a tailoring possible similar to a molecular engineering? and, of course, can new materials lead to new applications?

It is important to get an overview over the major influences of different components, for example, the inorganic groupings on the one hand and the organic groupings on the other hand. If one starts this consideration with examples of inorganic network or gel formers as "inorganics," like SiO_2, Al_2O_3, or TiO_2, one should expect chemical, optical, or mechanical properties related to these materials as bulk materials (glasses or ceramics). If one starts the consideration from the organic polymeric side, for example, with polyethyleneoxide (PEO), polymethylmethacrylate (PMMA), or polyethylene (PE), one should expect properties related to these properties like high thermal expansion, low Tg values, softness, low densities, and low n_D values. In addition to this, the influence of chemical functions, for example, by organofunctional groupings, is a third parameter, because its effect on the material properties depends on the structure, or on the arrangement of these groups in the structure or their interaction with the rest of the network. the network. Figure 38.3 is an attempt to show the connections between the main components and the influenced parameters. The question that arises is whether or not it is possible to tailor desired properties based on an experimental knowledge of the influence of different components.

38.3. PROPERTIES, COMPOSITION, AND STRUCTURES

The path of different developments of organically modified ceramics (ORMOCERs) showed us that in various cases properties could be predicted, that is, that new properties expected from the different elements (in this case, the element is a component, grouping, reaction condition, or similar) could be obtained. Other cases show that new unexpected properties are achieved. In the following, this will be demonstrated with a few examples.

38.3.1. Reactivity of Substituted Si Esters

As described above, for the introduction of organic groupings into an inorganic network a convenient way is the use of organoalkoxysilanes. The advantage of this type of molecules is that there is yet one assembling given: The organic group is covalently linked to an inorganic network former. In a cocondensation process together with other alkoxides, the organic phase only can be separated

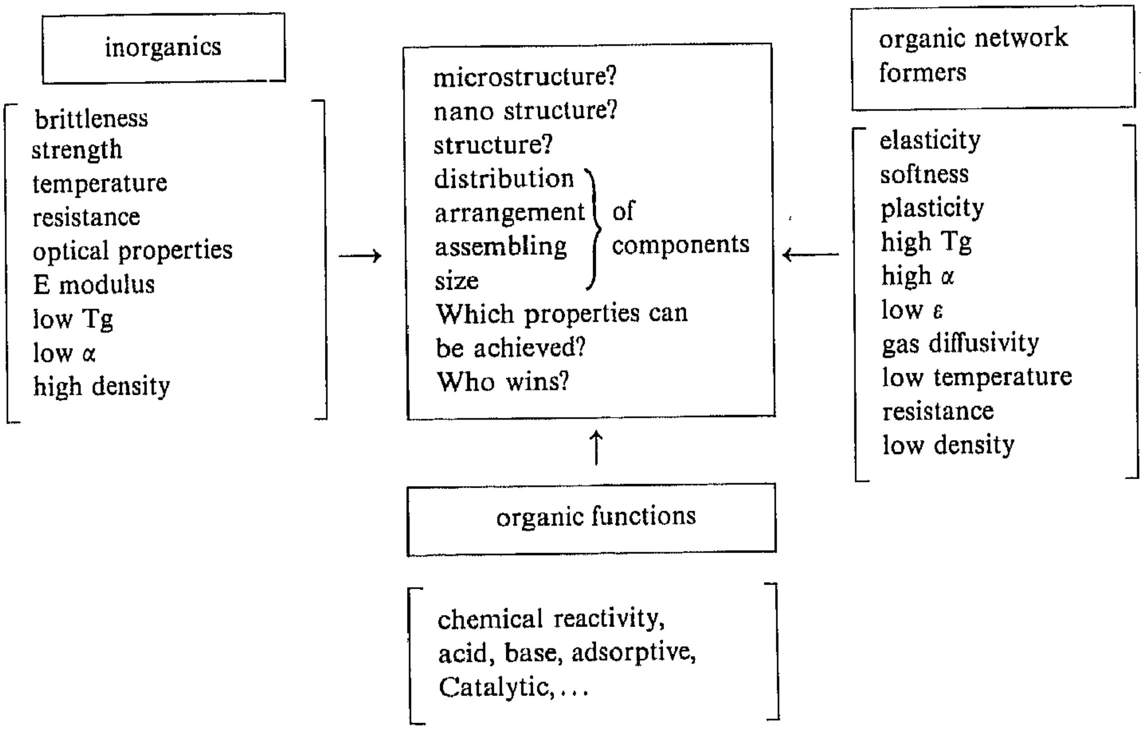


Figure 38.3. Possible influences of different components on ORMOCER properties.

from the inorganic one by including one partially inorganic network forming unit, but in this case various arrangements are possible (Fig. 38.4).

In Fig. 38.5, an example for a structure development according to step III is given.

The H_2O adsorption isotherm leads to the conclusion that the inside of the pores is covered to a great deal with hydrophobic CH_3 groups from the CH_3—Si≡ unit. This self-assembling reaction can be explained by the fact that during the hydrolysis and condensation process, where a maximum of OH groups appears, a separation effect takes place into $SiO_{n/3}(OH)_{4-n}$ and $CH_3SiO_{n/2}(OH)_{3-n}$ phases. This leads to the conclusion that hydrolysis and condensation rates should be different for the two different species, as one has expected anyway. As shown elsewhere [7], the hydrolysis rates actually are different, the striking point, however, is that hydrolysis of ≡Si—R group-containing silanes decreases almost linearly with increasing content of OH groups (Fig. 38.6).

This fact can be interpreted with the assumption of an increasing difficulty of the OH^- ion to substitution reaction due to the +I effect of the alkyl groups. In this case, the proton catalyzed mechanism is the only possible one (Fig. 38.7). This means, that based on rate differences, inhomogeneities occur, regardless of whether they are desired or not. Because the means for rate control are limited, especially if one wants to equilibrize hydrolysis and condensation rates of several components, one has to look for other reactions to overcome rate difference-based disadvantages for structure controlling. Yoldas [8] has pointed

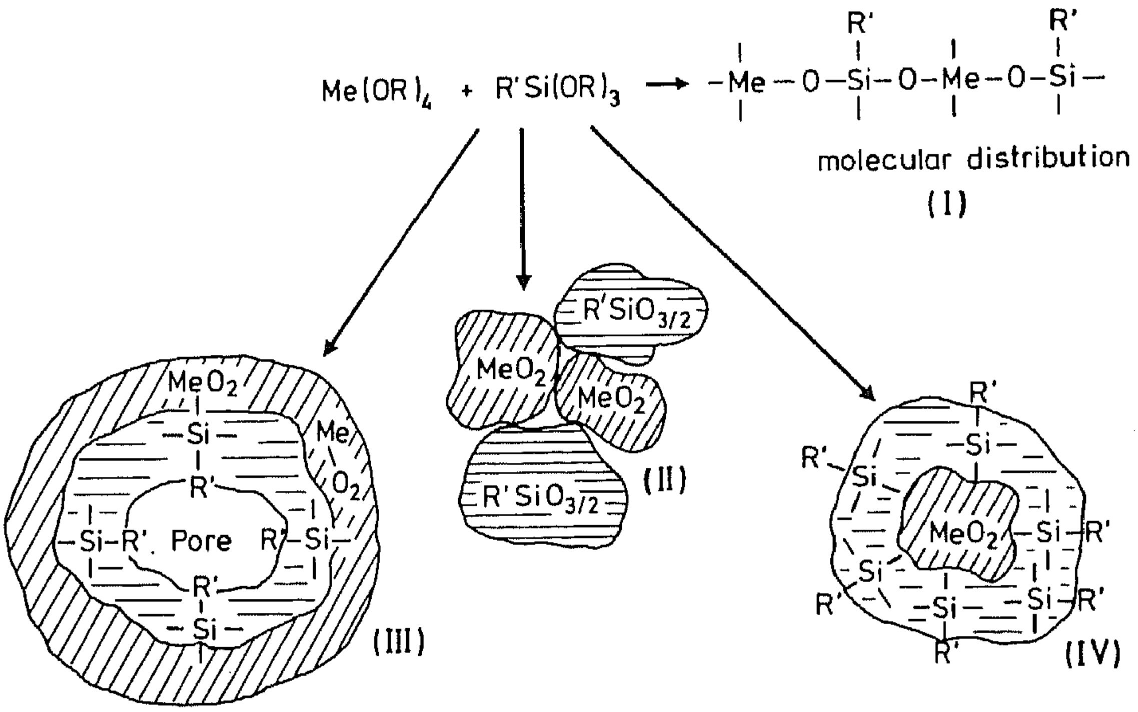


Figure 38.4. Some examples for different arrangements of inorganic–organic composites by sol–gel reactions.

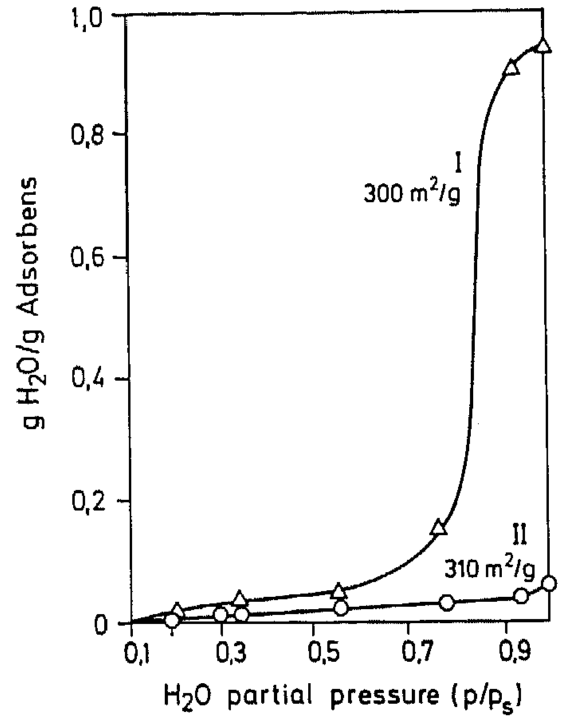


Figure 38.5. H_2O adsorption isotherm (25°C) of amino group containing SiO_2 gel (I) compared to $(CH_3)SiO_{3/2}:SiO_2 = 4:6$ gel (II).

out that by a fixation of one species to an already formed polymeric network, phase separation can be avoided or, as shown in Ref. 2, the so-called CCC (chemically controlled condensation) reaction can be applied successfully. The latter one allows control of the unit size as shown in Ref. 9 and keeps it small enough to cause light scattering and to exclude optical application. This was shown on a polymer based on $SiO_2/TiO_2/SiO_{3/2}$ epoxy. With chemical

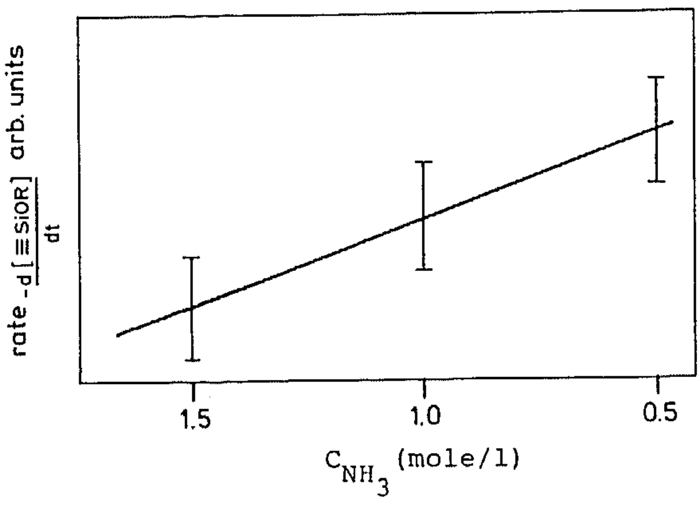


Figure 38.6. Dependence of hydrolysis rate of $(CH_3)_2Si(OC_2H_5)_2$ on NH_3 content: H_2O:OR stoichiometry = 1 :4; 50 vol% ethanol as solvent; 25°C.

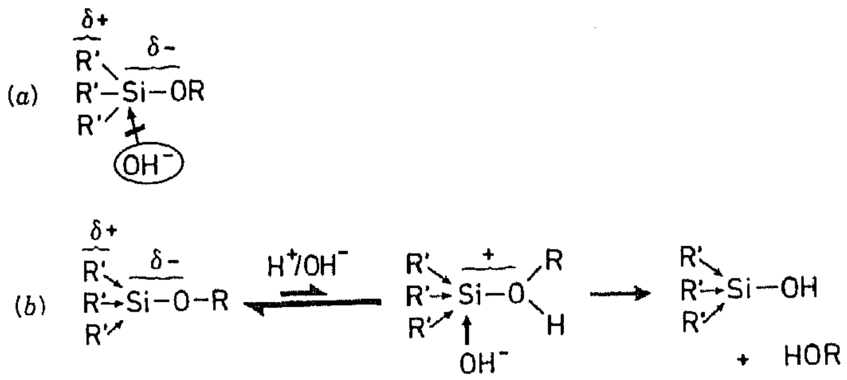


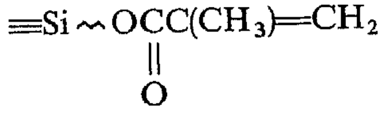
Figure 38.7. Proposed mechanism for the base-catalyzed hydrolysis of substituted silanes.

processing reactions like these, it is possible to incorporate substituted esters of various types into inorganic networks avoiding separation effects, and it is possible to tailor phase sizes if necessary.

38.3.2. Combination of Properties

Following are examples for the combination of properties. As described elsewhere [10], a contact lens material has been developed. The basic considerations of this material development resulted from *molecular* considerations of different structural units. For oxygen diffusion, a siliconelike unit having a $\equiv Si—CH_2—CH_2—$ grouping was chosen. For hydrophilicity (low wetting angle), a $—CH_2OH$ group was considered to be suitable. However, the combination of these functional silanes in a sol–gel process led to a reesterification reaction of the $\equiv Si(CH_2)_nOH$ to the $\equiv Si—R$ by destroying the hydrophilic $—CH_2OH$ groups. Therefore, the

group was chosen, and the ring opening was performed *after* the condensation. Now, the combination led to oxygen permeation and hydrophilicity, but the mechanical properties were poor, and the material was porous. The introduction of $Ti(OR)_4$ as a condensation catalyst led to dense, but extremely brittle material, which was not machinable to lenses. To reduce brittleness and increase flexibility,



$$\equiv Si \sim O\underset{\underset{O}{\|}}{C}C(CH_3){=}CH_2$$

was introduced, which was polymerized with methylmethacrylate (MMA). Now, mechanical properties were sufficient, but wettability decreased. The sub-

TABLE 38.1. Expected and Obtained Properties of a Molecular Composite of SiO_2, TiO_2, Si-Epoxy, Si-Methacrylate, MMA, and HEMA[a]

group	expected function		obtained function
$\equiv Si-CH_2-CH_2-$ (I)	good oxygen permeation	⟶	good
$\equiv Si-CH_2-CH_2-OH$ (II)	good wettability	⟶	poor
$\equiv Si\sim\sim\underset{O}{\bigtriangledown} \rightarrow \equiv Si\sim\sim\underset{OH}{CH}-\underset{OH}{CH_2}$ (III)	good wettability	⟶	good
$\equiv Si-$organics (I-III)	good flexibility	⟶	poor
$[SiO_4]^{4-}$	good strength	⟶	poor
$[TiO_4]^{4-}$	good densification behavior	⟶	good
$\equiv Si\sim\sim O\underset{\underset{O}{\parallel}}{C}-C(CH_3)=CH_2$ + MMA	high flexibility	⟶	good
HEMA	good wettability	⟶	good
unexpected – – – – – – – – – – – – –			strength increase scratch resistance low density (≈1.3)

Abbreviations used: MMA, methylmethacrylate; HEMA, hydroxyethylmethacrylate.

[a] These materials were prepared from $Si(OCH_3)_4$, $Ti(OC_2H_5)_4$, $(CH_3O)_3Si(CH_2)_2OCH_2CHCH_2O$, $(CH_3O)_3Si(CH_2)_2OCOC(CH_3)=CH_2$, and MMA by a sol–gel process according to Ref. 10.

stitution of MMA by hydroxethyl methacrylate (HEMA) increased wettability, and all other properties were sufficient. Surprisingly, the material showed a superior *scratch resistance*. In Table 38.1, the comparison between expected properties and those obtained is given.

Table 38.1 shows that the molecular tailoring is possible, but it only works if the structure formation can be controlled. For example, the strength of the inorganic network could not be transformed into the composite at the low processing temperatures of <130°C, whereas the flexibility of PPMA (polymethylmethacrylate) polymeric chains could be. The wettability of CH_2OH groups could not be transferred; the glycol groups acted as wetting groups if present. Ti in these composites seems to be present in a coordinated state (Fig. 38.8).

The photocatalytic activity of TiO_2 is well known. In combination with organics, TiO_2 can undergo a redox reaction by accepting an electron to be reduced to Ti^{3+} and oxidizing organic groupings. However, this is a property of the crystalline bulk TiO_2. Radiation of the composite of Table 38.1 causes the colorless material to change to blue, which changes back to colorless in the dark. The properties of the TiO_2 are maintained in the molecular environment of the composite. The potential achieved by UV radiation can be qualitatively measured by a device shown in Fig. 38.9. A voltage of ≈ 1.2 V could be found.

In this case, a photoelectronic property of the bulk could be transferred

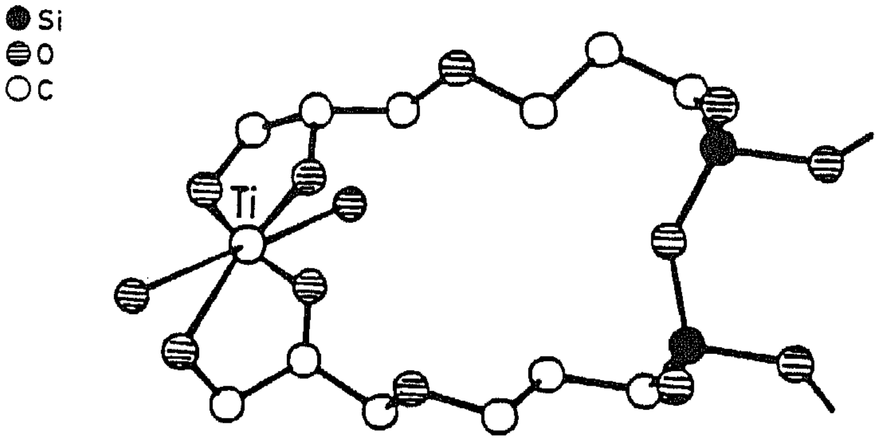


Figure 38.8. Coordination of Ti according to Ref. 11.

unexpectedly into a molecular composite. The disadvantage of this property is a reduced UV stability of these composites. This led to investigations to substitute Ti by Al or Zr. With Zr only weak, photoactivity was observed, and with Al no photoactivity was observed. One-to-one substitution of Ti by Al led to an unexpected drastic *increase* of brittleness and scratch resistance of coatings [9] and to an increase of UV stability by the factor of >20! Because structural evaluation is still under investigation, a structure–property relationship is not yet known. However, the consequence of these findings is an enlarged field of applications for outdoor purposes.

Due to the high costs of precursors, the main applications presently consist of coatings. Therefore, a variety of coating materials have been prepared. The main point in this case is the control of viscosity and curing behavior of the coated materials. The control of viscosity can be carried out according to two different mechanisms:

1. Partial hydrolysis and condensation (sol–gel control).
2. Control of the polymerization mechanisms of the organic grouping.

The main fields of application are hard coatings and soft materials like plastics, soft metals, paper wood, and even glass and ceramics.

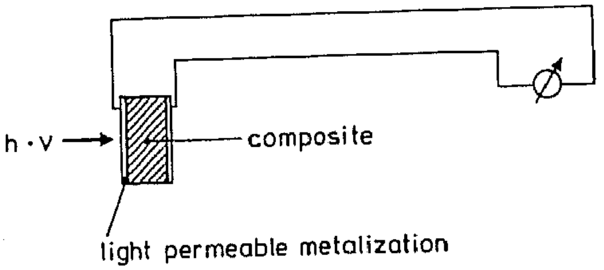
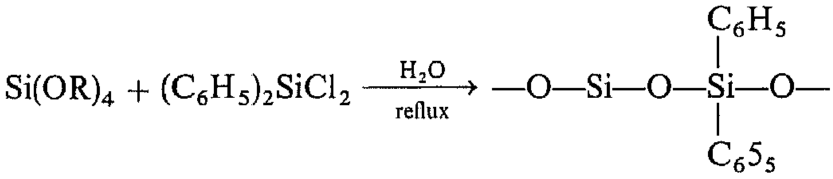


Figure 38.9. Device for detecting the $[TiO_4]^{4-}$ redox reaction in a composite according to Table 38.1.

For coating application, in most cases the addition of a third function is necessary, for example, reduction of H_2O permeation is required. This can be achieved by the introduction of groupings with hydrophobic properties, such as $\equiv Si(CH_2)_2CH_3$. The effect of this group in a scratch-resistant coating reduces the H_2O permeability to about 10% of the original permeability and makes this coating applicable as a scratch and corrosion protective coating on brass and aluminum.

The scratch-resistant properties of these materials could be maintained. The Al-based materials including polymerized epoxy and propyl groups show an excellent adhesion on metalized glass surfaces and a chemical and mechanical protection of the metal layer (Fig. 38.10), which otherwise would be chemically and mechanically unstable.

Investigations of the $—C_6H_5$ groups was carried out for reasons of the high thermal stability of the $\equiv Si—C\equiv$ bond in aryl-substituted silanes. With $(C_6H_5)_2Si=$ groupings it was possible to synthesize materials in combination with $Si(OR)_4$ or $Ti(OR)_4$ as precursors, which have temperature stabilities up to 350°C [$(C_6H_5)_2SiO:MeO_2 \approx 2:1$, (Eq. 1)] [12].



$$Si(OR)_4 + (C_6H_5)_2SiCl_2 \xrightarrow[\text{reflux}]{H_2O} —O—Si—O—\underset{C_65_5}{\overset{C_6H_5}{Si}}—O— \qquad (1)$$

However, these materials remain soluble in toluene or ethyl acetate. The infrared spectra of these materials show a surprising high OH content [13], even after 8 hr curing at 250°C. Traces of KOH reduce the OH content almost to zero. With fillers, like graphite or mica, high-temperature-resistant coatings (500°C in air) can be prepared. However, the surprising effect is the perfect *adhesion* of this system to glass surfaces and its *thermoplasticity*. Both properties had not been expected and were not described in literature. Based on these findings various adhesives could be developed. The introduction of the $=SiCH_3(CH=CH_2)$ group permitted to cure these materials by a radical polymerization without losing the good adhesive properties. The base-catalyzed sol–gel processing

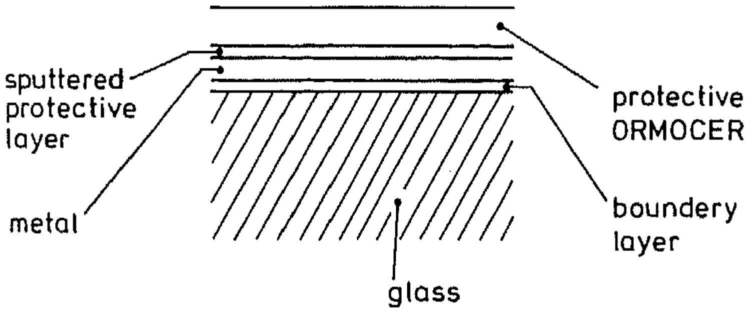


Figure 38.10. ORMOCER protection of metalized glasses.

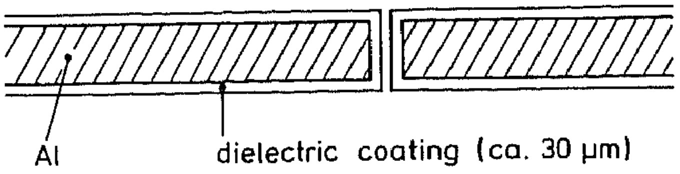


Figure 38.11. Metal core, printed circuit board.

combined with a high-temperature (280°C) curing under vacuum allowed the OH group content to be reduced to very low levels so that permittivity constants (ε) around 2.7 were possible. These types of coatings have been developed for metal core techniques for novel, printed circuit boards (Fig. 38.11) [14].

In order to make these materials depositable by electrophoretic deposition for the coating of sharp edges (cataphoretic coating), a third function in the form of electric charges had to be added. The cocondensation of ≈5 mol% of $-NH_2$ groups [from $(RO)_3Si{\sim}NH_2$] and the preparation of a stable emulsion led to a system that allowed a cataphoretic coating (Fig. 38.12).

After coating, a UV curing based on the vinyl group polymerization can be applied. Probably due to the low OH content and the additional organic crosslinking, a new unexpected property was found: These materials are very stable against bases, which is very unusual for silicate-based materials. In order to attack the surface, a 40% KOH solution at 50°C is necessary. The combination of low ε, low OH content, good thermal stability (280 to 300°C), and high chemical stability make these groups a good candidate for microelectronic application.

Another interesting question relates to the problem of the effect of the combination of two different basic properties of organic polymeric "networks" (linear and flexible) on the one hand and of inorganic network (stiff, brittle, and

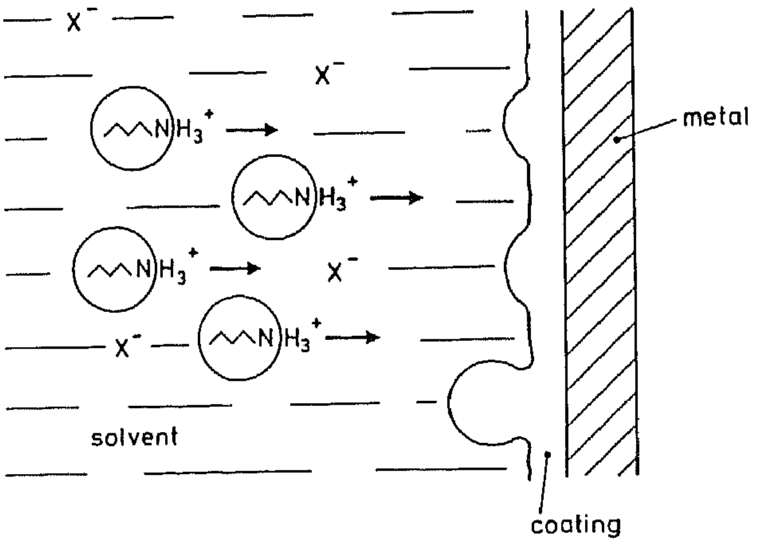


Figure 38.12. Scheme of the electrophoretic deposition process.

three-dimensionally crosslinked) on the other if these networks are not covalently bond, but exist independently of each other. In one example, the experiment was carried out with a soluble polymer (ethylvinyl acetate copolymer, EVA) and 50 wt% TiO_2 were added to a 5% solution of EVA in toluene (Fig. 38.13) [3]. In this case, the change of EVA properties was drastic as well as of the properties of TiO_2. The used EVA was soft and plastically deformable. $Ti(OR)_4$ under the applied reaction conditions would have formed a white powder. The "new" polymer is elastic, and the tensile strength is up to ≈20 MPa. Phase separation is difficult to be detected, but scanning electron microscopy indicates a range of ≈20 to 50 nm. It is surprising that despite its high TiO_2 content an elastic material results. The material was used for the coating of polypropylene, creating a sterilizable surface for medical use.

The combination of properties was investigated with a series of other examples. As a general rule, in most cases very interesting properties could be obtained, but the case of a "linear" addition of properties is the exception. For example, density does not follow the inorganic and organic increments: the density, even with high inorganic contents, remains low (Fig. 38.14). This shows that the oxygen chains or groupings govern density by chain movement or rotation, and an "open" structure results. Another example is the thermal expansion coefficient as a function of the numbers of Si–C bonds, which is given in Ref. 15.

38.4. MATERIALS

Numerous materials have been developed. One can distinguish between different groups of materials according to their properties or structures.

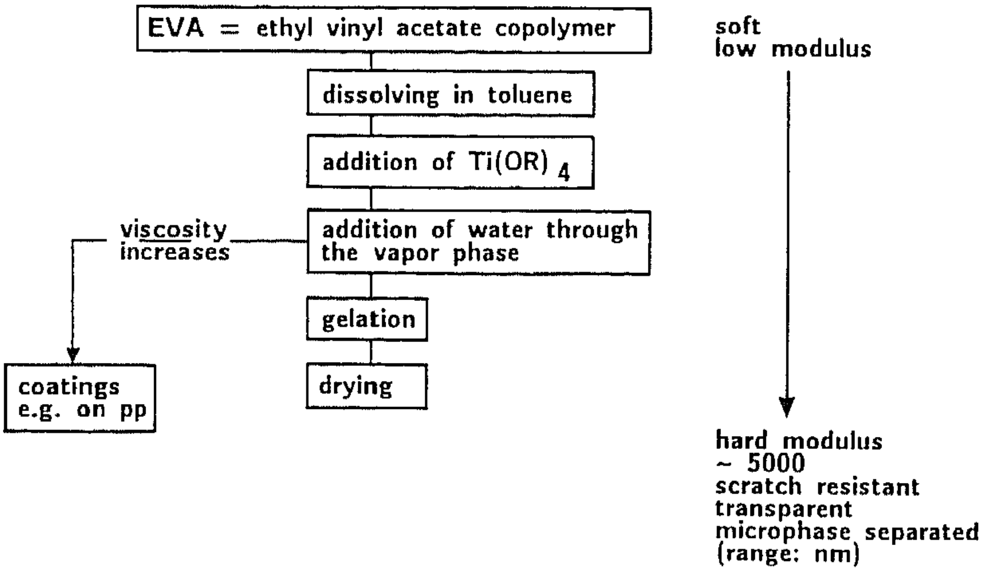


Figure 38.13. Scheme of the preparation of TiO_2/EVA copolymer.

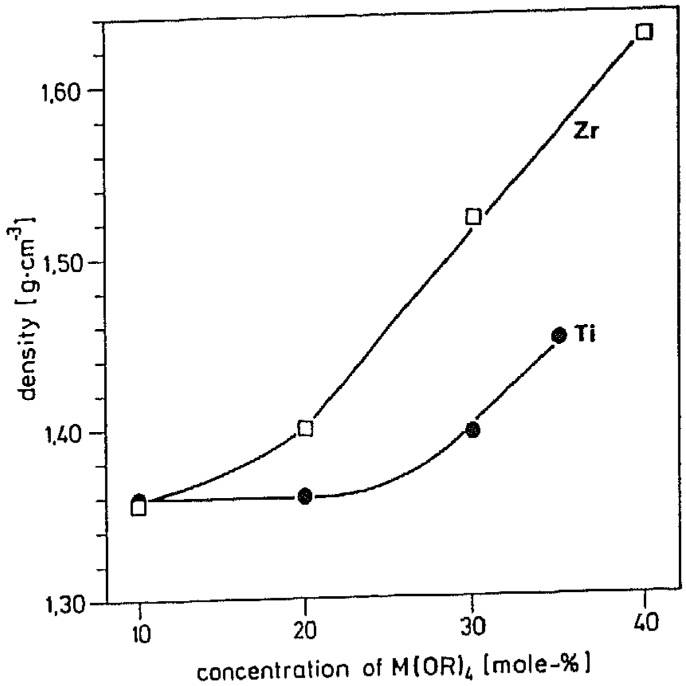


Figure 38.14. The density of ORMOCERS.

38.4.1. Porous Materials

They are characterized by a high content of inorganic network formers. The properties are influenced by composition and reaction parameters: It is possible to tailor microstructure (pore size from 4 nm to several micrometers can be established). The organic groupings can be used for special chemical properties, such as complexation of metals, acid or basic properties, hydrophobic or hydrophilic properties, selective adsorption, and surfaces with chemical links for covalent coupling of biochemical compounds. Some applications resulting from these general properties are various adsorbents for gas- and liquid-phase adsorption, membranes, carriers for catalysts and enzymes, sensors, ion exchangers, and materials for chromatography.

38.4.2. Thermoplastic Materials

They are characterized by high contents of the $(C_6H_5)_2SiO$ unit. With the addition of other network formers, the thermal properties can be varied [12]; with organics, mechanical properties and processing properties, as well as chemical properties, can be varied. Introduction of olefinic groupings (e.g., vinyl, allyl, or methacryl) can lead to photocurable behavior. Tailoring of $\equiv$SiOH or $\equiv$SiOR group contents leads to good adhesive properties on inorganic surfaces. Applications for these groups are adhesives, protective coatings, dielectrics for microelectronic application (structurizable coatings for packaging and housing), and ion conductive materials (H^+, Li^+).

38.4.3. Hard Materials

This group is characterized by inorganic network formers like Ti, Al, Zr, or Sn and polymerizable grouping bonds to Si ($\equiv\mathrm{Si}\sim\mathrm{R}$). R = methacryl, epoxy. Hardness and antiabrasive properties result from the inorganic backbone in combination with some flexibility by the organic polymer. The adaption to various substrates (metal and polymers) is possible, and other functions can be added by other organic groupings or fillers. Bulk materials can be prepared in the form of plates or rods, which can be machined to parts. Examples for applications are hard coatings, protective coatings, lubricating coatings, and lenses.

38.4.4. Interpenetrating Networks

This type is characterized by the fact that no chemical bond exists between the inorganic and organic backbone, whereas in the Sections 38.4.1 and 38.4.2 described materials the distribution of organics and inorganics can be controlled by the sol–gel reaction, in the latter type of materials the distribution reaction is controlled by a "phase formation" reaction, leading to phase separation effects. The chemistry, therefore, has to be investigated thoroughly, and not much data concerning inorganic–organic sol–gel techniques are available [16]. Applications are, for example, reinforcement of polymers on a nanosized level or creating new functions in polymers.

38.5. CONCLUSION AND FUTURE

The conclusion that can be drawn from the available data is that a tailoring of properties can be done successfully only in combination with the reaction control. It seems to be possible to predict functions from the properties of the used units, but it is rather difficult to predict the structure development based on the reactivities of the component in a complex environment. Based on sufficient experience, this tailoring is a combination of predictable basic features and an unknown part to be solved permanently.

Because there are huge numbers of parameters resulting from composition and reaction conditions, the field is only scratched. Important questions like structure formation mechanisms or size effects of the different phases are only investigated in a few examples. So, despite already having a short history, the future of the inorganic composite material will be interesting and exciting.

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